DOE RESEARCH GRANT
NO. DE-FG-03-93ER14315

"The Hydrophobic Character of Nonsulfide Mineral
Surfaces as Influenced by Double-Bond Reactions
of Adsorbed Unsaturated Collector Species"

PROGRESS REPORT

15 December 1992 - 14 December 1995

J. D. MILLER
Department of Metallurgical Engineering
412 W. C. Browning Building
University of Utah
Salt Lake City, UT 84112-1183

June 1995

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INTRODUCTION

Background

Froth flotation is a physico-chemical process that is used to separate particles in an aqueous suspension via differences in hydrophobicity as established by the interaction of various reagents at the solid/water, solid/gas and water/gas interfaces. Surfactants called collectors are added to the suspension to selectively adsorb at the surface of specific particles, rendering these particles hydrophobic. Regulators are employed to promote collector adsorption at the desired surfaces, while preventing such reactions at other surfaces. When air is dispersed into the suspension, the bubbles generated attach to hydrophobic particles. The resulting bubble/particle aggregates float to the suspension surface and are collected in a froth phase as a concentrate. Frothers are used to stabilize the froth and prevent the concentrate from collapsing back into the suspension tailings. Clearly, particulate separation by froth flotation is one of the most outstanding examples of applied surface chemistry, and is used in food, petroleum, pulp/paper, and mineral industries.

Flotation technology is now being developed to solve environmental problems including resource conservation, pollution prevention, and environmental remediation. Examples such as the separation of radionuclides from contaminated soils, the removal of dispersed oil from oily waste water, recycle of wastepaper to produce a clean cellulose product, and clean coal production demonstrate the utility and need for the development of flotation technology. The use of this technology is perhaps most significant in the mineral industry where in the U. S. alone over 640,000 tons/day of nonsulfide minerals are processed by flotation. In this regard, a research program has been in progress with DOE support from Grant # DE-FG03-93ER14315 to study

the fundamental features of collector adsorption phenomena in nonsulfide mineral flotation systems in order to increase our understanding of the interfacial chemistry for improved separation efficiencies and energy economy in mineral flotation processes.

Nonsulfide minerals systems are generally divided into three classes, viz. soluble salt minerals such as sylvite (KCl) and halite (NaCl), semisoluble salt minerals such as fluorite (CaF_2) and apatite ($\text{Ca}_5(\text{PO}_4)_3\text{X}$ where $\text{X} = \text{F}, \text{Cl}, \text{OH}$ or CO_3), and insoluble oxide minerals such as quartz (SiO_2) and alumina (Al_2O_3). Due to differences in mineral solubility and collector adsorption, a wide variety of flotation strategies has to be employed for the selective separation and efficient recovery of these nonsulfide minerals. For soluble salt minerals (alkali halide and oxyanions), collector solubility is an important issue because of the high ionic strengths (5 molar or greater) in these systems. Long chain tallow amines are used commercially for sylvite flotation from halite. Demand for potash, the mineral sylvite, has increased considerably in the last 40 years. Agricultural fertilizers account for about 95% of the world potash consumption. Other uses include high-quality glass production, electronic components and ceramics (1). Understanding of collector adsorption in soluble salt flotation systems has become even more important in view of the depletion of high grade potash reserves especially in the United States (2).

Semi-soluble salt minerals (alkaline earth and metallic oxyanions including fluorite, CaF_2) are often concentrated by flotation with tall oils, which are long chain saturated and unsaturated carboxylic acids such as stearic, oleic and linoleic acids. These collectors are thought to adsorb at the surface of semi-soluble salt minerals through chemical bonding of the carboxylate head group and the polyvalent mineral cation. Such reactions can occur with cations in the crystal lattice or with cations in solution due to the slight solubility of the mineral. Among the common

semi-soluble salt minerals, apatite ($\text{Ca}_5(\text{PO}_4)_3\text{X}$ where $\text{X} = \text{F}, \text{Cl}, \text{OH}$ or CO_3) is used for the production of fertilizers, while fluorite (CaF_2) is used as a flux in steel and glass-making, and to produce fluorine chemicals (1). Calcite (CaCO_3) is a common gangue mineral in many ore bodies. Other important semi-soluble salt minerals include brucite ($\text{Mg}(\text{OH})_2$) and hydromagnesite ($3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$) which are gaining new attention because of their attractive environmental profile (3).

Insoluble oxide and silicate minerals are also recovered by flotation. Furthermore, the ubiquitous presence of quartz and clay minerals such as kaolinite in all types of ores makes knowledge of their flotation behavior of utmost importance. Large quantities of low-grade oxide minerals of strategic metals such as titanium are contained in ore deposits in the southwestern United States. Utilization of these resources would be very useful in reducing the dependence on imports of these critical materials.

During the past two decades, flotation of nonsulfide minerals has grown substantially in the U. S. and around the world. For instance in 1965, approximately 240,000 tons/day of nonsulfide minerals were processed in the U. S. by flotation. This production capacity had grown to 560,000 tons/day in 1975 and about 640,000 tons/day in 1985 (4). Nevertheless, understanding of the interfacial chemistry and optimum conditions for improved separation efficiencies are incomplete.

Energy consumption in flotation has only been recognized as a significant process factor during the last 15 years. Most of the energy is used to generate bubbles and maintain particles in suspension. ERDA and NRC reports have concluded that initiatives to maximize flotation response not only will improve the utilization of our mineral resources but also will result in a

reduction in the energy consumed during flotation (5,6). Most previous strategies proposed to enhance flotation response have concentrated on new reagent schedules or on improving the performance of the flotation equipment.

Analytical techniques for detailed, in-situ, and real time observation of the solid/liquid interface have only been developed within the last ten years. The advent of these sophisticated experimental methods now allows for a more detailed investigation of the critical role that interfacial chemistry plays in flotation separations. Understanding the interfacial chemistry will allow for the design of new procedures for improved flotation separation efficiency and reduced energy consumption.

Program Objectives

The primary goal of this research program is to provide a basis for improved flotation separation efficiency in nonsulfide mineral systems by establishing the fundamental features of collector (surfactant) adsorption reactions and developing appropriate surface chemistry control strategies. In-situ real-time FT-IR/IRS measurements, preparation of transferred Langmuir-Blodgett (LB) films, nonequilibrium electrophoresis, vacuum and bench scale flotation, contact angle goniometry, laser Raman spectroscopy, linear dichroism spectroscopy, photo-correlation spectroscopy, and atomic force microscopy are being used to accomplish this goal. These advanced experimental techniques together with more traditional experimental methods are providing crucial information concerning collector adsorption phenomena in various nonsulfide mineral systems.

Specifically, the research program is designed and intended to describe collector adsorption phenomena in-situ and in real time including adsorption density, interfacial order,

surface bonding state, and reaction of unsaturated hydrocarbon chains. In addition, the significance of collector colloid adsorption continues to be examined based on nonequilibrium electrophoretic measurements, the study of solid phase defect states, and interparticle force measurements by AFM. Finally, preliminary attention is being given to the structure of interfacial water at hydrophilic and hydrophobic surfaces as determined by FTIR/IRS depth profiling.

Summary

This report summarizes the last thirty-six month period of Grant No. DE-FG03-93ER14315 (December 15, 1992 to December 14, 1995). Research has focussed on extending the previous results from model systems to various minerals representative of each nonsulfide mineral class. Several new research achievements have been realized for a variety of nonsulfide mineral flotation systems using advanced analytical instrumentation. DOE-supported research during this period has led to 16 presentations at special seminars and professional society meetings. Further, 15 publications have resulted from this work in a broad range of journals, including publications in *Langmuir*, *Applied Spectroscopy*, *Journal of Colloid and Interface Science*, *Journal of Physical Chemistry*, *Colloids and Surfaces* and in various engineering journals. All efforts to communicate these results to our colleagues are documented in APPENDICES II, III, and IV. Most importantly, during this grant period, six students were supported for their Ph.D. degrees in Metallurgical Engineering. See Appendix I, page 49. In addition, this DOE research program at the University of Utah prompted the principal investigator to organize the Engineering Foundation Conference, "Surface Characterization of Adsorption and Interfacial Reactions," which was held in January 1994. Representatives from academia, industry and government were present at this conference, and an international audience with delegates

from several countries including Australia, Finland, Germany, Sweden, etc. participated. This conference was organized by methodology according to the following topics: wetting phenomena, Raman/fluorescence spectroscopy, infrared spectroscopy, X-ray photoelectron spectroscopy, electrochemical analysis, surface forces, and scanning probe microscopies, and the conference proceedings were published in a special issue of *Colloids and Surfaces* (7).

As a result of the research performed during this grant period, fundamental in-situ measurements of surfactant adsorption were made for selected nonsulfide mineral systems using FT-IR/IRS with reactive internal reflection elements. Significant advancements have been achieved in development of the FT-IR/IRS technique for in-situ study of surfactant adsorption phenomena. The IRS adsorption density equation has been developed from first principles to quantify the extent of surfactant adsorption, and the validity of the adsorption density equation has been confirmed based on the examination of transferred Langmuir-Blodgett (LB) films. Furthermore, the order and organization of adsorbed surfactants have been established from linear dichroism spectroscopy. Finally, on the basis of this surface spectroscopic information and the results from the contact angle measurements, hydrophobicity and stability of adsorbed surfactants at mineral surfaces can be explained with improved understanding.

The surface charge/collector colloid adsorption mechanism developed from lattice ion hydration theory for alkali halides to explain soluble salt flotation has been extended to explain the anomalous behavior of KCl and the flotation of double salts such as schoenite, kainite, borax, etc. from their saturated brines. The physical characteristics of the adsorbing surfactant colloids at the salt surfaces in brine solutions were studied by photon correlation spectroscopy and atomic force microscopy to further substantiate the surface charge/collector colloid adsorption theory.

A research program is being initiated to examine the nature of the interparticle forces involved in soluble salt flotation systems.

In addition to surfactant adsorption studies, FT-IR/IRS has been used to spectroscopically characterize interfacial water near hydrophilic and hydrophobic surfaces. Interfacial water is being examined spectroscopically over certain distances from the surface by appropriate design of the geometry and optics of the internal reflection system. These preliminary spectroscopic results at different surfaces promise to provide important information regarding the nature of short-range interparticle forces significant in the flotation process. Ultimately, these forces control the kinetics of bubble attachment at the hydrophobic surface and the efficiency of the flotation separation.

IN SITU FT-IR INTERNAL REFLECTION SPECTROSCOPY

During the course of this grant in situ Fourier transform infrared internal reflection spectroscopy (FT-IR/IRS) with reactive internal reflection elements (IREs) has been developed to quantitatively describe the nature of adsorbed surfactants at mineral surfaces. In this experimental technique, the IRE is machined from a material of interest (either man-made single crystals or naturally occurring mineral crystals) and adsorption is monitored at the IRE surface, hence the term reactive IRE. On this basis, FT-IR/IRS has been shown to provide direct, real-time, spectral data which can be used to quantify surfactant adsorption reactions and explain a variety of interfacial phenomena occurring at mineral surfaces.

General Experimental Procedure

Shown in Figure 1 is a schematic representation of a light ray undergoing multiple internal reflections in a parallelepiped-shaped IRE. Two requirements must be met for total internal reflection to occur. First, the IRE must be optically denser, that is, have a higher refractive index than the sample phase. Second, the incident angle of the light beam within the IRE must be greater than the critical angle (θ_c) given by Snell's law ($\theta_c = \sin^{-1} n_2/n_1$). Upon total reflection at the IRE interface, an evanescent field is established at the surface. It is through this evanescent field that sampling of the adsorbed surfactant in the interfacial region occurs. Since the evanescent field decays exponentially from the surface, with a decay length on the order of wavelength of the light beam, and because of the relatively low bulk concentration of the surfactant, at least 90% and usually more than 95% of the signal comes from the adsorbed surfactant.

Figure 1. Schematic representation of light undergoing multiple internal reflections in a reactive IRE.

Figure 2 shows a schematic diagram of the liquid flow-through cell used for in-situ FT-IR/IRS experiments. The IRE, which is thoroughly cleaned by a combination of solvents and radio frequency plasma, is placed in the in-situ FT-IR/IRS cell. This cell is then placed in the FT-IR sample compartment chamber on a variable-angle holder manufactured by Harrick Scientific. At this point, the efficiency of the cleaning procedure is determined by collecting a spectrum of the cleaned crystal. A background spectrum of the IRE is collected and the surfactantless solvent (usually H₂O or D₂O) is injected into the inlet port. This solution is allowed to equilibrate with the IRE, and the solvent spectrum is recorded. Surfactant solution is then injected through the inlet port to replace the solvent and spectra of the adsorbing surfactant are recorded as a function

of time. Injections are performed using a syringe pump at an appropriate rate to insure that the surfactant concentration in solution does not change. The solvent spectrum is subtracted from the spectrum of the adsorbed species and the resultant spectrum is used to quantify and evaluate the state of the adsorbed surfactant.

Solution contact ATR cell

Figure 2. Exploded view of an in situ FT-IR/IRS flowthrough cell.

Adsorption Density Equation

Because of the high sensitivity of the FT-IR/IRS technique it is possible to detect submonolayer coverage of adsorbed species. Even more significant is that quantitative FT-IR/IRS is possible and an adsorption density equation has been developed to directly calculate the adsorption density, Γ (mol/cm²), of the adsorbed collector species from spectral data (8-10). The equation is:

$$\Gamma = [(A/N) - \epsilon C_b d_e] / 1000 \epsilon (2d_e / d_p) \quad (1)$$

where

- A = integrated absorbance (cm⁻¹)
- N = number of internal reflections
- ϵ = molar absorptivity of collector (l/cm².mol)
- C_b = Collector bulk concentration (M)
- d_p = depth of penetration (cm) = $\lambda / [2\pi n_1 (\sin^2 \theta - n_{21}^2)^{1/2}]$
- d_e = effective depth (cm) = $(n_{21} E_o^2 d_p) / 2 \cos \theta$
- λ = wavelength in the absorbance region (cm)
- n₂₁ = n₂/n₁ = ratio of the sample and IRE refractive indices
- E_o = electric field amplitude
- θ = incident angle (deg)

Importantly, the validity of this FT-IR/IRS adsorption density equation for quantitative analysis of surfactant adsorption has been confirmed independently by the FT-IR/IRS study of transferred Langmuir-Blodgett (LB) films (11). In these experiments, the adsorption densities of transferred LB monolayer films of stearic and oleic acids were calculated from the spectral data using the FT-IR/IRS adsorption density equation and compared with adsorption densities evaluated from the measured LB surface pressure-specific area (π -A) isotherms. The area per molecule for an LB monolayer at the air-water interface can be directly determined from the π -A isotherm and thus the adsorption density can be calculated from:

$$\Gamma = 1 / N_A \alpha \quad (2)$$

where N_A is Avogadro's number and α is the area per molecule measured from the π -A isotherm (Figure 3) at the surface pressure maintained during LB transfer.

Figure 3. Surface pressure-specific area isotherms for stearic, oleic, and linoleic acids.

The adsorption density values found from the established π -A isotherms for LB monolayer films of stearic and oleic acids were compared with the adsorption density values evaluated using the FT-IR/IRS adsorption density equation (Equation 1). As shown in Figure 4, for both stearic and oleic acids, the adsorption density values determined from the FT-IR/IRS spectra are in good agreement with the ones calculated from the established π -A isotherms. These results clearly

show that the FT-IR/IRS adsorption density equation is valid and can be used with confidence for quantitative analysis of surfactant adsorption phenomena.

In addition, a clear understanding of the importance of sample and incident beam areas in the use of this equation was developed during this grant period. It has been shown that for correct application of the adsorption density equation, the incident beam must not be reflected from uncoated surfaces of the internal reflection element. However, it is possible to correct data where this condition is not satisfied (12).

Figure 4. Adsorption density values for transferred LB monolayers of fatty acids calculated by the FT-IR/IRS adsorption density equation vs. those determined from the π -A isotherms.

Conformation and Orientation

Order, as applied to surfactants, is used to describe the organization of surfactant molecules. FT-IR/IRS has been successfully used to examine two types of order namely conformational and orientational order. Conformation can be considered as the relative flexibility of the adsorbed hydrocarbon chain caused by rotations about carbon-carbon single bonds. The hydrophobic character of fluorite, sapphire, and sylvite surfaces as influenced by the conformational order of adsorbed collectors has been described by studying the systematic shifts in the C-H stretching region of the FT-IR/IRS spectra of the adsorbed species (13).

During this grant period, polarized light FT-IR/IRS was used to study the orientational order of adsorbed collector species. The results from these experiments indicate that for both self-assembled and LB films of stearate molecules at a fluorite surface, the surfactant molecules are in the trans state with uniaxial distribution of both the hydrocarbon chains and the transition dipole moments of the CH₂ stretching vibration (14). On this basis, the average molecular orientation angles for such monolayers were determined from linear dichroism theory. Table 1 shows typical orientation angles of the alkyl chain and carboxylate head group for both transferred LB and self assembled monolayers of stearate, a straight chain saturated fatty acid collector, at the surface of a fluorite IRE. It can be noticed that both transferred LB and self-assembled monolayers of stearate molecules are highly ordered nearly normal to the surface, although the transferred LB layer shows a slightly greater orientational order. The influence of the molecular orientational order on the structure of the adsorbed collector and the hydrophobicity of the mineral surface under consideration is discussed in a subsequent section of this report, "Hydrophobicity and Stability of Adsorbed Surfactants".

Table 1. Orientation Angles (relative to surface normal) of Alkyl Chain and Carboxylate Head Group for Transferred LB and Self-Assembled Stearate Monolayers as Determined by Linear Dichroism Theory (14).

Nature of the Adsorbed Film	Adsorption Density (10^{-10} mol/cm ²)	Alkyl Chain (degrees)	Carboxylate (RCOO ⁻) (degrees)
Transferred LB	8	9-16	3-11
Self-Assembled	7	21-22	18

Identification of Surface Species

As mentioned previously, due to improved signal to noise ratio and fast data collection, FT-IR/IRS can be used to study the nature of surfactant adsorption even at submonolayer coverage. The transfer of LB monolayers to the crystal surfaces is an excellent method for the study of surfactant adsorption phenomena. These model monolayers have a well-defined structure which can be compared to the structure of the self-assembled monolayers found in typical flotation systems. During this grant period, the combined method, i.e., FT-IR analysis of transferred LB monolayers at the surfaces of the mineral crystals, has been used to study the fatty acid/fluorite and amine/sylvite systems to identify the nature of adsorbed surfactant species.

The FT-IR/IRS analysis of transferred LB monolayers of oleic and stearic acids at a fluorite surface clearly confirmed that the singlet at 1550 cm⁻¹ in the resulting spectrum is indicative of carboxylate chemisorption at the surface of calcium bearing semisoluble minerals. In addition, these results suggest that chemisorption and/or dehydration of carboxylate at the fluorite surface provides for complete resonance structure resulting in a singlet at 1550 cm⁻¹ whereas multilayer formation of the calcium dicarboxylate salt is not a favorable condition for complete resonance, resulting in a doublet at about 1575 and 1540 cm⁻¹ (15,16). In this way, the chemisorbed monolayer can be distinguished and conditions which favor its formation identified.

LB monolayers of octadecylamine species were transferred at a sylvite surface from the air/saturated KCl solution interface at different pH values (17). It was found from the FT-IR/IRS analysis of these LB monolayer films that the amine species at the sylvite surface is in the form of the free amine at pH values exceeding 11 whereas the surface amine species is in the form of amine hydrochloride at lower pH values as distinguished by the adsorbed band at 1504 cm^{-1} (Figure 5).

Figure 5. Formation of different octadecylamine species at a sylvite (KCl) surface depending on the subphase (saturated KCl solution) pH as examined by the FT-IR/IRS spectra of a transferred LB monolayer of octadecylamine.

Adsorption Kinetics

Using the in-situ FT-IR/IRS technique, direct measurements of oleate and linoleate adsorption kinetics have been made in real time during this grant period. These measurements have been used to determine the activation energies of oleate and linoleate collector adsorption at the fluorite surface. The calculated activation energies for oleate and linoleate adsorption are 42.1 and 30.4 kJ/mol respectively. Adsorption was found to follow simple first order kinetics in each case with a negligible effect from back reaction rates. The adsorption kinetics studied at different temperatures revealed that when the solution calcium concentration is minimized, only monolayer adsorption occurs irrespective of the oleate collector concentration.

Characterization of Interfacial Water

The properties of interfacial water are of great importance in froth flotation as well as in many other technological areas. Recent research suggests that the characterization of interfacial water is important in understanding the so called non-DLVO forces (structural/hydration forces) and their influence on particle dispersion and aggregation in aqueous systems particularly at high salt concentrations. In this regard, internal reflection spectroscopy offers excellent possibilities to spectroscopically characterize interfacial water at mineral surfaces. Most importantly, internal reflection spectroscopy with reactive internal elements should allow for the in-situ spectroscopic examination of interfacial water at specified distances (from a few tens of Angstroms to a few thousands of Angstroms) from the surface in real time. During this grant period, for the first time, interfacial water at hydrophilic and hydrophobic surfaces has been examined by FT-IR/IRS at different distances from the surface. The results are discussed in a subsequent section, "Spectroscopic Characterization of Interfacial Water".

SURFACTANT ADSORPTION REACTIONS

Soluble Salts

During the previous grant period, nonequilibrium electrokinetic measurements using laser-Doppler electrophoresis were reported for the first time for alkali halides and the sign of their surface charge thus determined. These new results are generally as had been expected from simplified lattice ion hydration theory with KCl, under normal circumstances, being the most significant exception. In this regard, lattice defects have been found to influence the surface charge of KCl and its flotation response. During this grant period, the influence of crystal lattice defects (F centers and oxygen imperfections) on the surface charge of KCl was studied by varying the concentration of these defects in the crystal lattice of KCl. In particular, the presence of oxygen defect states in the crystal lattice has been found to be responsible for KCl's unexpected behavior based on the simplified lattice ion hydration theory (18,19).

The concentration of oxygen defect states in KCl, as characterized by UV/Vis absorption, was varied in order to study their influence on the electrokinetic behavior and subsequently on the flotation response of KCl. At low oxygen contents (< 60 ppm) KCl is positively charged as expected from lattice ion hydration theory. However, typically, KCl contains substantial oxygen (> 300 ppm) sufficient to impart a negative surface charge. On this basis the selective flotation of KCl from NaCl has been explained by heterocoagulation with oppositely charged alkyl amine hydrochloride collector colloids.

In addition, the surface charge/collector colloid adsorption model developed has now been extended to successfully explain the flotation behavior of certain alkali oxyanions including nitrates and sulfates as well as hydrated double salts including schoenite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$)

and kainite ($\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$). As was done previously, the sign of the surface charge for these alkali oxyanions and double salts was established from both equilibrium and nonequilibrium electrokinetic measurements by laser-Doppler electrophoresis (Figure 6). These results together with the results from flotation/bubble attachment experiments indicate that the surface charge/collector colloid adsorption hypothesis accounts for the flotation response of many different soluble salt minerals when alkyl amines and carboxylates are used as collectors (20). These findings are important not only to further improve the efficiency of existing flotation circuits but also to develop new flotation strategies for the recovery of salts such as LiCl from saturated brine solutions.

Further, during this grant period, the physical characteristics of adsorbing collector colloids were studied at salt surfaces in brine suspensions to substantiate the surface charge/collector colloid adsorption mechanism. Techniques such as photon correlation spectroscopy, FT-IR, and atomic force microscopy were used for this purpose. Photon correlation spectroscopy measurements indicated that the size of the adsorbed aminehydrochloride collector colloids which control the flotation of alkali halides is on the order of a tenth of micron. Figure 7 shows an AFM image of the adsorption of positively charged, hydrophobic latex particles (model collector colloids, 200 nm in size) at a negatively charged KCl surface in saturated brine. Negatively charged carboxylate latex particles did not adsorb on the negatively charged KCl surface thus further substantiating the surface charge/collector colloid adsorption theory.

Figure 6. Nonequilibrium electrophoretic mobility distributions for potassium sulfate and sodium sulfate salts.

Figure 7. AFM image of the positively charged, hydrophobic amino latex particles (model collector colloids, 200 nm in size) at a KCl surface.

Semi-Soluble Salts

During this grant period, the effect of solution calcium concentration on the nature of oleate adsorption at fluorite surfaces has been more clearly defined using in-situ and ex-situ FT-IR/IRS techniques. These studies indicate that above a certain concentration of calcium and oleate ions in the bulk solution, collector colloid adsorption occurs at the fluorite surface and accounts for the surface hydrophobicity. In previous studies reported in the literature (16,21-23), the effect of calcium concentration was uncertain due to the difficulty in controlling the calcium concentration with high surface area powders. However, for studies during this grant period, in which a low surface area IRE crystal was used, calcium concentration was easily maintained. Results show that the nature of the adsorbed oleate can be controlled by controlling the bulk calcium concentration as illustrated in Figure 8. These spectral results show that at low calcium concentrations, adsorption occurs by chemisorption as indicated by the singlet at 1550 cm^{-1} whereas at high calcium concentrations, surface precipitation of calcium dioleate occurs at the surface as indicated by the appearance of a doublet at 1575 and 1535 cm^{-1} . These results suggest that surface precipitation or collector colloid adsorption occurs by reaction of carboxylate group with cations released from the lattice. In addition, the nature of the adsorption reaction and state of the adsorbed oleate was explained based on solution chemistry calculations from thermodynamic data (24).

Figure 8. Effect of calcium concentration on oleate adsorption at a fluorite surface. The doublet with predominant peaks at 1575 and 1535 cm^{-1} is indicative of calcium dioleate whereas the singlet at 1550 cm^{-1} is indicative of chemisorption. The Oleate concentration was 1×10^{-4} M and the pH adjusted to 9.8.

Insoluble Oxides

Previously, the in-situ FT-IR/IRS technique was used to determine the aggregative behavior of sodium dodecyl sulfate (SDS) in solution based on shifts in the positions of the $-\text{CH}_2$ stretching band. The SDS surfactant in solution was found to exist as different phases including monomer, micelle, and coagel depending on the SDS concentration (Figure 9). The phase behavior of SDS adsorbed at a sapphire (Al_2O_3) surface was found to be similar to that in solution based on the $-\text{CH}_2$ stretching band positions in the in-situ FTIR/IRS spectra generated

(25). During this grant period, the hydrophobic character of sapphire (Al_2O_3) surfaces in sodium dodecyl sulfate (SDS) solutions was examined with respect to the aggregative nature of the adsorbed surfactant phase as revealed in Table 2. It was found that, at equilibrium, sapphire surfaces having adsorbed SDS bilayers exhibited no contact angle. Conversely, when the adsorbed SDS appeared to be in a micellar state, the sapphire surfaces developed significant hydrophobic character with a well defined contact angle. The surface states as detected by in-situ FT-IR/IRS conformational analysis were found to be reversible with temperature.

Figure 9. Asymmetric CH₂ band position as a function of SDS concentration at 298 K.

Table 2. Hydrophobic Character of Sapphire Surfaces in Sodium Dodecyl Sulfate Solutions at pH 2.85 and 298 K (26).

Concentration M	Phase	Contact Angle degrees	Adsorption Density mol/cm ²
1.7×10^{-5}	cylindrical micelle	no attachment	5×10^{-11}
4.5×10^{-5}	cylindrical micelle	43.4 ± 2.7	8×10^{-11}
6.6×10^{-5}	cylindrical micelle	42.1 ± 1.6	1×10^{-10}
3.0×10^{-4}	coagel/cylin. micelle	34.4 ± 2.1	3×10^{-10}
4.4×10^{-4}	coagel	no attachment	5×10^{-10}
1.2×10^{-3}	coagel	no attachment	1×10^{-9}
3.2×10^{-3}	coagel	no attachment	1×10^{-9}

Research in Progress

Further research is in progress for the three nonsulfide mineral categories discussed in this section. In soluble salt systems, the composition of the amine collector species in saturated brine solutions is being determined by transmittance, FTIR microscopy, and FT-IR/IRS measurements. This research which is aimed at characterization of adsorbed collector species is important in establishing the hydrophobic character of salt minerals based on the composition of adsorbed collector colloids.

Experiments are in progress to determine the effect of the degree of collector unsaturation on adsorption phenomena at calcite and apatite minerals. This research will be directed towards understanding the effect of molecular orientation on surface hydrophobicity and polymerization reactions. In addition to interfacial water structure, molecular orientation and polymerization of adsorbed collectors will be investigated by in-situ spectroscopic examination of an IRE under electrochemical control.

In the category of insoluble oxides, research is in progress to describe the adsorption behavior of unsaturated collectors on alumina by in-situ FTIR/IRS and transferred LB films. In addition, the effect of fatty acid unsaturation on adsorption, polymerization, and subsequent hydrophobicity at a rutile (TiO_2) surface will be studied using in-situ FT-IR/IRS and transferred LB films. Spectroscopic characterization of interfacial water is also in progress at these oxide surfaces.

HYDROPHOBICITY AND STABILITY OF ADSORBED SURFACTANTS

Semi-soluble salt minerals are naturally hydrophilic and fatty acids are frequently used to create a hydrophobic state and thus modify their surface wetting properties. Without such modification, the separation of semi-soluble salt minerals by flotation can not be achieved. Also, such treatment facilitates the use of these semi-soluble salt minerals as fillers for plastics in the production of polymer-mineral composites. Therefore, an understanding of the surface chemistry of fatty acid adsorption at semi-soluble salt mineral surfaces is interesting from both a fundamental and a practical point of view.

It is evident from the in-situ FT-IR/IRS experiments that fatty acids adsorb at the surface of a semi-soluble salt mineral through chemisorption of a carboxylate group with lattice cations at low collector concentrations (27,28). At high solution concentrations of the collector and the cation, and at higher pH, surface precipitation or collector colloid adsorption occurs by reaction of carboxylate group with cations released from the lattice as mentioned previously. Because the fatty acid interacts not only with the lattice cation sites of the semi-soluble salt mineral but also with the dissolved cations in solution, the solution chemistry of these minerals and the pH of the

system play an important role in determining the hydrophobicity and stability of adsorbed species.

During this grant period, the hydrophobicity and stability of fatty acid monolayers at fluorite and calcite surfaces have been analyzed using sessile drop contact angle measurements with water and diiodomethane to further understand the differences in fatty acid adsorption at these surfaces (29).

Wetting Characteristics of an Apolar Liquid Sessile Drop - LB films

The wetting characteristics for transferred LB layers of fatty acids were observed to be the same at both fluorite and calcite surfaces when probed with an apolar liquid (diiodomethane). These contact angle results show little hysteresis and indicate that fatty acid monolayers are stable at both fluorite and calcite surfaces when exposed to an apolar liquid (Figure 10).

Figure 10. Advancing and receding contact angles for a transferred LB monolayer of stearic acid at fluorite (circles) and calcite (squares) surfaces as measured for a diiodomethane drop of varying size.

Wetting Characteristics of a Water Sessile Drop - LB films

The hydrophobicity and stability of transferred LB monolayers of fatty acids at fluorite and calcite surfaces were examined with advancing and receding contact angles using water drops of varying size at different pH values. The transferred LB layer of stearic acid exhibits good hydrophobicity and stability at the fluorite surface. The advancing contact angle was found to be 110 to 114 degrees and was not affected by the pH of the aqueous phase as shown in Figure 11. A contact angle hysteresis of 10 to 20 degrees, depending on the pH value, was observed. At pH 5.8, the transferred LB monolayer of stearic acid showed good stability during the time of contact angle measurement. The same advancing and receding contact angles were obtained when contact angle measurements were repeated at the same location of the monolayer as illustrated in Figure 12. These results indicate that carboxylate chemisorption causes immobilization of the transferred stearate molecules at a fluorite surface, thus accounting for the stability of the adsorbed monolayer.

On the other hand, a considerable difference in the water receding contact angles between the transferred LB monolayer of stearic acid at a fluorite surface and the transferred LB monolayer of stearic acid at a calcite surface was observed. For example, at pH 5.8, the receding contact angles for the transferred LB monolayer of stearic acid at the calcite surface were only 13 to 15 degrees compared to 100 to 102 degrees for the LB stearate monolayer at a fluorite surface as illustrated in Figure 13. Further, in the case of calcite both advancing and receding contact angles decreased significantly when the contact angle measurements were repeated at the same location of the monolayer. These results suggest that only some portion of the stearic acid might be adsorbed at the active sites of the calcite surface through carboxylate chemisorption

Figure 11. Advancing and receding contact angles for a transferred LB monolayer of stearic acid at a fluorite surface as measured for a water drop of varying size at different pH values (squares= pH 3.6, circles=pH 5.8, triangles=pH 11.0, and crosses=pH 12.0)

Figure 12. Advancing and receding contact angles for a transferred LB monolayer of stearic acid at a fluorite surface as measured for a water drop of varying size at pH 5.8. The measurements were performed for two runs at the same location on the LB monolayer (circles=first run, triangles=second run).

Figure 13. Advancing and receding contact angles for a transferred LB monolayer of stearic acid at fluorite (circles) and calcite (squares) surfaces as measured for a water drop of varying size at pH 5.8.

whereas the rest of the stearic acid molecules remain unreacted and are adsorbed at the calcite surface through weaker interactions, possible coulombic interaction/hydrogen bonding.

The kinetics of destabilization of transferred LB monolayers of fatty acid were also examined at fluorite, calcite, and quartz surfaces by monitoring contact angle change with time. These results again agree with the previous observation that transferred LB monolayers of stearic acid are less stable at quartz and calcite surfaces than at a fluorite surface.

Wetting Characteristics of a Water Sessile Drop - SA films

Self-assembled (SA) stearate monolayers were characterized by contact angle measurements with a water sessile drop. The advancing and receding contact angles for water drops at SA stearate monolayers were measured as function of surface coverage. The measured advancing contact angles increased significantly to about 112 degrees at a surface coverage (x) of $x=0.91$. On the other hand, receding contact angles of the SA stearate were zero below $x=0.31$ and increased to about 90 degrees at $x=0.71$. These results suggest that good hydrophobicity and stability of SA stearate can be obtained only beyond $x=0.71$.

LB vs SA Films

It is clear from comparison of the measured contact angles of LB and SA stearate layers that the receding contact angles for the transferred LB stearate monolayers are always greater than the receding contact angle for SA stearate monolayer by 17 to 25 degrees where as the measured advancing contact angles were the same in both cases. This may be due to the effect of molecular orientation. As shown in Table 3, the transferred LB stearate monolayer at a fluorite surface was found to be oriented at 13 degrees from the surface normal whereas the SA stearate monolayer was found to be oriented at 21 degrees from the surface normal, as determined by linear dichroism theory. These results suggest that molecular orientation of the adsorbed surfactant is an important factor which significantly influences the hydrophobicity/stability of surfactant monolayers and consequently the flotation response. Also, it is possible that the slight difference in adsorption density may contribute to the difference in hydrophobicity/stability.

Research in Progress

It is clear from these experiments that adsorbed surfactant monolayers (both LB and SA) are less stable at a calcite surface than at a fluorite surface. Research is in progress to examine the hydrophobicity and stability of multilayers at fluorite and calcite surfaces. These experiments are important since fatty acid reacts with both the lattice cations at the surface (chemisorption) and the dissolved cations (precipitation/collector colloid adsorption). In addition, efforts are underway to study the kinetics of destabilization and/or desorption of fatty acid at fluorite, calcite, and quartz surfaces by monitoring contact angle change with time.

Table 3. Contact Angle Data for Transferred LB and SA Stearate Monolayers at a Fluorite Surface (drop size varied from 2 to 6.5 mm, pH=5.8)

Type	Adsorption Density ($\times 10^{-10}$ mol/cm ²)	Molecular Orientation Angle (degrees)	Advancing Contact Angle (degrees)	Receding Contact Angle (degrees)
LB	8.1	13	110 to 114	100 to 102
SA	7.6	21	110 to 115	75 to 85

SPECTROSCOPIC CHARACTERIZATION OF INTERFACIAL WATER

In addition to surfactant adsorption studies, a research program has been initiated during this grant period to spectroscopically characterize interfacial water near hydrophilic and hydrophobic surfaces by in-situ FT-IR/IRS. The characterization of interfacial water structure near mineral surfaces is of great significance in flotation and in many other areas as well. For example, the nature and behavior of thin films during bubble attachment at the surface of a hydrophobic mineral surface and the stability of water films in the froth phase are excellent examples of the importance of interfacial water in the flotation process.

Silicon/Water interface

In-situ FT-IR/IRS has been used to spectroscopically characterize interfacial water near hydrophilic surfaces. Interfacial water is being examined spectroscopically over certain distances from the surface by appropriate design of the geometry and optics of the internal reflection system. The in-situ FT-IR/IRS spectra were analyzed by consideration of the OH stretching region ($3000 - 3800 \text{ cm}^{-1}$). Preliminary FT-IR/IRS experiments were conducted at a hydrophilic silicon surface in the mid-IR region. Figure 14 shows the absorbance spectra (non-normalized) of water in the OH stretching region as function of depth of penetration (d_p) from the silicon surface (30,31). The normalized spectra with respect to the number of internal reflections showed a decrease in the absorbance with an increase in d_p at larger d_p values away from the surface, thus deviating from the theory (30). Several changes in the spectra with regard to absorbance, peak shape, and position can be noticed from this figure as d_p is increased from 153 nm to 547 nm. It can be noticed from Figure 14 that a distinct change in the shape of the spectra occurred as d_p is increased. Specifically, the peak becomes broader as d_p is increased indicating changes in the relative intensities of certain bands such as those evident in the deconvoluted spectrum presented in Figure 15.

The broad peak in the spectral region shown in Figure 14 was deconvoluted using the Fourier self-deconvolution method. This unbiased method provides for useful band narrowing thus enabling the visual identification of broad and overlapping spectral features. Figure 15 shows the deconvoluted spectrum of water at a d_p of 153 nm along with the original spectrum. Three peaks centering around 3600 , 3400 , and 3200 cm^{-1} can be clearly seen from this figure. Other deconvoluted spectra of interfacial water are shown in Figure 16 for three different d_p values

Figure 14. Absorbance spectra of interfacial water at various depths of penetration (d_p) for the silicon/water system in the OH stretching region

Figure 15. Original and deconvoluted spectra of interfacial water at a silicon surface for a depth of penetration (d_p) of 153 nm in the OH stretching region

Figure 16. Deconvoluted spectra of interfacial water at various depths of penetration (d_p) for silicon/water system in the OH stretching region

ranging from 153 nm to 547 nm. The differences in these spectra as d_p is varied from 153 nm to 547 nm are immediately obvious and changes in the relative intensities of the three peaks centered about 3600, 3400, and 3200 cm^{-1} can be noticed from this figure. The peak at $\sim 3600 \text{ cm}^{-1}$, free OH stretch (32), is very weak at $d_p = 153 \text{ nm}$ and becomes very strong at $d_p = 547 \text{ nm}$ indicating that the amount of free OH increases as more and more bulk water is sampled at greater depths from the hydrophilic silicon surface. On the other hand, the relative intensities of the peaks ~ 3400 and $\sim 3200 \text{ cm}^{-1}$, hydrogen bonded OH stretch (32), decrease as the depth of penetration increases from 153 nm to 547 nm. These results suggest that hydrogen bonding is facilitated at the hydrophilic silicon surface. A closer look at the deconvoluted spectra for d_p values of 153 and 547 nm presented in Figure 16 clearly indicates that water structuring is prevalent near the hydrophilic silicon surface as is evident from the presence of the strong peak at $\sim 3200 \text{ cm}^{-1}$. The peak at $\sim 3100 \text{ cm}^{-1}$ in the deconvoluted spectra shown in Figure 16 seems to be related to the peak at 3600 cm^{-1} since they both decrease in intensity at smaller d_p values. This peak has been attributed to the first overtone of the OH bending mode in combination with the Fermi resonance (32).

It should be noted that the in-situ FTIR/IRS spectra presented in Figure 14 contain spectral information due to the presence of both surface and bulk water as discussed previously. However, it is clearly evident from the spectral features described above that the extent of water structuring (hydrogen bonding/bond ordering) decreases at greater distances from the silicon surface. Furthermore, the relatively high intensity of the peak centered at $\sim 3200 \text{ cm}^{-1}$ at the smallest d_p value (153 nm) is indicative of an ice-like structure in the arrangement of water molecules at the hydrophilic silicon surface. Unfortunately, the depth of penetration could not be

decreased below 153 nm for the silicon/water system considered due to design limitations of the available sampling accessories. Nevertheless, it is very clear from these spectral results that the in-situ FTIR/IRS technique can be used to distinguish between surface and bulk water as is evident from the distinct and obvious changes in the spectra of interfacial water with changes in the depth of penetration. Most importantly, it should be noted that there is a significant change in the shape of the water spectra at a distance from 273 to 446 nm where the peak due to free OH ($\sim 3600\text{ cm}^{-1}$) becomes very significant as shown in Figure 14.

Silicon/Heptane Interface

To further demonstrate that the changes in the spectra of interfacial water at various depths of penetration are due to changes in water structure near the surface, similar studies were conducted at the same silicon surface with a non-polar solvent, heptane. Figure 17 shows the absorbance spectra (non-normalized) in the CH stretching region for heptane at the silicon surface as a function of d_p . The total integrated absorbance normalized with respect to the number of reflections systematically increases with an increase in d_p , in excellent agreement with theory (31). It can be noticed from these spectra that there are few changes in the shape and the relative intensities of the various bands as d_p is varied from 182 nm to 1580 nm. By contrast, it is evident that changes in the spectral features of interfacial water at the hydrophilic silicon surface (Figures 14-16) are significant and are due to changes in the water structure at different distances from the surface. Such spectral changes are not observed for heptane and other nonpolar solvents (30).

Figure 17. Absorbance spectra of heptane at various depths of penetraion (d_p) for silicon/heptane system in the CH stretching region

Research in Progress

The spectral results from this work suggest that interfacial water near a hydrophilic surface has extensive hydrogen bonding as indicated by the presence of absorption bands characteristic of an ordered ice-like structure. Certainly additional work needs to be done in order to determine the range of the interfacial water structure at several other surfaces. Efforts are underway to examine the extent of water structuring or hydrogen bonding at different mineral surfaces as well as to increase the surface sensitivity of the FT-IR/IRS technique so that water structure closer to the interface can be more clearly detected with minimum interference from bulk water signals. It is expected that these spectroscopic results at different surfaces will provide crucial information on interfacial water structure to help explain the nature of structural/hydration forces which control many aspects of the flotation process.

ATOMIC FORCE MICROSCOPY

Atomic force microscopy (AFM), also known as scanning force microscopy, a recent development in surface analysis, produces images that mimic the sample topography by recording the interaction forces between the apex of a tip and a sample surface as the tip is scanned over the surface of the sample (33). The tip is fastened to a cantilever spring that has a lower spring constant than the effective spring constant between atoms. Thus, with sufficient sensitivity in the spring deflection sensor, the tip can reveal surface profiles with subnanometer resolution. The AFM can image nonconducting surfaces both in air and in aqueous environments. Therefore, the AFM has great promise for the measurement of interparticle forces involved in flotation. In this regard, A Digital Nanoscope E atomic force microscope was acquired during the grant period and

research is in progress in several different areas including characterization of the surface roughness of IREs used for adsorption density measurements and measurement of interparticle forces as a function of separation distances.

Collector Adsorption Phenomena

AFM is being used to characterize adsorbed collector colloids in soluble salt flotation systems as discussed previously and illustrated in Figure 8. Further, by using AFM, it has been demonstrated that the effect of surface roughness of the internal reflection element (IRE) on the FT-IR/IRS adsorption density calculation (Equation 1) is negligible. In order to determine the effect of roughness on surface area, topographic measurements were made with the AFM. The results of some of these measurements are shown in Figure 18. From this figure, it can be calculated that the steepest topography (located between 0.8 and 1.0 micron on the abscissa) has an ascent angle of only 4.75° . Because the area enlargement due to roughness is found as $1/\cos \theta$, the area enlargement for this steep portion of the cross-section shown in Figure 18 is only 0.34%. In addition, using the image processing software available with the Nanoscope AFM for two randomly selected 14.5×14.5 micron patches on a fluorite IRE surface, it was calculated that the area enlargement that can be attributed to surface roughness was approximately 0.1%; thus validating the adsorption density equation further. AFM topographical measurements at fluorite and calcite surfaces were also made to examine the influence of surface roughness on contact angle hysteresis at transferred LB and SA layers.

Research is in progress to characterize the adsorbed SA surfactants with regard to their positional and orientational order. Preliminary experiments are being conducted with a model substrate, mica (a layered aluminosilicate mineral) since it has been shown to provide an atomically flat plane layers.

Figure 18. Cross-sectional profile of a fluorite IRE surface as determined by AFM. (The raw data were converted from a gray scale format to the ordinate values using the AFM image and lowest and highest values along the scan line shown.)

Interparticle Forces

The greatest utility of atomic force microscopy in mineral research is for the measurement of interparticle forces. Interparticle forces are of great significance in flotation including such phenomena as aggregation, adhesion, and film thinning. These microprocesses largely depend on the particle-particle and bubble-particle interaction forces (34). A research program has been initiated during this grant period to determine the effect of adsorbed surfactants on the nature of interparticle forces responsible for selective flotation. For example, the results from particle interaction experiments suggest that both attractive and repulsive hydration forces exist and are

responsible for aggregation/dispersion behavior of soluble-salt particles in their saturated brines. Furthermore, the nature of the interaction forces responsible for the heterocoagulation of oppositely charged soluble salt mineral particles and hydrophobic collector colloids is unknown. AFM will be used to determine the nature of such forces involved in these flotation systems. Already, training with the AFM is complete and interparticle force measurements between insoluble oxide mineral particles as a function of pH and ionic strength are in progress. Figure 19 shows some preliminary AFM results from the interparticle force measurements between a silica sphere glued to the cantilever and an alumina substrate as a function of pH. Attractive, repulsive, and van der Waals forces between silica and alumina can be noticed from this figure depending on the variation of the sign of surface charge of these mineral surfaces as established by the pH of the system. It can be noticed from the Figure 19 that at pH values above 8 (Figures 19c, d, and e), a repulsive force is observed since both minerals bear a surface charge of the same sign. On the other hand, at pH values below 8, an attractive force can be noticed (Figures 19a and b) because of the oppositely charged silica and alumina surfaces and vdW interactions.

a

b

c

d

e

Figure 19. Force/radius vs. separation curves obtained by AFM at different pH values between a 15 μ silica (SiO_2) sphere and a sapphire (Al_2O_3) surface. a: pH=3.5, b: pH=4.5, c: pH=8, d: pH=10.1, e: pH=11.4.

FUTURE RESEARCH ACTIVITIES -- PROPOSAL RENEWAL

Particulate separation by froth flotation is one of the most outstanding examples of applied surface chemistry, and is used in food, petroleum, pulp/paper, and mineral industries. Further, flotation technology is now being developed to solve environmental problems including resource conservation, pollution prevention, and environmental remediation. Therefore, improvement in understanding interfacial flotation phenomena is important to develop energy efficient particulate separation processes.

Excellent progress has been made in characterizing and analyzing several nonsulfide mineral flotation systems as is evident from the number of publications which have resulted from this research program. Important topics investigated during the course of this grant period include further development and verification of the adsorption density equation, analysis of surfactant (collector) adsorption phenomena, molecular orientation and conformational order of adsorbed collector species, influence of defect states on the flotation response of KCl, and preliminary characterization of interfacial water. Research performed at the University of Utah has demonstrated the significance of these features in different nonsulfide flotation systems. Most importantly, in situ FT-IR/IRS continues to provide nonintrusive and real-time quantitative analysis of various aspects of mineral/collector adsorption phenomena. For example, depth profiling of interfacial water at mineral surfaces by in-situ FT-IR/IRS promises to provide crucial information with appropriate design changes in the geometry and optics of the experimental setup. Despite the tremendous progress made, many issues remain unresolved. In this regard, a proposal renewal has been prepared, which in addition to the continued development of in-situ FT-IR/IRS, includes several new surface chemistry techniques that will be developed to examine specific aspects of nonsulfide mineral flotation systems.

In the proposed research, two new surface spectroscopy techniques namely Raman internal reflection spectroscopy (IRS) and sum frequency generation (SFG) will be explored to study the interfacial water structure and collector adsorption phenomena. Multichannel Raman spectroscopy has already been used during the previous grant periods to study double bond reactivity of adsorbed unsaturated collector species at the fluorite and calcite surfaces using powder samples. However, in the proposed work, IRS with reactive internal reflection elements will be used to study the structure of interfacial water at a variety of nonsulfide mineral surfaces. Raman IRS offers the possibility for the examination interfacial water at distances as close as 10 nm from the surface if good collection optics and appropriate geometry of the internal reflection element can be established. Sum frequency generation (SFG), a technique based on nonlinear optics, will be evaluated for the study of interfacial phenomena occurring at mineral surfaces. SFG is a powerful surface spectroscopic tool that has recently been developed to probe different types of interfaces. The utility of this highly surface sensitive technique (designed to detect only monolayer features) will be examined for the interfacial water structure and molecular orientation of the adsorbed species at various nonsulfide mineral surfaces.

Langmuir-Blodgett deposition has proved to be an extremely important tool for study of the wetting characteristics of mineral surfaces. Preliminary research under the auspices of this grant has determined the influence of molecular orientation of fatty acid collector at fluorite and calcite surfaces on the stability and hydrophobicity of these surfaces. However, the relationship between orientation and double-bond interaction, stability and hydrophobicity of cationic collectors, and the study of other important nonsulfide minerals remain to be investigated.

Spectroelectrochemical techniques will be developed to probe the significance of electric fields on interfacial water structure as well as on conformational properties and double bond reactivity of adsorbed species. These experiments will involve single crystal electrodes simultaneously serving as internal reflection elements.

Atomic force microscopy (AFM), has demonstrated the ability to characterize the adsorbed collector colloids as well as the force-distance profiles in the vicinity of solid surfaces. This research program, initiated during the previous grant, is expected to provide significant breakthroughs with regard to the short-range forces involved in flotation systems and the effect of interfacial water structure, if any, on these interparticle forces.

Finally, adsorption phenomena for important flotation systems remain to be investigated. Rutile (TiO_2), apatite ($\text{Ca}_5(\text{PO}_4)_3\text{X}$ where $\text{X} = \text{F}, \text{Cl}, \text{OH}$ or CO_3), and scheelite (CaWO_4) minerals will be studied by in-situ FT-IR/IRS, LB, and Raman experimental techniques to establish the fundamental features of collector adsorption phenomena in these mineral flotation systems.

Already, the results obtained during the course of this grant have provided considerable insight into many aspects of interfacial phenomena critically important to flotation and many other surface chemistry related technologies. For example, the results from our DOE-supported research program have now generated interest from NTT (Nippon Telephone and Telegraph) in Japan who have asked us to help examine the interfacial characteristics of an advanced water repulsive material and who will provide modest support, \$15,000, for the collaborative effort. In addition, ZPM Inc. of CA has also expressed interest in our abilities in the analysis of interfacial phenomena and as part of their research and development effort supported by the European Economic Community will involve our laboratories in their program. Also, it should be noted that

the University of Utah has agreed to provide \$30,000 in partial support for the procurement of a new FTIR spectrometer. In view of the significant findings and the great potential for future breakthroughs, a renewal proposal has been submitted to the Office of Basic Energy Science, DOE, to extend this research program for an additional three year period.

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APPENDIX II: LIST OF PRESENTATIONS (1992-1995)

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3. J. D. Miller and M. R. Yalamanchili, "Fundamentals of Soluble Salt Flotation," presented at the Minerals Engineering '93, Cape Town, South Africa, August 23-27, 1993.
4. J. D. Miller, "Fundamental Aspects of Soluble Salt Flotation," Lecture for Faculty of Chemistry, Technical University of Gdansk, Poland, June 1, 1994.
5. J. D. Miller, "Fourier Transform Infrared Internal Reflection Spectroscopy (FTIR/IRS) for the Study of Surfactant Adsorption Phenomena," seminar presented at the University of Nevada, Reno, 14 Nov., 1994.
6. J. D. Miller, "The Surface Chemistry of Soluble Salt Flotation," RDTN Seminar of South Dakota School of Mines and Technology, Rapid City, South Dakota, 18 Nov., 1994.
7. M. R. Yalamanchili and J. D. Miller, "The Influence of Oxygen Defect States on the Surface Chemistry of Sylvite and its Flotation Response," presented at the 123rd SME Annual Meeting, Albuquerque, NM, Feb. 14-17, 1994.
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APPENDIX IV: COPIES OF PUBLICATIONS

1. J. J. Kellar, W. M. Cross, M. R. Yalamanchili, C. A. Young, "Surface Phase Transitions of Adsorbed Collector Molecules as Revealed by in situ FTIR/IRS," in: *Minerals and Metallurgical Processing*, Vol. 10, No. 2, 1993, pp. 75-80.

Surface phase transitions of adsorbed collector molecules as revealed by in situ FT-IR/IRS spectroscopy

J.J. Kellar, W.M. Cross, M.R. Yalamanchili, C.A. Young and J.D. Miller

Introduction

Researchers have long speculated regarding the adsorption state of collectors on mineral surfaces. Only recently have analytical techniques become available that allow direct in situ analysis of adsorbed layers. With reactive internal reflection elements (IREs), Fourier transform infrared spectroscopy coupled with internal reflection spectroscopy (FT-IR/IRS) allows for unobtrusive investigation of the adsorbed layer (Harrick, 1979). This technique has been used both for the in situ identification of adsorbed species and for the direct calculation of collector adsorption density in real time from infrared spectral data (Miller and Kellar, 1988).

The reactive mineral IRE serves both to internally reflect the infrared light and to act as a substrate at which collector adsorption can be monitored. Shown in Fig. 1 is a schematic of light being internally reflected in an IRE. As the light is totally reflected at the interface, an evanescent wave propagates a short distance (typically a few microns) away from the IRE, and sampling of the interfacial region occurs. Because of multiple internal reflections, great sensitivity can be obtained. Flotation systems for which this method has been demonstrated include CaF_2 /oleate, Al_2O_3 /dodecylsulfate, CaCO_3 /oleate, ZnS /xanthate and KCl /octylamine (Miller and Kellar, 1988; Kellar et al., 1989, 1990; Miller et al., 1990).

Of particular interest to flotation chemists is the conformational behavior of the alkyl chain of adsorbed collector molecules. In the simplest sense, conformation can be thought of as the relative flexibility of the hydrocarbon chain caused by rotations about carbon-carbon single bonds. The flexibility is described by the amount of gauche/trans conformations in the alkyl chain.

Figure 2 shows examples of gauche and trans conformations (rotational isomers or rotamers) in a hydrocarbon chain. These two conformations are observed when the terminal methylene groups in any four-carbon subchain are on the same side (gauche) or opposite sides (trans) of the plane of the middle carbon-carbon bond. A gauche conformer (rotamer) is thus a state of maximum potential energy, whereas a trans conformer is a state with minimum potential energy. The difference between these states has been found to be approximately 0.5 to 0.8 kcal/mole (Mead et al., 1986).

The relative number of butane molecules present as gauche conformers with respect to trans conformers can be calculated from the Boltzmann equation (Mead et al., 1986). At 25° C approximately 66% of the butane molecules are trans rotamers.

Fig. 1—Schematic of light undergoing multiple internal reflections in an IRE.

However at 100° C, only 33% of butane molecules are trans rotamers.

Exposing the hydrocarbon chain to a polar, rather than an apolar, medium should also cause an increase in the number of gauche butylene groups in a hydrocarbon chain, although this effect has been difficult to observe experimentally (Mead et al., 1986). Forming a crystalline hydrocarbon is equivalent to decreasing the temperature, which greatly increases the amount of trans butylene groups present in the chain.

From the preceding discussion, a picture of the solution species of concern can be developed. The collector monomer should exhibit the greatest number of gauche rotamers and most likely will look crumpled or balled-up to reduce the surface area in contact with water. The micellar form is expected to be aggregated, with the hydrocarbon chain existing in a less polar environment.

These characteristic conformational features have been examined by FT-IR spectroscopy for various liquid phases of alkanolic acids (Umemura et al., 1981; Cameron et al., 1982a; Yang et al., 1986; Wong, 1987; Wong and Mantsch, 1983; Cross et al., 1992), phospholipid membranes (Fringeli, 1980; Casal and Mantsch, 1985; Wong et al., 1988;

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Fig. 2 — Examples of trans (left) and gauche (right) butylene linkages. The asterisk indicates the gauche bond.

Mendelsohn et al., 1989; Casal and McElhany, 1990) and alkylsulfates (Kawai et al., 1983; Mantsch et al., 1984; Hui and Labes, 1987; Holler and Callis, 1989; Scheuing and Weers, 1990; Cross et al., 1991). Investigations have mainly followed two general trends:

- determining shifts in the position of the $-\text{CH}_2$ stretching bands (Umemura et al., 1981; Cameron et al., 1982a; Kawai et al., 1983; Casal and Mantsch, 1984; Mantsch et al., 1984; Wong and Mantsch, 1985; Yang et al., 1986; Wong, 1987; Hui and Labes, 1987; Wong et al., 1988; Scheuing and Weers, 1990; Cross et al., 1991) and, more recently,
- examining $-\text{CH}_2$ wagging bands that are specific to certain gauche or trans conformations (Holler and Callis, 1989; Mendelsohn et al., 1989; Casal and McElhany, 1990).

In both cases, these bands give data characteristic for each phase studied. Thus it is clear that phase transitions can be distinguished by specific infrared spectral changes. In terms of the $-\text{CH}_2$ stretching bands, higher wavenumbers are indicative of a high population of gauche rotamers. Conversely, lower wavenumbers are indicative of more trans rotamers.

In this paper FT-IR/IRS with reactive internal reflection elements has been used to examine some of the conformational characteristics exhibited in three flotation systems: CaF_2 /oleate, Al_2O_3 /dodecylsulfate and KCl /octylamine.

Experimental

Infrared spectra were recorded with a nitrogen gas- or dry-air-purged Digilab FTS-40 FT-IR spectrometer using a narrow-band liquid, nitrogen-cooled, mercury-cadmium-telluride detector. All spectra were at least 1024 co-added scans at resolutions of 8, 4 or 1 cm^{-1} , as noted in the text. A Twin Parallel Mirror

Reflection 320 liquid, internal reflection accessory (Harrick Scientific) was used with a Haake F3 constant-temperature bath to obtain thermostated in situ IRS spectra. Transmission spectra were collected with a Spectra-Tech demountable, liquid transmission cell with fluorite windows. All chemicals used were reagent-grade. Single-crystal minerals were machined and polished into 50- x 10-mm internal reflection elements. All IRE were 1 mm in thickness. IRE angles were verified by goniometric measurement.

Spectra of adsorbed collector were obtained by subtracting deuterium oxide, D_2O , spectrum from a D_2O /collector spectrum, both of which were ratioed against the clean IRE background. More complete experimental details can be found elsewhere (Miller and Kellar, 1988; Kellar et al., 1989, 1990, 1991; Kellar, 1991; Cross et al., 1991; Yalamanchili et al., 1991; Kellar et al., 1992).

Results and discussion

The conformational analysis of the surface state is based on a detailed examination of systematic shifts in the asymmetric $-\text{CH}_2$ and symmetric $-\text{CH}_2$ stretching vibrations. Specifically, liquid transmission spectra of collector/solution are compared with spectra of the adsorbed collector at the surface of particular mineral IRE. From similarities in the band position of these spectra, the conformations of adsorbed collectors are thus determined.

Shown in Table 1 is the frequency of the asymmetric $-\text{CH}_2$ stretching band for solution phases of various collectors common to froth flotation systems. The monomeric and micellar phases are well known to most flotation chemists. The liquid crystalline and coagel phases are somewhat less familiar. The most common liquid crystals found are hexagonal and lamellar. The hexagonal liquid crystal can be thought of as an aggregate

Table 1 — Asymmetric $-\text{CH}_2$ stretching frequency wavenumbers (cm^{-1}) for selected surfactants in various states.

Surfactant	Monomer	Micelle	Coagel	Liquid crystal	Solid	Reference
Sodium n-octanoate	2936	2928				Umemura, et al., 1981
Sodium oleate		2926	2920			Cameron, et al., 1982
Sodium dodecylsulfate	2934	2928	2918	2924		Cross, et al., 1991
n-octylamine hydrochloride	2937	2933			2924	Yalamanchili, et al., 1991
n-octylamine hydrochloride (KCl-saturated D_2O)	2935	2929			2924	Yalamanchili, et al., 1991

Fig. 3 — Frequency change (a) and corresponding spectra (b) of the asymmetric $-\text{CH}_2$ stretching band during oleate adsorption on a fluorite IRE at 25°C and $1 \times 10^{-5}\text{ M}$ oleate.

of cylindrical micelles with each micelle positioned according to a hexagonal lattice. The lamellar liquid crystals are planar, bilayered aggregates of single molecules. Common examples of liquid crystals are the thick soap/water mixture found on the bottom of soap dishes, as well as biological cell membranes.

The coagel phase is most often described as a poorly hydrated crystalline solid. In appearance this phase is usually opaque and microscopically heterogeneous, most resembling toothpaste. An example of a coagel occurs during the transformation of cell membranes in biological systems. These membranes are lamellar liquid crystals at normal body temperatures but transform to coagels when exposed to a body temperature drop of 5 to 10 degrees. Also, cholesterol buildup in arteries can result in coagel formation. The liquid crystalline and coagel phases each have a specific amount of conformational order (Tardieu et al., 1973; Collings, 1990).

From Table 1, one can determine the relative conformation of various phases. For example, the monomer of sodium dodecylsulfate has an asymmetric $-\text{CH}_2$ stretching frequency of 2934 cm^{-1} and a significant population of flexible gauche rotamers in comparison to the coagel phase, which has a frequency of 2918 cm^{-1} . At the lower frequency, the alkyl chain is predominantly in the all-trans conformation. Armed with bulk phase information regarding conformational states of the various surfactants, attention can now be turned to adsorbed collectors and their alkyl conformational state.

Fluorite/oleate

Recently, using in situ FT-IR/IRS, the fluorite/oleate flotation system was thoroughly investigated (Kellar, 1991; Kellar et al., 1991). In these analyses it was determined from infrared spectral data that, at solution concentrations less than $3 \times 10^{-5}\text{ M}$, oleate was chemisorbed. Also, at concentrations greater than this, a surface-precipitated calcium oleate resulted.

Conformational analysis has been performed for adsorbed oleate at concentrations that give these two, different, adsorbed oleate species. Shown in Fig. 3a is the band position of the asymmetric $-\text{CH}_2$ band as a function of adsorption density at 25°C from an oleate concentration of $1 \times 10^{-5}\text{ M}$. This dependence was established from peak maxima determined by a peak-picking algorithm (Digilab,

Fig. 4 — Conformation of the chemisorbed oleate species at the surface of fluorite for different levels of adsorption density revealing the transition from the gauche state at submonolayer coverage to the more rigid trans state at near monolayer coverage. Gauche bonds are designated with asterisks (*).

Fig. 5 — Change in frequency of the asymmetric $-\text{CH}_2$ stretching band as a function of temperature for equilibrium oleate adsorption on a fluorite IRE at each temperature.

1988) from the overlaid spectra (resolution 4 cm^{-1}) presented in Fig. 3b. Using a similar algorithm, Cameron and co-workers have shown that changes in peak maxima can be accurately determined for changes as small as a hundredth of a wave number (Cameron et al., 1982).

From Fig. 3 it can be seen that initially the adsorbed species have a band centered at 2924.5 cm^{-1} , but with continued loading on the fluorite IRE, the band shifts to 2920.0 cm^{-1} . The higher frequency position is associated with the alkyl chains of the adsorbed oleate having a large proportion of flexible gauche rotamers (the gauche state). The lower frequency, reached after 30 hours of equilibration, is associated with the alkyl chains being in a rigid, predominantly all-trans conformation (the trans state). It should be noted that the spectra presented in Fig. 3b are for adsorbed oleate species and not for oleate species in solution. Even in the worst case, the oleate species in solution ($1 \times 10^{-5}\text{ M}$) contribute less than 1% at the lowest adsorption density shown in Fig. 3a.

It appears that the initially adsorbed oleate species have few nearest neighbors, and consequently, the alkyl chains are highly mobile with a significant number of gauche rotamers. Upon further loading, the adsorbed oleate species begin to interact through van der Waals' forces. Consequently, the number of gauche bonds is reduced, and the alkyl chains stabilize in the more rigid trans state.

The actual number and position of the gauche bonds in the adsorbed species were not determined. However, it is believed that, with increased loading, the gauche bonds progress toward the tail-end of the hydrocarbon chain (Zerbi et al., 1981; Rabolt, 1987). This scenario is depicted in Fig. 4 from top to bottom and left to right. The transition state depicts the transformation from the gauche state at low adsorption density to the trans state at equilibrium ($1 \times 10^{-5}\text{ M}$ oleate) and explains the shift in band position described in Fig. 3. Unlike previous illustrations, Fig. 4 also pictures the chemisorbed oleate molecules being monocoordinated to the fluorite surface through the oxygen atoms in the polar head group. Such a hypothesis is supported by in situ infrared spectra that have positively identified chemisorbed oleate on fluorite (Kellar, 1991; Kellar et al., 1991).

After 30 hours of equilibration at 25°C , the temperature of the fluorite IRE and oleate solution was raised to 40°C , 60°C and 80°C . Each temperature was held for 10 hours. Shown in Fig. 5 is the band position of the asymmetric $-\text{CH}_2$ band at each of these temperatures. This increase in frequency with increased temperature is the reverse of what was witnessed at 25°C with an increase in oleate adsorption, namely a change in the alkyl

Fig. 6 — Adsorption isotherm for the physisorption of surfactant SDS at an alumina surface. CHMC indicates the critical hemimicelle concentration, and CMC shows the critical micelle concentration (adapted from Somasundaran et al., 1988).

chains from the rigid, predominantly trans state to the more mobile and disordered gauche form. The frequency shift occurs primarily between 25° and 40°C , which is the temperature range where Cameron et al. (1982a) found a coagel-to-micelle transition of sodium oleate. Thus, the results presented here for oleate adsorption suggest that, at room temperature, these adsorbed aggregates behave more like a gel or coagel; they resemble micelle only at elevated temperatures.

In addition to the conformational state of chemisorbed oleate a similar analysis was performed on surface-precipitated oleate. It was found that at both 25° and 40°C , the asymmetric $-\text{CH}_2$ stretching frequency remained constant between 2920 to 2921 cm^{-1} . From this behavior one can conclude that surface precipitated species have alkyl chains in the predominantly all-trans conformation. Furthermore, this packing of the calcium oleate remains, even at elevated temperatures.

Alumina/sodium dodecylsulfate

In the absence of chemisorption, the isotherm for collective adsorption at a mineral oxide surface is generally divided into four regions, as shown for the alumina/SDS (sodium dodecylsulfate) system in Fig. 6 (Scamehorn et al., 1982; Bitir and Harwell, 1987; Besio et al., 1988; Somasundaran et al., 1988). Region I is attributed to Henry's Law-type adsorption of monomers. The increase of adsorption in region II is often characterized as the onset of surface aggregation. The boundary between region I and II is called the critical hemimicelle concentration. The cause of the slope change in region III is more debatable and is ascribed to a reversal in sign of the surface charge (Somasundaran et al., 1988) or to the distribution of pair adsorption energies (Bitir and Harwell, 1987). Region IV usually occurs at a solution concentration exceeding the CMC (critical micelle concentration), and the plateau region is most often attributed to the solution monomer concentration attaining a constant value.

Comparison of the transition between regions I and II at regions II and III with the solution behavior of SDS has shown that there are very good correlations both between the adsorption density at the region I/II boundary and the CMC and between the adsorption density at the region II/III boundary and the micelle/coagel transition (Cross et al., 1991). This enables

Fig. 7—Effect of adsorption density on the asymmetric-CH₂ stretching band frequency. These in-situ FT-IR/IRS spectral data were obtained at different times for adsorption from various solutions.

the prediction of the surface phase for the adsorbed SDS species. These predictions are shown in Table 2.

Adsorbed SDS on alumina was evaluated for adsorption densities that correspond to regions II and III of Fig. 6. Shown in Fig. 7 is a plot of adsorption density determined from spectral data (Cross et al., 1991) vs. frequency of the asymmetric -CH₂ stretching band. For adsorption densities that correspond to region II of Fig. 6, it can be noted that a plateau frequency occurs at approximately 2924 cm⁻¹. In comparison to reported bulk SDS phases (Table 1), this value corresponds most closely to a hexagonal liquid crystal-type species. It is not possible at the present time to differentiate between the hexagonal liquid crystal and the cylindrical micelle that composes the liquid crystal solely on the basis of the asymmetrical -CH₂ stretching band.

In Fig. 7, the second plateau, at approximately 2922.5 cm⁻¹, corresponds to adsorption densities represented by region III of Fig. 6. The asymmetric -CH₂ stretching frequency of 2922.5 cm⁻¹ for the adsorbed SDS appears to be a mixture of coagel (2918 cm⁻¹) and liquid crystalline (2924 cm⁻¹) components. It is interesting to note that at adsorption densities greater than 1 x 10⁻⁹ mol/cm², the asymmetric -CH₂ stretching frequency decreases rapidly, indicative of a substantial increase in the trans character of the alkyl chains of adsorbed SDS molecules.

Sylvite/octylamine

The asymmetric -CH₂ stretching frequency also was monitored for the sylvite/*n*-octylamine flotation system (Yalamanchili et al., 1991). The primary difference between this system and the previous systems is that adsorption occurred from a saturated KCl brine that was necessary to prevent the dissolution of the IRE. Shown in Table 3 is the asymmetric -CH₂ stretching frequency as a function of *n*-octylamine adsorption density. As before, the adsorption density was determined from in situ spectral data.

The -CH₂ asymmetric stretching frequencies of adsorbed octylamine on the sylvite IRE do not change appreciably with time, as shown in Table 3. Initially, the adsorbed octylamine has an asymmetric -CH₂ stretching band position of about 2929 cm⁻¹, which decreases only slightly after about 10 hours of equilibration time. Of greater significance is the fact that the asymmetric -CH₂ stretching frequency for the adsorbed

Table 2 — Adsorption density, predicted surface phase, and predicted asymmetric -CH₂ stretching frequency for alumina/SDS at pH 6.5 and 0.1 M NaCl.

Region	Adsorption density (10 ⁻¹¹ x mol/cm ²)	Surface phase	Asymmetric -CH ₂ stretching frequency (cm ⁻¹)
I	<0.1	monomer	2934
II	0.1–15.0	micelle	2928, 2924
III	15.0–67.0	coagel	2920
IV	>67.0	coagel	2920

Table 3 — Asymmetric -CH₂ stretching frequencies of adsorbed octylamine at various adsorption densities.

Adsorption density (mol/cm ² x 10 ⁻¹⁰)	-CH ₂ stretching frequency (cm ⁻¹)
1.55	2928.0
2.80	2927.9
4.92	2924.0
3.51	2927.8
3.40	2927.5
4.02	2924.0
11.57	2927.9
21.27	2927.8

octylamine generally remains constant at about 2927 to 2928 cm⁻¹ throughout the complete adsorption isotherm (see Table 3). The anomalous results at 4.92 x 10⁻¹⁰ mol/cm² and at 4.02 x 10⁻¹⁰ mol/cm² may be due to crystallization or etching effects during the experiment.

These results suggest that, in the KCl/octylamine system, the surface state of the adsorbed species is of a micellar structure for both monolayer coverage and high adsorption densities. In contrast to these results, the surface state of the adsorbed species in the CaF₂/oleate and Al₂O₃/dodecylsulfate systems was found to have coagel- or liquid crystal-type structures at room temperature. Thus it appears that the high ionic strength conditions inhibit conformational changes that are favored in more conventional flotation systems.

Summary

It has been shown by inspection of FT-IR/IRS spectra that the alkyl conformation of adsorbed collectors can be determined. The conformations of adsorbed collectors were interpreted in terms of bulk solution phases of the collectors. Such analysis was performed on the CaF₂/oleate, Al₂O₃/SDS and KCl/octylamine flotation systems. It was found that each system has unique conformational behavior, depending upon variables such as adsorption density and temperature. For the CaF₂/oleate system, the adsorbed species resemble a coagel at room temperature. Raising the temperature of the chemisorbed species to 40° C caused the adsorbed oleate to become micellar. Liquid crystalline-adsorbed species were observed in the Al₂O₃/dodecylsulfate system at low adsorption densities. As the adsorption density increased, the adsorbed species resembled a coagel/liquid crystal mixture. In all cases, octylamine adsorbed by KCl appeared micellar in nature.

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Verification of the Internal Reflection Spectroscopy Adsorption Density Equation by Fourier Transform Infrared Spectroscopy Analysis of Transferred Langmuir-Blodgett Films

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Recent research has demonstrated the utility of the internal reflection spectroscopy (IRS) adsorption density equation for in situ study of surfactant adsorption phenomena. The IRS adsorption density equation has been examined by several researchers and in one form is $\Gamma = (A/N - \epsilon C_b d_e)/1000\epsilon(2d_p/d_e)$, where Γ is the adsorption density of adsorbed species, A/N is the absorbance per reflection, ϵ is the integrated molar absorptivity, C_b is the bulk concentration of the surfactant, d_e is the effective thickness, and d_p is the depth of penetration. Previously, the validity of the adsorption density equation had only been confirmed from solution depletion measurements using high surface area powders. Now a more direct examination of the IRS adsorption density equation has been completed in our laboratory using a Langmuir-Blodgett (LB) FTIR/IRS technique. Experimental results with LB films of 18C fatty acids transferred to the internal reflection element provide further confirmation of the validity of the adsorption density equation and thus clearly show that the adsorption density equation can be used, with confidence, for in situ and ex situ studies of surfactant adsorption phenomena.

Introduction

Internal reflection spectroscopy (IRS), alternatively referred to as attenuated total reflection (ATR), is a method for recording the spectrum of species which are in intimate contact with an internal reflection element (IRE). The technique was first proposed by Harrick¹ and independently by Fahrenfort² in the 1960s. Reviews of IRS have been given by several researchers.³⁻⁷ A combination of multiple internal reflection with Fourier transform infrared spectroscopy (FTIR) gives an improved signal/noise ratio over more conventional IR sampling and allows for the study of surfactant adsorption on single crystal IRE surfaces even at submonolayer coverage.

The adsorption of surfactants is important in many areas of technology including suspension stabilization, detergency, tribology, and flotation.⁸⁻¹¹ In recent years, FTIR/IRS has been used with reactive internal reflection elements (IREs) to determine in situ and in real time the adsorption density of surfactant at solid-liquid interfaces using the IRS adsorption density equation.¹²⁻¹⁵ Sperline et al.¹² calculated the adsorption density of cetylpyridinium chloride at the surface of a reactive zinc selenide IRE for

both aqueous and organic solutions. The results were validated, with a relative standard deviation $\pm 25\%$, by comparison with the Γ values determined by solution depletion experiments with high surface area powders. Subsequently, researchers at the University of Utah have developed the use of reactive internal reflection elements to study surfactant adsorption and measure adsorption densities using the IRS adsorption density equation. Many different internal reflection elements have been used including Al_2O_3 ,^{13,16-18} CaF_2 ,¹³⁻¹⁷ KCl,¹⁹ and CaCO_3 .²⁰ In this way adsorption isotherms were constructed and in several instances the validity of the IRS adsorption density equation was confirmed by solution depletion measurements using high surface area powders. Figure 1 compares in situ FTIR/IRS adsorption densities calculated from the IRS adsorption density equation¹⁴ with those determined by solution depletion using an ex-situ radiotracer technique.²¹ Based on these results the IRS adsorption density equation has been used to analyze protein adsorption phenomena.²²

Now, a more direct examination of the IRS adsorption density equation has been completed in our laboratory using a Langmuir-Blodgett (LB)²³⁻²⁶ FTIR/IRS technique.

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Figure 1. Comparison of the adsorption of oleate by fluorite using ex situ solution depletion (radiotracer)¹⁴ and in situ (FTIR/IRS)²¹ techniques.

In this paper, the adsorption densities of transferred LB monolayer films of stearic and oleic acids were calculated from FTIR/IRS spectra using the IRS adsorption density equation and compared with adsorption densities obtained from the measured LB surface pressure-area isotherms. Molecular orientation in the monolayer after transfer was examined by polarized light FTIR/IRS experiments and a detail discussion of these results will be presented in another publication.²⁷

Experimental Section

Materials and Equipment. Stearic acid (+99% pure) obtained from Johnson-Matthey and oleic acid (+99% pure) obtained from Sigma Chemical were used without further purification. Chloroform and carbon tetrachloride (99.99% pure) were used as received from EM Science. The LB film deposition system was a Lauda Langmuir film balance manufactured by SYBRON/Brinkmann. FTIR experiments were conducted with a dry-air purged Bio-Rad Digilab Division FTS-40 FTIR spectrometer equipped with a liquid-nitrogen-cooled wide-band mercury cadmium telluride (MCT) detector. All spectra were obtained at a resolution of 8 cm⁻¹. Deuterium oxide (+99.9% pure) was purchased from Cambridge Isotope Laboratories and was used as received. Milli-Q water (+18 MΩ) was used in all experiments. Calcium fluoride single-crystal parallelepiped internal reflection elements (50 × 10 × 2 mm, 75° acute angle) were purchased from Optovac, Inc. Calcium fluoride windows obtained from Spectra Tech, Inc., and germanium windows obtained from Harrick Scientific were used for molar absorptivity measurements.

LB Film Preparation. Monolayer spreading solutions were produced by dissolving stearic acid or oleic acid in chloroform; the concentrations of stearic and oleic acids were 7.6 and 4.8 mM, respectively. The monolayers were spread from the chloroform solutions on the surface of high purity water (+18 MΩ) with a large enough area to achieve complete spreading. Chloroform was permitted to evaporate for 30 min before compression of the Langmuir film. Surface pressure-area isotherms were measured using the Langmuir film balance at 23 °C.

For preparation of a monolayer, the Langmuir-Blodgett technique²³⁻²⁵ was applied. A calcium fluoride single crystal (50 × 10 × 2 mm, 75° acute angle) was used as the substrate. The substrate was dipped into the subphase (water) before spreading the monolayer solution. After chloroform was permitted to evaporate for 30 min, the substrate was withdrawn at a speed of 3 mm/min with the surface pressure held at the desired level.

Figure 2. Schematic of light undergoing multiple total internal reflections in an IRE (θ is the incident angle of light for internal reflection).

This transfer speed is in the range of typical speeds for transferring the initial monolayer onto a prepared substrate,²⁶ from 10 to about 1 mm/s, and therefore should ensure the uniform transfer of the monolayer to the substrate. While the monolayer was transferred onto the calcium fluoride surface, all the transfer curves were recorded so as to ensure that each monolayer was transferred at a constant pressure. The variation in the surface pressure of the transfer was within ± 1 mN/m. For multiple deposition experiments, the Y-type deposition method was used.

Transmission Spectroscopy. Liquid transmission measurements using a demountable liquid transmission cell with a spacer and calcium fluoride windows were conducted to determine molar absorptivities of stearic or oleic acid in carbon tetrachloride and sodium oleate in D₂O. The path length of the sample was evaluated more accurately using an interference fringe counting technique^{28,29} rather than by the specified thickness of the calcium fluoride windows. The calcium fluoride windows were used only for the molar absorptivity measurement of pure oleic acid. Even with the thinnest available (15 μ m), the absorbance of pure oleic acid at the frequencies was too high to be measured. Therefore, transmission measurements of pure oleic acid were carried out after spreading the oleic acid between the windows without a spacer in order to obtain band absorbances which obeyed the Beer-Lambert law. The path length of the pure oleic acid sample was found by an interference fringe counting technique or by applying the Beer-Lambert law in some cases. All the spectra were the result of 512 or 1024 coadded scans with the same IR beam size.

FTIR/IRS. Due to the nature of organic contaminants on such surface chemistry studies, the following cleaning procedure was applied to clean the IRE: First, the IRE was rinsed with acetone/water/methanol/water. Second, the IRE was placed in a Tegal plasma chemistry reactor and subjected to oxygen plasma for 30–40 min. In some cases, the surface of the IRE was polished with alumina powders (0.5 or 0.05 μ m) and washed with high purity water to create a fresh surface.

An internal reflection cell with a variable angle holder (Harrick Scientific) was used. The entrance face of the parallel calcium fluoride IRE was cut at a 75° angle and the variable angle holder was set at 42° giving an incident angle of 61° for each internal reflection. The background spectrum for the measurements was the single-beam spectrum of the clean IRE. Sufficient care was taken to reposition the IRE in its holder after the LB film was transferred. All spectra were recorded as 1024 coadded scans with the same IR beam size. Absorbance spectra of the LB films of stearic and oleic acids were recorded against the background spectra of a clean calcium fluoride IRE.

FTIR/IRS Adsorption Density Equation

Electric Field Amplitudes. IRS involves the internal reflection of light through an IRE. Figure 2 is a schematic representation of a ray of light undergoing multiple internal reflections in an IRE. For light to be totally internally reflected the following conditions must be satisfied:

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$$n_1 > n_2 \quad (1)$$

$$\theta > \theta_c, \quad \theta_c = \sin^{-1} n_{21} \quad (2)$$

where n_1 is the refractive index of IRE, n_2 is the refractive index of sample, $n_{21} = n_2/n_1$, θ is the incident angle of light for internal reflection, and θ_c is the critical angle. As the light is totally reflected at the IRE/sample interface, an evanescent wave passes from the IRE and decays exponentially into the sample. The propagating distance is typically a few micrometers or less away from the IRE surface. This wave consists of the three electric field vectors which can interact with the sample. The electric field amplitudes are given by³⁰

$$E_y = \frac{2 \cos \theta}{(1 - n_{21}^2)^{1/2}} \quad (3)$$

$$E_x = \frac{2 \cos \theta (\sin^2 \theta - n_{21}^2)^{1/2}}{(1 - n_{21}^2)^{1/2} [(1 + n_{21}^2) \sin^2 \theta - n_{21}^2]^{1/2}} \quad (4)$$

$$E_z = \frac{2 \cos \theta \sin \theta}{(1 - n_{21}^2)^{1/2} [(1 + n_{21}^2) \sin^2 \theta - n_{21}^2]^{1/2}} \quad (5)$$

For perpendicularly polarized light (transverse electric wave), $E_0^2 = E_y^2$, and for parallel polarized light (transverse magnetic wave), $E_0^2 = E_x^2 + E_z^2$.

Depth of Penetration and Effective Thickness. Harrick³⁰ arbitrarily defined the depth of penetration, d_p , to be the distance required for the electric field amplitude to fall to $1/e$ of its value at the surface

$$d_p = \frac{\lambda}{2\pi n_1 (\sin^2 \theta - n_{21}^2)^{1/2}} \quad (6)$$

where λ is the wavelength of the light.

Harrick³⁰ also defined an effective thickness, d_e , as the thickness of material which gives the same absorbance in transmission spectra at normal incidence as that found from IRS

$$d_e = \frac{n_{21} E_0^2 d_p}{2 \cos \theta} \quad (7)$$

Accordingly, the effective thicknesses for perpendicular (TE wave) and parallel (TM wave) polarization are, respectively⁷

$$d_{e,1} = \frac{2n_{21}d_p \cos \theta}{1 - n_{21}^2} \quad (8)$$

$$d_{e,2} = \frac{2n_{21}d_p \cos \theta (2 \sin^2 \theta - n_{21}^2)}{(1 - n_{21}^2) [(1 + n_{21}^2) \sin^2 \theta - n_{21}^2]} \quad (9)$$

Thus, the average effective thickness of the unpolarized radiation is approximated by⁶

$$d_e = \frac{d_{e,1} + d_{e,2}}{2} \quad (10)$$

Absorbance per Reflection. Tompkins³¹ derived an equation that described the absorbance per reflection for multiple IRS when a thin film is adjacent the IRE

$$\frac{A}{N} = \frac{n_{21} E_0^2 \epsilon}{\cos \theta} \int_0^{\infty} C(z) \exp\left(-\frac{2z}{d_p}\right) dz \quad (11)$$

where A is the integrated absorbance (cm^{-1}) due to internal reflections, N is the number of internal reflections, ϵ is the

integrated molar absorptivity ($\text{L}/\text{cm}^2 \text{mol}$), z is the distance from the IRE surface (cm), and $C(z)$ is the concentration as a function of distance from the IRE surface (mol/L). The number of internal reflections, N , can be found for parallelepiped geometry from the relationship

$$N = \frac{l}{h} \cot \theta \quad (12)$$

where l is the length of the IRE with adsorbed surfactant and h is the thickness of an IRE.

Molar Absorptivity. The molar absorptivity, ϵ , can be evaluated from transmission experiments and using the Beer-Lambert equation

$$A = \epsilon b C \quad (13)$$

where b is the thickness of sample (cm) and C is the surfactant concentration (mol/L). The thickness of the sample, b , can be estimated using the following equation and an interference fringe counting procedure^{22,29}

$$b = \frac{k}{2n(f_1 - f_2)} \quad (14)$$

where n is the refractive index of sample, f_1 and f_2 are the wavenumbers where counting starts and ends (cm^{-1}), and k is the number of fringes.

Adsorption Density Equation. By assuming a concentration step profile for species adsorbed or in intimate contact with the IRE, i.e., $C(z) = C_i + C_b$ for $0 < z < t$, and $C(z) = C_b$ for $t < z < \infty$ and substituting d_p and d_e into eq 11, together with the approximation that the thickness of the coated layer, t , is much less than d_p ($\exp(-2t/d_p) = 1 - 2t/d_p$) the absorption per reflection, A/N , is

$$A/N = \epsilon C_b d_e + \epsilon (2d_p/d_e) (C_i t) \quad (15)$$

Substituting $C_i t = 1000\Gamma$ and rearranging eq 15, the FTIR/IRS adsorption density equation similar to the one proposed by Sperline et al.¹² can be obtained

$$\Gamma = \frac{A/N - \epsilon C_b d_e}{1000 \epsilon (2d_p/d_e)} \quad (16)$$

where Γ is the adsorption density of adsorbed species (mol/ cm^2).

In some cases, the absorbance contribution due to transmission through adsorbed surfactant at the IR entrance and exit faces of the IRE might be considered and this correction will be discussed elsewhere.³² Generally, this contribution, if present, amounts to only a few percent of the calculated adsorption density and can frequently be ignored.³³ It is clear that this relative contribution to the total absorbance decreases with an increasing number of internal reflections.

To calculate the adsorption densities for deposited LB films, eq 16 should be modified as follows: The concentration of the LB film, $C(z)$, is a step function with $C(z) = C_i$ for $0 < z < t$ and $C(z) = 0$ elsewhere, i.e., $C_b = 0$. Therefore, for the LB films, the FTIR/IRS adsorption density equation is

$$\Gamma = \frac{A/N}{1000 \epsilon (2d_p/d_e)} \quad (17)$$

On the other hand the area/molecule can be directly determined for LB films found at the air/water interface

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Figure 3. Surface pressure-specific area isotherms for stearic acid and oleic acid.

during Langmuir experiments. Thus, the adsorption density of LB monolayer films can be monitored quantitatively from the surface pressure-area isotherm and a direct measurement of the adsorption density for the transferred monolayer can be made without introducing uncertain assumptions. It should be noted that, for good transfers, the orientation packing and characteristics of molecules on the substrate are expected to be similar to those on the water subphase.^{25,26} Although some researchers challenge this point,³⁴ it is expected that only small variations in packing density occur due to transfer.³⁵⁻³⁸ These effects can be minimized by careful control of experimental conditions. Therefore, the adsorption densities found from the surface pressure-area isotherms for LB films can be compared with the adsorption densities calculated using the FTIR/IRS adsorption density equation, eq 17.

Results and Discussion

Surface Pressure-Area Isotherms. Figure 3 shows the surface pressure-specific area (π -A) isotherms for stearic and oleic acids at the air/water interface as obtained using the Langmuir film balance. These isotherms were found to be in excellent agreement with the isotherms reported in the literature.^{39,40} As indicated by a rapid decrease in surface pressure, the monolayer of stearic acid ruptured at approximately 20 Å²/molecule. For oleic acid, the trend was quite different. The surface pressure increased up to 31 mN/m at about 27 Å²/molecule. As further compression occurred the surface pressure did not change appreciably. It appears that due to unsaturation, oleic acid has a higher effective molecular cross-sectional area, the liquid expanded state exists over a wider range of molecular areas, and oleic acid has a higher compressibility than that observed for stearic acid. Gaines²⁵ explained the expanded behavior of the oleic acid monolayer in terms of the effect of unsaturation on packing considerations. Based on packing in a crystal, oleic acid has an effective area of 22.5 Å²/molecule for compact packing and stearic acid has 20.5 Å²/molecule.⁴⁰ It is also known that the unsaturated C=C bond is more hydrophilic

Figure 4. Comparison of the FTIR/IRS spectra of trans LB films of stearic acid (1 and 5 monolayers) with the transmission spectrum of stearic acid in CCl₄ solution.

than saturated C—C bonds and upon compression attraction between the double bond and water molecule causes the packing area of oleic molecules to reflect an expanded state.

Characteristic of the Transferred LB Films. examination of the π -A isotherms, the spread monolayers of stearic acid were found to be in liquid condensed superliquid states³⁹ at the surface pressures of transfer, whereas the monolayers of oleic acid were in the liquid expanded state. Figure 4 compares the typical transmission spectrum of stearic acid in CCl₄ and the IRS spectra of transferred LB films of stearic acid. Of particular importance is that the peak at 1710 cm⁻¹ (free acid stretch in the transmission spectrum) is not evident in the transferred monolayer of stearic acid at the surface of the calcium fluoride IRE. Rather, a new absorption at 1550 cm⁻¹ has appeared. It seems clear that the transferred stearic acid molecules have reacted with calcium sites at the surface of the calcium fluoride IRE, resulting in a chemisorbed monolayer. As shown in Figure 5, the same result was obtained for the transferred monolayer of oleic acid. This single band in the vicinity of 1550 cm⁻¹ was confirmed by previous IR experiments on various calcium bearing minerals including fluorapatite (CaF₂),⁴¹ calcite (CaCO₃),⁴² and apatite (Ca₅X(PO₄)₃, X = F, OH, etc.).⁴² The free acid C=O stretching at 1701 cm⁻¹ reappeared for multilayer deposition, as in Figure 4c, indicating that only the fatty acid head of the first monolayer reacts with the surface calcium of the calcium fluoride IRE.

Molar Absorptivity by Transmission Experiment. Use of the FTIR/IRS adsorption density equation requires that the molar absorptivity, ϵ , be determined *a priori*. The molar absorptivities for oleic and stearic acid

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Figure 5. Comparison of the FTIR/IRS spectrum of a transferred LB monolayer film of oleic acid with the transmission spectra of pure oleic acid and oleic acid in CCl_4 solution.

Figure 6. Effect of unsaturation on absorbance (CH stretching region, Table I) as revealed by the Beer-Lambert plot from transmission spectra (CaF_2 windows).

revealed by $-\text{CH}$ stretching bands were determined by transmission experiments. Figure 6 shows the change in the integrated absorbance with respect to path length and concentration in carbon tetrachloride for stearic and oleic acids using calcium fluoride windows. As shown in Figure 6, the molar absorptivity ($\epsilon = A/bC$) of oleic acid as determined by Beer-Lambert law was found to be smaller than that of stearic acid, which is probably due to the decrease in the number of methylene groups and the effect of the single $\text{C}=\text{C}$ bond on the neighboring methylene groups. For example, the molar absorptivity of linoleic acid (18C fatty acid with two $\text{C}=\text{C}$ double bonds) was found to be even lower, ca. $21,800 \text{ L}/(\text{cm}^2 \text{ mol})$.⁴³

The effect of solvent polarity on the molar absorptivities of oleic acid and sodium oleate was also examined in order to use the IRS adsorption density equation with confidence. As shown in Figure 7 and Table I, the effect of solvent polarity on the absorbances of oleic acid and its

Figure 7. Effect of solvents on absorbance (CH stretching region, Table I) of oleic acid and its sodium salt revealed by the Beer-Lambert plot from transmission spectra (CaF_2 windows).

Table I. Molar Absorptivity Data

	concentration (M)	integrated range (cm^{-1})	ϵ ($\text{L}/(\text{cm}^2 \text{ mol})$)
stearic acid/ CCl_4	1.05×10^{-4} to 1.26×10^{-3}	3000–2800	67 600
oleic acid/ CCl_4	5.76×10^{-4} to 5.05×10^{-3}	3032–2802	43 300
sodium oleate/ D_2O	1.80×10^{-3} to 2.40×10^{-2}	3030–2820	42 600
linoleic acid/ CCl_4 ⁴³	3.00×10^{-4} to 5.00×10^{-3}	3025–2825	21 800

sodium salt was not appreciable. The integrated molar absorptivities shown in Table I were determined by a linear regression method with the bC term of the Beer-Lambert law as an independent variable and a zero intercept. The coefficient of determination values (R^2) are very close to 1 (>0.99) and indicate that the Beer-Lambert law is valid under these circumstances.

As further confirmation of the molar absorptivity values, it was desired to determine the molar absorptivity of pure oleic acid which was expected to be similar to those values determined from solution transmission measurements. However, even with the thinnest spacer available ($15 \mu\text{m}$), absorbance of pure oleic acid at the CH_2 asymmetric and symmetric stretching frequencies was too strong to allow analysis with the Beer-Lambert equation. Therefore, transmission experiments were made without a spacer between the windows and the windows were squeezed to create a thin film suitable for analysis with the Beer-Lambert equation. The thickness of the pure oleic acid in this thin film was determined by two different approaches: (1) application of the Beer-Lambert law at the $-\text{C}=\text{CH}$ stretching frequency and (2) the use of an interference fringe counting procedure.

In the case of the Beer-Lambert approach the measurements were made for two different windows, calcium fluoride and germanium. The Beer-Lambert law was applied to the $-\text{C}=\text{CH}$ band at 3005 cm^{-1} , the absorbance of which is small enough even with different spacers to allow a Beer-Lambert type analysis of pure oleic acid. Figure 8 plots the absorbance (peak height at 3005 cm^{-1}) of oleic acid with respect to bC . These bC values correspond to concentration of oleic acid in carbon tetrachloride, from 2.3×10^{-3} to 3.97 M (pure oleic acid). For example the bC value of $9.93 \times 10^{-3} \text{ cm M}$ corresponds to the concentration of pure oleic acid, 3.97 M , multiplied by the spacer thickness of $2.5 \times 10^{-3} \text{ cm}$. The data were found to obey the Beer-Lambert law, as shown in Figure 8 for CaF_2 windows. This curve was used as a calibration curve for calculating the thickness of pure oleic acid films, in the absence of a spacer, created by squeezing the windows together. By use of a linear regression method, the peak height molar absorptivity of oleic acid at 3005

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Figure 8. Calibration curve constructed from transmission measurements of pure oleic acid with spacers (CaF_2 windows). This relationship was used to determine the thickness (path length) of pure oleic acid films created by squeezing pure oleic acid between the windows without a spacer.

Table II. Comparison of Integrated Molar Absorptivity Values for Pure Oleic Acid

approach to determine path length (b)	b (cm)	A (3032–2802 cm^{-1})	ϵ ($\text{L}/(\text{cm}^2 \text{ mol})$)
Beer–Lambert law at 3005 cm^{-1} w/ CaF_2	3.0×10^{-4}	45.9	38 500
Beer–Lambert law at 3005 cm^{-1} w/Ge	2.4×10^{-4}	39.0	40 100
interference fringe counting	2.5×10^{-4}	39.0	39 600

cm^{-1} was estimated to be $57.9 \text{ L}/(\text{cm mol})$. With this peak height, the molar absorptivity value, and the spectrum of pure oleic acid, the Beer–Lambert equation allowed for the calculation of the path length for the pure oleic acid film ($b = \text{peak height at } 3005 \text{ cm}^{-1}/(57.9 \times 3.97)$). From the calculated path length (b), the concentration of pure oleic acid, 3.97 M , and the measured integrated absorbance (A), the integrated molar absorptivity (ϵ) was determined for the CH -stretching frequencies, again according to the Beer–Lambert law. Thus, the thickness of pure oleic acid films was calculated from FTIR transmission spectra with CaF_2 and Ge windows using this calibration curve. The calculated thickness values and the corresponding integrated molar absorptivities are listed in Table II.

For the interference fringe counting procedure, germanium windows were used to obtain better optical contrast. The refractive index of germanium is larger than that of oleic acid by about 2.5 units, while the difference in refractive indices between calcium fluoride and oleic acid is less than 0.1 unit. Accordingly, the reflectivity³⁰ can be improved by more than 600 times with germanium windows. In both the reflectivity calculation and the measurement of the interference fringe spacing, 1.5 was used as the index of refraction for oleic acid at the CH -stretching frequencies.^{3,44–46} Table II compares the results of our integrated molar absorptivity determinations. The three values are in very good agreement. It should be noted that pure oleic acid has a slightly smaller molar absorptivity (ca. $40\,000 \text{ L}/(\text{cm}^2 \text{ mol})$) when compared with oleic acid in carbon tetrachloride solution ($43\,300 \text{ L}/(\text{cm}^2 \text{ mol})$) or sodium oleate in D_2O ($42\,600 \text{ L}/(\text{cm}^2 \text{ mol})$). The variation would appear to be due to the interaction between the solvent molecules and hydrocarbon chain of oleic acid. These results are in good agreement with the results reported by Kellar et al.¹⁶ for a slightly different frequency range.

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Figure 9. Adsorption density vs. surface pressure for monolayer of stearic acid determined from the π -A isotherm and by the FTIR/IRS adsorption density equation after transfer of the LB film to the surface of a CaF_2 IRE.

Figure 10. Adsorption density vs. surface pressure for monolayer of oleic acid determined from the π -A isotherm by the FTIR/IRS adsorption density equation after transfer of the LB film to the surface of a CaF_2 IRE.

Adsorption Density of LB Films. The adsorption density was calculated both from the π -A isotherm and from the FTIR/IRS adsorption density equation. In the case of the π -A isotherm the adsorption density, Γ , calculated from eq 18

$$\Gamma = \frac{1}{N_A a}$$

where N_A is Avogadro's number (6.023×10^{23}) and a is area/molecule estimated from the π -A isotherm at a specified surface pressure. After the LB film was deposited at specified pressure, the adsorption density was calculated from FTIR/IRS adsorption density equation according to eq. 17.

$$\Gamma = \frac{A/N}{1000 \epsilon (2d/d_p)}$$

Since the transferred LB films are in contact with water rather than carbon tetrachloride, the molar absorptivities for stearic and oleic acids in the nonpolar solvent, carbon tetrachloride solution were used for the adsorption density calculations.

Figures 9 and 10 compare both sets of adsorption density values as a function of the surface pressure for transfer of the monolayer. The adsorption density values determined from FTIR/IRS spectra are in good agreement with the ones calculated from the surface pressure–area isotherms.

For the transferred LB monolayer film of stearic acid, there is quite good agreement between the adsorption density values evaluated using the FTIR/IRS adsorption density equation and the values calculated from the π -A isotherm.

was obtained, as can be seen from Figure 9. Based on crystal packing, the calculated adsorption density for a closely packed monolayer of stearic acid is 8.1×10^{-10} mol/cm². The transferred stearic acid monolayer at a surface pressure of 27 mN/m (the superliquid state) gave an adsorption density value of 7.4×10^{-10} mol/cm².

The FTIR/IRS spectra of the transferred LB monolayer of oleic acid gave adsorption density values close to the ones obtained from the π -A isotherm. An adsorption density of 7.4×10^{-10} mol/cm² is expected for crystal packing of oleic acid. As shown in Figure 10, an adsorption density of 6.1×10^{-10} mol/cm² was obtained for the transferred monolayer film of oleic acid at 25 mN/m which, when compared to 7.4×10^{-10} mol/cm², indicates that the oleic acid could not be compressed to the more compact state but remained in the liquid expanded state.

Conclusion

By comparison of calculated FTIR/IRS adsorption density values from π -A isotherms, prior to transfer, it was clearly shown for both stearic acid and oleic acid at

a calcium fluoride IRE that the FTIR/IRS adsorption density equation is valid and can be used, with confidence, for quantitative analysis of surfactant adsorption phenomena.

In addition, the single band in the vicinity of 1550 cm⁻¹, the characteristic peak of chemisorbed carboxylate at surface calcium sites was found from the FTIR/IRS spectra of LB monolayer films of stearic acid at the CaF₂ surface. The same result was found for LB monolayer films of oleic acid. The free acid C=O stretching band reappeared for LB multilayer deposition, indicating that only the fatty acid head group of the first monolayer reacts with the surface calcium sites of the calcium fluoride IRE.

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MODIFICATION AND SURFACE SPECTROSCOPY OF SEMI-SOLUBLE FILLER MATERIALS FOR POLYMER MATRIX COMPOSITES

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An ever increasing amount of mineral fillers are being used in the plastics industry. Of critical importance in filled polymer systems is the surface treatment of the fillers prior to their addition to the polymer matrix. Fatty acid species are often adsorbed onto semi-soluble filler materials in order to improve the mechanical properties of composites. This paper details the treatment of filler materials, including their modification and characterization by FT-IR spectroscopic methods. Fillers discussed include CaCO_3 , $\text{Mg}(\text{OH})_2$ and CaF_2 , all of which were modified by the adsorption of oleate species from aqueous solution. It will be shown that in some instances the surface treatments are substrate dependent, yielding different responses for properties such as adsorption density and chemical reactivity.

Introduction

During the past 30 years there has been increased use of filler materials in polymer matrices. Most often these fillers, which are usually mineral based and less expensive than the polymer, are added to the polymer resin to consume volume, and hence reduce the overall cost of the final product. In these cases the fillers are also referred to as extenders. In other instances fillers are added to the polymer to impart a specific quality to the composite. The focus of this paper is the surface treatment and characterization of semi-soluble filler materials.

Semi-soluble filler materials are arbitrarily defined as those which have a solubility product constant, K_{sp} , greater than 1×10^{-12} when normalized with respect to the metal cation of the crystalline filler material. The reason for defining semi-soluble fillers in terms of metal cation solubility is due to such fillers' ability to form metal soap species on their surface, as will be shown later.

Filler Surface Treatments

In order to enhance the properties of filled polymers, fillers are treated with surface active agents known as coupling agents. Typically a coupling agent has organic functionality for interaction with the polymer matrix and inorganic functionality for interaction with the filler. The use of coupling agents provides property improvements such as, increased tensile and flexural strengths and moduli, hydrolytic stability, and improved processability as a result of improved dispersion of the filler in the polymer and reduced viscosity of the system.

Silaceous fillers are commonly treated with silane coupling agents. Such fillers generally have very limited water solubility. Application of silane coupling agents onto fillers is either accomplished by intensive mixing of the silane ester with the filler or addition of the filler to a dilute aqueous solution of the hydrolyzed silane coupling agent¹. Titanate coupling agents are used with a variety of hydrophilic fillers. Titanates are typically applied directly to a fluidized bed of the filler or the filler is introduced into a dilute solvent or aqueous solution of titanate¹. Also used as coupling agents are chrome complexes, azidosilanes, chlorinated paraffins, and zircoaluminates^{1,2}.

Esters, for example, esterified fatty acids, and metal carboxylates, such as calcium stearate are used as processing aids for inorganic fillers, as well as, the acids of the esters. Fatty acids have the general formula R-COOH , where the acid endgroup interacts with the inorganic filler and the R represents typically a long chain alkyl group which has no chemical reactivity. To apply fatty acids to fillers, the filler is introduced into a dilute aqueous solution of the fatty acid. pH is a consideration due to the considerable variation in speciation of the fatty acid as a result of hydrogen ion concentration. Fatty acid pretreatment is common with semi-soluble fillers, and is the focus of this paper.

Numerous theories have been postulated regarding how coupling agents effect the changes observed. The most recognized theories include mechanical interlocking³, interpenetrating networks⁴, equilibrium⁵, and secondary forces^{3,6}. All of the theories require good wetting of the filler surface by the coupling agent and eventually the polymer matrix. No single theory is capable to explain the experimental data that exist, thus combinations of the above cited theories are used to explain particular data sets.

As mentioned earlier, a common pretreatment of semi-soluble fillers involves adsorption from aqueous solution of fatty acids such as stearic, $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$, and oleic, $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$, acids. To begin to explore the reasons for improved composite properties associated with the surface treatment of fillers polymers one must begin by investigating the interfacial phenomena associated with the adsorbed layer(s) at the filler particle surface. In this regard, our research groups have utilized Fourier transform infrared spectroscopy (FT-IR) as a means to obtain information on adsorbed layers⁷⁻¹⁰. Information obtained includes surfactant adsorption density, orientation and chemical reactivity. What follows is an overview of three fillers and some of the information obtained from these surface spectroscopy studies.

Calcium Carbonate, CaCO_3

Several forms of this mineral are used as filler materials including calcite, limestone, and marble as well as material precipitated from solution¹. Table I lists several properties of CaCO_3 of importance when used as a filler. CaCO_3 is by far the most common filler for polymers, with annual usage of approximately 680,000 tons. This filler is compounded with a variety of polymers.

FT-IR spectroscopy has been used to determine the adsorption density of oleate species at the surface of CaCO_3 ¹⁰. This research was performed in-situ on single crystals of naturally occurring calcite using a technique called internal reflection spectroscopy (IRS)¹³. Shown in Figure 1 is an adsorption isotherm for oleate on CaCO_3 . Three distinct regions can be seen on this isotherm. At low equilibrium concentrations (2×10^{-6} to 6×10^{-6} M), there exists a plateau region where only small variations in adsorption density are observed. Such plateau regions are a common feature for adsorption at low equilibrium concentrations on semi-soluble mineral fillers. Due to the opacity of CaCO_3 in certain regions of the infrared nothing definite can be said about the exact species which is adsorbed at low fatty acid concentrations.

However, it has been shown by several researchers on various semi-soluble minerals that the adsorbed layer under these conditions is one in which the polar carboxylic head group is bonded directly to lattice cations, in this particular case calcium, forming what a chemisorbed layer⁸. This layer is tenaciously bonded and extreme measures are required for removal. At higher oleate concentrations ($> 6 \times 10^{-6}$ M), the adsorption density sharply increases up to the maximum plateau (adsorption densities of over 2×10^{-3} mol/cm² at equilibrium concentrations from 6×10^{-5} to 5×10^{-4} M), and then decreases at concentrations $> 5 \times 10^{-4}$ M. In regions II and III of the adsorption isotherm multilayer adsorption is occurring. Once again, the oleate species adsorbed at these concentrations is not known. As will be shown later, however, multi-layer adsorption on semi-soluble fillers usually is the result of surface precipitation of the metal salt of the fatty acid, in this case the expected precipitate is calcium dioleate.

Table I Selected Properties of CaCO₃^{1,2,11,12}.

Hardness (Mohs')	3
Refractive Index (birefringent)	1.48-1.66
Specific Gravity	2.7
Solubility Product (25°C)	4.8×10^{-9}
Tensile Strength (psi)	2.5

Figure 1. Adsorption isotherm (25°C, pH 9.5) of oleate on CaCO₃ as determined by in-situ FT-IR spectroscopy.

Magnesium Hydroxide, Mg(OH)₂.

Mg(OH)₂ filler is produced by selective precipitation from brine solutions¹⁴. Precipitation of Mg(OH)₂ allows filler particles to be produced which have very uniform size and shape, as shown in Figure 2. The added cost of Mg(OH)₂ production compared to CaCO₃ can be justified because Mg(OH)₂ serves both as a filler and a flame retardant. Flame retardation occurs due to hydrolysis of Mg(OH)₂ which occurs at temperatures greater than 320°C¹⁵. The degradation temperature of Al(OH)₃, the most often used flame retardant filler, occurs at 220°C¹. Thus, use of Mg(OH)₂ occurs mainly with thermoplastics which require processing temperatures in excess of the degradation temperature of Al(OH)₃. Shown in Table II are selected properties of Mg(OH)₂ of importance when used as a filler/flame retardant material.

One of the most useful features of FT-IR spectroscopy is its ability to sample the interfacial region of a variety of different sample types. For instance, in the previous example the substrate was a monolithic single mineral crystal. However, in this case the FT-IR analysis of the surface layers on powdered Mg(OH)₂ the sampling technique used is called diffuse reflectance, sometimes referred to as DRIFT¹⁸. DRIFT, like its counterpart IRS, can be used to quantify adsorbed layers on filler materials. Shown in Figure 3 is an adsorption isotherm for oleate on Mg(OH)₂¹⁹. Like in the previous adsorption isotherm, at low equilibrium concentrations ($< 2 \times 10^{-4}$ M) a chemisorbed layer exists, and at higher concentrations adsorption of multi-layers of oleate occurs. Mg(OH)₂ is transparent throughout much of the infrared region, thus allowing information to be obtained regarding the nature of the adsorbed layers. In this regard, shown in Figure 4 is a DRIFT spectrum obtained after contacting Mg(OH)₂ with an oleate solution at pH 9.25. The band at 1571.6 cm⁻¹ has been assigned to the stretching vibration of a magnesium carboxylate²⁰, thus substantiating earlier claims concerning formation of adsorbed metal carboxylates on semi-soluble fillers.

Table II Selected Properties of Mg(OH)₂^{12,16,17}.

Refractive Index	1.57
Specific Gravity	2.4
Solubility Product (25°C)	1.5×10^{-11}
Young's Modulus (GPa)	64

Calcium Fluoride, CaF₂.

The use of CaF₂ as a filler material is limited to certain specialty applications¹. However, CaF₂ serves as a model substrate from which information can be obtained which is pertinent to many other semi-soluble fillers. Listed in Table III are selected properties of CaF₂ of importance when considered for use as a filler material. Extensive research on the surface chemistry of CaF₂ in fatty acid solutions has been undertaken in recent years^{4,9,22,23}. Thus, the surface chemistry associated with this mineral serves as the basis for much of our understanding of semi-soluble fillers. Shown in Figure 5 is an adsorption isotherm for oleate adsorption on CaF₂²⁴. The shape of the isotherm is very similar to that shown for the previous semi-soluble systems. Specifically, at low oleate concentrations sub-monolayer coverage of

chemisorbed oleate occurs and at higher concentrations surface precipitation of calcium dioleate occurs.

It was mentioned earlier that dispersion of the filler material is improved by the adsorption of fatty acid species. Increased dispersion can be related to the improved wettability of the filler by the liquid polymer. Factors which influence polymer wettability include the conformation of the alkyl chain of the adsorbed fatty acid molecule, as well as the orientation of the alkyl chain. Both of these properties have been quantified using FT-IR spectroscopy^{8,22}. Another property which influences dispersion and hydrolytic stability of a filled polymer is hydrophobicity, or the ability of the filler to resist penetration of water. A dramatic increase in hydrophobicity has been reported when adsorption by oleate on CaF_2 occurs at elevated temperatures ($>40^\circ\text{C}$) or in the presence of oxygen saturated solutions. This increase in hydrophobicity has been attributed to the reactivity of the unsaturated portion of the oleyl chain^{23,25}. It is interesting to note that a similar increase in hydrophobicity on CaCO_3 does not occur under similar conditions¹⁰.

Figure 2. Scanning electron micrograph of commercially available $\text{Mg}(\text{OH})_2$ filler particles.

Figure 3. Adsorption isotherm (25°C, pH 9.25) of oleate on $\text{Mg}(\text{OH})_2$ as determined by FT-IR spectroscopy.

Figure 4. DRIFT spectrum of oleate adsorbed on $\text{Mg}(\text{OH})_2$, equilibrium oleate concentration = 5×10^{-4} M

Table III Selected Properties of CaF_2 ^{12,21}.

Refractive Index (isometric)	1.43
Specific Gravity	3.18
Solubility Product (25°C)	3.9×10^{-11}

Figure 5. Adsorption isotherm (25°C, pH 9.5) of oleate on CaF_2 as determined by in-situ FT-IR spectroscopy.

Future Research

A wealth of information from adsorbed layers on semi-soluble fillers can be obtained using FT-IR spectroscopy. Future research will involve investigation of surface related phenomena and how they influence composite mechanical properties. For instance, does a filler with an oleate chemisorbed layer give a stronger composite than one filled with adsorbed multilayers? Also, future research will explore the role of oleate double bond reactivity on composite properties.

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Adsorption of collector colloids in the flotation of alkali halide particles

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ABSTRACT

On the basis of nonequilibrium electrophoretic mobility measurements by laser-Doppler electrophoresis, the sign of the surface charge of alkali halides in their saturated brines has been established. The results are generally as expected from simplified lattice ion hydration theory. This recent electrokinetic information coupled with the stability and prevalence of collector colloids in such soluble-salt flotation systems suggests that the selective flotation of alkali halides is due to the adsorption of oppositely charged collector colloids by heterocoagulation. Experimental flotation results confirm this surface charge/collector colloid adsorption model and are presented herein.

INTRODUCTION

The selective flotation of alkali halide salts such as KCl and NaCl is of great industrial significance and has been considered by flotation chemists for many decades. During the past 60 years, beginning with Halbach (1933), numerous researchers have advanced their models to explain the mechanism of collector adsorption in soluble-salt flotation systems. These models include formation of insoluble surface reaction products between collector anions and surface alkali cations (Halbach, 1933), an ion exchange model (Gaudin, 1957; Fuerstenau and Fuerstenau, 1956), a heat of solution model (Rogers and Schulman, 1957), a crystallography model (Bachman, 1951), a surface hydration model (Schubert, 1967), and a surface charge model (Roman et al., 1968). None of these hypotheses can be used to adequately explain flotation and the collector adsorption phenomena observed in these systems.

The surface charge model was rather controversial when it was first presented at the SME Annual Meeting in Los Angeles in 1967. Basically this model suggested that the alkali halide salts were charged in their saturated brines

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and that collectors adsorbed as ions or neutral molecular dipoles depending on the specific flotation system under consideration. The model was quite speculative, with the sign of the surface charge being predicted from simplified lattice ion hydration theory. Little direct experimental evidence was given to support the predicted surface charge, and identification of surface collector species was not reported at all.

The adsorption of collector colloids has not been considered as a mechanism to describe the selective flotation of soluble salt minerals. In this regard, the recent findings of Laskowski et al. (1988) are particularly germane. They reported that collector colloids have distinct electrokinetic properties and, for example, demonstrated that the dodecylamine collector colloid can be used to successfully float quartz. The proposed mechanism for adsorption of the amine colloid was suggested to be electrostatic attraction between the collector colloid and the quartz surfaces. Such a mechanism has not been proposed for soluble-salt flotation systems despite the overwhelming evidence that flotation is greatly enhanced when bulk precipitation of the collector occurs. Probably the most important reason for this lack of consideration is the notion that the contribution of electrostatic forces to the adsorption phenomena would be insignificant at the high ionic strengths associated with alkali halide flotation.

Recently, nonequilibrium electrokinetic measurements have been reported for alkali halides and the sign of their surface charge thus determined (Miller et al., 1992). On the basis of these measurements, it is now possible to examine the possibility of heterocoagulation between oppositely charged collector colloids and soluble-salt mineral particles. In this regard, both vacuum flotation experiments and bubble attachment studies have been completed to determine the significance of surface charge in the flotation of alkali halides and whether the adsorption of collector colloids is a tenable hypothesis. In addition, monosize latex particles have been used as model collector colloids to further characterize the adsorption phenomenon.

EXPERIMENTAL

Ultrapure alkali halides (>99.9%) used in this work were purchased from Alfa Research Chemicals. The collectors n-alkylamine hydrochloride and sodium laurate were obtained from Kodak Research Chemicals and were used as received. The latex particles used in this study were purchased from Polysciences Inc. Milli Q water (18 M Ω) was used in all experiments. Glassware used in the experiments was soaked in chromic acid, rinsed with pure water, soaked in 7 M KOH, rinsed in pure water, and dried just prior to use.

Electrophoretic mobility measurements were performed by a laser-Doppler electrophoresis technique. The Zetasizer 3 (Malvern Instruments Ltd., London, UK) was used for measuring the electrophoretic mobilities. Nonequilib-

rium electrophoretic mobility measurements of the alkali halide salt particles were made after injection into fresh water solutions. Dynamic measurements were possible because the laser-Doppler electrophoresis equipment measures the electrophoretic mobility of the dissolving particles in a matter of a few seconds (Malvern, 1990). Complete details of the experimental procedure are given elsewhere (Miller et al., 1992).

The vacuum flotation technique was used to study the flotation response of KCl and NaCl particles with n-alkylhydrochlorides and sodium laurate as collectors. A sample of from 0.5 to 3.0 grams of 200×270 mesh material was conditioned for about thirty minutes in a saturated brine containing the collector at a particular concentration. The flotation was then carried out for 3 minutes at 1×10^{-4} Torr vacuum. Subsequently, the float and nonfloat fractions were carefully recovered, dried, and weighed in order to determine the flotation recovery of the alkali halide under consideration. Ultrasonic dispersion was used to increase the sodium laurate collector colloid dispersion in saturated brines.

Bubble attachment experiments were completed using an electronic induction timer (Mineral and Coal Technologies, Virginia). Particles (100×150 mesh) of twenty-one alkali halides were conditioned in their respective saturated solutions in order to establish equilibrium. The collector colloid was prepared in the corresponding brine, the desired alkali halide particles were added, and the suspension was conditioned for an additional five minutes. It should be noted that the initial conditioning time for equilibrium is an important variable and in some cases the system was equilibrated for as much as 3 hours. The conditioned particles together with the solution (10 cc) were transferred to a small cell which was placed beneath the bubble holder. A captive bubble (generated using a microsyringe) of approximately 2 mm in diameter was held on the bubble tube and kept in contact with the bed of particles for a given time, typically 2 seconds. The tube with the bubble was then raised to its original position, and the bubble was observed through a microscope to determine whether attachment of particles at the bubble surface had occurred. The experiment was repeated several times for each alkali halide.

RESULTS AND DISCUSSION

Laser-Doppler electrophoresis

The nonequilibrium electrophoretic mobilities of alkali halides including fluorides, chlorides, bromides, and iodides have been measured during dissolution by laser-Doppler electrophoresis (Miller et al., 1992). The results were quite reproducible with respect to the sign of the electrophoretic mobility. Figure 1 shows typical electrophoretic mobility distributions for KCl and

Fig. 1. Nonequilibrium electrophoretic mobility distributions for KCl and NaCl (Miller et al., 1992).

NaCl. These distributions are determined for a large number of particles and the mean electrophoretic mobilities are determined from the distributions at the 95% confidence level. The details of the measurement are explained elsewhere (Miller et al., 1992; Malvern, 1990). It can be observed from this figure that KCl exhibits a negative electrophoretic mobility of -0.47 ± 0.26 ($\mu\text{m}/\text{sec})/(\text{v}/\text{cm})$, while NaCl exhibits a positive electrophoretic mobility of $+0.17 \pm 0.14$ ($\mu\text{m}/\text{sec})/(\text{v}/\text{cm})$. Table 1 presents the electrophoretic mobility results for 21 different alkali halides. As many as nine replicate measurements were made, and it should be emphasized that, for a given salt, the measured electrophoretic mobility was consistently of the same sign.

The validity of these nonequilibrium measurements was demonstrated by making equilibrium measurements for LiF and NaF. Table 2 presents the experimental results, which show the nonequilibrium electrophoretic mobilities to be equivalent in sign to the equilibrium electrophoretic mobilities measured after one hour of equilibration between the salt and aqueous solution.

Most importantly, these nonequilibrium electrophoretic mobility measurements can be used to establish the sign of the surface charge for each alkali halide salt, and these results are generally confirmed by lattice ion hydration theory (Miller et al., 1992). The results from the laser-Doppler electrophoresis are compared to the predictions using the simplified lattice ion hydration theory in Table 3. The gaseous ion hydration free energy values given in Table 3 were determined based on the Born model (Hunt, 1965), which still

TABLE I

Results from laser-Doppler electrophoresis experiments — nonequilibrium conditions

	Alkali halide	Mean electrophoretic mobility ($\mu\text{m}/\text{sec}$)/(v/cm)
Fluorides	LiF	+0.22
	NaF	+0.16
	KF	+0.08
	RbF	+0.06
	CsF	+0.58
Chlorides	LiCl	-0.64
	NaCl	+0.16
	KCl	-0.42
	RbCl	+0.21
	CsCl	+0.40
Bromides	LiBr	-0.32
	NaBr	-0.31
	RbBr	-0.46
	KBr	-0.09
	CsBr	+0.07
Iodides	LiI	-0.76
	NaI	-0.74
	KI	+0.08
	RbI	-0.25
	CsI	+0.04
	NaI·2H ₂ O	+0.04

TABLE 2

Comparison of nonequilibrium electrophoretic mobilities with equilibrium electrophoretic mobilities for two alkali halide salts (Miller et al., 1992)

Salt	Solubility	Mean electrophoretic mobility*, ($\mu\text{m}/\text{sec}$)/(v/cm)	
		Nonequilibrium	Equilibrium
LiF	0.27 g/100 cc	+0.22 (5)	+0.15 (8)
NaF	4.22 g/100 cc	+0.16 (4)	+0.10 (6)

*Number of observations reported in parentheses.

allows for the calculation of free energies that are accurate to within a few percent (Jayaram et al., 1989).

As can be noted from Table 3, the measurements for five salts are in disagreement with the predictions from the simplified lattice ion hydration theory; of particular interest are KCl and NaCl. These discrepancies might be

TABLE 3

Sign of the surface charge for selected alkali halides (Miller et al., 1992)

	Negative gaseous hydration free energies, kcal/mol		Sign of surface charge	
	Cation	Anion	Predicted ^a	Experimental ^b
<i>Fluorides</i>				
LiF	112.0	109.6	?	+
NaF	88.4	109.6	+	+
KF	71.1	109.6	+	+
RbF	65.9	109.6	+	+
CsF	58.2	109.6	+	+
<i>Chlorides</i>				
LiCl	112.0	82.5	-	-
NaCl	88.4	82.5	-	+
KCl	71.1	82.5	+	-
RbCl	65.9	82.5	+	+
CsCl	58.2	82.5	+	+
<i>Bromides</i>				
LiBr	112.0	75.7	-	-
NaBr	88.4	75.7	-	-
KBr	71.1	75.7	+	-
RbBr	65.9	75.7	+	-
CsBr	58.2	75.7	+	+
<i>Iodides</i>				
LiI	112.0	66.5	-	-
NaI	88.4	66.5	-	-
KI	71.1	66.5	-	+
RbI	65.9	66.5	?	-
CsI	58.2	66.5	+	+
NaI·2H ₂ O	NA	NA	NA	+

^aSimplified lattice ion hydration theory.^bElectrophoretic-mobility measurements by laser-Doppler electrophoresis.

due to the differences in lattice energy contributions of cation and anion in the salt, lattice defects and/or relaxation effects (Miller et al., 1992; Miller and Calara, 1976; Calara and Miller, 1976a,b). When gaseous ion hydration free-energy values based on enthalpies reported by Kanevskii (1949) are used, the lattice ion hydration theory predictions match most of the experimental results, with KCl, KBr, and RbBr being the only exceptions. Recent results indicate that the presence of oxygen defect states account for the deviation of KCl from the theoretical expectations dictated by the lattice ion hydration theory (Yalamanchili and Miller, 1993a).

The significance of these measurements has been demonstrated in the study of the dispersion and aggregation of alkali halide particles in saturated brines (Yalamanchili and Miller, 1993b) and in this paper the sign of the surface charge of alkali halides is used to describe the flotation response of alkali halides by the adsorption of collector colloids.

Flotation of KCl and NaCl

The nonequilibrium electrophoretic mobility results from the previous section allow for the sign of the surface charge to be predicted for alkali halides in their saturated brines. On this basis we can examine in more detail the hypothesis regarding the role of surface charge in the flotation of alkali halides. For example, the flotation response of KCl and NaCl salts was studied with dodecylamine hydrochloride and sodium laurate collectors.

It is known that most amine and carboxylate collectors used in alkali halide flotation systems form insoluble collector colloids at relatively low collector concentrations (Roman et al., 1968; Schubert, 1971). Generally the collector colloids have been found to be hydrophobic as determined in our laboratory by vacuum tube flotation experiments. Similar to the results reported by Roman et al. (1968), Fig. 2 shows that KCl floats well with $R_{12}NH_3Cl$ collector only after precipitation of the $R_{12}NH_3Cl$ collector colloid from solution. It has been reported that $R_{12}NH_3Cl_{(s)}$ is positively charged at natural pH as is

Fig. 2. Flotation recovery of KCl and NaCl as a function of dodecylamine hydrochloride concentration (Miller et al., 1992).

evident from the data presented in Fig. 3 (Laskowski et al., 1988). Because the charges on KCl (see Table 1) and $R_{12}NH_3Cl_{(s)}$ are opposite in sign, it is reasonable to suspect that heterocoagulation occurs between the positively charged $R_{12}NH_3Cl_{(s)}$ collector colloid and the negatively charged KCl particles at natural pH. This heterocoagulation event appears to account for the effective flotation of KCl with the hydrophobic $R_{12}NH_3Cl$ collector. Further, it is evident from Figure 2 that NaCl is not floated by the positively charged $R_{12}NH_3Cl_{(s)}$ collector colloid, because NaCl carries the same charge as the hydrophobic collector colloid (see Table 1), and heterocoagulation does not occur.

The flotation of KCl with the dodecylamine hydrochloride collector colloid represents a general phenomenon which has been found to occur for alkyl amines of different chain length, from C_8 to C_{18} as shown in Fig. 4. The relationship between collector colloid precipitation and salt flotation is most distinct in the case of dodecylamine and KCl. For octadecylamine, precipitation occurs at concentrations orders of magnitude less than the concentration required for effective flotation. It seems that in the case of octadecylamine, the flotation may be limited by the number concentration of the collector colloids and/or the kinetics for their adsorption by heterocoagulation. For example, the flotation response of KCl with octadecylamine is quite similar to the flotation response of KCl reported by Roman et al. (1968) with tetradecylamine which precipitates much closer to the point of flotation. Even though precipitation of the octadecylamine hydrochloride occurs at 5×10^{-9} M, the number concentration of these colloids is insufficient to realize the necessary ad-

Fig. 3. Effect of pH and concentration on the electrophoretic mobility of the dodecylamine hydrochloride collector colloid (Laskowski et al., 1988).

Fig. 4. Flotation recovery of KCl with octyl, dodecyl, and octadecyl amine hydrochloride collectors. Arrows indicate the solubility limit of the collectors.

sorption density at the KCl surface. These results suggest that a critical concentration of collector colloids is necessary for flotation, regardless of the chain length of the collector used. Research is in progress to further examine this possibility.

It should be mentioned that prior to the point of collector colloid precipitation, amine adsorption by KCl does occur reaching a monolayer coverage ($\sim 3.5 \times 10^{-10}$ mol/cm²) at an equilibrium concentration of 1×10^{-3} M in the case of octylamine collector (Yalamanchili et al., 1991). However, under these conditions the KCl surface shows little hydrophobicity and flotation is not significant as shown in Figure 4. In addition, of particular importance is that even after the precipitation of the octylamine hydrochloride colloid, KCl flotation never reaches 100 % and in fact is diminished at higher levels of collector addition (6×10^{-2} M). These results suggest that the hydrophobic character of the collector colloid is altered at higher concentration of octylamine. In fact, such is the case. In the absence of KCl particles, the octylamine hydrochloride collector colloid was found to be distinctly hydrophobic in KCl brine at 1×10^{-2} M whereas at 6×10^{-2} M, the collector colloid was hydrophilic.

Similar arguments made above for the amine collectors hold for the negatively charged $R_{11}COONa_{(s)}$ collector colloid. In this case, positively charged NaCl is floated, whereas negatively charged KCl is not floated with the carboxylate collector colloid, as shown in Fig. 5. It should be mentioned at this point that the dispersion of sodium laurate collector colloids in saturated brines was observed to be very poor. Consequently the flotation response of

Fig. 5. Flotation recovery of NaCl and KCl as a function of sodium laurate concentration (Miller et al., 1992).

NaCl with sodium laurate collector was very low. When an ultrasonic dispersion technique was used to increase the dispersion of the collector colloid, the flotation recovery of NaCl was significant as shown in Fig. 5.

Of course, in actual practice the composition of the collector colloid could vary in a multicomponent brine and the formation of more complex collector colloids would be possible in plant situations.

If the hypothesis of collector colloid adsorption is to be accepted, then the flotation of alkali halides should be sensitive to the pH of the system, not necessarily because the surface charge of the alkali halide salt changes (the H^+ should not be potential determining for most alkali halides), but because the charge of the collector colloid changes. In this regard, Fig. 6 shows that the flotation recovery of KCl almost ceases beyond a pH of about 11, which is the PZC of the $R_{12}NH_3Cl_{(s)}$ collector colloid (see Fig. 3). Clearly, above the PZC, the $R_{12}NH_3Cl_{(s)}$ collector colloid becomes negatively charged and no longer adsorbs on the negatively charged KCl. Under these circumstances the flotation of sylvite is no longer possible. It is important to note, also from Fig. 6, that the flotation recovery of NaCl improves for pH values greater than 11, which again indicates that the negatively charged $R_{12}NH_3Cl_{(s)}$ (above the PZC) adsorbs on the positively charged NaCl and facilitates flotation.

Generally, the surface charge of the alkali halide salt should be fixed by the solution activity of the potential determining lattice ions. In this regard, flotation of negatively charged KCl by dodecylamine hydrochloride was examined at natural pH as a function of potassium ion concentration. The results

Fig. 6. Flotation recovery of KCl and NaCl with dodecylamine hydrochloride as a function of system pH.

Fig. 7. Flotation recovery of KCl with dodecylamine hydrochloride as a function of total potassium concentration in solution.

presented in Fig. 7 show that when the potassium concentration is increased to about 40 grams of potassium per 100 grams of solution by the addition of potassium iodide (more soluble than KCl), flotation of KCl is not possible.

It appears that the higher concentration of potassium has reversed the charge of KCl, making it positive, and thus preventing the adsorption of the positively charged $R_{12}NH_3Cl_{(s)}$ collector colloid. In a similar way, activation and flotation of NaCl can be achieved with dodecylamine hydrochloride by the addition of excess chloride ions. When the chloride ion activity exceeds a certain level, the surface charge of NaCl reverses and the positively charged $R_{12}NH_3Cl_{(s)}$ collector colloid adsorbs at the negatively charged NaCl surface, thus effecting flotation.

The preceding results and discussion clearly indicate that the adsorption of collector colloids and subsequent flotation of KCl and NaCl salts are determined by interaction forces associated with the surface charge of the collector colloid and the surface charge of the alkali halide mineral. In the following section, this hypothesis has been further tested for 21 different alkali halides based on bubble attachment studies.

Bubble attachment studies

Table 4 presents the results of bubble attachment studies for alkali fluorides, chlorides, bromides, and iodides. This table also presents the experimentally determined sign of the surface charge and the expected flotation behavior/bubble attachment for these alkali halides. In all cases the solubility of the dodecylamine hydrochloride was exceeded as was evident from visual examination of the saturated brine prior to addition of specific alkali halide particles. Excellent agreement between theory and experiment is observed. Recall, however, that conditioning time for equilibration is an important variable. For example, in the case of LiCl, bubble attachment was significantly dependent on conditioning time, and attachment was only possible after more than two hours of conditioning time. This observation may help to explain previous inconsistencies in soluble-salt flotation behavior (Fuerstenau and Fuerstenau, 1956; Rogers and Schulman, 1957).

As is evident from Table 4, only two alkali halide salts, namely CsCl and CsBr, deviated from the expected flotation behavior according to the suggested adsorption mechanism of heterocoagulation between the collector colloid and the alkali halide particles. Further analysis is underway to explain these deviations.

It is also interesting to consider the flotation response of the NaI and $NaI \cdot 2H_2O$ systems. It may be recalled from Table 1 that anhydrous NaI is negatively charged as predicted by the lattice ion hydration theory, whereas $NaI \cdot 2H_2O$ is positively charged. This example clearly highlights the significance of hydration in the charging process. When water is introduced into the NaI crystal lattice, the hydration of the Na^+ in the lattice is substantial (Wells, 1962), in which case the iodide anion has a greater tendency to hydrate and leave the lattice surface site, thus resulting in a positive surface charge. The

TABLE 4

Bubble attachment studies for alkali halides with dodecylamine hydrochloride as collector

Alkali halide	Surface charge	Bubble attachment	
		Predicted	Experimental
LiF	+	N	N
NaF	+	N	N
KF	+	N	N
RbF	+	N	N
CsF	+	N	N
LiCl	-	Y	Y
NaCl	+	N	N
KCl	-	Y	Y
RbCl	+	N	N
CsCl	+	N	Y
LiBr	-	Y	Y
NaBr	-	Y	Y
KBr	-	Y	Y
RbBr	-	Y	Y
CsBr	+	N	Y
LiI	-	Y	Y
NaI	-	Y	Y
KI	+	N	Some
RbI	-	Y	Y
CsI	+	N	N
NaI·H ₂ O	+	N	N

bubble attachment experiments for NaI and NaI·2H₂O (see Table 4) further support the above results and discussion.

Collector colloid adsorption mechanism

It is clearly evident from our investigation that surface charge analysis of soluble salt systems is now possible based on reliable electrokinetic measurements by laser-Doppler electrophoresis. On the basis of this analysis, the nature of collector adsorption and the flotation behavior of alkali halide salts from their saturated solutions can be described satisfactorily by the heterocoagulation of collector colloids with alkali halide particles of opposite charge. The size of the collector colloids used in the flotation of alkali halides is on the order of a tenth of a micron as indicated by light scattering experiments (Yalamanchili, 1993). Attempts are being made to physically examine the adsorbed collector colloids at the salt surfaces using atomic force microscopy.

Also, recent studies on alkali halide particle interactions in saturated brines (Yalamanchili and Miller, 1993b) suggest that the surface charge of these salt particles plays a major role in the particle aggregation/dispersion behavior at high ionic strengths. These studies indicate that short range attractive hydration forces are responsible for the heterocoagulation between the oppositely charged hydrophilic particles at high ionic strengths. It would appear that a similar phenomenon accounts for the heterocoagulation which occurs between the hydrophobic collector colloid particles and the hydrophilic alkali halide particles. In this way the adsorption of collector colloids can be described as a heterocoagulation event between oppositely charged particles

Latex particles — model collector colloids

To substantiate the proposed collector colloid adsorption mechanism further, charged, monosize, hydrophobic latex particles are being used as model collector colloids to study the flotation of KCl and NaCl in saturated brines. In addition, the adsorption of these model collector colloids is being studied by SEM. Table 5 presents the physical and chemical characteristics of the model latex colloids used in this study. Amino (positively charged) and carboxylate (negatively charged) colloids were adsorbed on KCl and NaCl plates and SEM was used to examine the adsorption of these latex particles. Suspensions of latex particles ($0.2\ \mu\text{m}$ diameter) with a bulk concentration of 10^{12} particles/cc were used to examine adsorption at the KCl surface. Carboxylate latex particles of $0.31\ \mu\text{m}$ diameter were used for adsorption at NaCl surface. The adsorption was carried out for about one hour by dipping the salt plates in saturated brine suspensions containing the desired latex particles. The results from this study are presented by the representative SEM photographs shown in Figs. 8a and 8b. Figure 8a shows the adsorption of positively charged amino latex colloids at the negatively charged KCl surface whereas Fig. 8b shows the adsorption of negatively charged carboxylate latex colloids at the positively charged NaCl surface at a higher magnification. As is evident from Fig. 8a, approximately 80% of monolayer coverage is observed under these conditions. Preliminary analysis of the SEM results indicates that the surface

TABLE 5

Characteristics of latex model colloids

Latex	Electrophoretic mobility (μ/sec)/(v/cm)	Remarks
Amino	$+2.2 \pm 0.18$	Surfactant free; hydrophobic
Carboxylate	-3.3 ± 0.12	Surfactant free; hydrophobic

Fig. 8. (a) Adsorption of $0.2\ \mu\text{m}$ positively charged latex particles at negatively charged KCl surface. (b) Adsorption of $0.31\ \mu\text{m}$ negatively charged latex particles at positively charged NaCl surface.

concentration is about 10^{14} particles/cc or about two orders of magnitude greater than that of the bulk concentration. More detailed study of this phenomenon is in progress. No adsorption was observed when latex colloids of negative charge were used for adsorption at the negatively charged KCl surface. Similarly, positively charged latex particles did not adsorb at the positively charged NaCl surface. Finally, and most importantly, KCl was successfully floated using positively charged latex particles whereas practically no flotation was observed when negatively charged latex particles were used as

collector colloids for KCl. It is important to note that these suspensions of latex particles are surfactant free (Hoobler, 1992) and consequently the observed flotation response can not be attributed to the adsorption of ionic or molecular surfactant species. Clearly the results from these studies show once again that collector colloid adsorption occurs by heterocoagulation of oppositely charged particles and that this phenomenon accounts for the observed flotation response in soluble salt flotation systems.

SUMMARY AND CONCLUSIONS

Reliable nonequilibrium electrophoretic mobility measurements for alkali halide salts have been made by laser-Doppler electrophoresis for the first time (Miller et al., 1992). It is evident from the results presented that surface charge is indeed an important characteristic of alkali halide flotation systems. Generally the surface charge can be predicted from simplified lattice ion hydration theory, but there are exceptions, KCl being the most significant. Based on the experimentally determined surface charge, it seems that the flotation response of alkali halides and probably other soluble salts, e.g., NaNO_3 , KNO_3 , NaIO_3 , K_2SO_4 , and Na_2SO_4 (Yalamanchili, 1993) can best be explained by the adsorption of oppositely charged collector colloids rather than by the adsorption of collector ions and/or neutral molecular dipoles as originally suggested by Roman et al. (1968).

This heterocoagulation of charged collector colloids at oppositely charged salt surfaces appears to involve attractive hydration forces (Yalamanchili and Miller, 1992) and establishes the hydrophobic state as has been demonstrated quite extensively for KCl and NaCl. Of particular importance is the fact that the flotation response of KCl and NaCl is pH dependent in accordance with the electrokinetic behavior of the collector colloid. Further, the surface-charge/collector colloid adsorption model is substantiated by the dependence of KCl flotation on the dissolved potassium concentration.

Finally, bubble attachment studies for 21 different alkali halides and the results from the study of latex particles as model collector colloids significantly strengthen the proposed mechanism of collector colloid adsorption for soluble-salt flotation systems.

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FUNDAMENTAL ASPECTS OF SOLUBLE SALT FLOTATION

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ABSTRACT

The sign of the surface charge for alkali halides in their saturated brines has been established from nonequilibrium electrokinetic measurements. These surface charge results for alkali halides are generally as expected from simplified lattice ion hydration theory. Based on this electrokinetic information, it has been demonstrated that the flotation of alkali halide salts is due to the adsorption of oppositely charged collector colloids by heterocoagulation. For example, the classic flotation separation of KCl from NaCl with alkyl amines is thus explained.

Now, the surface charge/collector colloid adsorption hypothesis has been extended to successfully explain the flotation behavior of certain alkali oxyanions including nitrates and sulfates as well as double salts including schoenite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$) and kainite ($KCl \cdot MgSO_4 \cdot 3H_2O$). As was done previously for the alkali halides, the sign of the surface charge for these alkali oxyanion salts was established from nonequilibrium electrokinetic measurements by laser-doppler electrophoresis. These results together with the results from flotation/bubble attachment experiments indicate that the surface charge/collector colloid adsorption hypothesis accounts for the flotation response of many different soluble salt minerals when alkyl amines and carboxylates are used as collectors.

Keywords

Potash; collector colloid adsorption; oxyanions; halides; soluble salt flotation

INTRODUCTION

Soluble salt minerals comprise a variety of industrially significant materials including alkali halides such as KCl and NaCl, alkali nitrates such as KNO_3 and $NaNO_3$, alkali sulfates such as K_2SO_4 and Na_2SO_4 , and double salts such as carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$), kainite ($KCl \cdot MgSO_4 \cdot 3H_2O$), and schoenite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$). Generally, these salts are used as potassium and nitrogen sources for the production of agricultural fertilizers [1,2]. Potassium bearing minerals, ores, and refined products are known by the generic term potash. The future for the potash industry is very promising because potassium and nitrogen are essential as plant nutrients and will be required to maintain the world's food production.

In addition to traditional potash ores, naturally occurring brines (eg. the Dead Sea, the Great Salt Lake, etc.) contain dissolved potassium salts and are important secondary sources for commercial potash production. Nevertheless, the most important potash ore is sylvinitite, a mixture of sylvite (KCl) and halite (NaCl) with minor amounts of clay and other potassium minerals. Today, the majority of the sylvinitite ores in the world are concentrated by froth flotation involving brines fully saturated with respect to potassium and sodium chlorides [3,4]. Generally, the sylvinitite ores are concentrated in flotation plants

equipped with grinding, desliming, flotation, and drying circuits. The ore is pulped in a saturated brine and ground to liberate sylvite from halite, other salt minerals, and insoluble gangue minerals. The fine grained insolubles, largely clays and quartz, are removed in a desliming circuit by scrubbing/classification or by flocculation/flotation methods. Recent results indicate that air sparged hydrocyclone flotation is particularly effective for the removal of clays prior to KCl flotation [5]. The slurry of sylvite and halite is then treated in flotation cells where amine collectors along with frothers and extender oils are used to float sylvite from halite. Residual clay minerals are depressed during KCl flotation by employing depressants such as starch or guar gum.

While the flotation of KCl from NaCl by alkyl amines is a relatively simple process, the potash production from brine deposits is more complex. Lake brines contain a mixture of single, double, and hydrated salts depending on brine composition. These salts are eventually separated and converted into a marketable potash product, usually potassium sulfate. The practice at the Great Salt Lake Minerals Corporation, Utah typically involves the flotation of schoenite and its conversion to marketable potassium sulfate fertilizer [6]. For example, after the recovery of schoenite as a flotation concentrate, it is reacted with KCl to produce a K_2SO_4 product by controlled crystallization. This conversion process can generally be represented by the following reaction:

Potash production at the Dead Sea Works involves the separation of $MgCl_2$ by crystallization from the concentrated brines containing carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) and NaCl. Then, the mixture of KCl and NaCl (sylvinite) in the brine is treated in a flotation plant to separate KCl from NaCl. In addition, substantial quantities of magnesium chloride and bromine salts are recovered from this lake brine. It can be noted that there is no standard commercial procedure for the concentration of lake brines to produce potash products due to the complex salts found in these resources. Depending on the composition of a specific lake brine, an appropriate processing strategy must be established to maximize the efficiency of potash production.

Another interesting deposit is the caliche salts of the Atacama in northern Chile. These salts are rich in nitrates which are recovered by dissolution and fractional crystallization. In addition, lithium and iodine salts are recovered from this region [7,8]. Thus, it is expected that improved understanding of soluble salt flotation systems should lead to new process alternatives for the more effective utilization of these complex salt resources.

Even though the froth flotation practice has been fairly well established for the concentration of KCl, fundamental understanding of the interfacial phenomena in soluble salt systems has been very much limited. This is due to the inherent complexities of these systems such as high ionic strength, collector insolubility, and high viscosity of the brines. Several hypotheses have been advanced in the past to explain the collector adsorption mechanism in soluble salt flotation systems [9-16]. Generally, these hypotheses have been inadequate. Nevertheless, our recent research, stimulated by the findings of Roman et al [15], has provided a new perspective of soluble salt flotation and represents a significant breakthrough in understanding the flotation behavior of soluble salt minerals [17,18]. Specifically, it has been demonstrated that collector adsorption and flotation of soluble salt minerals involve heterocoagulation of oppositely charged collector colloids and soluble salt mineral particles. In the present work, the surface charge/collector colloid adsorption theory is used to explain the flotation behavior of a number of different soluble salt flotation systems including alkali halides, oxyanions, and certain double salts. First, however, the lattice ion hydration theory is reviewed and the predicted surface charge for alkali halides is compared with that determined experimentally by nonequilibrium electrophoresis.

LATTICE ION HYDRATION THEORY

The lattice ion hydration theory [19] describes the surface charge developed by non reactive ionic solids when placed in water. The sign of the surface charge is determined by the magnitude of the hydration

energy of the respective surface lattice ions. If the surface cation has a more negative hydration energy than the surface anion, then the surface will carry a negative charge. The converse is also true. The analysis can be further simplified. If the cation and anion are in equivalent crystal lattice positions such as in alkali halide salts, then the lattice energies for cation and anion are equivalent and the sign of the surface charge can be established simply from the hydration energies of gaseous ions [18-22]. This simplified theory was first demonstrated for silver halides as reported by De Bruyn and Agar [19]. The more complex case involving lattice energies has been considered by Miller and Calara [20-22]. Now, most recently, the validity of the theory has been demonstrated for the alkali halides [18].

The nonequilibrium electrophoretic mobilities for the simple alkali halides have been measured during dissolution by laser-doppler electrophoresis [18]. These results were quite reproducible with respect to the sign of the surface charge. Furthermore, the validity of these nonequilibrium electrophoretic mobility measurements was demonstrated by making equilibrium measurements for LiF and NaF [18]. Figure 1 shows typical electrophoretic mobility distributions for KCl and NaCl. It can be observed from this Figure that KCl exhibits a negative surface charge whereas NaCl exhibits a positive charge. Most importantly, these nonequilibrium electrophoretic mobility measurements are used to establish the sign of the surface charge for each alkali halide salt in its saturated solution as indicated in Table 1. It should be mentioned here that even though the double layer is compressed in saturated brines, a surface charge may still be present.

Fig.1 Nonequilibrium electrophoretic mobility distributions for KCl and NaCl [18].

The experimental results from laser-Doppler electrophoresis are compared to predictions using simplified lattice ion hydration theory in Table 1. It is evident that the sign of the surface charge as measured by laser-Doppler electrophoresis is generally in agreement with that predicted from simplified lattice ion hydration theory. However, there are a few exceptions. Many of these discrepancies were explained elsewhere in terms of the reliability of the gaseous ion hydration energy values calculated from the Born model [17]. It can be noticed from Table 1 that KCl deviates from expected behavior, according to lattice ion hydration theory, when the oxygen content of crystal lattice is in excess of at least 60 ppm. Recent results indicate that the presence of these oxygen defect states accounts for the deviation of typical KCl from theoretical expectations [23].

Finally, it should be noted that the significance of these surface charge results for alkali halides has been demonstrated in both particle interaction studies [24] and flotation experiments [25]. In the following sections, the role of surface charge in various soluble salt flotation systems is examined.

TABLE 1 Sign of the surface charge for selected alkali halides

	Negative Gaseous Ion Hydration Free Energies, kcal/mole		Sign of Surface Charge	
	Cation	Anion	Predicted ^a	Experimental ^b
Fluorides				
<i>LiF</i>	112.0	109.6	-	+
<i>NaF</i>	88.4	109.6	+	+
<i>KF</i>	71.1	109.6	+	+
<i>RbF</i>	65.9	109.6	+	+
<i>CsF</i>	58.2	109.6	+	+
Chlorides				
<i>LiCl</i>	112.0	82.5	-	-
<i>NaCl</i>	88.4	82.5	-	+
<i>KCl</i> ^c	71.1	82.5	+	-
<i>KCl</i> ^d	71.1	82.5	+	+
<i>RbCl</i>	65.9	82.5	+	+
<i>CsCl</i>	58.2	82.5	+	+
Bromides				
<i>LiBr</i>	112.0	75.7	-	-
<i>NaBr</i>	88.4	75.7	-	-
<i>KBr</i>	71.1	75.7	+	-
<i>RbBr</i>	65.9	75.7	+	-
<i>CsBr</i>	58.2	75.7	+	+
Iodides				
<i>LiI</i>	112.0	66.5	-	-
<i>NaI</i>	88.4	66.5	-	-
<i>KI</i>	71.1	66.5	-	+
<i>RbI</i>	65.9	66.5	+	-
<i>CsI</i>	58.2	66.5	+	+
<i>NaI·2H₂O</i>	NA	NA	NA	+

^aSimplified lattice ion hydration theory.^bElectrophoretic-mobility measurements by laser-Doppler electrophoresis.^cTypical KCl (Oxygen ~ 350 ppm) - reference 23^dLaser Quality KCl (Oxygen < 60 ppm) - reference 23

ALKALI HALIDES

On the basis of nonequilibrium electrokinetic results, the hypothesis regarding the role of surface charge in the flotation of alkali halides was examined in more detail. The flotation response of sylvite and halite salts was studied extensively with dodecylamine hydrochloride and sodium laurate collectors [15,25]. Figure 2 shows that KCl floats well with $R_{12}NH_3Cl_{(a)}$ collector only after precipitation of the $R_{12}NH_3Cl_{(a)}$ collector colloid from solution even though apparent monolayer adsorption occurs prior to the point of collector precipitation [26]. It is important to note that $R_{12}NH_3Cl_{(a)}$ is positively charged at natural pH [27]. Because the charges on KCl (see Table 1) and $R_{12}NH_3Cl_{(a)}$ are opposite in sign, it is reasonable to suspect that heterocoagulation occurs between the positively charged $R_{12}NH_3Cl_{(a)}$ collector colloid and the negatively charged KCl particles at natural pH. This heterocoagulation event appears to account for

the effective flotation of KCl with the hydrophobic $R_{12}NH_3Cl$ collector. Further, it is evident from Figure 2 that NaCl is not floated by the positively charged $R_{12}NH_3Cl_{(s)}$ collector colloid, because NaCl carries the same charge as the hydrophobic collector colloid (see Table 1), and heterocoagulation does not occur.

Fig.2 Flotation recovery of KCl and NaCl as a function of dodecylamine hydrochloride concentration [18].

Similar collector colloid precipitation arguments made above for alkyl amines also hold for the negatively charged carboxylate collector colloids. In this case, positively charged NaCl is floated, whereas negatively charged KCl is not floated with the negatively charged laurate collector colloid, as shown in Figure 3. It should be mentioned at this point that the dispersion of laurate collector colloids in saturated brines was observed to be very poor. Consequently the flotation response of NaCl with laurate collector colloid was very low. When an ultrasonic dispersion technique was used to increase the dispersion of the collector colloid, the flotation recovery of NaCl was significant as shown in Figure 3.

Fig.3 Flotation recovery of NaCl and KCl as a function of sodium laurate concentration [18].

The hypothesis of surface charge/collector colloid adsorption is further strengthened by the fact that the flotation behavior of both sylvite and halite is sensitive to the pH of the system, not because the surface charge of the alkali halide salt changes (the H^+ should not be potential determining for most alkali halides), but because the charge of the collector colloid changes. Further, the dependence of the flotation behavior of sylvite on the solution activity of the potential determining lattice ions further substantiates the surface charge/collector colloid adsorption hypothesis [25].

The flotation results for KCl and NaCl clearly indicate that the adsorption of collector colloids and subsequent flotation of these salts are determined by interaction forces associated with the surface charge of the collector colloid and the surface charge of the alkali halide particles. This hypothesis has been successfully tested by bubble attachment experiments for 21 different alkali halides and by the study of latex particles as model collector colloids [25]. For example, bubble attachment to KCl using different latex particles is reported in Table 2 and an SEM photograph of the KCl surface showing these attached, model collector colloids is presented in Figure 4.

TABLE 2 Latex particles as model collector colloids for KCl flotation

Latex Particle	Size (nm)	Electrophoretic Mobility ($\mu/\text{sec})/(\text{v/cm})$	Remarks	Bubble Attachment
Amino	200	$+2.4 \pm 0.13$	Surfactant Free Hydrophobic	Yes
Carboxylate	56	-3.3 ± 0.12	Surfactant Free Hydrophobic	No

Fig.4 SEM photograph showing the adsorption of 0.2 micron amino latex particles at the surface of KCl [25].

The surface charge/collector colloid adsorption hypothesis can be used to explain the improvement in the flotation response of coarse fractions of KCl when oils are used as extender collectors in the potash industry. Generally, these oil droplets have a negative surface charge at the natural pH (6-7) of saturated brines and do not adsorb at the negatively charged KCl surface unless amine collector colloids are present in the system. When amine is added to the KCl slurry containing the extender oil, the positively charged amine collector colloids act as a bridge between the negatively charged oil droplets and the negatively charged KCl particles. As a result, heterocoagulation occurs and thereby the attachment of air bubbles is facilitated. In this regard, Table 3 presents preliminary contact angle measurements for KCl/hexadecane and KCl/hexadecane/dodecyl amine systems. The contact angles reported were measured by the sessile drop method with a Rame-Hart contact angle goniometer. It can be noticed from Table 3 that no contact of the hexadecane drop was observed at the KCl surface in saturated brine. Weak attachment (contact angle 7°) was observed when dodecylamine at a concentration below the solubility limit was added to the brine of the KCl/hexadecane system. However, when the amine concentration exceeded the solubility limit, a much greater contact angle (52°) was observed as shown in Table 3. Of course, the exact nature of the interaction forces between the oppositely charged phases in this system is not clearly understood at this time and further work is in progress to explain the interparticle forces at these high ionic strengths.

TABLE 3 Contact angle measurements for hexadecane droplets in saturated brine at a KCl surface

System	Contact Angle
KCl/hexadecane	No Contact
KCl/hexadecane/ $R_{12}NH_3Cl$ (below solubility limit)	7°
KCl/hexadecane/ $R_{12}NH_3Cl$ (above solubility limit)	52°

Finally, it is interesting to consider the flotation response of LiCl with alkyl amine collectors. Several researchers in the past reported that LiCl can not be floated at all with any type of collector [11,12]. However, the surface charge/collector colloid adsorption hypothesis predicts that the negatively charged LiCl should float with the positively charged alkyl amine collector colloid. In fact, such is the case and LiCl flotation recoveries exceeding 90 % were obtained with amine collector colloids in our laboratory. It should be mentioned that the conditioning time for the preparation of LiCl brine was found to be very important and flotation with alkyl amine collector colloid was possible only when the LiCl brine had been slowly prepared during a period of about 2 hours in order to allow for heat dissipation.

It is expected that the surface charge/collector colloid adsorption phenomena may also occur in other soluble salt systems. In this regard, collector adsorption and flotation of selected oxyanion and double salts have been examined to determine the significance of surface charge in these systems. Nonequilibrium electrophoretic mobility measurements and vacuum flotation/bubble attachment studies have been completed for selected soluble salt systems including alkali nitrates, alkali sulfates, and double salts in order to examine the applicability of the surface charge/collector colloid adsorption theory to these systems.

OXYANIONS AND DOUBLE SALTS

Experimental

Potassium nitrate, sodium nitrate, potassium sulfate, and sodium sulfate reagents used in this study were obtained from Mallinkrodt, Inc. and were used as received. Kainite and schoenite samples were obtained

from the Great Salt Lake Minerals Corporation, Utah and were used as received. The collectors dodecylamine hydrochloride and sodium laurate were purchased from Kodak Research Chemicals and were used as received. Dodecylamine nitrate was synthesized in our laboratory and was used as collector for the flotation of alkali nitrates. Milli Q water of 18 M Ω was used in all experiments. Glassware used in this work was soaked in chromic acid, rinsed with large amounts of pure water, soaked in KOH, rinsed in pure water, and dried just prior to use.

Electrophoretic mobility measurements were done by laser-Doppler electrophoresis using the Zetasizer 3 (Malvern Instruments Ltd., London, UK). These nonequilibrium measurements were done by injecting the salt particles into fresh water solutions. Such dynamic measurements were possible because of certain features of the laser-Doppler equipment which are discussed with other details of the experimental procedure in the literature [18].

The vacuum flotation technique was used to study the flotation response of soluble salts under consideration with the selected collectors. A sample of from 0.5 to 3.0 grams of 100x140 mesh material was conditioned for about thirty minutes in a saturated brine containing the collector at a particular concentration. The flotation was then carried out for 3 minutes at 1×10^{-4} torr vacuum. Subsequently, the float and nonfloat fractions were filtered, dried, and weighed in order to determine the flotation recovery of a particular salt.

Finally, bubble attachment experiments for potassium and sodium sulfate salt particles were carried out using an electronic induction timer supplied by Mineral and Coal Technologies, Virginia. Particles (65x100 mesh) of the desired salt were conditioned in saturated solutions in order to establish equilibrium. The collector colloid was prepared in saturated brine, the desired salt particles were added, and the suspension was conditioned for an additional five minutes. The conditioned particles together with the solution (10 cc) were transferred to a small cell which was placed beneath the bubble holder. A captive bubble (generated using a microsyringe) of approximately 2 mm in diameter was held on the bubble tube and kept in contact with the bed of particles for a given time, typically 2 seconds. The tube with the bubble was then raised to its original position, and the bubble was observed through a microscope to determine whether attachment of particles at the bubble surface had occurred. The experiment was repeated several times for each salt.

Results and discussion

The nonequilibrium electrophoretic mobility measurements for sulfates, nitrates, kainite, and schoenite were determined during dissolution by laser-doppler electrophoresis. These results are presented in Table 4. Typical nonequilibrium electrophoretic mobility distributions for potassium and sodium sulfate salts are presented in Figure 5. It can be seen from this Figure that potassium and sodium sulfate salts differ in surface charge. Potassium sulfate exhibits a negative surface charge indicating that surface sulfate ions hydrate less than surface potassium ions whereas the electrokinetic behavior of sodium sulfate is exactly opposite to that of potassium sulfate. The validity of these nonequilibrium electrophoretic mobility measurements for soluble salts is once again demonstrated by measuring the equilibrium electrophoretic mobility which was possible for K_2SO_4 because of its low solubility (~ 12 gr/100 gr of water). It can be noticed from Table 4 that the sign of the surface charge in both equilibrium and nonequilibrium measurements is the same. The decrease in the magnitude of the electrophoretic mobility under equilibrium conditions appears to be due to the decrease in double layer thickness at high ionic strength. On the other hand, both potassium and sodium nitrate salts exhibit a negative surface charge. The inference from this data is that the surface nitrate ions tend to hydrate less than the potassium and sodium cations in the surface lattice thus resulting in negatively charged surfaces.

The double salts, schoenite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$) and kainite ($KCl \cdot MgSO_4 \cdot 3H_2O$) exhibit a negative and positive surface charge respectively. Although there is insufficient thermodynamic data available to examine these results in terms of lattice ion hydration theory, the reliability of this experimental analysis has been demonstrated for the alkali halides [18].

TABLE 4 Nonequilibrium electrophoretic mobilities for selected alkali oxyanions and mixed salts

Salt	Electrophoretic Mobility (μ/sec)/(V/cm)
K_2SO_4^a	-0.62 ± 0.13
Na_2SO_4	$+0.43 \pm 0.22$
KNO_3	-0.52 ± 0.16
NaNO_3	-0.86 ± 0.56
$\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ (schoenite)	$+0.25 \pm 0.19$
$\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$ (kainite)	-0.19 ± 0.12

^a Equilibrium electrophoretic mobility of $\text{K}_2\text{SO}_4 = -0.37 \pm 0.13$

Fig.5 Nonequilibrium electrophoretic mobility distributions for K_2SO_4 and Na_2SO_4 .

Flotation/bubble attachment experiments were conducted for the above mentioned oxyanions and double salts to examine the validity of the surface charge/collector colloid adsorption theory in these systems. Bubble attachment studies were conducted for K_2SO_4 and Na_2SO_4 salts with dodecylamine hydrochloride and sodium laurate collectors at a concentration of 1×10^{-4} M. Collector colloids were present at this concentration since it is above the solubility limit of these collectors. For negatively charged K_2SO_4 , bubble attachment occurred when the positively charged amine collector colloid was used as shown in Table 5. On the other hand, bubble attachment did not occur at the negatively charged K_2SO_4 surface

when the negatively charged sodium laurate collector colloid was used. Bubble attachment at the positively charged Na_2SO_4 surface was only possible when the negatively charged sodium laurate collector colloid was used and no bubble attachment was found with the positively charged amine collector colloid as shown in Table 5.

TABLE 5 Bubble attachment results for potassium and sodium sulfate salts in the presence of collector colloids

Salt	Bubble Attachment	
	Dodecylamine (1×10^{-4} M)	Laurate (1×10^{-4} M)
K_2SO_4 (Negative)	Yes	No
Na_2SO_4 (Positive)	No	Yes

The vacuum flotation technique was used to study the flotation response of potassium and sodium nitrates as a function of dodecylamine nitrate collector addition. Figure 6 shows that both NaNO_3 and KNO_3 salts float well with $\text{R}_{12}\text{NH}_3\text{NO}_3$ collector only after precipitation of the $\text{R}_{12}\text{NH}_3\text{NO}_3$ collector colloid from solution. Similar results were reported by Pizarro et al. [28,29]. The electrophoretic mobility of $\text{R}_{12}\text{NH}_3\text{NO}_3(\text{s})$ indicates that these collector colloids are positively charged at natural pH [17]. Because the surface charges are opposite in sign, it is expected that heterocoagulation occurs between the negatively charged potassium and sodium nitrate salts and the positively charged $\text{R}_{12}\text{NH}_3\text{NO}_3(\text{s})$ collector colloid. This heterocoagulation event appears to account for the effective flotation of both KNO_3 and NaNO_3 with the dodecylamine nitrate collector colloid and the results indicate that selective amine flotation of one salt from the other will be difficult because both carry the same surface charge. In the same way, it is evident from Figure 7 that neither KNO_3 nor NaNO_3 are floated with the sodium laurate collector colloid which carries the same sign of surface charge as the nitrate salts; thus heterocoagulation does not occur and flotation would not be expected according to the surface charge/collector colloid adsorption theory.

Fig.6 Flotation recovery of KNO_3 and NaNO_3 as a function of dodecylamine nitrate concentration.

Fig.7 Flotation recovery of KNO₃ and NaNO₃ as a function of sodium laurate concentration.

Vacuum flotation experiments for schoenite and kainite were carried out with amine and carboxylate collectors at two different collector concentrations. These collector concentrations were selected such that one concentration (7×10^{-6} M) is below and the other (1×10^{-4} M) is above the solubility limit of the collectors. Precipitation of the collector colloid was detected by visual observation of scattered light. The composition of the collector colloid precipitate is not known for certain but the surface charge of these collector colloids is assumed to be similar to the surface charge of collector colloids examined previously. The flotation results are presented in Table 6. It can be observed from this table that positively charged schoenite floated only with the negatively charged laurate collector colloid whereas negatively charged kainite floated only with the positively charged amine collector colloid. Practically no flotation was observed for both kainite and schoenite when the collector concentration was below its solubility limit, no matter which collector was used.

TABLE 6 Flotation response of double salts in the absence and presence of collector colloids

Double Salt	Flotation Recovery (%)			
	Dodecyl Amine		Laurate	
	7×10^{-6} M No Ppt.	1×10^{-4} M Ppt.	7×10^{-6} M No Ppt.	1×10^{-4} M Ppt.
Schoenite (Positive)	3	4	4	58
Kainite (Negative)	5	61	5	4

It is evident from these results that the flotation response of soluble salt minerals such as alkali nitrates, alkali sulfates, and double salts can best be explained by heterocoagulation of charged collector colloids with oppositely charged mineral surfaces. The surface charge/collector colloid adsorption theory which has been demonstrated for the flotation of alkali halides can therefore be extended to explain the collector adsorption phenomena observed in the flotation of alkali oxyanions and double salts. These results should

be particularly useful for improving the reagent schedule for potash flotation from lake brines and for the flotation of less common soluble salt minerals.

SUMMARY AND CONCLUSIONS

The surface charge/collector colloid adsorption theory has been demonstrated for the flotation of alkali halides from their saturated brines. The nonequilibrium electrokinetic measurements coupled with flotation studies of alkali halides suggest that the selective flotation of alkali halides is due to the adsorption of oppositely charged collector colloids rather than by the adsorption of collector ions and/or neutral molecular dipoles as previously suggested by other researchers.

Nonequilibrium electrophoretic mobility measurements for selected alkali oxyanions and double salts have been made by laser-Doppler electrophoresis to examine the validity of the surface charge/collector colloid adsorption hypothesis in these systems. The results from flotation/bubble attachment experiments for alkali oxyanions and double salts clearly indicate that indeed surface charge plays an important role in these soluble salt systems and selective flotation of these soluble salts can be explained by the surface charge/collector colloid adsorption theory.

Finally, it should be mentioned that the surface charge/collector colloid adsorption theory must, at this time, be limited to alkyl amine and carboxylate collectors. For example, it is reported in the literature that soluble salt flotation with alkyl sulfonates and alkyl sulfates is possible without collector precipitation, i.e. in the absence of collector colloids, and further examination of these systems is warranted.

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The Surface Charge of KCl as Influenced by Crystal Lattice Defects

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Recently, nonequilibrium electrokinetic measurements using laser-Doppler electrophoresis were reported for alkali halides and the sign of their surface charge was thus determined (13). These results are generally as expected from simplified lattice ion hydration theory with KCl, under normal circumstances, being the most significant exception. In this regard, lattice defects (*F* centers and oxygen imperfections) have been found to influence the surface charge of KCl and its electrophoretic mobility. In particular, the presence of oxygen defect states in the crystal lattice has been found to be responsible for KCl's unexpected behavior. The concentration of oxygen defect states in KCl, as characterized by UV/Vis absorption, was varied in order to study their influence on the electrokinetic behavior and subsequently on the flotation response of KCl. At low oxygen contents (<60 ppm) KCl is positively charged as expected from lattice ion hydration theory. However, typically, KCl contains substantial oxygen (>300 ppm), sufficient to impart a negative surface charge and this accounts for the selective flotation of KCl from NaCl by heterocoagulation with oppositely charged alkyl amine hydrochloride collector colloids. © 1994 Academic Press, Inc.

INTRODUCTION

Sylvite (KCl) is the most predominant potash mineral in the world potash deposits (1). Over 80% of the potash in the world today is produced by the selective flotation of sylvite from such salt deposits (2, 3). The flotation separation is based on controlled surface chemistry so that one mineral component of a particular mixture (e.g., KCl) is maintained in a hydrophobic state by the adsorption of an appropriate collector (surfactant) while the other particulate mineral components (e.g., NaCl, gangue, etc.) are maintained in their natural hydrophilic state. In this way, the hydrophobic particles attach to air bubbles dispersed throughout the suspension and are recovered as a froth phase during flotation. Other mineral particles which do not adsorb the collector are maintained in a hydrophilic state and remain in suspension, and separation is thus achieved.

Lattice Ion Hydration Theory and Flotation Chemistry

The difference in floatability of KCl and NaCl is amazing in view of the fact that these two alkali halides are so similar

chemically and crystallographically. Several hypotheses have been advanced in the past to explain collector adsorption phenomena observed in soluble salt flotation systems, with no agreement (4-11). However, results from recent research at the University of Utah indicate that collector adsorption in soluble salt flotation can best be explained by the heterocoagulation of the oppositely charged collector colloids and soluble mineral particles (12-17). Based on the nonequilibrium electrokinetic measurements for alkali halides by laser-Doppler electrophoresis reported by Miller *et al.* (13), the sign of the surface charge of alkali halides in their saturated brines has been established.

The surface charge results thus determined are generally as expected from simplified lattice ion hydration theory. The lattice ion hydration theory describes surface charge development by nonreactive ionic solids when placed in water. For simple uni-univalent salts such as alkali halides, the surface charge can be estimated simply from a comparison of the hydration free energies of the corresponding gaseous ions. For example, if the hydration free energy of the surface lattice cation is more negative than the hydration free energy of the surface lattice anion, then the surface will carry a negative charge. The converse is also true. Initially the simplified lattice ion hydration theory was demonstrated for silver halides (18) and more recently it was extended to take into consideration the lattice energy effects for more complicated nonreactive ionic solids such as calcium fluoride (19-21). Now, from nonequilibrium electrokinetic measurements the lattice ion hydration theory has generally been substantiated for alkali halides (13). These findings have been used together with the stability and prevalence of collector colloids to explain the flotation response according to the surface charge/collector colloid adsorption hypothesis for soluble salt flotation (13). Experimental flotation results for KCl and NaCl further confirm the validity of this hypothesis (16). Specifically, these results showed that negatively charged KCl floats only when positively charged alkylamine hydrochloride collector colloids are present in the system. On the other hand, KCl does not float with negatively charged sodium laurate collector colloids. In addition the flotation response of other soluble salt minerals including alkali oxyanions and double salts can be explained by the surface charge/collector colloid adsorption theory (17).

It is evident from this past work that the surface charge of alkali halides generally can be predicted from simplified lattice ion hydration theory. However, there are exceptions, KCl being the most important, as shown in Table 1 where the results from nonequilibrium electrophoretic measurements by laser-Doppler electrophoresis are compared to the predictions from lattice ion hydration theory. It can be noticed from this table that seven salts, viz. LiF, KCl, NaCl, KBr, RbBr, KI, and RbI, are in variance with the lattice ion hydration theory predictions. In the case of LiF, NaCl, KBr, KI, and RbI, the deviation from theory might be explained in terms of the reliability of the gaseous ion hydration free energy values (22). In almost all of these cases, the difference in cation and anion gaseous hydration free energies is very small and uncertainty in the thermodynamic values could lead to erroneous predictions. However, in the case of KCl, the difference between cation and anion hydration free energy

is greater than 10 kcal/mole, and other factors must account for the deviation from theory.

It can be noted from Table 1 that KCl was found to be negatively charged even though theory predicts KCl to be positively charged. Now research has shown that this deviation from theory is due to the presence of crystal lattice defects. In this regard, two different types of defect states, viz. *F* centers and oxygen imperfections, were considered in order to study their influence on the surface properties of KCl. A brief description of *F* centers and oxygen imperfections, provided in the following paragraphs, explains the nature and formation of these defects in alkali halide crystals.

Defect Structures

One of the most common and striking features of defects in alkali halide crystals is the coloration of the crystals which occurs under certain circumstances (23). For example, if KCl is heated in the presence of potassium vapor, the crystal becomes green with a blue tinge due to the introduction of excess potassium ions and electrons into the KCl crystal lattice according to the reaction:

These added potassium ions occupy either a normal lattice site or an interstitial site while the electrons occupy vacant anion sites, acting as small anions. The electrons occupying anion vacancies are called *F* centers. If a pair of electrons occupies an anion vacancy, then an *F'* center results. This process of introducing color centers into the crystal lattice is known as additive coloration. It should be noted that these *F* centers are extremely mobile when compared to Frenkel and Schottky defects. The rapid movement of these defects can be demonstrated by placing a colored crystal between an anode and cathode which, at a moderate temperature, results in the migration of the particular color of the crystal toward the anode.

F and *F'* centers can also be produced by irradiating alkali halide crystals. For example, irradiation of KCl with X-rays or alpha particles causes the reaction:

The electron thus set free may be trapped in an anion vacancy which leads to coloration of the crystal. When the KCl crystal is heated, the electrons rapidly find their way back to a neutral chlorine and the color is bleached immediately. Many natural minerals show such coloration (*F* centers) produced by long exposure to radiation in a natural environment.

In addition to *F* centers, the effect of oxygen defect states (O_2^- and O^{2-}) on the surface properties of KCl crystals was also studied. Oxygen can be present in the KCl crystal in two different forms namely, O_2^- and O^{2-} centers (24). If the

TABLE 1
Sign of the Surface Charge for Selected Alkali Halides (22)

	Negative gaseous ion hydration free energies, kcal/mole			Sign of surface charge	
	Cation	Anion	Δ^a	Predicted ^b	Experimental ^c
Fluorides					
LiF	112.0	109.6	2.4	—	+
NaF	88.4	109.6	21.2	+	+
KF	71.1	109.6	38.5	+	+
RbF	65.9	109.6	43.7	+	+
CsF	58.2	109.6	51.4	+	+
Chlorides					
LiCl	112.0	82.5	29.5	—	—
NaCl	88.4	82.5	5.9	—	+
KCl	71.1	82.5	11.4	+	—
RbCl	65.9	82.5	16.6	+	+
CsCl	58.2	82.5	24.3	+	+
Bromides					
LiBr	112.0	75.7	36.3	—	—
NaBr	88.4	75.7	12.7	—	—
KBr	71.1	75.7	4.6	+	—
RbBr	65.9	75.7	9.8	+	—
CsBr	58.2	75.7	17.5	+	+
Iodides					
LiI	112.0	66.5	45.5	—	—
NaI	88.4	66.5	21.9	—	—
KI	71.1	66.5	4.6	—	+
RbI	65.9	66.5	0.6	+	—
CsI	58.2	66.5	8.3	+	+
NaI · 2H ₂ O	NA	NA	NA	NA	+

^a Difference in cation and anion gaseous hydration free energies.

^b Simplified lattice ion hydration theory.

^c Electrophoretic-mobility measurements by laser-Doppler electrophoresis.

crystals are grown in an ambient atmosphere, the KCl melt reacts with oxygen to form KO_2 (O_2^- centers) as follows:

When excess potassium is introduced into the lattice, KO_2 present within the lattice is converted to K_2O (O^{2-} centers) according to the reaction:

Equation [4] can also be represented as

The symbol $\Box$ in Eq. [5] represents a vacancy in the crystal lattice. The introduction of excess potassium ions into the KCl lattice creates F centers (e^- at anion vacancies) in the crystal lattice as mentioned in the previous section. Therefore Eq. [5] can be rewritten as

It is clear from Eq. [6] that the number of O_2^- defects will be reduced by the presence of F centers in the crystal lattice thereby forming the O^{2-} defect pairs.

Research Objectives

In the present work, F centers and oxygen imperfections were created in KCl crystals at various levels of concentration in order to examine their influence on the electrokinetic properties of KCl. In particular, this work was done to determine if the deviation of KCl surface charge from that predicted by lattice ion hydration theory could be explained by the presence of crystal lattice defects. Vacuum flotation studies were then conducted to determine if these defects would influence the flotation response of KCl according to the surface charge/collector colloid adsorption model.

EXPERIMENTAL

Materials and Equipment

Several different sources of KCl were used in this study of defect states. Single crystals of optical quality KCl were obtained from Optovac, Inc. Another sample of KCl, ultra dry, <300 ppm oxygen, and 99.999% pure, was purchased from Aesar JM. This particulate material was used for growing a laser quality crystal by the Czochralski method (25) at the University of Utah Crystal Growth Laboratory. Finally, particulate KCl (analytical reagent grade) was purchased from Mallinckrodt and was used as received.

Color centers in KCl were produced by using an additive coloration apparatus at the University of Utah Laser Insti-

tute. The schematic of this apparatus is shown in Fig. 1. It should be noted that the apparatus has appropriate pressure gauges to monitor the alkali vapor pressure and temperature control system (26).

Other experiments involving thermal treatment of potassium chloride were carried out in a Lindberg tube furnace in oxygen and nitrogen atmospheres. Oxygen traps (Alltech Associates, Inc.) were used to reduce the oxygen levels in the nitrogen used to less than 1 ppm.

A Perkin-Elmer DU-7 UV/Vis spectrometer was used to record the UV/Vis spectra of KCl crystals. A Zetasizer 3 (Malvern Instruments Ltd., London, UK) was used for measuring electrophoretic mobilities. Flotation experiments were conducted by using a vacuum flotation cell.

Procedures

KCl crystals of size $10 \times 10 \times 25$ mm were exposed to potassium vapor in the additive coloration apparatus to create F centers. The crystals were maintained in an inert atmosphere at a temperature of 650°C for 24 h to achieve a uniform distribution of color centers throughout the crystal (26). Different alkali pressures were employed to achieve the variation in the number of color centers produced. UV/Vis spectra of KCl were recorded at a scan speed of 300 nm/min in the range from 200 to 600 nm. The UV/Vis spectra were obtained by ratioing the background of the empty sample compartment against the sample spectrum.

FIG. 1. Schematic of the additive coloration apparatus used to create F centers in KCl crystals.

In other experiments to control oxygen defect states, KCl crystals were thermally treated at a temperature of 650°C for at least 30 h in a tube furnace. Nitrogen (<1 ppm oxygen) and oxygen atmospheres were maintained in the tube furnace to remove oxygen from, or supply oxygen to, the KCl crystals. Only about 300 mg of KCl (125 micrometers) was treated in each test to ensure complete reaction. The oxygen levels in thermally treated KCl were determined by IRT Corporation, San Diego, by neutron activation analysis.

The nonequilibrium electrophoretic mobilities for KCl were measured by laser-Doppler electrophoresis. The details of this experimental procedure are given elsewhere (13).

Finally, the vacuum flotation technique was used to study the flotation response of KCl particles with dodecylamine hydrochloride as collector. Samples of from 0.5 to 3.0 g of 100-micrometer material were conditioned for about 30 min in a saturated brine containing the collector at a particular concentration. The flotation was then carried out for 3 min at 3×10^{-4} Torr vacuum. Subsequently, the float and non-float fractions were filtered, dried, and weighed in order to determine the flotation recovery of KCl.

RESULTS AND DISCUSSION

The presence of defects has been found to influence the surface as well as the bulk characteristics of alkali halides (23). Basically, these defects alter the charge neutrality on the cleavage planes leading to a change in the surface properties of alkali halides, including KCl. It should be noted that the surface charge considered in this work is due to the differential hydration of the surface lattice ions of the KCl crystal at the solution interface. The resulting surface charge due to lattice ion hydration should not be confused with the surface charge of KCl at the solid/gas interface which is due to the topographical nature of the surface and related to the relative sublimation potential of the surface ions (27–30). It is interesting to note, however, that the difference in the sublimation rates in KCl and NaCl crystals was attributed by some researchers to be due to the difference in the space charge at the KCl (negative) and NaCl (positive) surfaces (31). In the present work, certain types of crystal lattice defects such as *F* centers and oxygen imperfections have been created at various levels of concentration in order to examine their influence on the surface properties of KCl.

F Centers

Color centers or defects were produced in KCl crystals (Optovac) by a procedure known as additive coloration as described previously. The presence of *F* centers created at various alkali vapor pressures was confirmed and characterized by UV/Vis spectra of colored KCl crystals as shown in Fig. 2.

The absorption bands in Fig. 2 for KCl colorated at 24 Torr K vapor are due to the absorption by *F* centers (560

FIG. 2. Absorption spectrum of KCl colorated at 650°C and 24 Torr potassium.

nm, very strong) and their transitions, viz. L_1 (348 nm), L (288 nm, weak), L_3 (251 nm), and L_4 (201 nm) (24, 32). These band positions will be discussed further in the next section. Thus the presence of *F* centers in KCl crystals is indicated both by the color of the crystal and by the characteristic absorption frequencies of *F* centers as revealed in the UV/Vis spectrum. The number of different *F* center types produced in a crystal during a particular coloration procedure can be determined from the peak intensities of the UV/VIS spectra shown in Fig. 2. The color of the crystal also gives an indication about the approximate number density of *F* centers present in the crystal. For example, in a totally black crystal, the number density of *F* centers would be typically about 10^{18} *F*-centers/cm³, whereas in a pale blue or green crystal the number density would be about 10^{13} *F*-centers/cm³ (33). The calculation of the actual number of *F* centers produced, however, is beyond the scope of this research. The mathematical details for the calculation of *F*-center number density can be found in the literature (26, 34).

After characterizing the *F* centers in KCl crystals from UV/VIS spectra, nonequilibrium electrophoretic mobilities for these KCl crystals were measured to examine the influence of defect structures on their electrokinetic properties. These results are presented as electrophoretic mobilities in Table 2.

It may be recalled that KCl without *F* centers has a negative surface charge (see Table 1). However, nonequilibrium electrophoretic mobility results reveal that the sign of the surface charge for KCl changes from negative to positive when *F* centers are created, as shown in Table 2. Also, it can

TABLE 2

Nonequilibrium Electrophoretic Mobilities for KCl with *F* Centers Produced at 650°C and the Flotation Response with the Dodecylamine Hydrochloride Collector Colloid

Crystal	Coloration pressure	Electrophoretic mobility ($\mu\text{m/s}/(\text{V/cm})$)	Flotation recovery (%)
KCl	As received	-0.43 ± 0.19	96
KCl	14 torr K	$+0.21 \pm 0.16$	8
KCl	24 torr K	$+0.39 \pm 0.24$	7

be noted from Table 2 that the surface charge increased from $+0.21 \pm 0.16$ for KCl exposed to 14 Torr K vapor to $+0.39 \pm 0.24$ for KCl exposed to 22 Torr K vapor. From these results, it is clear that both the sign and the magnitude of the surface charge depends on the number of *F* centers present in the crystal lattice. Of course, it can be argued that the presence of excess K^+ ions in the crystal lattice makes the KCl surface positively charged. It appears that even though the K^+ ion has a more negative hydration free energy when compared to the Cl^- ion (see Table 1), the presence of excess K^+ ions introduced into the crystal lattice during additive coloration is sufficient to make the KCl surface positively charged.

Vacuum flotation results for negatively charged KCl with dodecylamine hydrochloride as collector at a concentration of $3 \times 10^{-4} M$ showed that flotation recoveries in excess of 95% can be obtained as indicated in Table 2. Of course, under these conditions the dodecylamine hydrochloride precipitates from the saturated brine as positively charged collector colloids and readily adsorbs on the negatively charged KCl (16). However, flotation recovery is drastically reduced to values below 10% when the KCl is positively charged by the introduction of *F* centers. These results clearly indicate that the presence of *F* centers in KCl significantly influence the surface properties and thereby the flotation response as shown in Table 2.

It should be mentioned that when excess cations are introduced into the alkali halide crystal lattice, excess electrons (*F* centers) will also be introduced into the crystal lattice (see Eq. [1]). There are conflicting reports in the literature regarding the energetics of electron hydration (35, 36). As such, there is very limited information on the thermodynamic characteristics of electron hydration. According to Krestov (35) the thermodynamic value for electron hydration will be equivalent to the values for proton hydration. If this position is true, then electrons should hydrate in preference to K^+ and Cl^- ions. Nonequilibrium electrophoretic mobility measurements and the flotation results for KCl crystals with *F* centers support the position that electron hydration is more energetically favorable than hydration of K^+ , tending to leave the crystal with a more positive charge.

It is clear from these experimental results that the presence

of defect structures can alter the surface properties of KCl and the behavior of the system can be rationalized in terms of lattice ion hydration theory.

Oxygen Defect States

In addition to the study of the effect of *F* centers and coloration on the surface charge of KCl, the effect of oxygen imperfections was also taken into consideration. In this regard, systematic studies were undertaken to examine the surface properties of KCl having varying amounts of oxygen. No coloration of the KCl crystals was observed when the oxygen content of the KCl crystal was varied.

As a first step in this study, an ultra pure laser quality KCl crystal was grown at the University of Utah crystal growth laboratory. The Czochralski method (25) was employed to grow the KCl crystal from a starting material with five-nines purity. The properties of the University of Utah laser quality KCl crystal were compared to those of the optical quality KCl crystal obtained from Optovac, Inc., and to the KCl reagent grade powder as shown in Table 3. It can be seen from this table that the University of Utah KCl crystal has a positive charge as predicted by lattice ion hydration theory whereas the Optovac KCl crystal and KCl reagent grade powder exhibit a negative surface charge. The oxygen levels as determined by neutron activation indicate that the Optovac KCl has a higher oxygen content than the University of Utah KCl as shown in Table 3. The higher oxygen levels in Optovac KCl appear to be due to the use of relatively less pure KCl as a starting material for crystal growth and the crystal growth procedure employed. For example, if the crystal is grown under ambient atmosphere, oxygen in the atmosphere could react with the KCl melt forming various defect states which are discussed in the following paragraphs.

TABLE 3
Nonequilibrium Electrokinetic Properties of KCl
from Various Sources

KCl source	Crystal growth/quality	Sign of surface charge	Oxygen* (ppm)
U of U crystal	Czochralski method/laser quality 99.999% KCl starting material	Positive	60 ± 8.6
Optovac crystal	Chlorine purging Not known/optical quality 99.5% KCl starting material	Negative	345 ± 13
Reagent grade powder	No purging Not applicable	Negative	Not measured

* Obtained from IRT Corporation, San Diego.

Unfortunately, Optovac, Inc., was unwilling to share information regarding their crystal growth procedures. However, it is most likely that one or all the reasons mentioned above could account for the presence of higher levels of oxygen in Optovac KCl crystals. In any event, it seems that the difference in oxygen levels in the University of Utah and Optovac crystals is responsible for the difference in the electrokinetic behavior of these KCl crystals.

The presence of O_2^- and O^{2-} defects can be characterized by their typical absorption frequencies in the UV/VIS region (24, 32). Figure 3 shows the absorption spectra for the Optovac and the University of Utah KCl crystals in the UV/Vis region. The presence of O_2^- defects in the Optovac KCl can be clearly seen from Fig. 3 as indicated by the band positions at 205 and 244 nm. On the other hand, it can be noted that the University of Utah KCl crystal is free of O_2^- defects as indicated by the absence of any absorption bands in the region of 200–250 nm. Fisher *et al.* (24) reported that both O_2^- and O^{2-} defects in KCl have a characteristic absorption band in the range of 200–250 nm. It should be mentioned that O_2^- defects could easily be converted into O^{2-} defects if the crystal is exposed to prolonged radiation even in the natural environment. However, neither the University of Utah nor Optovac crystals show any characteristic absorption due to O^{2-} defects. Typically, O^{2-} defects have multiple absorption bands at 440, 286, 215, and 194 nm (24) and clearly these multiple bands are absent in Fig. 3 which indicates that the University of Utah and Optovac

FIG. 3. Absorption spectra of the Optovac and University of Utah KCl crystals. Optovac KCl shows absorption due to O_2^- defects whereas the University of Utah KCl does not show any absorption due to oxygen defect states.

TABLE 4
Dodecylamine Hydrochloride Flotation of KCl
from Various Sources

KCl source	Sign of surface charge	Flotation recovery
U of U crystal	+	5
Optovac crystal	—	95
Reagent grade	—	94

crystals had not been exposed to long-term radiation since these crystals are free of O^{2-} defects.

Therefore it can be concluded that the absorption bands in Fig. 3 for the Optovac KCl are due to the presence of O_2^- defects, whereas the University of Utah KCl crystal is free of any oxygen defects which was expected since the University of Utah crystal was grown with extreme care to avoid oxygen contamination.

At this juncture, it is worthwhile to refer back to Fig. 2 which the F centers in KCl are described. Recall that KCl obtained from Optovac was used for the additive flotation experiments as mentioned before. The O_2^- defect states present in Optovac KCl crystals would obviously transform into O^{2-} defect states when excess potassium ions are introduced into the crystal lattice during the coloration process (see Eq. 5). Therefore, one should see the characteristic multiple absorption bands associated with O^{2-} defect states in Fig. 2 unless these O^{2-} defects form pairs with cations, in which case multiple bands due to O^{2-} defect states disappear and bands corresponding to the defect pairs would appear in the UV/Vis spectra. In fact, the spectrum presented in Fig. 2 shows that the O^{2-} did form defect pairs as revealed by the characteristic absorption band for $O^{2-} \cdot \square$ at 345 nm (24).

In any case, the UV/Vis spectra for Optovac KCl, University of Utah KCl and their nonequilibrium electrophoretic mobility results (see Table 3) suggest that O_2^- defects strongly influence the surface properties and are responsible for the deviation of normal KCl from predictions based on lattice ion hydration theory. Also, it is expected from nonequilibrium electrophoretic measurements that the positive surface charge of the reagent grade KCl is due to the presence of O_2^- defects.

Table 4 presents the results from vacuum flotation experiments conducted for KCl from different sources using dodecylamine hydrochloride as collector at a concentration of $3 \times 10^{-4} M$. Of course, at this concentration, the positively charged collector colloid precipitates from solution (16) can be seen from Table 4 that the flotation recovery of positively charged University of Utah crystal is very poor whereas Optovac and reagent grade KCl (negatively charged) show very good flotation recoveries.

The concentration of oxygen defects was varied to ex-

their influence on the electrokinetic properties of KCl. Optovac and reagent grade KCl particles were thermally treated in nitrogen atmospheres containing less than 1 ppm oxygen in a tube furnace as described in the experimental section. Similarly, the KCl crystal grown at the University of Utah was thermally treated in an oxygen atmosphere. Table 5 presents the results from these thermal treatment experiments. It can be noted from this table that when the University of Utah KCl was thermally treated at 650°C for about 27 h in an oxygen atmosphere, the surface charge reversed its sign and changed from positive to negative due to oxygen incorporation into the crystal lattice. In the case of Optovac and reagent grade KCl, the surface charge reversed its sign in the opposite direction, changing from negative to positive when these particles were thermally treated in the presence of nitrogen having less than 1 ppm oxygen. The sign of surface charge reversal in the case of University of Utah KCl indicates that oxygen has diffused into the crystal as suggested by the increase in oxygen level from 60 ± 9 ppm to 147 ± 9 ppm and thus accounts for the change in electrokinetic behavior. These results show that when KCl is sufficiently oxygen defect free, its electrokinetic behavior is predicted according to lattice ion hydration theory. However, generally KCl deviates from lattice ion hydration theory because of the typical level of oxygen defects found in the crystal lattice.

Similar conclusions can be drawn based on the results for both Optovac and reagent grade KCl particles. Both Optovac and reagent grade KCl (samples with high oxygen content) exhibited a negative surface charge before thermal treatment. When these KCl particles were thermally treated in the presence of nitrogen having less than 1 ppm oxygen, the sign of the surface charge reversed from negative to positive. Of course, KCl is expected to be positively charged according to lattice ion hydration theory. Presumably, oxygen present in the crystal has diffused out during the thermal treatment due to the low oxygen pressure in the atmosphere above the bed of the KCl particles. In fact the UV/Vis spectrum of a KCl plate (Optovac, $5 \times 5 \times 1$ mm), thermally treated at about 650°C in the presence of nitrogen (oxygen <1 ppm), revealed that oxygen had, indeed, been removed from the

FIG. 4. Comparison of absorption spectra of Optovac KCl thermally treated at 650°C in a nitrogen (oxygen <1 ppm) atmosphere for 30 h with the as-received Optovac KCl.

KCl plate as indicated by the absence of characteristic absorption bands associated with O_2^- defects in the range 200–250 nm as shown in Fig. 4.

The change in the electrokinetic behavior of Optovac KCl has been monitored with respect to the thermal treatment time. It took approximately 30 h of thermal treatment (650°C, $O_2 < 1$ ppm) for charge reversal of KCl to occur as shown in Fig. 5. These observations further substantiate the fact that oxygen defect states are responsible for the deviation of KCl from behavior expected according to lattice ion hydration theory. The results from this study suggest that the

TABLE 5

Thermal Treatment Experiments—The Effect of Oxygen

KCl source	Temp/atm (°C)	Time (h)	Nonequilibrium electrophoretic mobility	Oxygen (ppm)
U of U	As prepared	—	$+0.18 \pm 0.10$	60 ± 8.6
	650/ O_2	27	-0.26 ± 0.17	147 ± 9.0
Optovac	As received	—	-0.46 ± 0.20	345 ± 13.0
	650/ N_2	27	$+0.34 \pm 0.16$	Not measured
Reagent grade	As received	—	-0.42 ± 0.19	Not measured
	650/ N_2	27	$+0.32 \pm 0.16$	Not measured

FIG. 5. Nonequilibrium electrophoretic mobility of Optovac KCl thermally treated at 650°C in a nitrogen (oxygen <1 ppm) atmosphere as a function of time.

presence of oxygen inhibits the hydration of surface anionic species compared to the hydration of surface potassium ions which then results in a negatively charged KCl surface.

SUMMARY AND CONCLUSIONS

Deviation of KCl from the sign of the surface charge predicted according to lattice ion hydration theory has been explained in terms of defect states present in the crystal lattice. The results from the additive coloration experiments revealed that color center defects significantly influence the surface properties of KCl. Of even greater significance, however, is the finding that the presence of oxygen defect states accounts for the fact that KCl is negatively charged under normal circumstances and thus generally is in variance with the prediction from lattice ion hydration theory. Only at low oxygen contents was KCl found to become positively charged and conform to lattice ion hydration theory. For example, the surface charge of a specially grown laser quality KCl crystal with an oxygen content of about 60 ppm was found to be positive. Generally, the oxygen content of most KCl crystals (both natural and synthetically grown) is much higher (~350 ppm) and thus these KCl crystals are negatively charged, deviating from the prediction of lattice ion hydration theory.

Thermal treatment of these KCl crystals in appropriate atmospheres showed that the sign of the surface charge is controlled by the oxygen content of the KCl crystal. Experimental results suggest that for an oxygen content in excess of about 150 ppm, deviation of KCl from expected behavior, according to lattice ion hydration theory, should be anticipated. Flotation results further confirm the change in the surface properties of KCl due to the presence of defect states in the crystal lattice and, in addition, support the previously proposed collector colloid adsorption model for soluble salt flotation systems.

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Quantitative Fourier transform-infrared internal reflection spectroscopy (FT-IR/IRS) for adsorption density measurements

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Abstract

Use of the FT-IR/IRS adsorption density equation or any other equation based on the Beer–Lambert law can result in incorrect quantitative values when applied to cases where only part of the internal reflection element (IRE) is coated. Experimental methods that can lead to incorrect quantitative analyses are identified as well as methods to correct such problems. The validity of the (FT-IR/IRS) adsorption density equation is demonstrated using transferred Langmuir–Blodgett films of stearic and oleic acids with proper consideration of coated and uncoated dimensions of the IRE. Results from this study clearly show the FT-IR/IRS adsorption density equation can be used with confidence for quantitative analyses of surfactant adsorption phenomena.

Keywords: Adsorption density measurements; Beer–Lambert law; Internal reflection spectroscopy; Langmuir–Blodgett films; Quantitative spectroscopy

1. Introduction

Quantitative Fourier transform-infrared internal reflection spectroscopy (FT-IR/IRS) is an important analytical tool in surface chemistry. One common equation used in quantitative FT-IR/IRS surface analysis is the FT-IR/IRS adsorption density equation. Proper application of the FT-IR/IRS adsorption density equation requires some understanding of internal reflection spectroscopy, the effect of sample and incident beam sizes, and the variables used in the adsorption density equation.

1.1. Internal reflection spectroscopy (IRS)

Internal reflection spectroscopy (IRS), alternatively referred to as attenuated total reflection

(ATR) spectroscopy, was first proposed by Harrick [1] and independently by Fahrenfort [2] in the 1960s. Reviews of IRS can be found in the literature [3–7]. An improved signal/noise ratio due to multiple internal reflections allows the study of surfactant adsorption on single-crystal internal reflection element (IRE) surfaces even at submonolayer coverage.

1.2. Effect of sample and incident beam sizes

In some FT-IR/IRS applications, quantitative errors can arise [8]. An example of such quantitative errors is illustrated in Fig. 1. In Fig. 1 an IRE was coated by evaporating a sodium oleate solution along the central portion of the IRE. Two spectra were then taken, each with a different incident beam size. The resulting instrumental absorbance values were different, even though the

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Fig. 1. FT-IR/IRS spectra of sodium oleate coated only along a central strip (0.8 mm wide) of a fluorite IRE: spectrum a, small incident beam size, 2.9 mm height; spectrum b, large incident beam size, 9.6 mm height.

amount of exposed adsorbate remained the same. According to Beer's law, the absorbance should be proportional to the number of absorbing molecules encountered by the beam [9–11]. This discrepancy in absorbance values originates from improper application of Beer's law. Because Beer's law is the foundation for all quantitative spectroscopy, improper application will lead to significant errors in quantification.

1.3. FT-IR/IRS adsorption density equation

The FT-IR/IRS adsorption density equation was first proposed and applied by Sperline et al. [12] and later developed for different systems by Miller et al. [13–15]. The FT-IR/IRS adsorption density equation is

$$\Gamma = \frac{(A/N) - \epsilon C_b d_e}{1000\epsilon(2d_e/d_p)} \quad (1)$$

where Γ is the adsorption density (mol cm^{-2}), A the integrated absorbance (cm^{-1}), N the number of internal reflections, ϵ the molar absorptivity ($\text{l cm}^{-2} \text{ mol}^{-1}$), C_b the bulk concentration (mol l^{-1}), d_e the effective thickness (cm) and d_p the depth of penetration (cm). A more in-depth analysis of individual parameters is available in the literature [12,16–18].

The molar absorptivity ϵ can be evaluated from transmission experiments using the Beer–Lambert

equation:

$$A = \epsilon b C \quad (2)$$

where b is the thickness of sample (cm) and C the surfactant concentration (mol l^{-1}).

All of the independent variables can be calculated from optical considerations (N , d_p and d_e), measured spectroscopically (A and ϵ) or measured by other means (C_b). Knowing all of the necessary values allows straightforward calculation of the adsorption density in a variety of applications.

Researchers at the University of Utah have used mineral crystals as reactive IREs for in situ study of surfactant adsorption phenomena at mineral surfaces, and have applied the FT-IR/IRS adsorption density equation in quantitative analyses of the adsorbed species. Many different IREs have been used, including Al_2O_3 [13–15], CaF_2 [13,14,17], KCl [19] and CaCO_3 [20]. In addition, the FT-IR/IRS adsorption density equation has been used to analyze protein adsorption phenomena [21].

2. Experimental

Stearic acid (+99% pure) obtained from Johnson–Matthey, as well as oleic acid (+99% pure) and sodium oleate (+99% pure) obtained from Sigma Chemical were used without further purification. Chloroform and carbon tetrachloride (99.99% pure) were used as received from EM Science. The Langmuir–Blodgett (LB) monolayer films of stearic and oleic acids were prepared by a Lauda Langmuir film balance manufactured by SYBRON/Brinkmann. The detailed procedure for preparing the LB monolayer films is discussed elsewhere [17]. FT-IR experiments were conducted with a dry-air-purged Bio-Rad Digilab Division FTS-40 FT-IR spectrometer equipped with a liquid-nitrogen-cooled wide-band mercury cadmium telluride (MCT) detector. Calcium fluoride and germanium single-crystal parallelepiped internal reflection elements ($50 \text{ mm} \times 10 \text{ mm} \times 2 \text{ mm}$, 75° and 45° acute angles) were purchased from Optovac Inc. and Harrick Scientific. Calcium fluoride windows were obtained from Spectra Tech Inc.

Using a demountable liquid transmission cell with a spacer and calcium fluoride windows, liquid transmission measurements were conducted to determine molar absorptivities of stearic and oleic acids in carbon tetrachloride. All the spectra were the results of 512 or 1024 co-added scans at a resolution of 8 cm^{-1} . In each transmission test, wire mesh screens were used to prevent detector saturation. In these transmission experiments all portions of the beam that reached the detector passed through the sample chamber; therefore the screens did not quantitatively affect the results.

An internal reflection cell with a variable-angle IRS accessory (Harrick Scientific) was used. The entrance face of the parallelepiped calcium fluoride IRE was cut at a 75° angle and the variable-angle IRS accessory was set at 42° , giving an incident angle of 52.3° at each internal reflection. The germanium IRE was cut with a 45° face and utilized in the IRE accessory at 45° , resulting in an internal reflection angle of 45° . The background spectrum for all IRS measurements was the single-beam spectrum of the clean IRE. All spectra were obtained at a resolution of 8 cm^{-1} using 1024 co-added scans with an open internal aperture. The beam size was maintained at the same size for both background and absorbance measurements. Absorbance spectra were ratioed against the background spectra of a clean calcium fluoride IRE. Milli-Q water ($+18\text{ M}\Omega$) was used in all experiments.

3. Results and discussion

Many FT-IR/IRS applications can result in quantitative errors such as those illustrated by Fig. 1. In Fig. 1 it is shown that two very different absorbance values can be obtained from the same adsorbate coating. These two different absorbance values would lead to different calculated adsorption densities even though the sample adsorption density did not change. The discrepancy in measured absorbance values arises because the incident beam encounters both coated and uncoated sections of the substrate. One common method of FT-IR/IRS analysis involves the use of an in situ sampling accessory as shown in Fig. 2.

Accessories such as that shown in Fig. 2 cause adsorption to occur along the central portion of the IRE. With this type of adsorption pattern, the incident beam size may have a significant effect on the measured absorbance value.

3.1. Source of quantitative errors

The quantitative errors resulting from absorbance measurements in which the incident beam size is larger than the sample size can be explained from fundamental spectroscopy, beginning with the definition of absorbance. Absorbance is defined as [8–11,22–24]

$$A = \log_{10}(I_0/I) \quad (3)$$

where A is the absorbance, I_0 the detected intensity without sample present, and I the detected intensity with sample present.

Most spectroscopic instruments determine this value of absorbance. The absorbance value in Eq. (3) is not necessarily the true sample absorbance needed in quantitative calculations. Instead, the measured absorbance could be a mixture of the absorbance due to the sample-coated section and the non-absorbing, non-coated section, resulting in a diminished absorbance as illustrated in Fig. 3 according to Eq. (3). The true sample

Fig. 2. Schematic diagram of an FT-IR/IRS in situ sampling accessory (after Ref. [8]).

Fig. 3. Schematic representation of an IRE (as used in the FT-IR/IRS accessory shown in Fig. 2) being examined before and after the sample coating is applied with an incident beam height larger than the sample coating height.

absorbance is

$$A_s = \log_{10}(I_{0s}/I_s) \quad (4)$$

where A_s is the sample absorbance, I_{0s} the detected intensity from the sample-coated section before the sample coating is applied (see Fig. 4) and I_s the detected intensity from sample-coated section after the sample coating is applied (see Fig. 4). An example of an FT-IR/IRS experiment in which the true sample absorbance is measured is illustrated in Fig. 4.

Because intensity is defined as the power per unit area, there is a distinct and important difference between I and I_s that can easily be erroneously

Fig. 4. Schematic representation of an IRE (as used in the FT-IR/IRS accessory shown in Fig. 2) being examined for both background and sample responses with an incident beam height equal to the sample coating height.

ignored. I is the detected power per unit of overall beam area, which includes portions travelling through uncoated sections, whereas I_s is the detected power per unit area of beam travelling through coated section only. Thus a quantitative problem arises in cases where the portions of the beam travel through uncoated IRE sections. Writing I in terms of I_s , I_0 and "x", leads to

$$A = \log_{10} \left[\frac{I_0}{I_s + (1-x)I_0} \right] \quad (5)$$

where x is the fraction of incident beam which passes through the sample-coated section of the substrate before the sample coating is applied.

In most quantitative FT-IR/IRS experiments involving parallelepiped internal reflection elements (IREs), the area of the beam used for the background can be different from the area of the beam encountering the sample. This point is illustrated in Fig. 5 in which half of each IRE is coated with a transferred Langmuir–Blodgett monolayer.

3.2. Avoiding quantitative errors

The easiest way to prevent the quantitative errors associated with some FT-IR/IRS experiments is to make sure the incident beam does not encounter the non-coated portion of the IRE. This is illustrated in Fig. 5 using cases 2 and 3. The absorbance value determined by the instrument was $\log(2)$ in cases 2 and 3 — even though the incident beam heights are different, whereas in case 1 the absorbance is only $\log(\frac{4}{3})$. The important point is that in comparing case 1 to cases 2 and 3, the absorbance values determined by the instrument are not the same, despite the fact that the coating is the same in each case. In cases 2 and 3, the value of absorbance determined by the instrument will be the true sample absorbance rather than a mixture of sample and non-coated section absorbances as occurs in case 1.

3.3. Mathematical correction of quantitative errors

Accurate mathematical corrections are difficult to perform in many cases. The two major difficul-

Fig. 5. Schematic representation of the effect of beam and sample size on absorbance using Langmuir-Blodgett deposited films. For the sample coated section (shaded) half of the incident beam is assumed to be absorbed by the coating by the time the beam traverses that section of the IRE. Also, it is assumed that the incident beam intensity is uniform with respect to radial position.

ties are gasket interference and non-uniform incident beam intensity, which can vary considerably with different materials and instruments respectively. The gasket material used in applications such as that depicted in Fig. 2 can interfere with the evanescent field due to gasket roughness or simply by absorbing the infrared beam at the substrate-gasket interface. Under some conditions, gasket materials can eliminate the entire signal from the non-coated substrate, thereby effectively making the fraction of the incident beam passing through the sample-coated section equal to one.

The general form for mathematical correction is

$$A_s = -\log_{10}(1/x)(10^{-A} + x - 1) \quad (6)$$

However, applying Eq. (6) to experimentally obtained data requires knowledge about the incident beam intensity profile and the absorptive

characteristics of the gasket being utilized. If the beam intensity is uniformly distributed and the gasket non-interfering, the value of "x" can be easily determined by geometry.

Applying Eq. (6) to the idealized cases illustrated in Fig. 5, where "x" is equal to the ratio of the coated section height to the incident beam height, leads to the calculation of the true sample absorbance A_s from the instrumental absorbance A according to Eq. (6):

Case 1

$$A_s = -\log_{10}(2)[10^{-\log_{10}(4/3)} + (\frac{1}{2}) - 1] = \log_{10}(2) \quad (7)$$

Case 2

$$A_s = -\log_{10}(1)[10^{-\log_{10}(2)} + (1) - 1] = \log_{10}(2) \quad (8)$$

Case 3

$$A_s = -\log_{10}(1)[10^{-\log_{10}(2)} + (1) - 1] = \log_{10}(2) \quad (9)$$

Eqs. (7)–(9) give identical values for the sample absorbance, even though the measured absorbance values were different; therefore Eq. (6) provides an accurate way of correcting the idealized quantitative problem illustrated in Fig. 5.

In the idealized cases shown above, it was assumed that beam divergence can be neglected. To confirm the validity of this assumption, two in situ tests were conducted. In one test the beam height was reduced to the sample height at the entrance face of the IRE. In the other test, the beam height was reduced to that of the sample at both the entrance and exit faces of the IRE. The resulting absorbance values agreed to within 2%, indicating that the effect of divergence was negligible in this study.

In many spectrometers, the beam intensity profile can essentially be considered uniform near the beam center; however, the extent to which uniformity can be assumed depends upon the internal aperture. For a BioRad Digilab FTS-40, the beam intensity profile is represented in Fig. 6 for an internal aperture of 1.0 cm.

Using the intensity profile in Fig. 6, the fraction of the incident beam traversing through a sample-coated parallelepiped IRE can be calculated as the

Fig. 6. Intensity profile for a BioRad Digilab FTS-40 FT-IR spectrometer determined using a variable circular aperture and calipers. Intensity is defined as response per unit area (cm^2) and the radial position is defined as distance from maximum beam intensity (cm). The internal aperture was set at 1.0 cm and the response measured at 2920 cm^{-1} .

ratio of the integral over the sample contact region to the integral over the beam contact region. For the example given in Fig. 1, numerical integration yielded $x=0.28$ for the beam size used for spectrum a and $x=0.113$ for the beam size used for spectrum b. Applying Eq. (6) with these values for x at each point in the baseline corrected spectra leads to the sample absorbance spectra shown in Fig. 7.

The sample absorbance values between the corrected a and b spectra agree within 20% of each other. The remaining discrepancy can be attributed to beam alignment errors in the intensity profile and absorbance measurements, as well as to inaccuracies in other measurements.

Fig. 7. Comparison of spectra a and b from Fig. 1 which have been mathematically corrected using Eq. (6).

Figs. 1 and 7 represent data from ex situ tests which were more easily controlled than in situ tests. To illustrate the quantitative errors associated with sample and incident beam sizes for in situ experiments, two tests were conducted under the same conditions. In one test, the background and absorbance values were measured with a beam height slightly smaller than the sample chamber height. In the other test the beam size was approximately three times the chamber height. The measured integrated absorbance for these tests is shown in Fig. 8 as a function of time.

The ratio of the true sample absorbance to the measured sample absorbance, which is defined as the correction factor in this discussion, is 1.8 for the data sets in Fig. 8. The measured fraction of the beam that travelled through the sample-coated section of the IRE was 0.44. This value of x leads to a correction factor of 2.3 using Eq. (6) with a measured (non-integrated) absorbance value of 0.01 at 2925 cm^{-1} ; thus the experimentally measured correction factor of 1.8 from Fig. 8 is 22% lower than the calculated correction factor of 2.3 using Eq. (6). Some of the discrepancy between the measured and calculated values may have resulted from solution seepage under the portions

Fig. 8. Comparison of integrated absorbance values ($3030\text{--}2820 \text{ cm}^{-1}$) obtained from two in situ adsorption tests. The pH was 9.5, the temperature was 25°C , and the oleate concentration was $1 \times 10^{-5} \text{ M}$. In test A the entrance face of the IRE was masked to make the incident beam height equal to the sample chamber height. In test B the beam height was considerably larger than the sample chamber height.

of the gasket that lie inside the “O”-ring (see Fig. 2). Though the agreement between the mathematical correction and experiment is not excellent, the magnitude of the error is close to two and the necessity of the mathematical correction for experiments in which the incident beam height was greater than the sample height is evident.

3.4. Confirmation of the adsorption density equation

The validity of the FT-IR/IRS adsorption density equation has been examined in our laboratory making use of LB monolayer films and the true sample absorbance. In this paper, the adsorption densities of transferred LB monolayer films of stearic and oleic acids were calculated from the obtained spectra using the FT-IR/IRS adsorption density equation and compared with adsorption densities evaluated from the measured LB surface pressure–specific area (π - A) isotherms.

To calculate the adsorption densities for ex situ FT-IR/IRS spectra of thin films such as transferred LB films, Eq. (1) should be modified as follows: the concentration of the LB film, $C(z)$, is a step function with $C(z) = C_i$ for $0 < z < t$ and $C(z) = 0$ elsewhere, i.e. $C_b = 0$. Therefore, for the ex situ FT-IR/IRS spectra, the FT-IR/IRS adsorption density equation is

$$\Gamma = \frac{A/N}{1000\epsilon(2d_e/d_p)} \quad (10)$$

It should be noted that, for good transfers, the transfer ratio is very close to unity [25,26]. Although some researchers challenge this point [27], it has been shown that only small variations in packing density occur due to film transfer [28,29]. These effects can be minimized by careful control of experimental conditions.

On the other hand, the adsorption density of transferred LB monolayer films can be monitored quantitatively from the π - A isotherm; therefore a direct measurement of the adsorption density for the transferred monolayer is possible without introducing uncertain assumptions. The area per molecule for an LB monolayer at the air–water interface can be directly determined from the π - A isotherm and thus the adsorption density can be calculated

from Eq. (11):

$$\Gamma = \frac{1}{N_A \alpha} \quad (11)$$

where N_A is Avogadro's number (6.023×10^{23}) and α the area per molecule measured from the π - A isotherm at the surface pressure maintained during LB transfer.

Fig. 9 shows the π - A isotherms for stearic and oleic acids at the air–water interface as obtained using the Langmuir film balance. These isotherms were found to be reproducible and in excellent agreement with the isotherms reported in the literature [30,31]. The adsorption density values of the transferred LB monolayer films of stearic and oleic acids were monitored quantitatively from the established π - A isotherm using Eq. (11) prior to transfer.

Use of the FT-IR/IRS adsorption density equation requires that the molar absorptivity ϵ be determined a priori; thus the molar absorptivities for oleic and stearic acids as revealed by $-\text{CH}$ stretching bands were determined by transmission experiments and are listed in Table 1. The integrated molar absorptivity values of stearic and oleic acids were determined by a linear regression method with the bC term of the Beer–Lambert law as an independent variable and zero as the

Fig. 9. Surface pressure–specific area isotherms of stearic and oleic acids (after Ref. [17]).

Table 1
Molar absorptivity data

Compound/Solvent	Concentration (M)	Integration range (cm^{-1})	($\text{l cm}^{-2} \text{mol}^{-1}$)
Stearic acid/ CCl_4	1.05×10^{-4} – 2.52×10^{-2}	3000–2800	58500
Oleic acid/ CCl_4	5.76×10^{-4} – 5.05×10^{-2}	3032–2802	43300

intercept. The coefficient of determination values (R^2) for these tests are greater than 0.99, indicating that the Beer–Lambert law is valid under these circumstances.

The adsorption density values found from the established π -A isotherms for LB monolayer films of stearic and oleic acids were compared with the adsorption density values evaluated using the FT-IR/IRS adsorption density equation. As shown in Fig. 10, for both stearic and oleic acids, the adsorption density values determined from the FT-IR/IRS spectra are in good agreement with the ones calculated from the established π -A isotherms. These results clearly show that the FT-IR/IRS adsorption density equation is valid and can be used with confidence for quantitative analysis of surfactant adsorption phenomena.

Fig. 10. Adsorption density values of the transferred LB monolayer films of fatty acids determined by the FT-IR/IRS adsorption density equation vs. the values evaluated from the π -A isotherms shown in Fig. 8.

4. Conclusions

Fundamental analysis of the definition of absorbance indicates that spectroscopic techniques in which the sample does not cover the entire substrate can lead to serious quantitative errors. In the case of FT-IR/IRS experiments in which the incident beam travelled through both sample-coated and uncoated portions of the IRE, it has been shown that measured sample absorbances can be significantly less than true sample absorbances. The causes of such errors have been identified and methods to correct these errors were discussed. Therefore quantitative analyses using equations such as the FT-IR/IRS adsorption density equation must only be used with the true sample absorbance as described herein.

FT-IR/IRS analysis of transferred LB films of fatty acids (using true sample absorbance values) showed that the adsorption density values calculated from the FT-IR/IRS adsorption density equation are in good agreement with the ones determined from the π -A isotherms, thus confirming the validity of this equation. These results indicate that the FT-IR/IRS adsorption density equation can be confidently used with true sample absorbance values in quantitative adsorption studies.

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NOTES

Effect of Sample and Incident Beam Areas on Quantitative Spectroscopy

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Index Headings: Quantitative spectroscopy; FT-IR/internal reflection spectroscopy.

INTRODUCTION

Quantitative spectroscopy is based upon the Bouguer-Lambert-Beer law, often referred to as Beer's law, which is expressed as:¹⁻⁴

$$A = \log\left(\frac{I_0}{I}\right) = abc \quad (1)$$

where A is the absorbance, I_0 is the background intensity, I is the intensity measured with the sample present, a is the absorptivity, b is the sample thickness, and c is the sample concentration.

As represented in Eq. 1 the Bouguer-Lambert-Beer law is simple, yet it contains an important subtlety that to our knowledge is not explicitly discussed in the literature, though inferences can be made from the available literature.^{7,8} Because intensity is defined as the power per unit area, the incident beam or background intensity, I_0 , is the power per unit of incident beam area, whereas the intensity measured with a sample present, I , is the power per unit of sample area exposed to the incident beam. Most spectroscopic instruments measure power but not areas; thus, they cannot determine the intensity values required in Eq. 1. Fortunately, when the area encountered by the background incident beam and the area of sample encountered by the incident beam are the same, it is mathematically correct to replace intensity with power or detector response in Eq. 1; however, when the areas are different, calculating the absorbance on the basis of detected signal will lead to substantial error in quantitative analyses.

This note identifies both the general conditions that lead to such errors as well as the magnitude of these errors. In addition, techniques to eliminate these errors are discussed. A more thorough treatment of such errors and mathematical corrections is provided elsewhere.⁹

QUANTITATIVE INTERNAL REFLECTION SPECTROSCOPY

The quantification of internal reflection spectra is considerably more complex than that of transmission spectra, yet, because of the physical arrangement of common internal reflection accessories, the quantification of internal reflection spectra is more likely to result in errors.

FT-IR/IRS (Fourier transform infrared internal reflection spectroscopy) commonly involves an accessory similar to that shown in Fig. 1 for *in situ* adsorption studies. From Fig. 1 it is apparent that adsorption can occur only where the gasket does not contact the internal reflection element (IRE); therefore, the adsorbate will contact the IRE only on the central portion of the IRE, as illustrated in Fig. 2. The fact that the entire IRE is not coated in such a setup must be considered in quantitative analysis of adsorption phenomena.

Quantifying the adsorbate on the IRE can be accomplished with the use of the adsorption density equation that was initially derived by Sperline et al.¹⁰ and was further developed and confirmed at the University of Utah by Miller and Kellar¹¹ and by Jang and Miller.¹² The adsorption density equation is:¹¹

$$\Gamma = \frac{\left(\frac{A}{(l/t)\cot\phi} - C_s\epsilon d_s\right)}{1000\epsilon\left(\frac{2d_s}{d_p}\right)} \quad (2)$$

In Eq. 2, Γ is the adsorption density (mol/cm²), A is the integrated absorbance (cm⁻¹), l is the adsorbate coating length (cm), t is the IRE thickness (cm), ϵ is the molar absorptivity of surfactant [L/(cm²·mol)], C_s is the surfactant bulk concentration (mol/L), d_p is the depth of penetration (cm), d_s is the effective depth (cm), and ϕ is the incident angle of internal reflection. This equation relies upon the instrumental calculation of absorbance, and, therefore, the area encountered by the incident beam and the sample-coated area encountered by the beam will not be accounted for in cases where they are different. The adsorption density equation does, however, account for the adsorbate coating length, leaving only the exposed

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FIG. 1. Illustration of typical internal reflection cell also known as attenuated total reflection (ATR) cell: (1) clamp screw; (2) clamp; (3) solution inlet; (4) stainless steel cell; (5) rubber seal; (6) gasket; (7) internal reflection element; (8) solution chamber; (9) solution outlet.

adsorbate and incident beam heights to be considered in order to completely account for the exposed adsorbate and incident beam areas when parallelepiped IREs are used. When cylindrical IREs are used, the exposed adsorbate and incident beam circumferences are the same; thus, only the adsorbate coating length, which is already included in the adsorption density equation, needs to be considered in order to completely account for the areas.

As discussed previously, quantification errors will result if the incident beam reaches the detector without encountering the sample-coated section. For the internal reflection case using parallelepiped IREs, use of the adsorption density equation, which includes the adsorbate coating length, will result in errors when the effective incident beam height is larger than the exposed adsorbate height. These errors can be illustrated by first taking background spectra with different beam heights, each created by placing sheets of foil with rectangular slits of different heights in front of a clean internal reflection element (IRE) mounted in a cell such as that shown in Fig. 1 with a nonabsorbing gasket. Next, an adsorbate layer of height, h_a , which is less than the foil slit heights, h_i , is coated in the central portion of the IRE, as shown in Fig. 2. Finally, absorbances for each adsorbate sample are measured for each of the incident beam heights against the background at the same incident beam height. Figures 3 and 4 illustrate the different spectra that can be recorded by applying such a technique.

Figure 3 shows FT-IR/IRS spectra generated by evaporating a solution with the desired adsorbate along the

FIG. 2. Illustration of the internal reflection element (IRE) used in the ATR cell shown in Fig. 1. h_i is the incident beam height; h_a is the adsorbate coating height; l is the adsorbate coating length.

FIG. 3. *Ex situ* spectra of oleate adsorbed at a fluorite surface. Background spectra were collected with the use of foil sheets to control the incident beam heights of (1) 0.9 mm; (2) 2.9 mm; (3) 6.0 mm; and (4) 10.0 mm. After the background spectra were taken, the adsorbate was deposited in the center of the IRE by evaporating an oleate solution along a narrow strip of the IRE with the use of Teflon® guides. After the adsorbate was coated on the IRE, an absorbance spectrum was collected against the background spectrum taken with the same slit height. Note the adsorbate coating of height 0.9 mm remained the same throughout the test series. The IRE was a 52- × 10- × 2-mm fluorite parallelepiped with 75° ends. A Harrick twin-parallel-mirror, variable-angle ATR accessory was utilized at a 42° setting.

central portion of the IRE using Teflon® guides. The resulting coating resembles that depicted in Fig. 2. The spectra shown in Fig. 3 were obtained without gaskets present. The spectra shown in Fig. 4 were obtained *in situ* with aluminum foil gaskets. From Figs. 3 and 4, each of which involves a constant adsorption density, it is clear that the calculated adsorption density, which is deter-

FIG. 4. *In situ* spectra of oleic acid adsorbed at a sapphire surface. Background spectra were collected with the use of foil sheets with slit heights of (1) 3.6 mm, (2) 7.1 mm, and (3) 10.0 mm with water present in the cell (note that the water was allowed to equilibrate with the IRE for 4 h prior to the time when background spectra were taken). After the background spectra with water were taken, the adsorbate solution of 10^{-3} M sodium oleate in pH 2 deionized water (18 MΩ-cm) was injected into the cell as an emulsion. After 10 min the cell was flushed with water (pH 2), and the system equilibrated for approximately one half of an hour. After the adsorbate was coated on the IRE, an absorbance spectrum was collected against the background spectrum taken with the same slit height. The IRE was a 52- × 10- × 1-mm sapphire parallelepiped with 60° ends. A Harrick twin-parallel-mirror, variable-angle ATR accessory was utilized at a 60° setting.

TABLE I. Comparison of calculated and actual adsorption density values from both *ex situ* and *in situ* adsorption tests. The integrated absorbance values from the FT-IR/IRS spectra of CaF_2 and Al_2O_3 IRE substrates coated with oleate were used to calculate the adsorption density with the use of Eq. 2. The molar absorptivities used were 36,500 and 5215 [$\text{L}/(\text{cm}^2 \cdot \text{mol})$] for the $\text{CaF}_2/\text{oleate}$ (2825–3025 cm^{-1}) and $\text{Al}_2\text{O}_3/\text{oleate}$ (2820–2878 cm^{-1}) systems, respectively—as shown in Figs. 3 and 4.

Data source	System	Integrated absorb. (cm^{-1})	h_i/h_s	Actual ads. dens. ($\mu\text{mol}/\text{m}^2$)	Calculated ads. dens. ($\mu\text{mol}/\text{m}^2$)	Error (%)
Figure 3	CaF_2/OI	7.23	1.0	18.4	18.4	0
Figure 3	CaF_2/OI	4.23	3.2	18.4	10.7	41.8
Figure 3	CaF_2/OI	2.74	6.7	18.4	6.96	62.2
Figure 3	CaF_2/OI	1.75	11.1	18.4	4.45	75.8
Figure 4	$\text{Al}_2\text{O}_3/\text{OI}$	1.97	1.0	32.6	32.6	0
Figure 4	$\text{Al}_2\text{O}_3/\text{OI}$	1.13	1.9	32.6	18.7	42.6
Figure 4	$\text{Al}_2\text{O}_3/\text{OI}$	0.65	2.6	32.6	10.7	67.1

* The actual adsorption density is that determined from Eq. 2 with the appropriate spectrum in which $h_i/h_s = 1$, allowing the instrument to determine the true sample absorbance. (When $h_i/h_s > 1$ the area encountered by the incident beam is greater than the exposed sample area; therefore, the areas will not cancel out in Eq. 1, leading to an incorrect determination of absorbance, as explained previously.)

mined on the basis of the measured absorbances, will vary considerably within each test—leading to serious errors in the calculation of adsorption density, as shown in Table I.

Often FT-IR/IRS spectroscopists utilize gaskets that in some cases eliminate the incident beam in the region surrounding the adsorbate by either dispersing or absorbing the beam to such an extent that the only signal reaching the detector is that which travels through the sample chamber. Such gaskets effectively change the incident beam height to that of the adsorbate height, thereby eliminating quantification errors. In cases where gaskets are not used or do not sufficiently eliminate the incident beam around the adsorbate periphery, an opaque mask with a slit height less than or equal to the adsorbate height can be placed in front of the IRE to make $h_i/h_s \leq 1$, thus ensuring proper quantitative use of equations such as the adsorption density equation.

SUMMARY AND CONCLUSIONS

The results from this study show that serious errors in quantitative spectroscopy can result if the effects of sample and incident beam areas are neglected. Specifically, such errors arise when the area encountered by the incident beam is larger than the area of sample exposed to

the beam. Under such circumstances analysis of the sample with the use of the Bouguer–Lambert–Beer law or equations relying on this law results in a calculated sample absorbance value that is less than the true sample absorbance value. These errors can affect spectroscopic results from the use of a variety of accessories, although FT-IR/IRS is particularly susceptible to these errors because of the physical setup of IRS sample accessories. Accurate application of the adsorption density equation in FT-IR/IRS experiments can be made when the effective incident beam height is equal to the exposed adsorbate coating height. The effective incident beam height can be made equal to that of the exposed adsorbate coating height either by using a gasket which eliminates the beam in the region not coated by the adsorbate or by placing an opaque mask with a slit height that is less than the height of the adsorbate in front of the IRE.

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DISCUSSION

Flotation of boron minerals

Minerals and Metallurgical Processing, August 1993
M. S. Celik et al.

Discussion by M.R. Yalamanchili and J.D. Miller

The authors, M. S. Celik et al., should be recognized for their efforts to describe the flotation behavior of boron minerals. In the case of borax and other soluble salt minerals, analysis of the flotation chemistry has been difficult because of the high ionic strengths associated with these soluble salt systems. However, considerable progress has been made in this area, and recently a surface charge/collector colloid adsorption model was proposed by Miller and his coworkers to explain the collector adsorption phenomena observed in soluble salt flotation systems (Miller et al., 1992; Yalamanchili et al., 1993; Miller and Yalamanchili, 1994; Yalamanchili and Miller, 1994a; Yalamanchili and Miller, 1994b). In this work, the sign of the surface charge of alkali halides in their saturated brines was established on the basis of nonequilibrium electrophoretic mobility measurements by laser-Doppler electrophoresis (Miller et al., 1992). Generally, these results are what would be expected from the simplified lattice-ion-hydration theory. This electrokinetic information coupled with the stability and prevalence of collector colloids in such soluble salt flotation systems indicates that the selective flotation of alkali halides is due to the adsorption of oppositely charged collector colloids by heterocoagulation.

Experimental flotation/bubble attachment results for 21 different alkali halides (Yalamanchili et al., 1993; Yalamanchili and Miller, 1994b) confirmed that the flotation response of soluble salt minerals with weak electrolyte collectors can best be explained by the adsorption of oppositely charged collector colloids rather than by the adsorption collector ions and/or neutral molecular dipoles as originally suggested by many researchers (Fuerstenau and Fuerstenau, 1957; Schubert, 1967; Roman et al., 1968). In addition, the flotation of certain alkali oxyanions (Pizarro et al., 1993) and double salts such as schoenite and kainite can be explained by the same collector colloid adsorption mechanism (Miller and Yalamanchili, 1994).

The borax flotation results reported by Celik et al. need to be examined in terms of the above mentioned surface charge/collector colloid adsorption model. Unfortunately, the authors seem to be unaware of this recent work that nicely describes soluble salt flotation with weak electrolyte type collectors such as amines and carboxylates. In view of our past work, the flotation characteristics of borax were of particular interest, and, in this regard, the results of dodecyl amine flotation of borax reported by Celik et al. have been examined in further detail in the light of experimental results from our laboratory.

In our research, a vacuum flotation technique was used to study the flotation response of borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), which has a solubility of 39 g/L at 25 °C) with dodecyl amine hydrochloride as collector. These chemicals were purchased from Eastman Kodak and used as received. Saturated solutions of borax at desired pH values were prepared by continuously stirring the salt solutions over a period of about 10 hrs. It should be mentioned that the conditioning time to achieve equilibrium is an important variable and can significantly change the flotation response of some soluble salts (Yalamanchili et al., 1993). Collector was added to the saturated borax solutions containing about one gram of 100x150 mesh borax particles, and conditioning was done for about 20 minutes prior to flotation.

The borax flotation recoveries from saturated brine are presented in Fig. 1 as a function of collector addition at the natural pH of 9.3, as reported both by Celik et al. and as measured in our laboratory. In addition, the region of precipitation for the dodecyl amine hydroborate is included in Fig. 1. It can be seen in Fig. 1 that the flotation response curves are separated by about one order of magnitude in $\text{R}_{12}\text{NH}_3\text{Cl}$ collector addition. The flotation results of Celik et al. show that the maximum borax recoveries can be obtained below the solubility limit of the dodecyl amine hydroborate collector. However, in our experiments borax flotation seems to occur only after the precipitation of the dodecyl amine hydroborate collector as might be expected from the collector colloid adsorption model (Yalamanchili et al., 1993) if borax were negatively charged. Further analysis by nonequilibrium and equilibrium electrophoretic mobility measurements for borax indicates that borax is negatively charged at the natural pH of 9.3, as discussed below. The reliability of the nonequilibrium electrophoretic measurements has been demonstrated previously for alkali halides and alkali oxyanions (Miller et al., 1992; Miller and Yalamanchili, 1994).

The equilibrium and nonequilibrium electrophoretic measurements for borax were found to be consistent and are presented in Table 1. These results provide clear evidence that borax carries a negative surface charge in its saturated brine (pH 9.3), and the sign of the surface charge of borax reverses and becomes positive if the pH is reduced to 8.6. The equilibrium between borax and its saturated brine can be described by the following reaction:

It appears that the oxyanions of the borax lattice provide

Fig. 1 — Flotation recovery of borax as a function of dodecylamine

Table 1 — Equilibrium and nonequilibrium electrophoretic mobilities for borax		
pH	Electrophoretic mobility, ($\mu\text{m}/\text{sec})/(\text{v}/\text{cm})$	
	Equilibrium (high ionic strength)	Nonequilibrium (low ionic strength)
8.6	$+0.13 \pm 0.10$	$+0.18 \pm 0.10$
9.3	-0.16 ± 0.14	-0.42 ± 0.15

weak acid sites at the surface which readily undergo protonation. Furthermore, it should be noted from the results presented in Table 1 that the absolute values of the electrophoretic mobilities are influenced by the ionic strength, as expected from classical double-layer theory.

It was found that the amine hydroborate collector colloid is positively charged at the natural pH of the borax brine, and it appears that the heterocoagulation event between the negatively charged borax particles and the positively charged hydrophobic amine hydroborate collector colloids accounts for the effective flotation of borax. Flotation tests and nonequilibrium electrophoretic mobility measurements for borax were done at different pH values to further substantiate the validity of the collector colloid adsorption hypothesis for borax flotation. In this regard, Fig. 2 presents the nonequilibrium electrophoretic mobility of borax as a function of pH. As is evident in Fig. 2, borax is positively charged below a pH value of about 9. Therefore, it is expected that amine flotation of borax should not be effective below this pH, and, in fact, such is the case, as shown in Fig. 3. Below the pzc of borax ($\text{pH} \approx 9$), flotation recovery is very low because both borax and collector colloid are positively charged, and heterocoagulation does not occur. On the other hand, flotation recovery of borax increases above its pzc due to heterocoagulation of the oppositely charged amine hydroborate collector colloids and borax particles. Figure 3 also shows that the flotation recovery of borax begins to drop around pH 11, since the amine hydroborate collector colloids are expected to become negatively charged under these conditions. In the borax system, the sign of the surface charge for both the soluble salt and the collector colloid is determined by the pH of the system; whereas in most alkali halide systems, only the sign of the surface charge of collector colloid is influenced by pH.

It is evident from the above results and discussion that borax flotation is readily explained by the surface charge/collector colloid adsorption model. However, the reasons for the discrepancy between our flotation results and the results

Fig. 2 — Nonequilibrium electrophoretic mobility of borax as a function of pH.

Fig. 3 — Dodecylamine flotation of borax as a function of pH.

reported by Celik et al. are not clearly understood (see Fig. 1). The differences in the reported flotation results reported could be due to:

- the borax sample used for flotation (Celik et al. used natural borax samples for their studies, whereas we used a borax sample obtained from Eastman Kodak),
- the procedure used for preparation of saturated brines,
- the difference in flotation equipment used (column vs. vacuum flotation), or
- a mistake in the calculation of collector addition.

In any event, it is important to note that the experimental results from the study of amine flotation of borax support the surface charge/collector colloid adsorption model for soluble salt flotation systems (Miller et al., 1992, Yalamanchili et al., 1993, Miller and Yalamanchili, 1994).

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Reply by M.S. Celik and M. Hancer

The discussion of Yalamanchili and Miller that addresses the paper by Celik et al. (1993) is an excellent attempt to describe the flotation behavior of borax with dodecylamine hydrochloride (DAH). The analysis of flotation chemistry of soluble salt minerals has been difficult due to the presence of high ionic strengths in these systems. A recent model proposed by Miller and his co-workers has been a major breakthrough in explaining the collector adsorption phenomena observed in soluble salt flotation systems (Miller et al., 1992; Yalamanchili et al., 1993; Miller and Yalamanchili, 1994; Yalamanchili and Miller 1994a).

A remarkable accomplishment by Miller et al. (1992) was that, for the first time, a measurement of the surface charge of alkali halides in their saturated solutions by laser-Doppler electrophoresis technique was reported in the literature. The results were generally found to agree with the simplified lattice hydration theory with the exception of KCl. This electrokinetic information, together with the flotation response of a number of soluble salt minerals, led to the formulation of a heterocoagulation mechanism involving the adsorption of oppositely charged colloids at the salt surface.

It should be noted that this plausible explanation for soluble salt minerals has not been verified in this study for boron minerals. Boron minerals exhibit a spectrum of solubilities ranging from the sparingly soluble colemanite (0.8 g/l) to the highly soluble borax (49 g/l at 25 °C). However, compared to the solubility of halite (350 g/l), the solubility of borax is rather low. Also, the natural pH of all hydrated boron minerals occur in alkaline buffered pH of around 9.3. The anion of boron minerals ($B_4O_7^{2-}$) is of a larger size than those of halides.

In our research, a column cell was used in microflotation experiments. Natural borax crystals of ultra purity, obtained from the Kirka borax deposit, were used to measure the flotation response of borax with DAH. The borax used for preparing the saturated solutions was obtained from the Bandirma Acid Bolic Plant and had a specified purity >99.5 %. DAH was purchased from Eastman Kodak and was used as-received. Collector was added to the saturated borax solutions containing 2 grams of 65x100 mesh borax particles, and the suspension was conditioned for 10 minutes. A description of the flotation column and details of the flotation procedure are given elsewhere (Hancer and Celik, 1993b; Celik et al., 1993).

To answer the queries posed by the referenced discussion, the procedure used in the flotation tests can be summarized as follows:

- Saturated borax solutions were prepared either by heating to a certain temperature and then cooling to 25°C or by continuously stirring the salt solution over a period of 10 hrs to simulate the procedure given in the above referenced discussion.
- In addition to the natural borax sample, a synthetic borax of 65x100 mesh, obtained from the Bandirma Acid Boric Plant, was used.

Fig. 1 — Solubility of borax at 25°C as a function of pH.

Fig. 2 — Flotation recovery of borax as a function of dodecylamine hydrochloride addition (DAH).

- Turbidity tests were conducted to identify the precipitation boundaries of the dodecylamine hydroborate collector.

The solubility of borax as a function of pH is shown in Fig. 1. The solubility data exhibit a minimum in the range of pH 9 to 10, that corresponds to the solubility of about 49 g/l at 25°C. The minimum solubility is usually regarded as the point-of-zero-charge (pzc) for oxide minerals. Whether a coincidence or not, the pzc agrees with that obtained from the nonequilibrium electrophoretic measurements. The data for borates, if available, should be examined in view of the simplified lattice ion hydration theory.

Figure 2 presents the flotation recoveries of borax as a function of DAH concentration at natural pH (9.3). In Fig. 2, the results by Yalamanchili and Miller, Celik et al. (1993), Hancer et al. (1993), along with the present study, are illustrated. In addition, the precipitation domain for the

dodecylamine hydroborate is included. It is evident from Fig. 1 that the flotation response curves are still different by over one order of magnitude in DAH addition. The four sets of results shown in Fig. 2 were obtained as follows:

- The results reported by Celik et al. (1993) were obtained by heating the brine solution at 90°C and then cooling it to 25°C (90⇒25).
- The data reproduced from Hancer et al. (1993) were obtained by heating the brine solution to 35°C and then cooling it to 25°C (35⇒25).
- The curve referred as "this study" was done under the same conditions, i.e., the saturated solution was prepared at 25°C by stirring for 10 hrs, as did Yalamanchili and Miller, except that the mineral was natural (25⇒25).
- This set was obtained as above except for using the synthetic borax mineral. However, there is a fair agreement between the precipitation boundaries reported by the two studies.

It is interesting to note that the four sets of results obtained in our laboratories over a period of about two years with three different investigators agree very well. It is clear that the differences between our flotation results and those reported by Yalamanchili and Miller are not resolved. If the reasons cited by Yalamanchili et al. are revisited:

- there is no difference between natural and synthetic borax (as confirmed in Fig 2),
- the procedures used in the preparation of saturated brines show only marginal differences,
- there can not be a mistake in calculation of collector concentration as three different investigators performed the experiments over a period of about two years (10^{-3} M of stock solution of DAH contained 0.2218 g/l collector), and
- the only difference that remains between the two studies is the type of flotation cell used. We used a column microflotation cell and Yalamanchili and Miller used vacuum flotation cell.

The agreement between the precipitation boundaries suggests that the type of equipment may be responsible for the observed differences rather than the solution conditions.

In summary, though an excellent model for halides, we are

not in a position to support the surface charge/collector colloid adsorption model for borax flotation. However, it should be emphasized that a similar observation between the negatively charged barium dodecylsulfate collector colloids and positively charged colemanite surface was found to enhance the flotation of colemanite (Celik et al. (1993)). This finding independently supports the adsorption of collector colloids for a system other than amine.

Since no precipitation was observed over the flotation range, the induced hydrophobicity may be more conveniently described by the adsorption of collector ions and/or neutral molecular dipoles, as originally suggested by other researchers (Fuerstenau and Fuerstenau, 1957; Schubert, 1967; Roman et al., 1968). The improvement observed in saturated solutions was ascribed to a salting-out effect accompanying the enhanced surface activity of the surfactant due to the CMC reduction at such high salinities (Celik et al., 1993). Finally, we may suggest that the authors test their findings on borax using a microflotation apparatus such as the Hallimond Cell.

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INTERACTION OF ALKALI HALIDE PARTICLES IN THEIR SATURATED BRINES AND THE SIGNIFICANCE OF ATTRACTIVE HYDRATION FORCES

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KEY WORDS

Alkali Halides, Hydration Forces, Surface Charge, Brines

ABSTRACT

The sign of the surface charge of alkali halides in their saturated brines was established from the results of nonequilibrium electrophoretic mobility measurements and is supported by simplified lattice ion hydration theory. Based on these surface charge results, the extent of alkali halide particle interactions in their saturated solutions was examined by optical microscopy. The microscopic observations indicate that the sign of the surface charge has a significant effect on the extent of particle dispersion/aggregation. The results suggest that short range hydration forces due to water dipole ordering in the interfacial region are responsible for dispersion/aggregation of alkali halide particles in their saturated brines. *Most significantly, it seems that the aggregation between oppositely charged particles is best explained in terms of an attractive hydration force arising from hydrogen bonding due to an asymmetric structure of water dipoles.*

INTRODUCTION

The interaction of soluble salt particles in their saturated brines is of interest from both a fundamental and practical perspective. The state of particle dispersion/aggregation has not been described from first principles due to the high ionic strengths involved in these systems. Nevertheless, progress has been made and the sign of the surface charge of alkali halide particles has been established from nonequilibrium electrophoresis measurements[1]. These results are shown in Table 1 for 21 different alkali halides. Generally, the sign of the surface charge was found to be in agreement with that predicted from simplified lattice ion hydration theory with few exceptions.

The lattice ion hydration theory[2] describes the surface charge developed by non reactive ionic solids when placed in water. The sign of the surface charge is determined by the magnitude of the hydration energy of the respective surface lattice ions. If the surface cation has a more negative hydration energy than the surface anion then the surface will carry a negative charge. The converse is also true. The analysis can be further simplified. If the cation and anion are in equivalent positions such as in the alkali halides, then the lattice energies for cation and anion are equivalent and the sign of the surface charge can be established simply from the hydration energies of gaseous ions[2-5]. This theory was first demonstrated for the silver halides as reported by De Bruyn and Agar[2]. More recently the validity of the theory has been demonstrated for the alkali halides[1]. As shown in Table 2 the experimental results from laser-Doppler electrophoresis are compared to predictions using simplified lattice ion hydration theory. The agreement between the experimental results and the predictions from theory has been found to be very good with few exceptions. Further, the validity of the nonequilibrium electrophoretic measurements was also demonstrated by the results from flotation experiments for selected alkali halides[6].

An important consequence of the electrophoretic mobility measurements is that the stability(interaction) of these alkali halide suspensions can now be examined in terms of the sign of the alkali halide surface charge. In this regard, the extent of particle interaction has been studied by optical microscopy for three different systems viz., KCl/NaCl, KCl/CsCl and quartz/NaCl and finally an attempt has been made to describe the interaction forces between these alkali halide particles in their saturated brines.

MICROSCOPIC OBSERVATIONS

The alkali halides(ultrapure grade, 99.9%) used in this work were purchased from Alfa Research Chemicals. Milli-Q(18M Ω) water was used in all experiments.

The alkali halide particles were sized and narrow size fractions were used for examination. In some cases, particle size was controlled so that different alkali halide particles could be distinguished in a binary mixture. Saturated solutions of desired salt particles or salt particle mixtures were prepared and suspensions of individual particles as well as binary mixtures were made at equal particle concentrations(~ 5% solids) for optical microscopic examination. The particle dispersion/aggregation behavior of the suspensions was observed using a Carl-Zeiss AxioPlan optical microscope(Model D-7082) with a MC 100 35 mm camera attachment. In the case of the quartz/NaCl system, the particles were observed in NaCl brine. All observations were made at the natural pH values of the solutions under consideration.

RESULTS AND DISCUSSION

As described in the previous section, the interaction of alkali halide particles was studied in their saturated brines for three different systems namely KCl/NaCl,

KCl/CsCl and quartz/NaCl and the particle dispersion/aggregation behavior is shown in the photographs presented in Figures 1, 2 and 3.

PARTICLE DISPERSION/AGGREGATION

Figure 1 presents the dispersion/aggregation behavior of KCl/NaCl particles in their saturated solutions. It is evident in Figure 1a that KCl itself is dispersed in its saturated brine. The same is evident for NaCl as shown in Figure 1b. However, when these particles are mixed a strong aggregation between oppositely charged (see Table 1) KCl and NaCl particles is evident as can be seen in Figure 1c. Similar findings have been reported by Roman et al. [7]. In view of the electrophoretic mobility measurements these results suggest that the sign of the surface charge has a significant effect on the extent of particle aggregation even at these high ionic strengths (~4M). This correlation of suspension stability with the sign of the surface charge at high ionic strengths has been found for all systems examined. For example, when NaCl is mixed with CsCl (both salts being positively charged as shown in Table 1) no aggregation occurs and the particles remain dispersed as shown in Figure 1d.

Observations similar to the KCl/NaCl system have been found for the KCl/CsCl system as shown in Figure 2. First, Figure 2a and 2b show the dispersion of positively charged CsCl particles at two different sizes (~15 μ and ~60 μ) thus indicating that repulsive forces responsible for the dispersed state are not particularly particle size dependent. When the positively charged CsCl particles are mixed with negatively charged KCl particles, substantial aggregation occurs as revealed in Figure 2c. Again the correlation of stability with surface charge is further evident.

The third system examined was the quartz/NaCl system. Quartz particles should be negatively charged at the natural pH of a saturated NaCl solution. Figure 3a shows that the quartz particles are dispersed in saturated NaCl solution. Figure 3b shows the dispersed state of NaCl particles in their saturated solution. Again when these particles are mixed extensive aggregation occurs as shown in Figure 3c.

The results clearly indicate that when oppositely charged particles are present in a binary mixture, significant aggregation occurs relative to the behavior of the individual salt particles at the same particle concentration, in which case they remain dispersed. These observations provide evidence that the sign of the surface charge plays an important role in the particle dispersion/aggregation behavior at these high ionic strengths. The following section is devoted to a discussion of the possible nature of the interaction forces responsible for the dispersion/aggregation behavior of the alkali halide particles in their saturated brines.

Figure 1. Particle interaction photographs for the KCl/NaCl system.
(a) KCl (~35μ) particles in saturated brine
(b) NaCl (~20μ) particles in saturated brine
(c) Mixed KCl (~40μ) / NaCl (~40μ) particles in saturated brine
(d) Mixed NaCl (~20μ) / CsCl (~200μ) particles in saturated brine

Figure 2. Particle interaction photographs for the KCl/CsCl system.
(a) CsCl($\sim 15\mu$) particles in saturated brine
(b) CsCl($\sim 60\mu$) particles in saturated brine
(c) Mixed KCl($\sim 100\mu$) / CsCl($\sim 60\mu$) particles in saturated brine

Figure 3.

Particle interaction photographs for the Quartz/NaCl system.

(a) Quartz(-200 mesh) particles in saturated brine

(b) NaCl(-20 μ) particles in saturated brine

(c) Mixed Quartz(-100 μ) / NaCl(-100 μ) particles in saturated brine

INTERACTION FORCES

The forces acting between interfaces in aqueous solution include electrostatic, van der Waals and hydration forces[8]. The DLVO theory combines double layer electrostatic interactions with van der Waals attractive forces to describe the total interaction between any two surfaces. The repulsive double layer interaction force between two like surfaces in aqueous solution is an exponential function of the separation distance. The magnitude and range of the electrostatic repulsive force depend on the amount of charge on the surface and on the ionic strength of the solution respectively. At small separations, the van der Waals attraction, which is essentially insensitive to electrolyte concentration and pH, overpowers the double layer repulsion, the surfaces are attracted and eventually are expected to adhere when they come into contact. However, in many cases this does not happen due to the presence of other non-DLVO forces at molecular distances. Israelachvili and others[9-13] showed that the DLVO theory fails to explain interaction forces between particles when they approach closer than a few nanometers in aqueous solutions at high salt concentrations. The basic reason for the failure of the DLVO theory is that the bulk water properties differ in the interfacial region corresponding to small separation distances and consequently the interaction forces are quite different from those predicted from the DLVO theory. The non-DLVO forces which occur at short ranges are known as structural or hydration forces.

The hydration forces which are now known to determine the interaction of surfaces at small distances of separation were unrecognized until recently. In the past decade, However, there has been significant progress in measuring and characterizing these hydration forces which have been found to be repulsive between like surfaces. It is believed that the hydration force arises due to the ordering of interfacial water molecules. The ordering of water molecules depends on many factors such as the geometry and coordination number of aqueous species, the type of interface involved, and the physical and chemical nature of the surfaces involved[8,14]. Generally, hydration forces have been considered to be repulsive in nature[8,15].

Several researchers in the past decade have measured the hydration forces in different systems by using Israelachvili's surface force apparatus[9-13]. Pashely and Israelachvili[16,17] measured a short range repulsive force between mica surfaces at high salt concentrations which they attributed to the work required to dehydrate the adsorbed ions at small distances of separation. Pashely[18] reported a repulsive hydration force of approximately 10 mN/m (~ 1 mJ/m²) between curved mica surfaces (at a separation distance of < 1 nm) immersed in 1 M KCl solutions. Similar values were reported by Claesson for curved mica surfaces in NaI solutions[11]. Recently, Butt[12] measured these hydration forces between mica and a silicon nitride tip in aqueous solutions containing very high salt concentrations (>3M) using an atomic force microscope. Clearly van der Waals attractive forces are not particularly significant under these conditions. In this regard the possibility of attractive hydration forces should not be ignored especially in view of the results from this study.

It is evident from previous work that hydration forces have been found to be repulsive and that these forces can be much larger than either of the two DLVO forces at small separation distances. However, the results from our present work suggest the existence of both repulsive and *attractive* hydration forces as indicated by the photographs presented in Figures 1,2 and 3. It seems that the sign of the surface charge greatly influences the orientational and positional ordering of water molecules near charged surfaces resulting in either repulsive or *attractive* forces between the surfaces involved. In this regard, the work done by Marcelja et al.[19] is very interesting. They suggested that a polar surface will perturb interfacial water molecules and the propagation of this perturbation via water-water interactions will result in a force that extends over several molecular layers. The strength of the perturbation of the water structure depends on the charge present at the surface. This approach was favored by Rand et al.[13] to describe the hydration forces between phospholipid bilayers.

To explain the experimental results presented in Figures 1,2 and 3, the interfacial structure of the respective brine solutions must be taken into consideration. As a first approximation, we can consider the interfacial region, several molecular diameters, to consist of water dipoles with some ordering as established by the sign of the surface charge. For example, consider the system KCl/NaCl. It may be recalled from Table 1 that KCl and NaCl are oppositely charged.

When these two surfaces are immersed in their saturated solutions, they perturb the water structure near the surfaces in an asymmetric manner resulting in an attractive dipole interaction as shown hypothetically in Figure 4. This attractive force which should not be confused with the hydrophobic attraction described by Israelachvili[8] causes the NaCl and KCl particles to aggregate as shown in Figures 1a and 1b. For the case of two like charged surfaces the water molecules orient themselves in a symmetric fashion(see Fig.4) near the two surfaces leading to a dipole repulsion force between the surfaces resulting in particle dispersion as shown in Figures 2a and 2b for CsCl and 1d for the NaCl/CsCl system. It should be noted that it is not yet clear the role of the surfaces in producing these observed forces. However, the results from the current investigation suggest that the sign of the surface charge plays a major role in determining the nature of the hydration force between the surfaces. It is expected that the sign of the surface charge determines the ordering of the water dipoles and that the hydration force which can be either *attractive* or repulsive is simply described by dipole type interactions. This explanation for the observed particle aggregation (heterocoagulation) in saturated brines relies on the notion that the sign of the surface charge alters the dipolar structure of interfacial water so that attraction occurs due to hydrogen bonding via appropriately oriented dipoles at the respective surfaces. Similar conclusions can be drawn even if realistic and more complicated situations involving hydrated ionic species present at the charged interfaces are taken into consideration. It is clear that additional research is warranted, particularly infrared and dielectric spectroscopy as well as atomic force microscopy and/or surface force apparatus measurements, in order to examine the structure of interfacial solutions at these alkali halide surfaces and determine the

REPULSIVE HYDRATION FORCE Symmetric Water Dipole Structure

ATTRACTIVE HYDRATION FORCE Asymmetric Water Dipole Structure

Figure 4. Schematic diagram showing the influence of interfacial water structures on the nature of the interaction forces for the KCl/KCl, NaCl/NaCl, and KCl/NaCl systems. Note the change in the interfacial water structure with the change in the sign of the surface charge.

exact nature of the proposed short range *attractive* hydration forces between oppositely charged surfaces at high salt concentrations.

SUMMARY AND CONCLUSIONS

The measurements of nonequilibrium electrophoretic mobility can be used to predict the sign of the surface charge of alkali halides in their saturated brines. Generally, the sign of the surface charge was found to be in agreement with that predicted from simplified lattice ion hydration theory. Based on the experimentally determined surface charge results, the extent of alkali halide particle interactions in their saturated solutions can be explained. It is evident from microscopic observations that the sign of the surface charge has a significant effect on the extent of particle dispersion/aggregation.

The interaction forces responsible for the dispersion/aggregation behavior of the alkali halide particles in their saturated solutions appear to be hydration forces active at small separation distances. Importantly, the results suggest that *attractive* hydration forces due to asymmetric dipole ordering at the surfaces account for aggregation of oppositely charged salt particles.

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LIST OF FIGURE CAPTIONS

- Figure 1. Particle interaction photographs for the KCl/NaCl system.
- (a) KCl($\sim 35\mu$) particles in saturated brine
 - (b) NaCl($\sim 20\mu$) particles in saturated brine
 - (c) Mixed KCl($\sim 40\mu$) / NaCl($\sim 40\mu$) particles in saturated brine
 - (d) Mixed NaCl($\sim 20\mu$) / CsCl($\sim 200\mu$) particles in saturated brine

- Figure 2.** Particle interaction photographs for the KCl/CsCl system.
(a) CsCl($\sim 15\mu$) particles in saturated brine
(b) CsCl($\sim 60\mu$) particles in saturated brine
(c) Mixed KCl($\sim 100\mu$) / CsCl($\sim 60\mu$) particles in saturated brine
- Figure 3.** Particle interaction photographs for the Quartz/NaCl system.
(a) Quartz(-200 mesh) particles in saturated brine
(b) NaCl($\sim 20\mu$) particles in saturated brine
(c) Mixed Quartz($\sim 100\mu$) / NaCl($\sim 100\mu$) particles in saturated brine
- Figure 4.** Schematic diagram showing the influence of interfacial water structures on the nature of the interaction forces for the KCl/KCl, NaCl/NaCl, and KCl/NaCl systems. Note the change in the interfacial water structure with the change in the sign of the surface charge.

Table 1. Results from Laser-Doppler Electrophoresis Experiments — Nonequilibrium Conditions[1].

<u>$\mu\text{m/sec/v/cm}$</u>	Alkali Halide	Number of Observations	<u>Electrophoretic mobility,</u>		
			Range	Mean	
	Fluorides				
	LiF	5	+0.175 to	+0.271	+0.221
	NaF	4	+0.112 to	+0.171	+0.162
	KF	5	+0.061 to	+0.083	+0.084
	RbF	9	+0.04 to	+0.135	+0.065
	CsF	3	+0.486 to	+0.813	+0.582
	Chlorides				
	LiCl	4	-0.497 to	-0.733	-0.641
	NaCl	5	+0.124 to	+0.216	+0.163
	KCl	6	-0.33 to	-0.467	-0.421
	RbCl	3	+0.164 to	+0.27	+0.213
	CsCl	4	+0.325 to	+0.495	+0.397
	Bromides				
	LiBr	7	-0.224 to	-0.375	-0.320
	NaBr	3	-0.252 to	-0.342	-0.311
	RbBr	3	-0.388 to	-0.496	-0.459
	KBr	5	-0.078 to	-0.106	-0.086
	CsBr	3	+0.064 to	+0.081	+0.072
	Iodides				
	LiI	4	-0.741 to	-0.803	-0.761
	NaI	8	-0.662 to	-0.791	-0.741
	KI	4	+0.057 to	+0.109	+0.079
	RbI	4	-0.098 to	-0.348	-0.253
	CsI	3	+0.025 to	+0.061	+0.041
	NaI·2H ₂ O	4	+0.026 to	+0.05	+0.039

Table 2. Sign of the Surface Charge for Selected Alkali Halides[1].

<u>Sign of Surface Charge</u>	<u>Negative Gaseous Hydration Free Energies, kcal/mole⁽¹⁷⁾</u>		<u>Predicted^a/ Experimental^b</u>
	Cation	Anion	
Fluorides			
LiF	112.0	109.6	? +
NaF	88.4	109.6	++
KF	71.1	109.6	++
RbF	65.9	109.6	++
CsF	58.2	109.6	++
Chlorides			
LiCl	112.0	82.5	--
NaCl	88.4	82.5	- +
KCl	71.1	82.5	+ -
RbCl	65.9	82.5	++
CsCl	58.2	82.5	++
Bromides			
LiBr	112.0	75.7	--
NaBr	88.4	75.7	--
KBr	71.1	75.7	+ -
RbBr	65.9	75.7	+ -
CsBr	58.2	75.7	++
Iodides			
LiI	112.0	66.5	--
NaI	88.4	66.5	--
KI	71.1	66.5	- +
RbI	65.9	66.5	? -
CsI	58.2	66.5	++
NaI·2H ₂ O	NA	NA	NA+

^aSimplified lattice ion hydration theory.^bElectrophoretic-mobility measurements by laser-Doppler electrophoresis.

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REMOVAL OF INSOLUBLE SLIMES FROM POTASH ORE BY AIR-SPARGED HYDROCYCLONE FLOTATION

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ABSTRACT

The presence of insoluble mineral components, typically clay minerals, in potash ores has always been a problem to the potash industry, particularly in the processing of low grade sylvinite ores. The insoluble slimes must be removed prior to potash flotation because of their high affinity for amine collectors used in the subsequent flotation of sylvite. In this regard, air-sparged hydrocyclone (ASH) flotation was examined as a process alternative for the removal of such insoluble slimes from potash ores. The effects of reagent concentration and ASH operating variables on the recovery of insolubles were studied for a typical plant feed from the Saskatchewan potash field. Results indicate that, for single stage ASH flotation, over 70% of the insolubles could be floated from a potash feed containing about 7% insolubles with salt recoveries in the underflow product exceeding 92%. These results with a 2-inch air sparged hydrocyclone suggest that high specific capacity ASH flotation, 100 times the specific capacity of conventional flotation, is a viable process alternative for the removal of insoluble slimes from potash ores.

Keywords

Potash flotation; air-sparged hydrocyclone; desliming

INTRODUCTION

The presence of insoluble slimes in potash ores is a processing problem of some significance to the potash industry. These insolubles must be removed prior to potash flotation because of their high adsorptive capacity for amines which are generally used as collectors in the subsequent sylvite flotation step. This problem is even more serious in low grade sylvinite ores such as the ore presently mined at the Carlsbad operations in New Mexico. Most of the rich potash ore containing small amounts of insoluble slimes has already been depleted during the past 50 years, thus leaving large reserves of low grade ore typically containing from 4% to 8% insolubles [1]. Generally, the effective removal of insolubles from potash ores has always been of concern in the potash industry and is a problem which is not limited to the New Mexico potash ores. The insoluble slimes are usually removed by scrubbing of the ore in brine followed by hydrocyclone classification to separate slimes from the salt particles [2]. Insoluble slimes that remain with the ore after this desliming procedure are depressed by reagents such as guar gum or starch to prevent the flotation of residual slimes during sylvite flotation.

Conventional Technology

The disadvantages of this conventional desliming by scrubbing and hydrocyclone classification are potash losses as fine sylvite particles in the insoluble slimes product and the significant amount of process brine

required for the desliming operation. Therefore, improved or new methods are required for the more efficient removal of insoluble slimes in order to reduce potash losses to the insoluble slimes product, to lower the process brine requirement, and to improve grade and recovery in the subsequent sylvite flotation for final product recovery. In this regard, flocculation-flotation technology for the removal of insoluble slimes has been offered as an alternative to desliming by scrubbing and hydrocyclone classification [1,3-4]. In this method, the insoluble slimes are flocculated prior to collector addition in order to reduce their surface area and facilitate their flotation. This method was successfully implemented for processing potash ores containing from 4% to 8% insolubles at the Cominco operations in Saskatchewan, Canada [4]. The reagents used at Cominco include a nonionic polyacrylamide flocculant and a cationic collector (primary amine) for selective flocculation-flotation of fine insoluble slimes in conventional flotation cells. In the present work, the air-sparged hydrocyclone was used to examine its viability for the flotation of insoluble slimes from such potash ores.

Air Sparged Hydrocyclone - Background

The concept of air-sparged hydrocyclone flotation was developed in the early 1980s in order to achieve fast flotation of fine particles in a centrifugal field. The air-sparged hydrocyclone which has at least 100 times the specific capacity of conventional column and mechanical flotation machines, has shown great potential for the flotation of variety of industrial minerals as well as for de-inking flotation in wastepaper recycling, wastewater treatment, and fine coal cleaning [5-11].

AIR-SPARGED HYDROCYCLONE

Fig.1 Perspective of the air-sparged hydrocyclone [8]

Figure 1 shows a perspective drawing of an air-sparged hydrocyclone which consists of two concentric right-vertical tubes, a conventional cyclone header with a vortex finder at the top, and froth pedestal/underflow structure at the bottom. The feed slurry is fed tangentially through the cyclone header to develop a swirl flow inside the ASH unit. Air is sparged through the inner porous tube and is sheared into numerous air bubbles by the high-velocity swirl flow of the suspension. The hydrophobic mineral particles in the slurry, after attachment to these air bubbles, are transported into the froth phase which forms at the free surface of the vortex. The froth phase moves towards the vortex finder of the cyclone header and is discharged as an overflow product. Most of the aqueous phase with hydrophilic particles is discharged as the underflow product through the annular opening between the inner porous tube and the froth pedestal. The ASH capacity is at least 200-400 gallons per minute per cubic foot of cell volume. For example, about 300, 000 gallons of suspension can be processed per day by using one ASH unit with an inside diameter of 6 inches and a length of 60 inches.

Research Objective

In view of the above, a study was undertaken in order to examine the possibility of using ASH flotation technology for the removal of insoluble slimes from sylvinite potash ores. The present study was divided into two parts. In the first part, the flotation of a pure kaolin clay sample from sylvinite-saturated brine was studied as a function of reagent concentration and ASH operating variables. The reagent schedule and the ASH operating variables established from these experiments were then used to study the flotation response of insoluble slimes from potash ore obtained from plant operations in the Saskatchewan potash field of Canada.

EXPERIMENTAL

The kaolin sample (Spers 100, coarse particle type, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, median particle size = 1.8-2.0 μm) used in this study was purchased from Albion Chemicals and was used as received. This sample contained 45.5% SiO_2 , 38.5% Al_2O_3 , 1.7% TiO_2 , 0.3% Fe_2O_3 and traces of soda, potash, and magnesia. Octadecylamine hydrochloride (Kodak) was used as collector for kaolin flotation from saturated brine.

Samples of Lanigan sylvinite ore along with flocculation and flotation reagents were obtained from the Potash Corporation of Saskatchewan, Saskatchewan, Canada. The reagents obtained included Percol E-10 (a nonionic high molecular weight flocculant) and Sherex MG-185-A3 (neutralized 12-15 C primary amine collector).

Flotation experiments were carried out using an ASH-2C unit with an internal diameter of 1.875 inches and a length of 18.5 inches manufactured by Advanced Processing Technologies, Inc., Salt Lake City, Utah. Flotation experiments were conducted as described below.

Brine Preparation

Saturated brine solution was prepared by adding ore to water (35 % solids by weight) and stirring for at least 12 hours. Later, the undissolved solids and slimes were allowed to settle at the bottom of the sump for about 5 hours. The clear saturated brine was then decanted and used for flotation experiments in both cases viz. pure kaolin and insolubles from sylvinite ore.

Reagent Preparation

Percol-E10 powder (0.5 gr) was added to a dry 100 cc screwtop bottle. The dry powder was then wetted with an addition of 3 cc methanol. Water was added to make up a 100 cc solution and the bottle was closed immediately and was shaken vigorously for about 20 seconds. The solution preparation was completed in the following 2 hours with occasional hand shaking of the bottle. Percol solutions were diluted to 0.05 % (by weight) before use in order to ensure rapid and uniform incorporation of the flocculant into the system. Fresh percol solutions were used for each experiment.

A 2 % solution of the neutralized amine collector, Sherex MG-185-A3 was prepared and used in the flotation experiments for the sylvinitic ore. In flotation experiments with kaolin, octadecylamine hydrochloride was used as the collector. Solutions of appropriate concentration of this collector were prepared and used in the kaolin flotation experiments.

Insoluble Slimes Flotation

The kaolin sample (median particle size 1.8-2 μm) was used as received. On the other hand, the Lanigan sylvinitic ore received from the Potash Corporation of Saskatchewan was roll crushed and dry screened to obtain -60 mesh material for use in this study.

In both cases, a known weight of sample/ore, at the desired percent solids, was added to 250 liters of brine and was scrubbed with good mixing for 20 minutes. Percol E-10 flocculant was added at 150 g/t of insol and the feed slurry was conditioned for 5 minutes. The required amount of collector was then added and the slurry was conditioned for an additional 5 minutes. The vortex finder diameter, the underflow opening and the air flowrate were set at desired levels. The slurry was then pumped to the ASH at the desired slurry flowrate in the range of 50 - 100 lpm. After attaining a steady state flowrate of the suspension, overflow and underflow samples were collected in 5 gallon containers and the sampling time was recorded. The pump was shut off following collection of the product samples. The vortex finder diameter, the underflow opening and/or the air flowrate rate values were changed to different levels, and several experiments were conducted as described above at desired slurry flowrates. Product samples were weighed, filtered, dried and weighed for further analysis. The dried overflow and underflow products were then analyzed for their insoluble contents by simply dissolving the product samples in tap water. After dissolution, the product samples were filtered, dried and weighed to calculate the insoluble content in the products. In the case of kaolin flotation experiments, the products were simply weighed, filtered, dried, and weighed again for determination of the flotation recovery of kaolin.

In some experiments, both the flocculant and the collector were added simultaneously to the conditioning tank to ascertain the effect of conditioning time on the recovery of insoluble slimes.

RESULTS AND DISCUSSION

The ASH flotation results from this study were analyzed to examine the effect of the dimensionless variables A^* (overflow area/underflow area) and Q^* (air flowrate/slurry flowrate), and the reagent schedule on the flotation response of kaolin and on the removal of insoluble slimes from -60 mesh sylvinitic ore.

Kaolin Flotation

Flotation of kaolin from sylvinitic saturated brine was carried out in the first part of this study in order to establish a reagent schedule as well as appropriate ASH operating variables for efficient removal of insoluble slimes from potash ore. In all kaolin flotation experiments, a suspension containing 5 % solids was used as feed to the ASH. Octadecylamine hydrochloride was used as collector in all kaolin flotation experiments.

Table 1 presents the ASH flotation results at a collector level of 500 g/t and a flocculant level of 150 g/t for two different Q^* values with an A^* value of 1.00 and a slurry pressure of 12 psi. These particular values were chosen in these initial experiments based on past experience from other ASH flotation systems. However, as can be seen from this table, very poor kaolin recoveries were obtained. Collector level was found to be the reason for these low flotation recoveries and subsequently the octadecylamine hydrochloride addition was increased to 700 g/t and flotation experiments were conducted as a function of both A^* and Q^* .

TABLE 1 Recovery of kaolin at two different Q^* values
Collector = 500 g/t, Flocculant = 150 g/t, $A^* = 1.00$

Q^*	Kaolin Recovery (%)
4.0	19
6.0	34

Figure 2 shows the kaolin recovery as a function of slurry pressure at different Q^* values. Better recoveries were obtained at a slurry pressure of 12 psi and a Q^* value of 6.0 as shown in this figure. It can be noticed that lower Q^* values resulted in poor kaolin recoveries. At a fixed slurry pressure, a lower value of Q^* implies a lower air flow rate. Clearly, at lower Q^* values, there is insufficient air and insufficient froth phase results in lower kaolin recoveries. A detailed discussion of the effect of flow phenomena on ASH flotation is given by Das and Miller [12]. A maximum recovery of about 80 % was obtained at a slurry pressure of 12 psi, a Q^* value of 6.0, a collector level of 700 g/t and a flocculant level of 150 g/t as shown in Figure 2. It should be mentioned here that longer conditioning times (>25 minutes) resulted in decreased flotation recoveries due to the degradation of the flocs in the conditioning tank as well as in the ASH. This could be the reason for incomplete flotation recovery of kaolin in these experiments since further increase in collector addition (900 g/t) did not result in an increase in the flotation recovery beyond 80 %.

Fig.2 Recovery of kaolin as a function of slurry pressure and Q^*

From the above set of experiments, it was clear that a Q^* value of about 6.0 and a slurry pressure of 12 psi would be appropriate for obtaining maximum recoveries. These conditions were used in subsequent flotation experiments to examine the influence of the dimensionless area ratio (A^*) on the flotation recovery of kaolin. Table 2 presents the results as a function of A^* for two different Q^* values. It is evident from these results that an A^* value of 1.00 provides for better kaolin recoveries from the saturated brine. At $Q^* = 4.0$, kaolin recoveries were low irrespective of the dimensionless area (A^*) indicating that the airflow rate is too low for efficient recovery of kaolin. However, at $Q^* = 6.0$, a maximum recovery of 80% was obtained corresponding to an A^* value of 1.00 whereas recoveries decreased at other A^* values. It should be noted that the change in A^* value was brought about by changing the underflow

opening area and not by changing the overflow opening area (vortex finder diameter). A 13/16" vortex finder was used in all these experiments.

Flotation experiments with kaolin were concluded by studying the influence of the method of reagent addition to the conditioning tank. In these experiments, both the flocculant and the collector were added simultaneously to the conditioning tank and samples were taken immediately without any appreciable conditioning time.

TABLE 2 Flotation recovery of kaolin as a function of A^* at two different Q^* values. Slurry pressure was 12 psi.

A^*	Underflow Annular Opening (%ASH Radius)	Kaolin Recovery (%)	
		$Q^* = 4.0$	$Q^* = 6.0$
1.10	8.93	28	61
1.00	9.88	30	80
0.92	10.83	22	41

These flotation experiments resulted in poor kaolin recoveries (about 30% maximum) indicating that a minimum conditioning time is required for better flotation. On the other hand, conditioning times longer than about 25 minutes resulted in degradation of the flocs as mentioned previously.

Flotation of kaolin clay from brine clearly indicated that ASH flotation technology can be used to remove insoluble clay slimes from saturated brines prior to sylvite flotation. In addition, appropriate conditions including the reagent schedule and ASH operating variables were established for kaolin flotation. This information was then used in the ASH flotation experiments for the removal of insoluble slimes from potash ore samples obtained from plant operations in Saskatchewan, Canada.

Flotation of Insoluble Slimes from Potash Ore

ASH flotation tests were done using potash samples obtained from Saskatchewan, Canada. These potash ores typically contain from 4% to 8% insoluble slimes. These insolubles typically consist of one-third clay minerals ($-2\mu\text{m}$) such as kaolinite and illite and two-thirds non-clay minerals ($-150\mu\text{m} + 2\mu\text{m}$) such as dolomite, hematite, silica etc. [4]. In the preliminary ASH flotation experiments, -60 mesh feed at 30% solids was used. These experiments resulted in choking of the ASH unit even at 8 rotations (13.68% of ASH radius) for the underflow opening. The percent solids was then decreased to 10% in subsequent experiments to avoid these problems.

Tables 3 and 4 show the results from ASH flotation experiments for potash ore under different operating conditions at collector and flocculant concentrations of 690 g/t of insol and 150 g/t of insol respectively. It can be noticed from Table 3 that salt recoveries in the underflow exceeded 90% for all the A^* values between 0.44 (8 rotations of underflow opening) and 0.59 (four rotations of underflow opening). Salt recoveries in the underflow as high as 96% were obtained at an A^* value of 0.44 while the insolubles content in the underflow was reduced to 1% with an insolubles recovery exceeding 70%. The insolubles content in the underflow increased when the underflow opening was reduced to 4 rotations (9.88% of ASH radius) indicating that lower A^* values should be used for better salt recoveries as well as lower insolubles content in the underflow. All these experiments were conducted at a Q^* value of 5.8 and a slurry pressure of 12 psi. Other experimental conditions included 5 minutes conditioning time after the addition of flocculant and collector similar to the conditions used for kaolin flotation. As mentioned previously, a change in A^* in these experiments was brought about by changing the underflow opening area and not by changing the vortex finder diameter which was fixed at 13/16".

TABLE 3 ASH flotation of insoluble clay slimes from potash ore.
 Collector = 690 g/t, Flocculant = 150 g/t, Feed size = -60 mesh,
 $Q^* = 5.8$, Slurry pressure = 12 psi

A^*	Grade, % Insol			OF Distribution, %		UF Distribution, %	
	Feed	O 'Flow	U 'Flow	Insol	Salt	Insol	Salt
0.44	4.4	32	1	62	4	38	96
0.47	4.0	40	1	77	5	23	95
0.54	4.4	28	2	59	7	41	93
0.59	6.0	25	4	40	8	60	92

TABLE 4 ASH flotation of insoluble clay slimes from potash ore.
 Collector = 690 g/t, Flocculant = 150 g/t, Feed size = -60 mesh,
 $A^* = 0.47$, Slurry pressure = 12 psi

Q^*	Grade, % Insol			OF Distribution, %		UF Distribution, %	
	Feed	O 'Flow	U 'Flow	Insol	Salt	Insol	Salt
4.0	6.1	5	26	15	5	85	95
5.0	5.0	22	10	38	5	62	95
6.0	5.8	34	1.5	72	7	28	93

Table 4 presents flotation results as a function of the dimensionless flowrate, Q^* , at an A^* value of 0.47 at which best salt and insolubles recoveries were obtained in the earlier experiments. Collector and flocculant dosages were maintained at the same level. Feed size was -60 mesh and the percent solids was maintained at 10% in these experiments. Again, salt recoveries as high as 93% and insolubles content as low as 1.5% were obtained in the underflow stream at a Q^* value of 6.0. Recovery of insolubles in the overflow stream was observed to be poor at lower Q^* values due to a lack of sufficient air flowrate for froth phase formation in the ASH unit [12]. Similar results were found in the kaolin flotation experiments discussed previously.

ASH Technology for Insoluble Slimes Flotation

Judging from the preliminary results presented above, it appears that removal of insoluble slimes from potash ores by ASH flotation is a viable process alternative to the conventional flotation method. Salt recoveries in the underflow product exceeding 92% were obtained while the insolubles content was decreased to as low as 1% in the underflow product from about 6% in the feed material. These results are comparable to the results obtained from kaolin flotation experiments in spite of the complex nature (chemical composition and size range) of the insoluble slimes found in actual potash ores. Most importantly, the results from this study were obtained from a single stage ASH flotation and were comparable to the salt and insolubles recoveries obtained from a two stage flocculation-conventional flotation circuit at Cominco operations [4].

The collector consumption for the ASH flotation in a 2 inch diameter unit is higher than that for conventional flotation. However, the reagent demand for larger diameter ASH units is expected to be significantly reduced as has been observed in other applications [13].

Finally, it should be mentioned that in the flocculation-conventional flotation method for insolubles removal, regulation of collector dosage is very critical to prevent sylvite from floating. Generally, collector dosage is controlled to a starvation level to prevent the flotation of sylvite along with the insoluble slimes [4,14]. The control of the collector dosage becomes even more critical when the

concentration of insoluble slimes in the feed is low. However, the ASH flotation of insoluble slimes was observed to be insensitive to the collector dosage with regard to the flotation of sylvite. Even at 900 g/t collector level, salt recoveries in the underflow product never decreased below 92%. This clearly indicates that control of the ASH flotation circuit is easier when compared to that of flocculation-conventional flotation circuits and salt losses into the insoluble slimes product are always very low in ASH flotation in spite of the high collector dosages.

SUMMARY AND CONCLUSIONS

The results from the preliminary testing suggest that the removal of insoluble slimes from sylvinitic ores by ASH flotation can be successfully accomplished and generally can be considered as a process alternative in the flotation of potash ores. Insol recoveries as high as 80% were obtained in the initial ASH experiments with kaolin in brine suspension. Based on these results, experiments with actual potash samples from plant operations were designed and carried out. In these experiments, salt recoveries in the underflow product exceeded 92% and in some cases more than 95% recovery could be achieved. The insolubles content of the feed material is typically reduced from about 6% insolubles to as low as 1% insolubles at an insolubles recovery exceeding 70%. Although the collector consumption for the ASH flotation in an ASH-2C unit is higher than that for conventional flotation, it is expected to be reduced considerably for larger diameter ASH units as has been observed for other systems [13].

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**Molecular Orientation of Langmuir-Blodgett and Self-Assembled
Monolayers of Stearate Species at a Fluorite Surface
as Described by Linear Dichroism Theory**

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ABSTRACT

Polarized light Fourier transform infrared internal reflection spectroscopy (FT-IR/IRS) experiments indicate that for both Langmuir-Blodgett (LB) and self-assembled (SA) monolayers of stearate molecules at a fluorite (CaF_2) surface the surfactant molecules are in the trans state with uniaxial distribution of both the hydrocarbon chains and the transition dipole moments of the CH_2 stretching vibration. On this basis the average molecular orientation angles for such monolayers were determined from linear dichroism theory. In the case of LB stearate monolayer the average molecular orientation angle was found to be 9 to 16 degrees from the surface normal whereas in the case of the SA stearate monolayer the average molecular orientation angle was found to be about 21 degrees from the surface normal.

INTRODUCTION

The preparation of organic thin films such as Langmuir-Blodgett (LB) and self-assembled (SA) monolayers has been under serious consideration for the development of advanced materials because of the possibility to construct molecular assemblies at a surface with planned structure and properties.⁽¹⁻⁴⁾ LB monolayer films are formed by the dynamic transfer of a mono-molecular layer of surfactant molecules from the air/water interface of a Langmuir trough to a solid substrate whereas SA monolayers are formed at an appropriate substrate by spontaneous adsorption from a solution of surfactant with reactive functionality. It has been demonstrated by several researchers that SA monolayers are structurally similar to LB monolayers of same compound.⁽⁵⁻⁸⁾ Typical examples of SA monolayers are organosilanes on silicon,⁽⁵⁾ thiols on gold,⁽⁶⁾ and fatty acids on aluminum oxide.^(7, 8)

Only certain types of molecules can form LB and SA monolayers and are known as amphiphilic molecules. The amphiphilic molecule is composed of a polar group and a nonpolar group and adsorbs at the interface between air and water, or between a nonpolar solvent and water. The amphiphilic property of surfactant molecules causes the concentration and orientation of surfactant molecules at a surface and consequently alters the surface energy, thereby modifying the surface properties of the system. Therefore, fundamental study of surfactant monolayers at a solid substrate is essential for the development of improved methods of surface modification. The polar head group-substrate interaction and the hydrocarbon chain-hydrocarbon chain interaction are the major factors in constructing LB and SA monolayers. Polarized light Fourier transform infrared internal reflection spectroscopy (FT-IR/IRS) has been successfully used to determine molecular orientation assuming uniaxial distribution of transition dipole moments with respect to the surface normal.⁽⁹⁻¹¹⁾

Recent FT-IR/IRS studies have shown that fatty acid molecules form SA monolayers at a fluorite surface.^(12, 13) It has been well established from FT-IR studies

that these fatty acid molecules react with the surface calcium sites of the fluorite (CaF_2) to form a chemisorbed monolayer.(12, 14-16) FT-IR/IRS examination of transferred LB monolayers of oleic and stearic acids also indicates that the fatty acid head group of the first monolayer reacts with the surface calcium sites of fluorite to form a chemisorbed monolayer(13, 17) (*these transferred LB monolayers of stearic and oleic acids will be referred to as the LB stearate and oleate monolayers*). Figure 1 clearly shows the spectral similarity between the FT-IR/IRS spectra of a transferred LB stearate monolayer at a fluorite surface (CaF_2) and a SA stearate monolayer formed at a fluorite surface from aqueous solution. As shown in Figure 1, the singlet at about 1550 cm^{-1} is characteristic of chemisorbed carboxylate monolayer and has been distinguished from the acid state and the calcium dicarboxylate salt. The stearate molecules adsorbed from even the nonpolar chloroform solution were also found to react with the surface calcium sites at the fluorite surface to form the chemisorbed stearate. Carboxylate chemisorption of SA and LB fatty acid monolayers at a fluorite surface and their spectral features are discussed elsewhere in more detail.(18) Also, a recent contact angle study shows that the SA stearate monolayer is very stable at a fluorite surface and has a hydrophobicity similar to that of the LB stearate monolayer at a fluorite surface.(19)

In this contribution, the assumption concerning uniaxial distribution of surfactant molecules has been examined using polarized light FT-IR/IRS experiments. Average molecular orientations of SA and LB stearate monolayers at a fluorite surface have been determined using linear dichroism theory . The FT-IR/IRS adsorption density equation for LB and SA stearate monolayers was used to evaluate the adsorption densities of these monolayers taking into consideration important conditions which must be satisfied for the correct use of the equation.(20, 21)

EXPERIMENTAL SECTION

Materials

Stearic acid ($\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$) with purity more than + 99 % (Aldrich Chemical Co.) and sodium stearate ($\text{CH}_3(\text{CH}_2)_{16}\text{COONa}$) with purity more than 99 % (Sigma Chemical Co.) were used as received. Spectrograde chloroform (CHCl_3) was obtained from EM Science. Reagent grade calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) and sodium hydroxide (NaOH) were obtained from Mallinckrodt, Inc.. A Millipore Milli-Q water system, supplied with deionized water, provided water with a resistivity of +18 M Ω and surface tension of 72.4 ± 0.4 at 22 °C. The pH of this high purity water was stabilized at $\text{pH } 5.8 \pm 0.1$ after equilibrating with carbon dioxide from the atmosphere.

Fluorite (CaF_2) single-crystal parallelepiped internal reflection elements from Optovac Inc. were used with acute angles which varied from 72 to 75° as measured by a goniometer. Due to the possibility of organic contamination in such surface chemistry studies, fluorite IREs were placed in a Tegal plasma chemistry reactor and subjected to argon plasma for 30 to 40 minutes. In some cases, the surface of the IRE was polished with alumina powders (0.5 or 0.05 micron) and washed with high purity water to create a fresh surface.

LB Film Preparation

For preparation of a transferred monolayer, the Langmuir-Blodgett technique^(1, 2) was applied. The LB film deposition system was a Lauda Langmuir Film Balance manufactured by SYBRON/Brinkmann. The film balance was kept in a special housing to provide a dust-free environment. The experiments were performed at room temperature. The substrate (fluorite single crystal) was dipped into the subphase (water) before spreading the monolayer solution. Monolayer spreading solution was produced by dissolving stearic acid in chloroform; the concentration of stearic acid was 7.6 mM. The monolayers were spread from the chloroform solutions on the surface of high purity water

with a large enough area to achieve complete spreading. Chloroform was permitted to evaporate for 20 to 30 minutes before compression of the Langmuir film. The substrate was withdrawn at a speed of 3 mm/min. with the surface pressure held at the desired level. In some cases calcium distearate monolayers were transferred. For calcium distearate, 1×10^{-3} M calcium ions (as $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) was added to the high purity water and the subphase pH was controlled to 9.2 ± 0.2 with NaOH before spreading of stearic acid monolayer. During LB experiments the surface pressures for transfer were maintained at 20 to 23 mN/m and the variation in the surface pressure of the transfer was within ± 1 mN/m. All the transfer curves were recorded so as to ensure that each monolayer was transferred at a constant pressure.

SA Monolayer Preparation

1.4×10^{-3} g of sodium stearate was dissolved in 0.5 liter of Milli-Q water which had been heated to 75 - 80 °C. The solution was diluted with water to 3×10^{-7} M and the solution pH was initially adjusted to $\text{pH } 9.5 \pm 0.1$ with NaOH. A clean fluorite IRE was immersed into the stearate solution. The solution was covered with aluminum foil during the reaction. After reaction with mild agitation for a given time (10 minutes to 5 hours), the solution pH was measured and the fluorite IRE was washed with pure water at $\text{pH } 9.5 \pm 0.1$ and dried. The final pH was usually lower than the initial pH of the solution (by about one pH unit).

FT-IR Spectroscopy

FT-IR experiments were conducted with a dry-air purged Bio-Rad Digilab Division FTS-40 FT-IR spectrometer equipped with a liquid-nitrogen-cooled wide-band mercury cadmium telluride (MCT) detector. An internal reflection cell with a variable angle holder (Harrick Scientific) and a Brewster's angle polarizer (Single Diamond Polarizer, Harrick Scientific) was used to measure polarized light FT-IR/IRS spectra. The incident angle for

internal reflection was calculated using the procedure described in the manual for the variable angle holder. The background spectrum for all FT-IR/IRS measurements was the single-beam spectrum of the clean IRE and absorbance spectra of the LB films were ratioed against the background spectra of the clean calcium fluoride IRE. The polarizer was set at 0° and 90° , giving absorbance parallel and perpendicular to the plane of incidence, respectively. In all cases, substantial care was taken to reposition the IRE in its holder after the LB film was transferred. The size of the IR beam was adjusted to pass only through the portion of the IRE with the transferred LB monolayer film. The same IR beam size was used for both background and sample spectra in order to satisfy conditions for use of the adsorption density equation. Detailed analysis of the effect of sampling area on adsorption density measurements is provided elsewhere.^(20, 21) All the spectra were the results of 1024 co-added scans at resolution 8 cm^{-1} . The spectra are presented without further noise reduction or smoothing.

INTERNAL REFLECTION SPECTROSCOPY AND LINEAR DICHROISM THEORY

When light travels through one medium to another, transmission, absorption and/or reflection will occur depending upon the optical properties of these media and angle of incidence. As the angle of incidence increases, reflectivity increases. In the cases where the refractive index of the first medium is larger than that of the second, the reflectivity becomes unity for angles of incidence larger than the critical angle, i.e., total internal reflection will occur at the interface. Internal reflection spectroscopy (IRS), alternatively referred to as attenuated total reflection (ATR), was first proposed by Harrick⁽²²⁾ and independently by Fahrenfort⁽²³⁾ in the 1960s. Reviews of IRS have been given by several researchers.⁽²²⁻²⁷⁾ This surface sensitive experimental technique involves the internal reflection of light through an internal reflection element (IRE). Figure 2 is a schematic representation of a ray of light undergoing multiple internal reflections in an IRE.⁽¹⁷⁾ The

IRE can be machined from a material of interest (either synthetic single crystals or naturally occurring mineral crystals). As the light is totally reflected at the IRE/sample interface, an evanescent wave is formed from the surface of the IRE which decays exponentially into the sample:

$$E = E_0 \exp\left(-\frac{z}{d_p}\right) \quad (\text{Eq. 1})$$

where d_p is the decay distance and depends on the wavelength of the light. Typically d_p extends a few microns or less away from the IRE surface for mid infrared radiation. It is through the evanescent wave that spectroscopic sampling occurs. The evanescent wave consists of the three electric field vectors which can interact with the sample. The electric field amplitudes at the interface, but in the rarer medium are given by⁽²⁴⁾

$$E_y = \frac{2 \cos \theta_i}{(1 - n_{21}^2)^{1/2}} \quad (\text{Eq. 2})$$

$$E_x = \frac{2 \cos \theta_i (\sin^2 \theta_i - n_{21}^2)^{1/2}}{(1 - n_{21}^2)^{1/2} [(1 + n_{21}^2) \sin^2 \theta_i - n_{21}^2]^{1/2}} \quad (\text{Eq. 3})$$

$$E_z = \frac{2 \cos \theta_i \sin \theta_i}{(1 - n_{21}^2)^{1/2} [(1 + n_{21}^2) \sin^2 \theta_i - n_{21}^2]^{1/2}} \quad (\text{Eq. 4})$$

where θ_i is the angle of internal reflection and n_{21} is the ratio of the refractive indices of the rarer medium (air or solution phase) to the denser medium (IRE). It should be noted that Equations 2 to 4 are applicable when the thickness of the thin film on the IRE is negligible compared to d_p as is the case for monolayer films. However, when the thickness of the thin film is smaller than but not negligible compared to d_p , the electric field amplitudes in the z direction, E_z , should be modified by taking the refractive index of the thin film into account while E_y and E_x are independent of the refractive index of the thin film.^(24, 26)

Fourier transform infrared (FT-IR) spectroscopy has been extensively used for both qualitative and quantitative analyses of chemical compounds due to the development of

various experimental techniques and increased sensitivity of the instrument. A combination of multiple internal reflection with Fourier transform infrared spectroscopy (FT-IR/IRS) gives an improved signal/noise ratio and fast data collection which allows for the study of surfactant adsorption at an IRE surface even at submonolayer coverage. Recently, researchers at the University of Utah have developed the use of mineral crystals as reactive internal reflection elements (IREs) for in-situ FT-IR/IRS analysis of collector adsorption phenomena involved in flotation technology.(28-33) Many different internal reflection elements have been used including Al_2O_3 (31), CaF_2 (28-30), KCl (32), and CaCO_3 (33). In such a way collector adsorption phenomena including the nature of collector adsorption, the adsorption density and the orientation of the adsorbed species can be studied quantitatively.

Adsorption Density Equation

The FT-IR/IRS adsorption density equation was initially derived by Sperline et al.(34) and later developed for different systems by Miller et al..(28-30) The FT-IR/IRS adsorption density equation is given below:

$$\Gamma = \frac{A_{\text{IRS}}/N - \epsilon C_b d_e}{1000 \epsilon (2d_e/d_p)} \quad (\text{Eq. 5})$$

where A_{IRS} = integrated absorbance (cm^{-1}) from IRS spectrum,

N = number of internal reflections,

ϵ = integrated molar absorptivity of collector ($l/(\text{cm}^2 \text{ mol})$),

C_b = bulk concentration of the surfactant (mol/l),

d_p = depth of penetration (cm),

d_e = effective thickness (cm).

Detailed definitions of individual parameters and derivation of the FT-IR/IRS adsorption density equation are provided elsewhere.(16, 24, 28, 34) The integrated molar absorptivity, ϵ , can be evaluated from transmission experiments using the Beer-Lambert Equation,

$$A_{\text{Transmission}} = \epsilon b C \quad (\text{Eq. 6})$$

where $A_{\text{Transmission}}$ = integrated absorbance (cm^{-1}) from transmission spectrum,

b = thickness of sample (cm),

C = surfactant concentration (mole/l).

Note that all the independent variables can be calculated from the dimension of the IRE (N) and optical properties (d_e and d_p).⁽²⁴⁾ Other variables are measured spectroscopically (A and ϵ), or set at a desired level (C_b). In previous publications, the validity of the FT-IR/IRS adsorption density equation was confirmed by the FT-IR analysis of transferred Langmuir-Blodgett monolayer films.^(17, 20)

Linear Dichroism Spectroscopy

Order, as applied to surfactants, is used to describe the interactions and organization of surfactant molecules. Orientation of surfactant molecules is of particular interest because highly oriented surfactant monolayers have quite different macroscopic properties than unoriented bulk materials. The average angle of molecular orientation for surfactant molecules can be determined by linear dichroism spectroscopy.^(9-11, 35-38)

Dichroic Ratio: The dichroic ratio for a band in the FT-IR/IRS spectra, R^{IRS} , is the key parameter used in the analysis of the molecular orientations and is determined by polarizing the incoming light and ratioing the absorbance under perpendicular and parallel polarization states. The dichroic ratio for a band, R^{IRS} , is defined as the ratio of absorption for radiation polarized parallel ($A_{\parallel}$) to the plane of incidence to that polarized perpendicular ($A_{\perp}$) to the plane of incidence:

$$R^{\text{IRS}} = \frac{A_{\parallel}}{A_{\perp}} = \frac{E_x^2 k_x + E_z^2 k_z}{E_y^2 k_y} = \frac{k_x E_x^2}{k_y E_y^2} + \frac{k_z E_z^2}{k_y E_y^2} \quad (\text{Eq. 7})$$

where E_x , E_y , E_z are the components of electric field vector and k_x , k_y , k_z are the components of the absorption coefficient in the coordinate system as established by the geometry of the experiment. For internal reflection spectroscopy, the three dimensional nature of the evanescent field offers an easy choice for the experimental coordinate system, which can be defined such that the y direction is normal to the plane of incidence, and the z direction is normal to IRE surface as shown in Figure 3. Thus, for perpendicularly polarized light (transverse electric wave, TE wave), $E_o^2 = E_y^2$, and for parallel polarized light (transverse magnetic wave, TM wave), $E_o^2 = E_x^2 + E_z^2$. The electric field amplitudes can be calculated using Equations. 2 to 4.

Uniaxial Distribution of Transition Dipole Moments: Determination of the molecular orientation angle of alkyl chains of surfactant molecules must be made based upon the assumption that all the alkyl chains are in the trans state with uniaxial distribution of the transition dipole moments of the CH_2 stretching vibrations with respect to the surface normal, i.e., $k_x = k_y$. The assumption of uniaxial distribution of transition dipole moments for the CH_2 stretching vibrations of surfactant molecules with respect to the surface normal, $k_x = k_y$, can be examined by using the following two methods. The first method is polarized light FT-IR/IRS experiments at two different angles of incidence.⁽³⁸⁾ The electric field amplitude changes with the angle of incidence whereas the x, y and z components of absorption coefficient are constant, resulting in a different dichroic ratio for each angle of incidence. Therefore, performing polarized light FT-IR/IRS experiments at two different angles of incidence gives two independent forms of Equation 7, as shown below;

$$R^{\text{IRS}}_1 = \left(\frac{k_x}{k_y}\right)\left(\frac{E_x^2}{E_y^2}\right)_1 + \left(\frac{k_z}{k_y}\right)\left(\frac{E_z^2}{E_y^2}\right)_1 \quad (\text{Eq. 7a})$$

$$R^{\text{IRS}}_2 = \left(\frac{k_x}{k_y}\right)\left(\frac{E_x^2}{E_y^2}\right)_2 + \left(\frac{k_z}{k_y}\right)\left(\frac{E_z^2}{E_y^2}\right)_2 \quad (\text{Eq. 7b})$$

where 1 and 2 represent the two different angles of incidence. Solving Equations 7a and 7b simultaneously for the k_x/k_y value,

$$\frac{k_x}{k_y} = \frac{R^{IRS}_1 \beta_2 - R^{IRS}_2 \beta_1}{\alpha_1 \beta_2 - \alpha_2 \beta_1} \quad (\text{Eq. 8})$$

where $\alpha_1 = (E_x^2/E_y^2)_1$, $\beta_1 = (E_z^2/E_y^2)_1$, $\alpha_2 = (E_x^2/E_y^2)_2$ and $\beta_2 = (E_z^2/E_y^2)_2$. If $k_x/k_y = 1$, i. e., $k_x = k_y$, the transition dipole moments of the surfactant molecules are uniaxially distributed with respect to the surface normal.

The second method to evaluate the assumption of uniaxial distribution of the transition dipole moments with respect to the surface normal is done by comparing the dichroic ratios of the transferred LB films by changing the dipping direction of the IRE by 90 degrees around the z axis,^(39, 40) as shown in Figure 4. When the LB transfer is carefully carried out under the same conditions the k_x and k_y values for the y direction of dipping (0° rotation) are expected to be the same as the k_y and k_x value for the x direction of dipping (90° rotation), respectively. Namely, $k_{x(0^\circ \text{ rotation})} = k_{y(90^\circ \text{ rotation})}$, $k_{y(0^\circ \text{ rotation})} = k_{x(90^\circ \text{ rotation})}$ and $k_{z(0^\circ \text{ rotation})} = k_{z(90^\circ \text{ rotation})}$. As is clear from Equations 2 to 4, the electric field amplitude is only a function of the angle of incidence and refractive indices of the system, which means that changing the dipping direction does not alter the electric field amplitude. Therefore, performing polarized light FT-IR/IRS experiments with the LB film prepared by two different dipping directions gives two independent forms of Equation 7, as shown below;

$$R^{IRS}_{0^\circ} = \left(\frac{k_x}{k_y}\right)_{0^\circ} \left(\frac{E_x^2}{E_y^2}\right) + \left(\frac{k_z}{k_y}\right)_{0^\circ} \left(\frac{E_z^2}{E_y^2}\right) \quad (\text{Eq. 7c})$$

$$\begin{aligned} R^{IRS}_{90^\circ} &= \left(\frac{k_x}{k_y}\right)_{90^\circ} \left(\frac{E_x^2}{E_y^2}\right) + \left(\frac{k_z}{k_y}\right)_{90^\circ} \left(\frac{E_z^2}{E_y^2}\right) \\ &= \left(\frac{k_y}{k_x}\right)_{0^\circ} \left(\frac{E_x^2}{E_y^2}\right) + \left(\frac{k_z}{k_x}\right)_{0^\circ} \left(\frac{E_z^2}{E_y^2}\right) \end{aligned} \quad (\text{Eq. 7d})$$

where 0° and 90° represent the y direction of dipping and the x direction of dipping, respectively. Solving Equations 7a and 7b simultaneously for the k_x/k_y value gives

$$\left(\frac{k_x}{k_y}\right)_{0^\circ} = \left(\frac{k_y}{k_x}\right)_{90^\circ} = \frac{R^{IRS}_{0^\circ} + \alpha}{R^{IRS}_{90^\circ} + \alpha} \quad (\text{Eq. 9})$$

where $\alpha = E_x^2/E_y^2$. It is very clear that when the measured dichroic ratios are the same for the 0 and 90 degrees rotation the assumption of uniaxial distribution of the transition dipole moments is valid.

Molecular Orientation Based upon Uniaxiality

If all the alkyl chains of surfactant are in the trans state and the assumption of $k_x = k_y$ is verified, the average angle of molecular orientation angle for the surfactant molecules can be calculated based upon the following relationships. For the surfactant molecules whose transition dipole moment is oriented at an angle of ϕ from the director, (10, 35, 38)

$$k_x = k_y = KM^2 \left[\frac{S \sin^2 \phi}{2} + \frac{1 - S}{3} \right] \quad (\text{Eq. 10})$$

$$k_z = KM^2 \left[S \cos^2 \phi + \frac{1 - S}{3} \right] \quad (\text{Eq. 11})$$

where K is a constant and M is the transition dipole moment (the transition moment vector deviates by an angle ϕ from the director). S is the order parameter and was first defined by Stein (41, 42) as

$$S = \frac{3 \cos^2 \theta - 1}{2} \quad (\text{Eq. 12})$$

where θ is the angle between the director and the surface normal. It should be mentioned that in the above expressions (Equations 10 to 12), the angle θ is an average angle of the director with respect to the z axis and the angle ϕ is an average angle of the transition dipole moment as it rotates around the director. See Figure 3.

The director can be the molecular axis (in this case θ is the molecular orientation angle, the angle between the molecular axis and the surface normal, the z axis) or the transition dipole moment of specific group vibration (in this case θ is the orientation angle of a specific transition dipole moment, the angle between the transition dipole moment and the surface normal, the z axis. For clarity, we will use symbol θ_i^M for this angle). Therefore, orientations of surfactant molecules and transition dipole moments can be determined using Equations 10 to 12.

Determination of the Average Molecular Orientation, θ : It is well known from geometrical considerations that the transition dipole moments of the CH_2 stretching vibration are oriented at 90° to the molecular axis. Accordingly, substituting $\phi = 90^\circ$ and Equation 12 into Equations 10 and 11 gives

$$k_x = k_y = \frac{KM^2 (2 - \sin^2\theta)}{4} \quad (\text{Eq. 10a})$$

$$k_z = \frac{KM^2 \sin^2\theta}{2} \quad (\text{Eq. 11a})$$

Substituting Equations 10a and 11a into Equation 7 gives,

$$R^{\text{IRS}} = \frac{E_x^2}{E_y^2} + \frac{2 E_z^2 \sin^2\theta}{E_y^2 (2 - \sin^2\theta)} \quad (\text{Eq. 13})$$

Rearranging Equation 13, the molecular orientation angle, θ (the angle between the molecular axis and the z axis), is

$$\theta = \sin^{-1} \left[\frac{2 E_x^2 - 2 R^{\text{IRS}} E_y^2}{E_x^2 - R^{\text{IRS}} E_y^2 - 2 E_z^2} \right]^{1/2} \quad (\text{Eq. 14})$$

Equations 13 and 14 are essentially the same equations used to determine the dichroic ratio of transition dipole moments as a function of molecular orientation angle as reported by

Sperline et al.⁽¹¹⁾ to determine the orientation angles of the alkyl chain and the asymmetric vibration of the OSO_3^- group for sodium dodecyl sulfate (SDS) adsorbed at a sapphire surface and as reported by Ahn and Franses⁽⁴⁰⁾ to determine the average alkyl chain orientation at germanium and silicon surfaces based upon the uniaxial model.

Determination of the Average Transition Dipole Moment Angle, θ_i^M : If we consider the transition dipole moment as the director, $\phi = 0$. Substituting $\phi = 0$ and Equation 12 into Equations 10 and 11 gives

$$k_x = k_y = \frac{KM^2 \sin^2 \theta_i^M}{2} \quad (\text{Eq. 10b})$$

$$k_z = KM^2 \cos^2 \theta_i^M \quad (\text{Eq. 11b})$$

Substituting Equations 10b and 11b into Equation 7 gives,

$$R^{\text{IRS}} = \frac{E_x^2}{E_y^2} + \frac{2 E_z^2}{E_y^2 \tan^2 \theta_i^M} \quad (\text{Eq. 15})$$

Rearranging Equation 15 gives

$$\theta_i^M = \tan^{-1} \left[\frac{2 E_z^2}{R^{\text{IRS}} E_y^2 - E_x^2} \right]^{1/2} \quad (\text{Eq. 16})$$

Equations 15 and 16 are essentially the same equations used by Sperline et al.⁽¹¹⁾ and Ahn and Franses⁽⁴⁰⁾ to determine a dichroic ratio of the transition dipole moment as a function of its angular displacement (θ_i^M). Specifically, Sperline et al.⁽¹¹⁾ examined the orientation angle of the symmetric vibration of the OSO_3^- band for sodium dodecyl sulfate (SDS) adsorbed at a sapphire surface whereas Ahn and Franses⁽⁴⁰⁾ considered the orientations of the CH_2 asymmetric and symmetric stretching vibrations, θ_{as}^M and θ_s^M , at germanium and silicon surface. Cropek and Bohn⁽⁹⁾ used a different form of Equation 15 to determine the orientation angle for the long axis of a phenyl ring at a quartz surface. Once the orientation

of the transition moments have been established in relation to the molecular axis, the average orientation angle of the alkyl chain of the surfactant molecule can be determined base upon geometrical considerations. For straight chain surfactants, the transition moments of the CH₂ symmetric and asymmetric vibrations and the hydrocarbon chain axis are mutually perpendicular, as described in Figure 3c. Therefore, the average orientation angle of the alkyl chain, θ , can be calculated from the trigonometry, i.e.,

$$\cos^2\theta_{as}^M + \cos^2\theta_s^M + \cos^2\theta = 1 \quad (\text{Eq. 17})$$

Rearranging Equation 17 gives

$$\theta = \sin^{-1} \left[1 - \cos^2\theta_{as}^M + \cos^2\theta_s^M \right]^{1/2} \quad (\text{Eq. 18})$$

RESULTS AND DISCUSSION

Average Angle of Molecular Orientation for a Transferred LB Stearate Monolayer

In order to determine the average angle of molecular orientation for adsorbed surfactant molecules, it is assumed that all the alkyl chains of the surfactant are in the trans state and the transition dipole moments of the CH₂ stretching vibration modes are uniaxially distributed with respect to the surface normal, i.e., $k_x = k_y$.

Evaluation of Assumptions: From the surface pressure-specific area isotherm, the molecular area of the LB stearate monolayer transferred at a fluorite surface was found to be about 20 Å²/molecule, which is molecular area is the cross-sectional area of an all-trans alkyl chain.⁽⁴⁴⁾ As revealed by the frequencies of the CH₂ asymmetric and symmetric stretching vibration in the FT-IR/IRS spectra of the transferred LB stearate monolayers in the dry state (at $2917 \pm 1 \text{ cm}^{-1}$ and $2850 \pm 1 \text{ cm}^{-1}$ for the CH₂ asymmetric and symmetric stretching bands, respectively), it is also evident that the stearate molecules are all in the

trans state. The typical peak frequencies of the CH₂ asymmetric and symmetric stretching vibrations for trans-state alkyl chain are reported to be 2918 and 2851 cm⁻¹, respectively.(5, 6)

As discussed in the pervious section, the k_x/k_y values were determined by performing the polarized light FT-IR/IRS experiments at two different angles of incidence and solving Equation 8. The k_x/k_y values determined are shown in Table 1 and were found to be reasonably close to 1, i.e., 0.96 to 1.10 for the CH₂ asymmetric stretching and 1.03 to 1.11 for the CH₂ symmetric stretching vibration.

As an independent method for evaluating the uniaxiality of the transition dipole moments of the asymmetric and symmetric CH₂ stretching vibration modes, polarized light FT-IR/IRS experiments were performed after LB transfer of the stearate monolayer for two different dipping directions. Solving Equation 9 with the two measured dichroic ratio values and the calculated electric field amplitudes gave the k_x/k_y of the asymmetric and symmetric CH₂ stretching vibration modes values. As shown in Table 2, the evaluated k_x/k_y values for the asymmetric and symmetric CH₂ stretching vibration modes were found to be 0.96 and 1.01 respectively. The results from these two independent experimental methods suggest that the assumption of uniaxial distribution of the transition dipole moments for the asymmetric and symmetric CH₂ stretching vibration modes are fairly reasonable, thus enabling us to estimate the average orientation angle of the alkyl chain of the transferred LB stearate monolayer.

Average Angle of Molecular Orientation: In the previous section it was found that stearate molecules after LB transfer at a fluorite are in the trans state and are uniaxially distributed with respect to the surface normal. On this basis the average angle of molecular orientation for transferred LB stearate monolayers was determined using Equation 14. and the results are presented in Table 3. In addition, the average orientation angles of the transition dipole moments of the CH₂ asymmetric and symmetric stretching vibration modes were

determined using Equation 16. The average angle of molecular orientation for the transferred LB monolayer was calculated by solving Equation 18 with the average orientation angles for the transition dipole moments. See Table 4. As is clear from Tables 3 and 4, good agreement was obtained for these two different approaches and the LB stearate monolayer transferred at a surface pressure of 20 to 23 mN/m (adsorption density of 7.9×10^{-10} to 8.3×10^{-10} mol/cm²) was found to be oriented at 9 to 16 degrees from the surface normal.

Using the same molecular orientation analyses for the LB monolayer of calcium distearate transferred at a surface pressure of 22 mN/m it was found that each hydrocarbon chain of the calcium distearate is oriented at 13° to 16° from the surface normal. By way of comparison a polarized light IR transmission study of 15 LB monolayers of behenic acid and calcium dibehenate at a fluorite surface showed that the hydrocarbon chain of the behenic acid layers was oriented at 21 to 29 degrees from the surface normal whereas the hydrocarbon chain axis makes an angle of 3 to 13 degrees with the surface normal for the calcium dibehenate layers.⁽⁴³⁾

Average Angle of Molecular Orientation for SA Stearate Monolayers and Submonolayers

Evaluation of Assumptions: Figures 5 and 6 show the frequencies of the CH₂ asymmetric and symmetric stretching vibration bands of SA stearate monolayers and submonolayers in the dry state. It was found that the frequencies of the CH₂ stretching vibrations of SA stearate monolayers and submonolayers are 2919 ± 1 cm⁻¹ for the asymmetric vibration and 2851 ± 1 cm⁻¹ for the symmetric vibration. Since the peak frequencies of the CH₂ stretching asymmetric and symmetric vibrations are very close to those found for typical trans alkyl chains (2918 and 2850 cm⁻¹),^(5, 6) it seems clear that the adsorbed molecules are mostly in the trans state. The k_x/k_y values for the CH₂ asymmetric and symmetric stretching vibration modes of SA stearate monolayers and submonolayers were calculated

using Equation 8 and are listed in Table 5. It seems from Table 5 that at low coverage (below 2.5×10^{-10} mol/cm²) the calculated k_x/k_y values for the CH₂ asymmetric and symmetric stretching vibration modes were found to deviate significantly from 1. However, at higher adsorption densities (3.5×10^{-10} mol/cm² or higher), the calculated k_x/k_y values for the CH₂ asymmetric and symmetric stretching vibration modes were found to be reasonably close to 1, i.e., 1.05 and 1.03 respectively at an adsorption density of 7.6×10^{-10} mol/cm². Based upon the results in Table 5, it seems that uniaxiality of the asymmetric and symmetric CH₂ stretching vibration modes is a reasonable assumption for the SA stearate monolayer at an adsorption density of 3.5×10^{-10} mol/cm² or higher. The average angle of molecular orientation for the SA stearate monolayers can be determined based upon this assumption, whereas at low SA stearate coverage the calculated k_x/k_y values for the asymmetric and symmetric CH₂ stretching vibration modes deviate significantly from 1 and the average angle of molecular orientation for such SA stearate submonolayers may not be determined with any confidence.

Average Angle of Molecular Orientation: The average angle of molecular orientation for the SA stearate monolayer was determined using both Equation 14 and Equations 16 and 18 assuming the uniaxiality of the transition dipole moments for the CH₂ stretching vibration modes, an assumption which is not satisfied at low surface coverage ($< 3.5 \times 10^{-10}$ mol/cm²). See Figure 7. It was found that the average angle of molecular orientation for the SA stearate species was not dependent upon the adsorption density. A similar finding was reported from the polarized light FT-IR/IRS study of LB monolayer films of dipalmitoylphosphatidylcholine at a germanium surface.⁽⁴⁵⁾ It seems clear from Figure 7 that the SA stearate species are oriented at 21 to 23 degrees from the surface normal, regardless of surface coverage, for adsorption densities exceeding 3.5×10^{-10} mol/cm² and less than monolayer coverage. The average angle of molecular orientation for the SA

stearate monolayer at an adsorption density of 7.6×10^{-10} mol/cm² was found to be about 21 degrees from the surface normal.

Hydrophobicity Consideration: Further evidence of the similarity between LB and SA monolayers of stearate species is revealed from contact angle measurements. Table 6 compares advancing and receding contact angles of the LB and SA stearate. As shown in Table 6, the advancing contact angle of 112° for the SA stearate monolayer (7.6×10^{-10} mol/cm²) is almost the same as that of LB stearate monolayer whereas the receding contact angle for the SA stearate monolayer is about 20 degrees less than the receding contact angle for the LB stearate monolayer, indicating that the SA stearate monolayer are slightly less stable than the LB stearate monolayer. Further discussion on the hydrophobicity and stability of LB and SA monolayers are provided in another contribution.⁽¹⁹⁾

CONCLUSION

Average molecular orientations of Langmuir-Blodgett (LB) and self-assembled (SA) stearate monolayers at a fluorite surface were determined from linear dichroism theory. It was shown from the surface pressure-specific area isotherm and/or FT-IR/IRS experiments that the surfactant molecules in the LB monolayer and the SA monolayer are in the trans state with uniaxial distribution of both hydrocarbon chains and transition dipole moments of the CH₂ stretching vibrations. Specifically, the axial distribution of surfactant molecules was experimentally examined using polarized light Fourier transform infrared internal reflection spectroscopy (FT-IR/IRS) to evaluate the validity of the assumption of uniaxiality of surfactant molecules at a fluorite (CaF₂) surface. The results demonstrate that stearate species are uniaxially distributed at a fluorite surface for both the LB monolayer and the SA monolayer at adsorption densities of higher than 3.5×10^{-10} mol/cm².

The molecular area of the LB stearate monolayer transferred at a fluorite surface was found to be the same as the cross-sectional area of an all-trans alkyl chain (about 20

A²/molecule). Also, the frequencies of the CH₂ stretching vibrations of LB stearate monolayers ($2917 \pm 1 \text{ cm}^{-1}$ for the asymmetric vibration and $2850 \pm 1 \text{ cm}^{-1}$ for the symmetric vibration) were shown to be similar to the typical peak frequencies of the CH₂ asymmetric and symmetric stretching vibration for trans-state alkyl chains (2918 and 2851 cm^{-1}), indicating that the adsorbed molecules are in the trans state.

Similarly, in most of the SA stearate monolayers the observed frequencies of the CH₂ stretching vibration bands were $2919 \pm 1 \text{ cm}^{-1}$ for the asymmetric vibration and $2851 \pm 1 \text{ cm}^{-1}$ for the symmetric vibration, which suggests that the adsorbed molecules are mostly in the trans state.

The average angle of molecular orientation for the LB stearate monolayers was found to be 9 to 16 degrees from the surface normal whereas the average angle of molecular orientation for the SA stearate layers at approximate monolayer coverage ($7.6 \times 10^{-10} \text{ mol/cm}^2$) was found to be about 21 degrees from the surface normal. In addition, it was found that the adsorption density of the stearate molecule has no significant influence on the molecular orientation of adsorbed stearate species. For example, the molecular orientation angle of SA stearate species was found to have little variation (20 to 26 degrees from the surface normal) with respect to the extent of surface coverage (from a tenth of a monolayer to full monolayer coverage).

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Table 1. The k_x/k_y Values for Transferred LB Stearate Monolayers as Determined by Polarized Light FT-IR/IRS Analysis at Two Different Angles of Incidence. (θ_i is the angle of incidence for each polarized light FT-IR/IRS experiments, k_x/k_y calculated from Eq. 8)

Type	i	θ_i	$(\frac{E_x^2}{E_y^2})_i$	$(\frac{E_z^2}{E_y^2})_i$	R_{IRS_i} for CH_2^{as}	R_{IRS_i} for CH_2^s	k_x/k_y for CH_2^{as}	k_x/k_y for CH_2^s
LB1 (23 mN/m)	1	52.3	0.287	1.426	0.379	0.360	0.96	1.03
	2	61.0	0.409	1.182	0.479	0.475		
LB2 (20 mN/m)	1	51.7	0.273	1.453	0.376	0.368	0.99	1.09
	2	62.4	0.421	1.158	0.502	0.515		
LB3 (22 mN/m)	1	51.0	0.256	1.488	0.296	0.292	1.10	1.11
	2	58.3	0.382	1.236	0.433	0.431		
LB4 (23 mN/m)	1	51.6	0.271	1.458	0.329	.352	0.96	1.04
	2	60.4	0.404	1.192	0.444	0.478		

Table 2. The k_x/k_y Values for a Transferred LB Stearate Monolayer as Determined by Polarized Light FT-IR/IRS Analysis for Two Different Dipping Directions (In both cases surface pressure for LB transfer was maintained at 23 mN/m. The $(k_x/k_y)_{0^\circ}$ was calculated using Eq. 9 with an incident angle for internal reflection of 52.3° .)

Type	Dipping Direction	$\left(\frac{E_x^2}{E_y^2}\right)$	RIRS for CH_2^{as}	RIRS for CH_2^{s}	$(k_x/k_y)_{0^\circ}$ for CH_2^{as}	$(k_x/k_y)_{0^\circ}$ for CH_2^{s}
LB	y axis (0° rotation)	0.287	0.354	0.366	0.96	1.01
	x axis (90° rotation)		0.379	0.360		

Table 3. Molecular Orientation of Transferred LB Stearate Monolayers using Eq. 14. (θ is the molecular orientation angle, the angle between the molecular axis and the surface normal. The incident angles for internal reflection are provided in Table 1. For LB5, the incident angle for internal reflection was 52.3 °.)

Surface Pressure	E_x^2	E_y^2	E_z^2	RIRS for CH_2^{as}	RIRS for CH_2^{s}	θ for CH_2^{as}	θ for CH_2^{s}
LB1	0.858	2.992	4.267	0.379	0.360	14°	13°
(23 mN/m)	0.769	1.881	2.222	0.479	0.475	14°	13°
LB2	0.840	3.073	4.467	0.376	0.368	15°	15°
(20 mN/m)	0.723	1.717	1.989	0.502	0.515	15°	16°
LB3	0.811	3.169	4.715	0.296	0.292	9°	9°
(22 mN/m)	0.844	2.209	2.730	0.433	0.431	12°	11°
LB4	0.835	3.087	4.503	0.329	0.352	11°	13°
(23 mN/m)	0.789	1.952	2.329	0.444	0.478	11°	14°
LB5	0.858	2.992	4.267	0.354	0.366	12°	13°
(23 mN/m)							

Table 4. Molecular Orientation of Transferred LB Stearate Monolayers using Eqs. 16 and 18. (θ_{as}^M and θ_s^M are the transition moment orientation angles for the CH_2 asymmetric and symmetric stretching vibration modes, the angle between the transition dipole moment and the surface normal. θ is the molecular orientation angle, the angle between the molecular axis and the surface normal. The incident angles for internal reflection are provided in Table 1. For LB5, the incident angle for internal reflection was 52.3° .)

Surface Pressure	E_x^2	E_y^2	E_z^2	RIRS for CH_2^{as}	RIRS for CH_2^s	θ_{as}^M	θ_s^M	θ
LB1	0.858	2.992	4.267	0.379	0.360	80°	81°	14°
(23 mN/m)	0.769	1.881	2.222	0.479	0.475	80°	80°	14°
LB2	0.840	3.073	4.467	0.376	0.368	79°	80°	15°
(20 mN/m)	0.723	1.717	1.989	0.502	0.515	79°	79°	16°
LB3	0.811	3.169	4.715	0.296	0.292	83°	84°	9°
(22 mN/m)	0.844	2.209	2.730	0.433	0.431	82°	82°	11°
LB4	0.835	3.087	4.503	0.329	0.352	82°	81°	12°
(23 mN/m)	0.789	1.952	2.329	0.444	0.478	83°	80°	12°
LB5	0.858	2.992	4.267	0.354	0.366	81°	81°	13°
(23 mN/m)								

Table 5. The k_x/k_y Values for SA Stearate Monolayers as Determined by Polarized Light FT-IR/IRS Analysis at Two Different Angles of Incidence. (θ_i = angle of incidence for each polarized light FT-IR/IRS experiment. k_x/k_y calculated from Eq. 8.)

Adsorption Density	θ_i	$(\frac{E_x^2}{E_y^2})_i$	$(\frac{E_z^2}{E_y^2})_i$	R_{IRS_i} for CH_2^{as}	R_{IRS_i} for CH_2^s	k_x/k_y for CH_2^{as}	k_x/k_y for CH_2^s
1.2×10^{-10} (mol/cm ²)	51.3	0.264	1.473	0.513	0.474	1.15	1.30
	60.1	0.401	1.198	0.632	0.628		
2.5×10^{-10} (mol/cm ²)	51.3	0.264	1.473	0.565	0.547	0.84	0.64
	55.3	0.342	1.315	0.594	0.556		
3.4×10^{-10} (mol/cm ²)	51.3	0.264	1.473	0.457	0.433	1.09	1.13
	60.1	0.401	1.198	0.575	0.562		
3.5×10^{-10} (mol/cm ²)	51.3	0.264	1.473	0.483	0.476	1.05	1.00
	60.1	0.401	1.198	0.588	0.573		
7.6×10^{-10} (mol/cm ²)	51.3	0.264	1.473	0.470	0.459	1.05	1.03
	60.1	0.401	1.198	0.577	0.565		
11.0×10^{-10} (mol/cm ²)	51.6	0.271	1.458	0.520	0.522	1.07	1.10
	57.0	0.366	1.267	0.591	0.596		

Table 6. Contact Angle Data for Transferred LB and SA Stearate Monolayers at a Fluorite Surface.

Type	Adsorption density ($\times 10^{-10}$ mol/cm ²)	Advancing Contact Angle(°)	Receding Contact Angle(°)
LB	8.1	111 $\pm$ 2	100 $\pm$ 2
SA	7.6	112 $\pm$ 3	81 $\pm$ 3

Figure 1. Comparison of the FT-IR/IRS spectra of SA and LB stearate monolayers at a fluorite surface with the transmission spectrum of stearic acid in carbon tetrachloride solution.

Figure 2. Schematic of light undergoing multiple total internal reflections in an IRE and the evanescent field created at each reflection⁽¹⁷⁾ (θ is the incident angle of light for internal reflection).

a) Laboratory axes for polarized light FT-IR/IRS experiment

b) Description of the orientation director and the transition dipole moment

c) Orthogonality among the molecular axis and the transition dipole moments (τ) of the asymmetric/symmetric CH_2 stretching vibration modes

Figure 3. Schematic of the coordination system used for describing general uniaxial orientation and orientation directors.

Direction of LB Transfer

a) LB transfer with vertical IRE orientation

Direction of LB Transfer

b) LB transfer with Horizontal IRE orientation

Figure 4. Schematic diagram of IRE orientation during LB transfer.

Figure 5. CH₂ asymmetric vibration frequency for SA stearate monolayers as determined from FT-IR/IRS spectra vs. adsorption density.

Figure 6. CH₂ symmetric vibration frequency for SA stearate monolayers as determined from FT-IR/IRS spectra vs. adsorption density.

Figure 7. Average angle of molecular orientation (degrees from the surface normal) for SA stearate layers vs. adsorption density. $\Gamma_{\text{monolayer}} = 8.3 \times 10^{-10} \text{ mole/cm}^2$.

13. M. R. Yalamanchili, A. Atia, J. Drelich, and J. D. Miller, "Characterization of Interfacial Water at Hydrophilic and Hydrophobic Surfaces by In-Situ FTIR/Internal Reflection Spectroscopy," in: *Proceedings of the 34th CIM Conference of Metallurgists*, Vancouver, British Columbia, August, 1995, in press.

**CHARACTERIZATION OF INTERFACIAL WATER AT
HYDROPHILIC AND HYDROPHOBIC SURFACES BY
IN-SITU FTIR/INTERNAL REFLECTION SPECTROSCOPY**

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ABSTRACT

In-situ FTIR/internal reflection spectroscopy (FTIR/IRS) has been used to spectroscopically characterize interfacial water near hydrophilic (silicon single crystal) and hydrophobic (polymer-coated germanium single crystal) surfaces. Interfacial water was examined spectroscopically over certain distances from the surface by appropriate design of the geometry and optics of the internal reflection system. The in-situ FTIR/IRS spectra were characterized by consideration of the OH stretching region ($3000\text{--}3800\text{ cm}^{-1}$) associated with the vibrational spectra of the interfacial water. Preliminary spectral results indicate the prevalence of an ice-like structure at the hydrophilic silicon surface, whereas at the hydrophobic surface the ice like structure is not so prevalent and there appears to be a significant decrease in hydrogen bonding.

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INTRODUCTION

The characterization of interfacial water structure near hydrophilic and hydrophobic surfaces is of great importance in colloid and surface science areas including flotation, solid-liquid separation, dispersions and emulsions, flocculation, adsorption, and corrosion as well as in the preparation of thin films (1-4). Recent research suggests that the structural features of interfacial water determine the nature of interaction forces which control the aforementioned phenomena (5). Thus it is expected that the fundamental aspects of wetting phenomena are determined to a great extent by the structure and properties of interfacial water. For example, the nature and behavior of thin films during bubble attachment at the surface of a hydrophobic particle and the stability of water films in the froth phase are excellent examples of the importance of interfacial water in the flotation process. It has become evident then that the characterization of interfacial water is very important in understanding the so called non-DLVO interparticle forces (structural/hydration forces) and their influence on particle dispersion and aggregation in aqueous systems. Several researchers (5) have provided experimental evidence for the existence of these short-range forces. Specifically, the attractive forces measured between hydrophobic surfaces were found to have decay lengths up to about 60 nm (6). However, the origin of these forces is still unknown although it is widely believed that changes in the interfacial water structure are responsible for the existence of such hydrophobic attractive forces (7,8).

Although there has been some progress in the area of modeling the structure of water near surfaces, there is very little experimental evidence to support the model predictions. In part, this has been due to the lack of a suitable technique to examine interfacial water structure. However, in recent years new analytical techniques have been developed such as internal reflection spectroscopy (IRS) and nonlinear optical spectroscopy, to study solid/liquid interfaces (9-11). Already, these techniques have opened up new avenues to probe solid/liquid interfaces in-situ with much improved surface sensitivities. Each of these spectroscopic techniques has its advantages and disadvantages with respect to the characterization of interfacial water.

The non-linear optical spectroscopy techniques such as second harmonic generation (SHG) and sum frequency generation (SFG) which are based on second-order non-linear optical processes occurring at solid/liquid interfaces provide for extremely high surface sensitivities and thus the characteristics of monomolecular interfacial species can be studied (10,11). However, these techniques can not be used to simultaneously detect both surface and bulk species since these non-linear processes are forbidden in centrosymmetric media such as bulk water. On the other hand, internal reflection spectroscopy (IRS) with reactive internal reflection elements can provide spectral information regarding both surface and bulk species. The use of IRS in conjunction with mid-FTIR, near-FTIR, and Raman spectroscopy techniques will allow for a systematic depth profiling of water from the surface into the bulk. The drawback of this technique is the relatively low surface sensitivity which prevents the isolated examination of the first few layers of water although a region as small as 30 nm from the surface can be examined (12). Since most of the signal (absorption) comes from the first few layers at the surface, as will be evident from discussion in the following sections, in-situ IRS can provide important information about interfacial water properties.

SPECTRAL FEATURES OF WATER STRUCTURE

There is considerable spectroscopic evidence which supports the existence of structure in liquid water. However, the interpretation of this evidence is varied and numerous models have been advanced in the past to explain the experimental results. These models generally fall into one of two broad categories viz. mixture and continuum models (13,14). Briefly, mixture models of liquid water assume the existence of two types of water molecules: hydrogen bonded and non-hydrogen bonded. The unbonded water molecules are identified as monomeric water and the bonded water may have many different species depending on the number and configuration of the hydrogen bonds. On the other hand, continuum models assume that all water molecules are tetrahedrally coordinated as in ice and there is very little, if any, hydrogen-bond breakage. These continuum predict that the distorted hydrogen bonds give rise to a continuous distribution of hydrogen bond strengths resulting in a broad OH stretching spectrum.

Each of the above approaches explains certain properties of water but leaves other characteristics unexplained. For example, the observation of a band near 3600 cm^{-1} which has been attributed to broken

hydrogen bonding (free OH) is not accounted for by the continuum models. It is not the intention of the authors of the present work to consider these opposing theories in greater detail. An excellent treatment of these two approaches to explain the structure of liquid water is given elsewhere (13). In the following paragraph, the general spectral characteristics that reveal the structure of water are considered.

Three different bands centered about 3600, 3400, and 3200 cm^{-1} have been identified in the OH stretching region of the vibrational spectra for water as shown in Table 1. The OH stretching bands were observed to shift from above 3600 cm^{-1} at high temperature to below 3200 cm^{-1} in the spectra of ice at low temperature. Spectral features between 3000 and 3500 cm^{-1} are generally attributed to the existence of hydrogen bonded OH stretching with different degrees of bond ordering. For example, the peak at $\sim 3600 \text{ cm}^{-1}$ is attributed to the non-hydrogen bonded free OH stretching vibration. The peak at $\sim 3400 \text{ cm}^{-1}$ has been assigned to a water structure with partial hydrogen bonding and the peak at $\sim 3200 \text{ cm}^{-1}$ is generally attributed to the symmetric OH stretching mode associated with tetrahedrally coordinated water molecules as in ice. In any event, these spectral features in the OH stretching region can be used as indicators of the degree of hydrogen bonding, in other words, the degree of structure present in water.

Table 1. Spectral features of water structure in the OH stretching region

Region	Band Position (cm^{-1})	Band Assignment	Ref.
3600 cm^{-1} Free Water or Weak Hydrogen Bonding	3715	Free OH Stretch	15
	3691	Free OH Stretch	16
	3682	Free OH Stretch	17
	3680	Free OH stretch	18
	3650	Free OH Stretch, High Temp.	17
	3620-3650	Free OH Stretch	19
	3615	Free OH Stretch	20
3400 cm^{-1} Incomplete Tetrahedral Coordination or Hydrogen Bond Disorder	3446 and 3496	Sym and Anti Sym OH Stretch	21
	3450	Bonded OH Stretch	21
	3420	Bonded OH Stretch Bifurcated hydrogen bonds	20
	3400	Bonded OH Stretch One H strongly bonded and the other weakly bonded	17
	3400	Bonded OH Stretch in H-bonded clusters	22
	3380	Bonded OH Stretch H-Bonding between oxygens	23
3200 cm^{-1} Complete Tetrahedral Coordination	3200	OH Stretch Ice-like Structure	17
	3200	Coupled Sym OH Stretch Tetrahedrally coordinated water	18
	3200	OH Stretch, Supercooled ice	24
	3200	OH Stretch, Ice-like structure	12

RESEARCH OBJECTIVES

In this present work, the in-situ FTIR internal reflection spectroscopy (IRS) technique was used to study in real time the structure of the interfacial water present at various depths from the surface under consideration. Silicon/water and polymer-coated germanium/water systems were selected as model systems to study the spectral characteristics of interfacial water as a function of distance from the surface by in-situ FTIR/IRS in the MIR region. The spectral features including band position, shape, and intensity were examined at different distances from the surface in order to distinguish surface water from bulk water. Specifically, the OH stretching region of the vibrational spectra for interfacial water was studied in order to examine the degree of water structuring as a function of distance from the interface and as a function of temperature.

FTIR/INTERNAL REFLECTION SPECTROSCOPY

Total Internal Reflection

Internal reflection spectroscopy (IRS), alternatively referred to as attenuated total reflection (ATR) spectroscopy, allows for in-situ real time spectroscopic measurements of interfacial phenomena. Consequently, IRS has become a powerful analytical tool for in-situ surface analysis in many areas of colloid and surface science (25). Shown in Figure 1 is a schematic representation of a ray of light undergoing total internal reflection in a parallelepiped shaped internal reflection element (IRE). Two requirements must be met before total internal reflection can occur. First, the IRE must be optically denser, that is, have a higher refractive index, than the sample ($n_1 > n_2$). Second, the incident angle of the light beam in the IRE must be greater than a critical angle, θ_c :

$$\theta_c = \sin^{-1} (n_2/n_1) \quad (1)$$

where n_2 and n_1 are the refractive indices of the sample and the IRE respectively. When the incident angle is greater than the critical angle, total internal reflection occurs. As the light is totally reflected at the interface, an exponentially decaying evanescent wave is set up in the rarer outer phase (sample). It is through this evanescent wave that sampling occurs. The exponential decay of the evanescent field into the sample describes the decrease in the electric field perpendicular to the surface, the Z direction. Thus the electric field at some distance Z from the nonabsorbing interface is expressed as (26):

$$E = E_0 \exp ((-2\pi/\lambda_1)/\sin^2\theta - n_{21}^2)^{1/2} Z) \quad (2)$$

where E_0 is the electric field amplitude at the surface, $\lambda_1 = \lambda/n_1$ is the wavelength of the radiation in the denser medium, λ is the wavelength in free space, θ is the incident angle, $n_{21} = n_2/n_1$, and Z is the distance from the surface.

It should be mentioned here that the total internal reflection theory is simplified by assuming an infinite plane wave at an interface between semi-infinite nonabsorbing media (26). Even though these assumptions are unrealistic, they make the treatment of internal reflection theory relatively easy and the properties of the evanescent field can be adequately described by Equation 2. The validity of the internal reflection theory developed based on the above mentioned assumptions has been demonstrated by several researchers in the past for a variety of applications in the area of interfacial phenomena (9,25,27). Equation 2 can be simplified as:

$$E = E_0 \exp (-\eta Z) \quad (3)$$

where η is the exponential constant that is equal to $2\pi n_1 (\sin^2\theta - n_{21}^2)^{1/2} / \lambda$.

Figure 1. Schematic of light ray undergoing multiple total internal reflections in an IRE.

Depth of Penetration

The depth of penetration of the evanescent field is an important parameter in internal reflection spectroscopy and is particularly significant in the present work. For a nonabsorbing rarer phase, Harrick (9) defined the depth of penetration as the distance from the IRE where the electric field amplitude falls to $1/e$ of its value at the surface. The depth of penetration, d_p , as defined by Harrick is equal to $1/\eta$ and is given by:

$$d_p = \lambda / (n_1 2\pi (\sin^2 \theta - n_{21}^2)^{1/2}) \quad (4)$$

The nomenclature involved with d_p is unfortunate since it is often mistaken as the actual depth that is sampled in the IRS experiment. Since the electric field is 37% of its surface value at d_p , the depth actually sampled is greater than d_p . However, the spectral information obtained is most indicative of the spectral characteristics closest to the surface and the contribution of spectral information away from the surface is significantly less according to the exponential decay of the electric field amplitude (Equation 3). It should be mentioned here that the model system (silicon/water) considered in the present study has an outstanding feature, i. e., a large value of $\langle E_z^2 \rangle$ at the critical angle. This allows for an intense interaction with species at the interface. In other words, the interfacial water species concentrated in the first few layers will experience most of this electric field, hence the resulting spectrum contains important information about interfacial water species.

As mentioned above, the equation for depth of penetration (Equation 4) was derived based on the assumption that the second medium (rarer medium) is a nonabsorbing medium. For relatively low absorbing media such as adsorbed organic surfactants and polymer films, the validity of this equation has been demonstrated by several researchers in the past (9,25,28). However, for highly absorbing rarer medium, such as water, used in this present work, Equation 4 should be modified by taking into account the complex refractive index comprised of the real (n) and imaginary (κ , attenuation index) parts (29):

$$d_p = \lambda / (n_1 2\pi (\sin^2 \theta - n_{21}^2 (1 + i\kappa)^2)^{1/2}) \quad (5)$$

Figure 2 shows the variation in the depth of penetration (calculated using Equation 5) as a function of the incident angle for the silicon/water system being examined in this study. The critical angle for obtaining total internal reflection in this case is approximately 23 degrees as calculated from Equation 1. It can be observed from Figure 2 that the depth of penetration decreases as the incident angle increases.

Figure 2. Variation of depth of penetration as a function of incident angle for the silicon/water system.

Depth Profiling by In-Situ FTIR/IRS

As evident from the above, in-situ FTIR/IRS with reactive internal reflection elements should be a powerful analytical technique to study the spectral characteristics of interfacial water. Specifically, it is expected that interfacial water present at various distances from the surface can be described based on the in-situ FTIR/IRS spectral information. In other words, spectral characteristics including band position, intensity, and shape can be examined at different distances from a surface by simply varying the incident angle of the IR beam in the IRE (see Figure 2). The incident angle can, in turn, be varied by changing the face angle of the IRE and the optics of the experiment as will be explained in the experimental section. For the silicon/water system examined in this study, d_p values (as calculated from Equation 5) ranging from 153 nm to about 550 nm were possible, with the available sampling accessories and optics, for the study of interfacial water by in-situ FTIR/IRS in the MIR region.

Surface Water vs. Bulk Water

Internal reflection spectroscopy will allow for the analysis of interfacial water in the region anywhere from a few nanometers to a few hundreds of nanometers near a surface depending upon the optical properties of the solid surfaces and the type of spectroscopy used, i. e., mid-IR (MIR), near-IR (NIR), and Raman. For example, when using Raman internal reflection spectroscopy with a silicon internal reflection element, typically d_p values as small as 30 nm can be obtained even though a significant effort is required to enhance the extremely weak water signals generated with this method. In the MIR, the smallest d_p value possible for the silicon/water system examined was 153 nm with the available sampling accessories. It can be noticed from Figure 2 that it becomes very difficult to decrease the d_p beyond a certain value at larger incident angles, further away from the critical angle. However, by going to the NIR, these d_p values can be further decreased and typically a d_p value of about 100 nm can be obtained for the silicon/water system. Of course for the FTIR/IRS study of interfacial water in the NIR region, the IRE must be transparent. Fortunately, most minerals are transparent in the near-IR region which facilitates the study of interfacial water in regions closer to the surface.

It is now clear that the smallest region close to the surface that can be sampled by in-situ FTIR/IRS is in the range of about 150 nm, i. e., about 500 molecular layers from the surface for the silicon/water system in the MIR region. This then raises the question, "Are we really going to be able to

see surface water?". The answer to this important question depends on several factors including the extent of interfacial water structuring and the surface sensitivity of the technique used. As discussed in the previous section on depth of penetration, the electric field amplitude decays exponentially into the second phase and the majority of the signal comes from the near surface regions even though the total sampling depth is greater than the calculated characteristic depth of penetration. This means that the in-situ FTIR/IRS spectra of interfacial water contains information about both surface water and bulk water. As will be discussed in the following section, surface water can be clearly distinguished from the bulk water by the presence of certain band frequencies in the OH stretching region of the water spectra. In fact, in-situ FTIR/IRS will sample both surface and bulk water simultaneously unlike the case for sum frequency generation (SFG) method where bulk water is not sampled at all (10).

EXPERIMENTAL

Materials

Single crystal silicon and germanium internal reflection elements (50x10x2 mm) used in this study were purchased from Harrick Scientific, NY. Acetone and methanol used in chemical cleaning of the internal reflection elements (IREs) were of reagent grade. Heptane (99%) solvent used in some in-situ FTIR/IRS experiments was purchased from Aldrich and was used as received. The fluorochemical polymer (Fluorad FC-722, 3 M) was used to create a hydrophobic coating at the germanium surface. Millipore (18 M Ω) water was used in all the experiments.

Procedures

All the silicon and germanium IREs used in this present study were 50x10x2 mm in dimension. However, the face angles on these IREs were different in order to vary the incident angle and achieve the various d_p values desired for the study of interfacial water. The IREs were cleaned before each and every experiment to avoid contamination problems. The cleaning of these IREs involved two steps. In the first step, the IREs were thoroughly cleaned and rinsed with acetone/water/methanol/water. Later, the IREs were placed in a Tegal plasma chemical reactor and subjected to argon plasma for 60 minutes prior to the FTIR/IRS experiments.

The germanium crystal was coated with a oleophobic-hydrophobic fluorochemical polymer by a spreading technique. The FC-722 polymer is available as a 2% solution in a fluorocarbon solvent (boiling point of 56 °C). This solution was diluted to 0.3-0.5% with an analytical grade solvent, fluorocarbon 113 (1,1,2-trichloro-1,2,2-trifluoroethane; Horiba Instruments Inc.) and then spread over the surface of the clean germanium crystal using a microsyringe. Solvent was evaporated first in the ambient atmosphere at a room temperature of 20-22 °C for 5-10 minutes and next in a clean vacuum oven at temperature of 80-90 °C for 0.5-1 hour. The remaining polymer coating formed a film at the germanium crystal surface with a thickness of 30-50 nm as determined by profilometry.

Spectra of interfacial water were recorded with a Digilab FTS-40 FT-IR spectrometer using a wide-band liquid-nitrogen cooled MCT detector. A twin parallel-mirror reflection 320 internal reflection accessory (Harrick Scientific, NY) was used to hold the stainless steel IRS cell. This liquid IRS cell has a sampling length of 40 mm on both sides of the silicon IRE. IREs with different face angles were used to obtain a desired depth of penetration value for each experiment. The angle on the base plate was also varied in order to obtain different incident angles (always larger than the critical angle for total internal reflection) and consequently different depth of penetration values for these FTIR/IRS experiments. Figure 2 shows a range of typical depth of penetration values that can be obtained at different base plate readings and incident angles with silicon IREs of different face angles.

Interfacial water spectra were generated by taking the absorbance spectrum after injection into the flow-through IRS cell against the background spectrum of the clean IRE. All spectra were the result of 1024 co-added scans at a resolution of 8 cm⁻¹.

Contact angle measurements (sessile drop method) were done on IREs by using a Rame-Hart contact angle goniometer. These measurements were carried out before and after cleaning the IREs as mentioned above to monitor the surface state and establish its hydrophilic or hydrophobic character prior to each FTIR/IRS interfacial water experiment.

RESULTS AND DISCUSSION

The in-situ FTIR/IRS spectra of interfacial water generated at hydrophilic silicon and hydrophobic polymer coated germanium surfaces were studied by examining in detail the OH stretching region between 3000 and 3800 cm^{-1} . This region of the interfacial water spectrum forms a broad band which can be deconvoluted into several peaks. The origins and the interpretation of the band frequencies in this region still remain controversial. However, two important regions can be identified in this spectral range without any uncertainty as discussed previously. The spectral features surrounding 3600 cm^{-1} can be assigned to the stretching vibration of non-hydrogen bonded or free OH (17,18). On the other hand, the spectral features between 3000 and 3500 cm^{-1} can be ascribed to the stretching vibrations of the hydrogen bonded OH (17,18).

These peaks in the spectral region from 3000 to 3800 cm^{-1} can be used as indicators of the extent of hydrogen bonding present in interfacial water. The extent, or the degree, of hydrogen bonding reflects the extent of structuring of interfacial water. In view of the above, the in-situ FTIR/IRS spectra of interfacial water at silicon surfaces were examined by the analysis of the spectral features in the region from 3000 to 3800 cm^{-1} in order to describe the structure of interfacial water at a hydrophilic silicon surface. Similar spectral features were used by other researchers to characterize interfacial water by Raman IRS (12) and sum frequency generation (18,30) near sapphire and quartz surfaces respectively.

Silicon/Water System

In-situ FTIR/IRS experiments were conducted using three different silicon IREs at various depth of penetration values in order to characterize interfacial water based on spectral information. Extreme care was taken to maintain a similar surface state for each in-situ experiment conducted. Contact angle measurements were conducted to ensure that contaminant free and hydrophilic silicon surfaces had been prepared for each experiment. Contact angles of zero were observed for the argon plasma cleaned silicon crystals indicating a hydrophilic surface. The IREs were transferred to the FTIR sample compartment (dry air purged) immediately after plasma cleaning to avoid any further contamination from the atmosphere.

It should be mentioned that the surface of silicon single crystals used in this study were found to be very hydrophilic (complete spreading of water) as was evident from the zero contact angles observed after the silicon crystals were cleaned in argon plasma. Also, there was no FTIR spectroscopic evidence for the presence of a hydride layer reported to form due to the dissociation of water at the silicon surface (31).

Figure 3 shows the absorbance spectra of water in the OH stretching region as a function of depth of penetration, d_p , from the silicon surface. These spectra have been normalized with respect to the number of internal reflections so that the integrated absorbance can be compared (32). Several changes in the spectra with regard to absorbance, peak shape, and position can be noticed from this figure as d_p is increased from 153 nm to 547 nm. It can be noticed from Figure 3 that a distinct change in the shape of the spectra occurred as d_p is increased. The peak becomes broader as d_p is increased indicating changes in the relative intensities of certain bands as will be clear from the deconvoluted spectra presented in the following paragraphs.

The broad peak in the spectral region shown in Figure 3 was deconvoluted using the Fourier self-deconvolution method available with the Bio-Rad software. This unbiased method provides for useful band narrowing thus enabling the visual identification of broad and overlapping spectral features. These methods have been successfully used by other researchers in the past to study bulk water (12). Figure 4 shows the deconvoluted spectrum of water at a d_p of 153 nm along with the original spectrum. Three peaks centering around 3600, 3400, and 3200 cm^{-1} can be clearly seen from this figure. Other deconvoluted spectra of interfacial water are shown in Figure 5 for three different d_p values ranging from 153 nm to 547 nm. The differences in these spectra as d_p is varied from 153 nm to 547 nm are immediately obvious and changes in the relative intensities of the three peaks centered about 3600, 3400, and 3200 cm^{-1} can be noticed from this figure. The peak at $\sim 3600 \text{ cm}^{-1}$ (free OH stretch) is very weak at $d_p = 153 \text{ nm}$ and becomes very strong at $d_p = 547 \text{ nm}$ indicating that the amount of free OH increases as more and more bulk water is sampled at greater depths from the hydrophilic silicon surface. On the other hand, the relative intensities of the peaks ~ 3400 and $\sim 3200 \text{ cm}^{-1}$ (hydrogen bonded OH stretch) decrease as the depth of penetration increases from 153 nm to 547 nm. These results suggest that hydrogen bonding is facilitated at the

Figure 3. Absorbance spectra of interfacial water as a function of depth of penetration for the silicon/water system in the OH stretching region.

Figure 4. Deconvoluted spectrum of water at silicon at a depth of penetration of 153 nm along with the original spectrum in the OH stretching region.

Figure 5. Deconvoluted spectra of interfacial water at various depth of penetration values in the OH stretching region.

hydrophilic silicon surface. A closer look at the deconvoluted spectra for d_p values of 153 and 547 nm presented in Figure 6 clearly indicates that water structuring is prevalent near the hydrophilic silicon surface as is evident from the presence of the strong peak at $\sim 3200 \text{ cm}^{-1}$. The peak at $\sim 3100 \text{ cm}^{-1}$ in the deconvoluted spectra shown in Figure 5 seems to be related to the peak at 3600 cm^{-1} since they both decrease in intensity at smaller d_p values. This peak has been attributed to the first overtone of the OH bending mode in combination with the Fermi resonance (17,21).

It should be noted that the in-situ FTIR/IRS spectra presented in Figure 3 contain spectral information due to the presence of both surface and bulk water as discussed previously. However, it is clearly evident from the spectral features described above that the extent of water structuring (hydrogen bonding/bond ordering) decreases at greater distances from the silicon surface. Furthermore, the relatively high intensity of the peak centered at $\sim 3200 \text{ cm}^{-1}$ at the smallest d_p value (153 nm) is indicative of an ice-like structure in the arrangement of water molecules at the hydrophilic silicon surface. Unfortunately, the depth of penetration could not be decreased below 153 nm for the silicon/water system considered due to limitations discussed previously. Nevertheless, it is very clear from these spectral results that the in-situ FTIR/IRS technique can be used to distinguish between surface and bulk water as is evident from the distinct and obvious changes in the spectra of interfacial water with changes in the depth of penetration. Most importantly, it should be noted that there is a significant change in the shape of the water spectra in the region from 273 to 446 nm where the peak due to free OH ($\sim 3600 \text{ cm}^{-1}$) becomes very significant as shown in Figure 3.

Silicon/Heptane System

To further demonstrate that the changes in the spectra of interfacial water at various depths of penetration are due to changes in water structure near the surface, similar studies were conducted at the silicon surface with a non-polar solvent, heptane. Figure 6 shows the absorbance spectra (non-normalized) in the CH stretching region for heptane adsorption at the silicon surface as a function of d_p . It can be noticed from these spectra that there are few changes in the shape and the relative intensities of the

Figure 6. Absorbance spectra of heptane at silicon surface as a function of depth of penetration in the CH stretching region.

Figure 7. Deconvoluted spectra of interfacial water at germanium and polymer-coated germanium surfaces at a depth of penetration of 128 nm in the OH stretching region.

various bands as d_p is varied from 155 nm to 1808 nm. By contrast with these results in Figure 6, it is evident that the changes in the spectral features of interfacial water at the hydrophilic silicon surface (Figures 3-5) are significant and are not due to bulk spectral distortions (9) but rather are due to changes in the water structure at different distances from the surface. Such spectral changes are not observed for nonpolar solvents.

Polymer-Coated Germanium/Water System

In-situ FTIR/IRS experiments were conducted to spectroscopically characterize interfacial water near a hydrophobic surface (polymer-coated germanium single crystal). A germanium single crystal was used for these studies simply because of its high refractive index. Also, the fluorochemical used for the hydrophobic coating adhered better at the germanium crystal rather than at the silicon surface. Because of the relatively small thickness of the polymer coating (50-80 nm), Equation 5 still can be used to calculate depth of penetration values for this system. The hydrophobicity of the polymer-coated germanium IRE was characterized by sessile drop contact angle measurements which yielded a contact angle of 120° thus indicating a highly hydrophobic surface. Extreme care was taken for the preparation of a uniform hydrophobic film without discontinuities. Examination of these surfaces by optical microscopy indicated that the coating was of high quality. For the purpose of comparison, spectra of interfacial water were also generated at the argon plasma cleaned, hydrophilic germanium surface.

Figure 7 shows the deconvoluted spectra of interfacial water at the hydrophilic germanium surface and at the hydrophobic polymer-coated germanium surface for a depth of penetration of 128 nm in the OH stretching region. Three bands, centering around 3600, 3400, and 3200 cm^{-1} can be seen in these spectra. The relative intensities of these peaks in the water spectrum at the hydrophilic germanium surface indicate the prevalence of more hydrogen bonding similar to the spectral results obtained at the hydrophilic silicon surface at a comparable depth of penetration. Water spectrum at the hydrophobic polymer-coated germanium crystal shows a decrease in the relative intensity of the band at $\sim 3200 \text{ cm}^{-1}$ (hydrogen bonded OH stretch) whereas the band at $\sim 3600 \text{ cm}^{-1}$ (free OH stretch) is much more accentuated when compared to that at the hydrophilic germanium surface as shown in Figure 7. This clearly indicates a decrease in interfacial water structuring near the hydrophobic surface. Similar results were obtained near specially prepared hydrophobic silicon surfaces (32).

SUMMARY AND CONCLUSIONS

The spectral results from this work suggests that interfacial water near a hydrophilic surface has more hydrogen bonding and an ordered ice-like structure whereas at a hydrophobic surface there appears to be a decrease in the water structuring or hydrogen bonding. These results are in contrast to Drost-Hansen's concept of a clathrate like water structure near hydrophobic surfaces (33) as well as the recent Raman IRS study of interfacial water by Nickolov et al. (12). However, similar results were reported by Du et al. from their SFG experiments for water near hydrophobic and hydrophilic surfaces (30,34). Certainly, additional work needs to be done in order to determine the range of the interfacial water structure at these surfaces. It should be noted that even though the spectra of interfacial water were obtained for significant distances from the surface, because of the high intensity of the electric field amplitude near the surface, it is possible to identify spectral features due to water structure in the regions close to the surface. Efforts are underway to examine the extent of water structuring at different surfaces as well as to increase the surface sensitivity of the FTIR/IRS technique so that water structures closer to the interface can be more clearly detected with minimum interference from bulk water signals. For example, by creating an oxide film at the silicon surface, interfacial water in the first few water layers near the oxide film can be examined with much greater surface sensitivity (35).

In conclusion, it has been demonstrated that the in-situ FTIR/IRS technique can be used to spectroscopically characterize interfacial water at hydrophilic and hydrophobic surfaces. Using this method, the structure of water at different distances from the surface was examined by using appropriate optics and crystal geometries. For the first time, interfacial water has been distinguished from bulk water by analysis of the OH stretching region of the vibrational spectra at different distances from the surface. Preliminary results indicate that a hydrogen bonded ice-like structure prevails at a hydrophilic surface whereas interfacial water structure is diminished near hydrophobic surfaces.

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**Comments on "Nature and Structure of Adsorption Layer on Apatite
Contacted with Oleate Solution. 1. Adsorption and Fourier
Transform Infrared Reflection Studies"**

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The recent paper by Mielczarski et al. (Langmuir 1993, 9, 2370-2382) provides a spectroscopic analysis of oleate adsorption at the surface of hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$). Careful review of this paper suggests that analysis of the adsorption phenomena and spectral features of the adsorption state should be reconsidered.

The major point to be discussed is the chemisorbed oleate monolayer and its spectral features. Specifically, Mielczarski et al. state that this condensed monolayer is characterized by a doublet at 1572 and 1540 cm^{-1} due to the carboxylate absorbance of the oleate species. However, with a different oleate source, they observed a singlet at about 1550 cm^{-1} which was interpreted as a carboxylate band caused by "impurities" in their surfactant. The authors suggest that this latter spectral feature is indicative of disorganization of the adsorbed layer.

Previous Research

Many researchers have established that chemisorbed oleate monolayers at the surfaces of calcium-bearing semi-soluble minerals such as apatite, calcite (CaCO_3) and fluorite (CaF_2) are characterized by a singlet at about 1550 cm^{-1} , not a doublet. As early as 1965 Peck and Wadsworth⁽¹⁾ recognized this feature for chemisorbed oleate at fluorite and barite (BaSO_4) surfaces. A doublet characteristic of bulk calcium dioleate is observed only at higher adsorption densities. These characteristic spectral features have been

discussed recently in a review article by Finkelstein⁽²⁾ and published results from spectroscopic studies are presented in Table 1. The singlet has been attributed to monocoordination of the carboxylate group with a lattice cation at the surface (chemisorption)⁽¹¹⁾ and the doublet has been attributed to bicoordination of two carboxylate groups with a calcium cation released from the lattice (surface precipitation).

For example, the diffuse reflectance spectra of adsorbed oleate at the surface of hydroxyapatite were reported by Gong et al.⁽⁴⁾, and these spectra distinctly show the 1550 cm^{-1} singlet at neutral pH and low oleate concentrations where adsorption is confined to monolayer coverage. As is clear from Figure 1, a singlet at 1550 cm^{-1} was found for adsorption from an oleate solution of 2×10^{-5} M and a predominant doublet at 1574 and 1539 cm^{-1} was observed at higher oleate concentrations under which condition a surface precipitation reaction occurs and multilayers of calcium dioleate are found on the surface. This doublet is the same as that found for bulk precipitated calcium dioleate. In the same paper,⁽⁴⁾ it is shown that after ultrasonic washing, the doublet disappeared leaving a singlet. Other ex-situ infrared spectroscopic studies have shown similar results at neutral pH. See Table 1. This clearly demonstrates that the singlet at 1550 cm^{-1} represents a strongly bonded chemisorbed oleate whereas the doublet at 1574 and 1539 cm^{-1} represents the weakly attached calcium dioleate precipitates.

In addition, a recent in-situ Fourier transformed infrared internal reflection spectroscopic (FT-IR/IRS) study of adsorbed oleate at a fluorite (CaF_2) single crystal surface identified the calcium oleate chemisorption peak as a singlet at 1549 cm^{-1} whereas a doublet at 1576 and 1540 cm^{-1} was observed for adsorption in the surface precipitation region.⁽⁶⁾ The in-situ FT-IR/IRS technique is particularly advantageous because adsorption density measurements are accurately determined based upon the optical properties of the substrate/surfactant system.^(6, 12-14) It should be noted that for different solution conditions where the calcium dioleate precipitate becomes the predominant species (high pH and sufficient calcium and oleate concentrations), a doublet characteristic of

precipitated carboxylate, can be obtained even at less than monolayer coverage, but this should be distinguished from chemisorbed oleate and is to be discussed in a separate contribution.⁽¹⁵⁾

In summary, these spectral features of oleate adsorption (i.e., a singlet band for chemisorbed carboxylate and a doublet band for surface precipitated carboxylate) have been observed at apatite surfaces and the surfaces of other calcium-bearing semi-soluble salt minerals such as fluorite (CaF_2) and calcite (CaCO_3) as shown in Table 1. Unless the same "impurities" were present in all of the above mentioned systems it appears that the explanation offered by Mielczarski et al. is lacking. The issue of fatty acid purity will be discussed further in the following section on transferred Langmuir-Blodgett (LB) monolayers.

Transferred LB Monolayers

The question on the spectral features of fatty acid chemisorption at the surface of semi-soluble salt minerals can be further clarified by FT-IR/IRS analysis of transferred LB monolayers of carboxylates (+ 99 % purity, Aldrich) at a fluorite surface⁽¹⁴⁾. An LB monolayer is created at the air/water interface and the surface pressure-specific area (π -A) isotherm provides information on the molecular packing and ordering of the surfactant under carefully controlled conditions. Appropriate transfer of the LB monolayer to a crystal surface assures a well-assembled surfactant monolayer at the surface of interest and an independent, quite accurate measure of adsorption density from π -A isotherms.

The FT-IR/IRS spectrum of a transferred LB monolayer of oleic acid on CaF_2 (adsorption density of $6 \times 10^{-6} \text{ mol/m}^2$) showed that the transferred oleic acid had reacted with the fluorite surface as was evident from the disappearance of the free acid C=O stretching band at around 1700 cm^{-1} and the presence of a singlet at about 1550 cm^{-1} , characteristic of chemisorbed carboxylate, as shown in Figure 2.⁽¹⁴⁾ This spectral feature for chemisorbed carboxylate can be further confirmed by the FT-IR/IRS examination of

transferred LB monolayers of stearic acid (+ 99 % purity), which have an even more-ordered structure than oleic acid.⁽¹⁶⁾ (It was found from the π -A isotherm study that stearic acid molecules have a minimum cross-sectional area of about 20 Å² which occurs at a surface pressure of 50 mN/m whereas oleate molecules have a minimum cross-sectional area of about 27 Å² which occurs at a surface pressure of 31 mN/m.) Thus, transferred LB monolayers of stearic acid are expected to be more densely packed than those of oleic acid, as was found from FT-IR/IRS experiments. Furthermore, the dichroic ratios of the chemisorbed transferred monolayers as measured by polarized light FT-IR/IRS experiments indicate that these transferred monolayers are highly ordered.⁽¹⁶⁾ For example, the chemisorbed transferred stearate monolayers were found to be oriented at 9 to 16 degrees from the normal to the surface, as might be expected for LB monolayers of straight chain fatty acids.^(17, 18) It is clear from these results that even for this very condensed, well-ordered state, the chemisorption band for stearate at the fluorite surface is a well defined singlet at about 1550 cm⁻¹.⁽¹⁴⁾ *In no case was a doublet found for these well-ordered chemisorbed monolayers.*

It should be noted that even when an LB monolayer of well ordered calcium distearate is transferred the spectrum reveals just a singlet.⁽¹⁵⁾ Based upon the orientation analysis from FT-IR/IRS polarization experiments, the transferred calcium distearate is oriented at 15 to 16 degrees from the normal to the surface.⁽¹⁶⁾ *In no case was a doublet found for these well-ordered monolayers.* Only when a monolayer of randomly organized calcium distearate is formed at the surface or when multilayers of calcium distearate are formed is a doublet observed. The same is true for oleate and other alkyl carboxylates. It should be noted that neither the singlet band for well-ordered carboxylate monolayers nor the doublet band for randomly organized multilayers are sensitive to the polarization state in the FT-IR/IRS experiment⁽¹⁶⁾ and so it appears that orientation of the carboxylate group does not account for the singlet/doublet issue.

Perhaps the most significant finding from the FT-IR/IRS studies⁽¹⁵⁾ is that transferred LB monolayers of calcium distearate have much less water present at the surface than calcium distearate adsorbed from solution, suggesting that the hydration state of carboxylate in the monolayer may have an influence on the singlet/doublet issue. Mielczarski et al. show that bulk precipitated calcium dioleate which initially had a doublet at about 1575 and 1540 cm^{-1} gave a spectrum with a singlet at about 1560 cm^{-1} when exposed to a vacuum and high temperatures. They also show that this behavior is reversible when exposed to moisture. Similar results have been obtained previously by other researchers.^(19, 20) It is possible that this spectral change of bulk calcium dioleate may account for the characteristic singlet observed for chemisorbed carboxylate monolayers, in which case the chemisorbed monolayer would be expected to be substantially dehydrated at the mineral surface.

In view of the foregoing discussion, the conclusion by Mielczarski et al. that the doublet for the carboxylate stretching bands at 1572 and 1540 cm^{-1} is indicative of a well-organized, close-packed structure of a chemisorbed oleate monolayer can not be supported. Since high purity fatty acids (+ 99 % purity) were used for the LB monolayer experiments as well as for experiments involving spontaneous adsorption from solution,^(3, 7, 12-15) the "impurity" explanation offered by Mielczarski et al. is rejected and their results should be reconsidered in the context of these comments.

Summary

In summary, for calcium-bearing semi-soluble salt minerals such as apatite, calcite and fluorite, carboxylate chemisorption at monolayer coverage is characterized by a singlet at approximately 1550 cm^{-1} , whereas a bulk or surface precipitated carboxylate is randomly organized, hydrated to a greater extent, and is characterized by a doublet at approximately 1575 and 1540 cm^{-1} . It is very clear from the FT-IR/IRS analysis of transferred LB monolayers of oleate and stearate that these well-ordered chemisorbed carboxylate

monolayers are characterized by a singlet at approximately 1550 cm^{-1} . In this regard, it is evident that the doublet for the carboxylate stretching bands at 1572 and 1540 cm^{-1} reported by Mielczarski et al. for oleate adsorption by apatite is not indicative of a well-organized, close-packed structure of a chemisorbed oleate monolayer, but rather is indicative of adsorbed calcium dioleate, substantially hydrated, and formed by a surface precipitation reaction or adsorbed from solution as a collector colloid.

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Table 1. Characteristic Band Positions (cm^{-1}) for Adsorbed Oleate at the Surfaces of Calcium-Bearing Semi-Soluble Minerals in Neutral or Slightly Alkaline pH. (Modified from Ref. 3)

Mineral	Carboxylate Band Positions (cm^{-1})		Reference	Experimental Method
	Chemisorption	Surface Precipitation		
Hydroxyapatite	1550	1574, 1539	4	DRIFT
Fluoroapatite	1550	1577, 1541	5	DRIFT
Calcite	1551	1569, 1534	3	ex-situ FT-IR/IRS
Fluorite	1549	1573, 1535	6	in-situ FT-IR/IRS
Fluorite	1551	1575, 1537	7	ex-situ FT-IR/IRS
Fluorite	1550	1575, 1538	8	Transmission
Fluorite	1555		1	Transmission
Fluorite	1555	1575, 1540	9	DRIFT
Fluorite	1555	1576, 1540	10	DRIFT

Figure 1. Diffuse reflectance spectra of adsorbed oleate species at the hydroxyapatite surface treated with sodium oleate at pH 8.0. Sodium oleate concentrations were a) 2×10^{-5} M, b) 5×10^{-5} M, and c) 1×10^{-4} M (Adapted from Ref.2).

Figure 2. Comparison of FT-IR/IRS spectrum of a transferred LB monolayer of oleate with the transmission spectrum of oleic acid in CCl₄ solution (Adapted from Ref. 14).

15. W. H. Jang, J. Drelich, and J. D. Miller, "Wetting Characteristics and Stability of Langmuir-Blodgett Carboxylate Monolayers at the Surfaces of Calcite and Fluorite," in: *Langmuir*, 1995, in press.

**Wetting Characteristics and Stability of Langmuir-Blodgett Carboxylate Monolayers
at the Surfaces of Calcite and Fluorite**

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ABSTRACT

Although surface chemistry fundamentals of semisoluble minerals have been studied by many researchers, detailed understanding of these systems is still incomplete. In-situ Fourier transform infrared internal reflection spectroscopy (FT-IR/IRS) techniques have recently been used to successfully describe the adsorption of carboxylates at semisoluble mineral surfaces. However, the wetting characteristics of these adsorbed films require further consideration. In this regard, the hydrophobicity and stability of transferred Langmuir-Blodgett (LB) monolayers of fatty acids at fluorite and calcite surfaces has been studied by contact angle measurements with water and diiodomethane.

Generally, it was found that the transferred LB monolayers of fatty acids at a calcite surface are unstable whereas such monolayers transferred at a fluorite surface are stable, as revealed from advancing and receding contact angle measurements. These results are believed to be due to incomplete reaction of the fatty acid monolayer at the calcite surface. In addition it was found that a closely packed well-ordered stearate monolayer similar to that of a transferred LB monolayer, can be formed at fluorite surfaces by spontaneous adsorption and self-assembly from aqueous solutions.

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INTRODUCTION

Semisoluble salt minerals such as fluorite (CaF_2), calcite (CaCO_3), apatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{F}, \text{OH}, \text{Cl})_2$), scheelite (CaWO_4), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), magnesite (MgCO_3), and barite (BaSO_4) are commonly used by industry in the production of raw materials for fillers, fluxes, fertilizers, cements, chemicals, etc. These semisoluble salt minerals are naturally hydrophilic and fatty acids are frequently used to establish a hydrophobic state and thus modify their surface wetting properties. Without such modification the separation of semisoluble salt minerals by flotation cannot be achieved. Also, such treatment facilitates the use of these semisoluble salt minerals as fillers for plastics in the production of polymer-mineral composites. In this regard, an understanding of the surface chemistry of fatty acid adsorption at semisoluble salt mineral surfaces is important from both a fundamental and a practical point of view.

It has been recognized from infrared studies that a fatty acid adsorbs at the surface of a semisoluble salt mineral through chemisorption of a carboxylate group with a lattice cation at low collector concentrations, typically less than $1.0 \times 10^{-5} \text{ M}$.⁽¹⁻⁵⁾ At higher concentrations of the collector and/or the cation, and at higher pH values, surface precipitation or collector colloid adsorption occurs by reaction of the carboxylate collector with cations released from the lattice.⁽²⁻⁸⁾ Because the fatty acid interacts not only with the lattice cation sites of the semisoluble salt mineral but also with the dissolved cations in solution, the solution chemistry of these minerals and the pH of the system play an important role in determining the nature of the adsorbed species.

Oleate adsorption isotherms at the surfaces of semisoluble salt minerals have been established by several researchers.⁽⁹⁻¹³⁾ Figure 1 presents the adsorption isotherms for oleate at fluorite⁽⁹⁾ and calcite⁽¹²⁾ surfaces ($\text{pH} \approx 9$) as determined using in-situ FT-IR/IRS (note that the original isotherms from References 9 and 12 have been reconstructed using correction factors of 2.3 for fluorite and 1.2 for calcite, based upon sampling area considerations⁽¹⁴⁾). Although the shape of the oleate adsorption isotherm is almost the

same at both fluorite and calcite surfaces the adsorption density values differ significantly. At an equilibrium oleate concentration less than 1.0×10^{-5} M (monolayer region) the adsorption densities of oleate at a fluorite surface (from 4.6 to 6.3×10^{-10} mol/cm²) are found to be about three times larger than the adsorption densities at a calcite surface (from 1.4 to 2.2×10^{-10} mol/cm²). On the contrary, at an oleate concentration greater than 1×10^{-5} M, the adsorption density of oleate at a calcite surface is found to be considerably higher than at a fluorite surface (multilayer region of precipitated calcium dioleate-the collector colloid). It has been suggested that the well-packed chemisorbed oleate monolayer at the fluorite surface inhibits the release of lattice calcium ions to solution and thus minimizes the surface precipitation phenomenon.⁽¹²⁾ Note that the maximum monolayer adsorption density for oleate determined from the surface pressure-specific area isotherm is 6.1×10^{-10} mol/cm², i.e., $27 \text{ \AA}^2/\text{molecule}$.⁽¹⁵⁾ On the other hand, such a closely-packed chemisorbed oleate monolayer is not formed at a calcite surface (1.4 to 2.2×10^{-10} mol/cm²). This low surface coverage at a calcite surface does not prevent calcium release and the subsequent precipitation of calcium dioleate at the surface.⁽¹²⁾

It has been proposed that for the chemisorbed monolayer region the increased adsorption density of oleate at the fluorite surface, when compared to that at the calcite surface, is due to a difference in the crystallographic structures of the minerals.⁽¹²⁾ The average distance between the calcium ions is $3.86 \text{ \AA}$ along the natural (111) cleavage plane for fluorite, and $4.05 \text{ \AA}$ and $4.99 \text{ \AA}$ along the natural (014) cleavage plane for calcite.⁽¹⁶⁾ Based upon the distance between calcium ions, the calculated densities of lattice calcium ions at the fluorite and calcite surfaces are 14.5×10^{-10} mol/cm² and 8.3×10^{-10} mol/cm², respectively. Thus, in both cases, the lattice calcium ions are in excess of that required for the chemisorption of an uniform and densely-packed oleate monolayer in one to one coordination with surface calcium sites. In this regard, such simple calculations do not explain the different adsorption density values determined at fluorite and calcite surfaces. Not all surface calcium ions are involved in the chemisorption reaction of oleate and the

maximum monolayer adsorption density is determined by the dimensions of the surfactant species and its organization at the surface. Some research has been reported on this issue^(16, 17) which describes this molecular arrangement at the surface.

The difference in the mechanism of adsorption of fatty acids at fluorite and calcite surfaces is not fully understood. The stability of the fatty acid monolayers at fluorite and calcite surfaces has not been studied. It is not clear why a self-assembled, densely-packed and stable monolayer of carboxylate is not formed at a calcite surface by adsorption from aqueous solutions whereas such a densely-packed and stable monolayer of carboxylate is self-assembled at a fluorite surface. On this basis, it is particularly interesting to investigate if the formation of well-packed and stable monolayer of fatty acid at a calcite surface is possible under certain experimental conditions. The stability of the transferred LB monolayers was examined using the sessile-drop contact angle technique. Both advancing and receding contact angles were measured for polar (water) and apolar (diiodomethane) drops of varying size. The usefulness of this experimental technique in the examination of surface chemistry phenomena associated with flotation systems will be demonstrated.

Ideal solid surfaces with homogeneity and smoothness at the atomic/molecular level are extremely difficult to prepare; nearly all surfaces examined are, to some extent, heterogeneous and rough.⁽¹⁸⁾ Even uniform and closely-packed LB films, when transferred at a smooth and pure surface, may still be unstable when in contact with certain liquids. Obviously, the film instability affects the contact angle measurements. A liquid in contact with nonideal surfaces (heterogeneous, rough, and /or unstable films) exhibits more than one contact angle. Two contact angles are important in the characterization of such surfaces; (1) the advancing contact angle, θ_A , which is the largest contact angle for the system and is measured for the advancing liquid front, and (2) the receding contact angle, θ_R , which is the smallest contact angle for the system and is measured for the receding liquid front. The difference between the advancing and receding contact angles ($\theta_A - \theta_R$) is called the contact angle hysteresis. The contact angle hysteresis is a good parameter to

describe the quality of surfaces examined and does not exceed a few degrees for well prepared and stable surfaces. Elimination or, at least, minimization of contact angle hysteresis is required for accurate and reproducible characterization of surfaces. This may be accomplished by careful surface preparation (using a substrate with a smooth surface, cleaning the solid substrate, and careful transfer of the homogeneous LB monolayer), handling, and preservation.

The advancing and receding contact angles were measured using the sessile-drop technique for a drop of varying size. The effect of drop size on advancing and receding contact angles has been demonstrated for several systems by Drelich and Miller.⁽¹⁹⁾ It was shown that the contact angle/drop size relationship becomes an important feature of the three-phase system, especially when the surface exhibits imperfections, i.e., the surface is heterogeneous and/or rough.⁽²⁰⁻²²⁾ For such systems, the contact angle hysteresis may vary significantly with drop volume and examination of the relationship between contact angle hysteresis and drop size is a way to obtain more information regarding the quality of the surface being examined.

EXPERIMENTAL SECTION

Materials: Fluorite (CaF_2) single-crystal parallelepiped internal reflection elements with a dimensions of 52 x 10 x 2 mm and 52 x 14 x 2 mm and acute angles of 72 to 75° were purchased from Optovac Inc.. Optically pure, naturally cleaved calcite (CaCO_3) crystals of Iceland Spar (Mexico) were purchased from Ward's Natural Science Establishment, Inc. Before experimentation both the fluorite and calcite crystals were placed in a Tegal plasma chemistry reactor and subjected to argon plasma for 30 to 40 minutes to remove any organic contaminants. In some cases, the surfaces of the crystals were polished with alumina powders (0.05 micron) on Texmet[®] polishing pads (Buehler) and washed with high purity water to create a fresh surface.

The chemicals used in the experiments were as follows: stearic acid ($\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$) with purity greater than 99 % (Aldrich Chemical Co.), oleic acid ($\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$) with purity greater than 99 % (Sigma Chemical Co.), sodium stearate ($\text{CH}_3(\text{CH}_2)_{16}\text{COONa}$) with purity greater than 99 % (Sigma Chemical Co.), diiodomethane (CH_2I_2) with purity greater than 99 % (Janssen Chimica), reagent grade calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, Mallinckrodt, Inc.), reagent grade sodium hydroxide (NaOH , Mallinckrodt, Inc.), reagent grade hydrochloric acid (HCl , EM Science), and spectrograde chloroform (CHCl_3 , EM Science). A Milli-Q water system, supplied with distilled water, provided high purity water with a resistivity of $+18 \text{ M}\Omega$, and a surface tension of 72 ± 0.4 at 22°C . The pH of this high purity water was stabilized at $\text{pH } 5.8 \pm 0.1$ after equilibrating with the atmosphere.

Langmuir-Blodgett (LB) Film Preparation and Transfer: A Lauda Langmuir Film Balance (Langmuir trough) manufactured by SYBRON/Brinkmann was used for LB film preparation and transfer. The film balance was kept in a special housing to provide a dust-free environment. The experiments were performed at room temperature (22 to 23°C). The Langmuir trough was filled with water from a Milli-Q system ($\text{pH } 5.8 \pm 0.1$). In selected experiments, Milli-Q water with $1 \times 10^{-3} \text{ M}$ calcium ions (as $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) and $\text{pH } 9.2 \pm 0.2$ (adjusted with NaOH) was used in order to maintain conditions for the formation of calcium distearate.

The compounds to be studied (stearic acid and oleic acid) were weighed on a balance and dissolved in chloroform (7.6 and 4.8 mM , respectively). The monolayers were spread from the spreading solutions onto the subphase with a Hamilton syringe (typically $40 \mu\text{L}$). The solvent was permitted to evaporate completely (20 to 30 minutes). The surface pressure of the monolayer was measured as a function of the area occupied by the amphiphilic molecule for the surface pressure-specific area isotherm studies.

For LB deposition, the mineral crystal (fluorite or calcite) was dipped into the subphase (water) before spreading the monolayer. After spreading, the solvent permitted to evaporate completely and the film was transferred from the subphase onto the crystal surface at a speed of 3 mm/min with the surface pressure held at the desired level. In all LB experiments a constant film pressure was maintained at 23 mN/m for stearic acid and calcium distearate and 24 mN/m for oleic acid. The corresponding molecular areas were found to be 20 Å²/molecule for stearic acid, 40 Å²/molecule for calcium distearate and 30 Å²/molecule for oleic acid. While the monolayers were transferred at the crystal surfaces, all the transfer curves were recorded to ensure that each monolayer was transferred at a constant pressure. The variation in the film pressure was found to be within ± 1 mN/m. Details of the Langmuir-Blodgett technique are provided elsewhere.⁽²³⁻²⁶⁾

Self-Assembled (SA) Monolayer Preparation: For SA monolayer preparation 1.4 x 10⁻³ g of sodium stearate was dissolved to 0.5 liter of Milli-Q water which had been heated to 75 - 80 °C. The solution was diluted with water to 3 x 10⁻⁷ M and the initial pH was typically adjusted to pH 9.5 $\pm$ 0.1 with NaOH. In selected experiments, the solution pH was adjusted to higher or lower pH values. A clean fluorite crystal was clamped in Teflon-coated tweezers and suspended in the solution of sodium stearate. The solution was agitated with a magnetic stirrer at a constant speed. The solution was isolated from the atmosphere by covering it with aluminum foil. After reaction for a given time (10 minutes to 5 hours), the fluorite IRE was rinsed with water at pH 9.5 $\pm$ 0.1 and dried in a vacuum.

Adsorption Density Determinations: Fourier transform infrared internal reflection spectroscopy (FT-IR/IRS) experiments were conducted with a Bio-Rad Digilab Division FTS-40 FT-IR spectrometer equipped with a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector. The spectrometer was purged with dry air supplied by a Balston 75-60 air dryer. Digilab software, version 4.45, was used for spectral manipulation with

the SPC 3200 data station. An internal reflection cell with a variable angle holder (a twin-parallel mirror reflection 320 internal reflection accessory, Harrick Scientific) was used to measure the FT-IR/IRS spectra. The dial reading of the variable angle holder was adjusted to satisfy the condition for total internal reflection inside the IRE. Then, the intensity of the infrared beam internally reflected through the IRE was maximized by adjusting the mirrors of the variable angle holder. After alignment of the IRE, the spectrometer was purged with dry air for at least 30 minutes before a background spectrum of the clean IRE was collected in order to minimize possible interferences from water vapor.

Substantial care was taken to reposition the IRE in its holder for ex-situ internal reflection experiments. Absorbance spectra of the surfactant films (LB or self-assembled films) were ratioed against the background spectra of a clean calcium fluoride IRE. All the spectra were the result of 1024 co-added scans at a resolution of 8 cm⁻¹. In all cases, the size of the IR beam was adjusted to pass through only the area of the transferred LB monolayer film with the same IR beam size for both background and sample spectra to eliminate any error that could be caused by the difference between IR beam area and the sample area. Detailed analysis of the effect of sampling area on adsorption density measurements is provided elsewhere.^(14, 27)

The FT-IR/IRS adsorption density equation was initially derived by Sperline et al.⁽²⁸⁾ and later developed for different systems by Miller et al..⁽²⁹⁻³¹⁾ The FT-IR/IRS adsorption density is given below:

$$\Gamma = \frac{A_{IRS}/N - \epsilon C_b d_e}{1000 \epsilon (2d_e/d_p)} \quad (\text{Eq. 1})$$

where A_{IRS} = integrated absorbance (cm⁻¹) from IRS spectrum,

N = number of internal reflections,

ϵ = integrated molar absorptivity of collector (l/(cm² mol)),

C_b = bulk concentration of the surfactant (mol/l),

d_p = depth of penetration (cm),

d_e = effective thickness (cm).

The N , d_e and d_p values can be calculated from optical constants of the system (wavelength in the absorbance region, refractive indices of the IRE and the sample, and incident angle for internal reflection). The integrated absorbance due to internal reflections, A , can be determined from FT-IR/IRS spectra. The integrated molar absorptivity, ϵ , can be evaluated from transmission experiments using the Beer-Lambert equation.^(32, 33) The validity of the FT-IR/IRS adsorption density equation has been confirmed by the FT-IR/IRS analysis of transferred LB films.^(14, 15) Because calcite is not transparent in the mid-IR range, the adsorption densities of transferred LB monolayers of stearic acid and calcium distearate at a calcite surface were determined from the π -A isotherms.^(15, 26)

Contact Angle Measurements: The sessile drop technique for contact angle measurements was employed in these studies using a NRL goniometer (Ramè-Hart, Inc.). The optical system of the NRL goniometer has independently-rotatable crosshairs and an internal protractor-readout calibrated in one-degree increments. The supporting stage of the instrument is calibrated on the vertical axes in 0.02 mm divisions and this allows for accurate measurement of the drop base diameter.

The mineral substrate (fluorite or calcite) with the transferred LB monolayer or with the adsorbed monolayer was placed on Teflon posts in a rectangular glass chamber. The glass chamber with the substrate was partially filled with liquid and covered with a polyethylene film to maintain conditions of constant humidity. A liquid drop (water or diiodomethane) was introduced onto the substrate through a microsyringe and the needle was maintained in contact with the drop. A special precaution was taken in the measurements to avoid vibrations of the needle and to avoid distortion of the drop shape by the needle. The three-phase contact line of the liquid drop was made to advance or recede by adding or withdrawing a small volume of liquid and the advancing and receding contact

angles were measured after 15 to 30 seconds on both sides of the drop (the average contact angle value was taken for each drop diameter). The contact angles were measured for a liquid drop of varying size at room temperature (22 to 23 °C).

RESULTS AND DISCUSSION

Wetting Characterization of LB Monolayers with an Apolar Liquid: LB monolayers of stearic acid in the condensed state (i.e. having a molecular cross-sectional area of 20 Å²/molecule, as determined from the π -A isotherm) were transferred at both fluorite and calcite surfaces. A diiodomethane drop was placed at a freshly deposited and dried monolayer and both advancing and receding contact angles were measured. As shown in Figure 2, the same wetting characteristics were obtained for both transferred LB monolayers. The advancing and receding contact angles for the LB monolayer of stearic acid were found to be 74 to 76 degrees and 64 to 66 degrees, respectively, for a drop base diameter of 3 to 7 mm. Also, it appeared that the prepared LB monolayers remained stable during the contact angle measurements for a diiodomethane drop. The same advancing and receding contact angles were obtained when contact angle measurements were repeated at the same location on the transferred monolayer.

When the drop size was reduced to a drop base diameter of approximately 2 mm, both advancing and receding contact angles were found to decrease by 5 to 6 degrees. It was found from the surface roughness analysis by atomic force microscopy that the fluorite crystal had an average surface roughness of about 5 nm with a maximum of 100 nm whereas the calcite crystal had a surface roughness of 7 to 15 nm with a maximum of 100 to 300 nm depending upon the specific locations examined. Therefore, both the fluorite and calcite surfaces exhibit surface irregularities which could affect, to a certain extent, both the contact angle hysteresis and the contact angle/drop size relationship. Also, although the system examined appeared to be stable during contact angle measurements the effect of diiodomethane on the destabilization of the transferred LB monolayer of stearic acid cannot

be ignored. For example, Johnson and Dettre⁽³⁴⁾ observed that LB monolayers of stearic acid and barium stearate deposited onto glass slides were slowly desorbed into hexadecane during contact angle measurements (note that the contact angle hysteresis was only 1 to 2 degrees in these measurements).

The advancing contact angles as measured for the larger drops were 74 to 76 degrees (Figure 2), and are close to the contact angles, 73 to 74 degrees, which were measured at a highly ordered-CH₃ surface of a self-assembled octadecyltrichlorosilane (OTS) monolayer on SiO₂.⁽³⁵⁾ This similarity between the contact angles measured in this study and those published in the literature indicates that the transferred LB monolayers of stearic acid at fluorite and calcite surfaces remained closely-packed during the advancing contact angle measurements. For such systems, in which the interaction involves only the dispersion components of the transferred LB monolayer of stearic acid and the diiodomethane (apolar surface-apolar liquid), the surface tension (γ_s) of this monolayer can be calculated based on Fowkes' concept⁽³⁶⁾ and by using the following equation:

$$\gamma_s = \frac{\gamma_L (\cos \theta + 1)^2}{4} \quad (\text{Eq. 2})$$

where γ_L is the surface tension of the apolar liquid ($\gamma_L = 50.8$ mN/m for diiodomethane) and θ is the contact angle as measured for the apolar liquid at the solid surface (the advancing contact angle for diiodomethane at the transferred LB monolayer of stearic acid was 74 to 76 degrees). The surface tension of a closely-packed LB monolayer of stearic acid calculated using Equation 2 was 19.6 to 20.7 mN/m.

Further, LB monolayers of oleic acid were transferred at fluorite and calcite surfaces for contact angle measurements. In both cases the molecular cross-sectional area of the transferred LB monolayer of oleic acid was 30 Å²/molecule, as determined from the π -A isotherm. The contact angles as measured for diiodomethane at the transferred LB monolayers of oleic acid are presented in Figure 3. Again, the same advancing (54 to 58

degrees) and receding (40 to 43 degrees) contact angles were obtained for transferred LB monolayers of oleic acid at both the fluorite and calcite surfaces. Also, the same advancing and receding contact angles were obtained when contact angle measurements were repeated at the same location on the transferred monolayer. No significant decrease in contact angle with decreasing drop size was observed for these systems. On the other hand, the observed scatter in contact angle data with varying drop size suggests that the contact angle measurements were affected by surface imperfections, probably surface irregularities. Larger contact angle hysteresis was observed for the transferred LB monolayers of oleic acid (12 to 18 degrees) than for the transferred LB monolayers of stearic acid (about 10 degrees). Such a difference may be due to a difference in molecular arrangements. Note that one stearic acid molecule covered $20 \text{ \AA}^2$ of the crystal surface whereas one oleic acid molecule covered $30 \text{ \AA}^2$ of the crystal surface. As a simple calculation, there might be one-third of the surface area ($10 \text{ \AA}^2$) which was not covered by the oleate species (of course, a detailed calculation of the surface heterogeneity should also include the hydrocarbon chain conformation and the presence of C=C bond). If this hypothesis is correct, such a surface needs to be considered as heterogeneous and the surface tension of a transferred LB monolayer of oleic acid cannot be calculated based on Equation 2 which requires homogeneity.

Hydrophobicity and Stability of Transferred LB Monolayers of Fatty Acids at a Fluorite Surface: The hydrophobicity of transferred LB monolayers of fatty acids at a fluorite surface was examined with the sessile drop contact angle technique. Both advancing and receding contact angles were measured for water drops of varying size at different pH values. The contact angle data are presented in Figures 4 and 5. The advancing contact angle for water was found to be 110 to 114 degrees and was not affected by the pH of the aqueous phase, as shown in Figure 4. Note that the advancing contact angle of 110 to 114 degrees is a characteristic value for closely-packed methyl groups of organic LB films and

self-assembled monolayers.^(35, 37, 38) A contact angle hysteresis of 10 to 20 degrees, depending on the pH value, was observed for water drops with a base diameter of 2 to 6.5 mm (see Figure 4). Contact with water at different pH values did not cause any noticeable change in the contact angles of the LB monolayer of stearic acid at a fluorite surface during the time of the contact angle measurement (experimental data not show here). For example, at pH 5.8 the same advancing and receding contact angles were obtained when contact angle measurements were repeated at the same location on the transferred monolayer (see Figure 5). FT-IR/IRS analysis of the transferred LB monolayers of fatty acids at a fluorite surface showed that the carboxylate head group of the fatty acid monolayer reacts with surface calcium sites of the fluorite surface to form a chemisorbed monolayer.⁽¹⁵⁾ It is probable that carboxylate chemisorption at a fluorite surface after LB transfer caused immobilization of the stearate molecules at the fluorite surface, thus providing substantial stability for this monolayer. A similar stability has been observed for a chemisorbed OTS monolayer at a mica surface.⁽³⁸⁾

Smaller receding contact angles were measured for water drops at alkaline pH values (see Figure 4). These contact angle data indicate that a transferred LB monolayer of stearic acid at a fluorite surface which has reacted to form the chemisorbed monolayer exhibits some instability in a strongly alkaline environment. This relatively small instability of the transferred LB chemisorbed monolayer of stearate at a fluorite surface in water of high pH requires further investigation. A small decrease in both advancing and receding contact angles with decreasing drop size, especially for drops with a base diameter smaller than 2 mm, was obtained (see Figure 4). As mentioned in the previous section, this may be due to the surface roughness of the fluorite crystal.

Further, an LB monolayer film of calcium distearate was transferred at a fluorite surface. The hydrophobic properties and stability of this transferred LB calcium distearate monolayer were also examined by contact angle measurements using water drops of varying size at different pH values. The contact angle data are shown in Figure 6. The

advancing contact angles of 109 to 114 degrees were found to be very similar to those measured for the transferred LB chemisorbed monolayer of stearate, 110 to 114 degrees (see Figure 5). However, the receding contact angle values for the transferred LB calcium distearate monolayer were found to differ from those measured for the transferred LB chemisorbed monolayer of stearate. As shown in Figures 5 and 6, the contact angle hysteresis as measured for water drop at pH 5.8 was 20 to 30 degrees for the transferred LB calcium distearate monolayer at the fluorite surface whereas it was about 10 degrees for the transferred LB chemisorbed monolayer of stearate at the same surface.

The transferred LB calcium distearate monolayer was found to be unstable in acidic and alkaline solutions. As shown in Figure 6, the contact angle hystereses were found to be roughly 40 to 50 degrees at pH 3.6 and 40 to 110 degrees at pH 11.0 depending upon the drop size. Also, significantly smaller advancing contact angles were observed for repeated measurements with drops of solutions (experimental data not shown here). Therefore, it can be concluded that a transferred LB calcium distearate monolayer at a fluorite surface is much less stable than a transferred LB chemisorbed monolayer of stearate at the same surface. It seems clear that after contact with water, some disorganization of the transferred LB calcium distearate monolayer occurred through desorption, molecular reorientation, and probably water penetration. It can be speculated that the calcium distearate monolayer is attracted to the fluorite surface through Coulombic interaction. Such a monolayer is expected to be less stable than a chemisorbed stearate monolayer. Of course, stability through Coulombic interaction is greatly influenced by the pH of the system.

Further, contact angle measurements for a transferred LB monolayer of oleic acid at a fluorite surface were conducted. As in the case of transferred stearic acid monolayers, the transferred oleic acid monolayer reacted with the fluorite surface to form a chemisorbed monolayer of oleate.⁽¹⁵⁾ The advancing and receding contact angles were measured for water drops of varying size at different pH values and the contact angle data are presented

in Figure 7. The molecular area of the transferred LB chemisorbed monolayer of oleate was found to be $30 \text{ \AA}^2/\text{molecule}$. The advancing contact angle was found to be 100 to 104 degrees at pH 3.5 and at pH 5.8 when contact angle measurements were performed on freshly deposited monolayers. The receding contact angles were primarily between 58 and 65 degrees at pH values of 3.5 and 5.8. Both the advancing and receding contact angles decreased slightly when contact angle measurements were repeated at the same location on the transferred LB monolayer (experimental data not shown here). This change was quite clear when contact angle measurements were conducted with a water drop of pH 11.1. The advancing and receding contact angles were found to be 95 to 98 and approximately 20 degrees, respectively (Figure 7). Also, the advancing contact angles decreased by 40 degrees when contact angle measurements were repeated at the same location on the transferred monolayer (experimental data not shown here). It seems very clear that because of the larger molecular spacing of the transferred LB chemisorbed monolayer of oleate ($30 \text{ \AA}^2/\text{molecule}$) than that of the transferred LB chemisorbed monolayer of stearate ($20 \text{ \AA}^2/\text{molecule}$) and the presence of the more polar C=C bond in the hydrocarbon chain, water molecules can penetrate the oleate monolayer more easily and lead to reorganization of oleate species at the surface, thus affecting the wetting characteristics of the transferred oleate monolayer.

Hydrophobicity and Stability of LB monolayers at a Calcite Surface: The advancing contact angles for a water drop (pH 5.8) at a calcite surface with a transferred LB monolayer of stearic acid (perhaps only partially reacted and chemisorbed) were found to be 105 to 108 degrees which are 5 degrees smaller than those measured in the case of fluorite. In the case of receding contact angle measurements, a considerably larger difference was observed between the two minerals. As shown in Figure 8, the receding contact angles for a transferred LB monolayer of stearic acid at a calcite surface were only 13 to 15 degrees compared to 100 to 102 degrees for a transferred LB monolayer of stearic acid at a fluorite

surface. It was observed that both the advancing and receding contact angles for a water drop (pH 5.8) at a transferred LB monolayer of stearic acid at the calcite surface decreased significantly when the contact angle measurements were repeated at the same location on the transferred monolayer (experimental data not shown here). These experimental results briefly demonstrate the instability of transferred LB stearate monolayers at the calcite surface. The destructive effect of the aqueous phase on transferred LB monolayers of stearic acid at a calcite surface increased with an increase in the pH of the aqueous phase, as shown in Figure 9.

A similar contact angle/drop size relationship to that observed for fluorite was obtained when a calcium distearate monolayer was transferred at a calcite surface (see Figure 9). Even repeated measurements showed similar advancing and receding contact angles for both systems. In view of these experimental results, it seems that the adsorption force(s) between the transferred LB stearate monolayer and the calcite surface are similar in nature to the adsorption force(s) between the transferred LB calcium distearate monolayer and the calcite surface. It has been reported that fatty acid molecules are chemisorbed at a calcite surface.⁽⁵⁾ However, this might not necessarily be true for all of the molecules of the transferred LB monolayer of stearic acid. It is expected that only some portion of the transferred LB monolayer might be adsorbed at the active sites of the calcite surface through carboxylate chemisorption whereas the rest of the transferred monolayer remains unreacted in the acid form and is adsorbed at the calcite surface through weaker interactions, possibly Coulombic interaction/hydrogen bonding.

Fluorite vs. Calcite: As shown in Figures 2 and 3, the same wetting characteristics were obtained for LB monolayers of fatty acids at both fluorite and calcite surfaces when probed with an apolar liquid (diiodomethane). In this regard, it seems evident that the instability of the transferred LB monolayer of fatty acid at a calcite surface when in contact with the aqueous phase is due to a greater tendency for hydration of the calcite surface. Just after

argon plasma cleaning, the advancing contact angles for the fluorite and calcite surfaces were always close to zero (< 10 degrees). On the other hand, the advancing contact angle for the fluorite surface was found to increase (up to 27 degrees) after being in contact with air for 30 minutes whereas there was no change in the contact angle of the calcite surface.⁽³⁹⁾ The hydration free energies of CO_3^{2-} and F^- are reported as -402.6 kJ and 26.6 kJ, respectively.⁽⁴⁰⁾ The polarizability (α) values for calcite and fluorite were calculated from the Clausius-Mosotti equation⁽⁴¹⁾ which is defined as:

$$\alpha = \frac{M}{\rho} \times \frac{3}{4\pi N_A} \times \left(\frac{\epsilon_r - 1}{\epsilon_r + 2} \right) \quad (\text{Eq. 3})$$

where M , ρ and ϵ_r are the molecular weight, density, and relative dielectric constant of the sample, respectively. N_A is Avogadro's number. As listed in Table 1, the polarizability of calcite (approximately $1 \times 10^{-23} \text{ cm}^3/\text{molecule}$) is significantly greater than that of fluorite (approximately $6.6 \times 10^{-24} \text{ cm}^3/\text{molecule}$), which may contribute to the higher hydration tendency of the calcite surface. However, the effect of polarizability on fatty acid adsorption at the surfaces of semisoluble minerals requires further study. Based upon the contact angle data, hydration free energy, and polarizability, it is speculated that the trend towards greater hydration of the calcite surface leads to weaker adsorption force(s) between the LB monolayer of fatty acid and the calcite surface. Thus in the aqueous phase water is able to penetrate the monolayer and results in the disorganization/desorption of the unreacted portion of the fatty acid monolayer.

Time-Dependent Contact Angle Measurements: The kinetics of destabilization of LB monolayers in contact with water drops were examined for several systems by monitoring the contact angle change as a function of time. In these experiments a drop of water (pH 5.8) with a base diameter of 5 mm was placed on an LB monolayer (both stearate and oleate). The contact angle changes for the transferred LB monolayers of oleic and stearic

acids are presented in Figures 10 and 11, respectively. The initial contact angle ($t = 0$ min.) corresponds to the advancing contact angle which was measured 15 to 30 seconds after the drop was placed at the surface.

As shown in Figure 10, the contact angle for a water drop at the transferred LB monolayer of oleic acid at a fluorite surface ($30 \text{ \AA}^2/\text{molecule}$) decreased from 100 degrees to 89 degrees in 30 minutes. A few degrees of change in the contact angle is expected for most systems due to the equilibration and phase saturation of the system. Hayes and Ralston⁽⁴²⁾ postulated that an imbalance in interfacial energies in the vicinity of the three-phase contact line exists for even longer times than examined here. However, this hypothesis cannot be validated from these experimental results. The instability of LB monolayers at mineral surfaces can have a significant effect on contact angle relaxation. The contact angle of a transferred LB monolayer of oleic acid at a calcite surface was found to decrease rapidly during the first 5 minutes (by 23 degrees). In 30 minutes, the contact angle of the LB oleate monolayer decreased from 84 to 40 degrees.

The destructive effect of the aqueous phase over time on a transferred LB monolayer of stearic acid ($20 \text{ \AA}^2$ per molecule) was found to be less pronounced (see Figure 11). After 25 minutes the contact angle of the transferred LB monolayer of stearic acid at fluorite and calcite surfaces, decreased by 7 and 15 degrees, respectively. These results agree with the previous observations that LB monolayers of fatty acids are less stable at a calcite surface than at a fluorite surface. Note that destabilization of the transferred LB monolayer of stearic acid by the aqueous phase is even more pronounced at a quartz surface (see Figure 11).⁽²⁶⁾ Of course, chemisorption does not occur at the quartz surface and the transferred LB monolayer remains as stearic acid and is attracted to the quartz surface through weak intermolecular forces. This clearly shows that choosing a surfactant with proper functionality is essential for hydrophobization of the surface.

Hydrophobicity and Stability of Self-Assembled Stearate Monolayers at a Fluorite Surface:

The advancing and receding contact angles for water drops of varying size (pH 5.8) at stearate monolayers self-assembled (SA) at the fluorite surface were measured as a function of surface coverage. Surface coverage (x) of the fluorite surface by SA stearate was determined spectroscopically. The maximum monolayer coverage ($x = 1$) corresponds to $8.3 \times 10^{-10} \text{ mol/cm}^2$, as determined from the LB study⁽¹⁵⁾

Figure 12 shows the change of the advancing contact angle as a function of drop base diameter for different levels of surface coverage (x). The measured advancing contact angles increased significantly with a surface coverage of up to 0.5. At $x = 0.15$, advancing contact angles of less than 40 degrees were observed. The advancing contact angles increased to 98 - 103 degrees at $x = 0.51$. Further increase in surface coverage from $x = 0.51$ to $x = 0.91$ changed the advancing contact angle by only about 10 degrees.

In contrast, the receding contact angle values obtained for fluorite crystals with self-assembled stearate at submonolayer coverage (Figure 13) decreased continuously with decreasing drop size over a range of drop base diameter from 2 to 6.5 mm. Examination of larger drops is required in order to identify characteristic values of the receding contact angle for level of surface coverage. The receding contact angles of the SA stearate were found to be close to zero at $x = 0.30$ or below, as shown in Figure 13. At $x = 0.51$, the receding contact angles were found to be mostly 55 - 65 degrees. Further increase in surface coverage up to $x = 0.71$ changed the receding contact angles by about 20 degrees. However, the measured receding contact angles did not change appreciably with an increase in surface coverage from $x = 0.71$ to 0.91. These results along with the results from the advancing contact angle measurements suggests that good hydrophobicity and stability of SA stearate can be obtained at $x = 0.71$ and further increase in surface coverage does not enhance the hydrophobicity appreciably even at coverage greater than 0.71. The observed receding contact angles were no larger than 75 to 85 degrees.

It is clear from comparison of the measured contact angles of LB and SA stearate layers that the receding contact angles for the transferred LB stearate monolayer is always greater than the receding contact angle for the SA stearate monolayer by 17 to 25 degrees (see Table 2⁽²⁶⁾). Based upon linear dichroism theory, it was found that the transferred LB monolayer of stearic acid at a fluorite surface is oriented at 13 degrees from the surface normal whereas the SA stearate monolayer at $x = 0.91$ (adsorption density of 7.6×10^{-10} mol/cm²) is oriented at 21 degrees from the surface normal.^(17, 26) In addition, it was found that the adsorption density of the stearate molecule has no significant influence on the molecular orientation of adsorbed stearate species.^(17, 26) These results suggest that formation of a stearate monolayer with perfect homogeneity and an molecular orientation angle equivalent to that of the LB monolayer by self-assembly is not possible at a fluorite surface, although the SA monolayer is still of fairly high quality. See table 2.

SUMMARY AND CONCLUSIONS

It has been shown in previous research that transferred LB monolayers of fatty acids react completely with the fluorite surface to form a chemisorbed carboxylate monolayer. Such a reaction appears to be incomplete at a calcite surface and this difference in the extent of the reaction between fluorite and calcite accounts for distinct differences in wettability and stability of the monolayer film.

The hydrophobicity and stability of fatty acid monolayers at fluorite and calcite surfaces have been analyzed using the contact angle-sessile drop technique. The wetting characteristics for the transferred LB monolayers of fatty acids were observed to be the same at both fluorite and calcite surfaces when probed with an apolar liquid (diiodomethane). The contact angle results indicate that the transferred LB monolayers of fatty acids are stable during the contact angle measurements when exposed to an apolar liquid (diiodomethane).

The hydrophobic properties and stability of transferred LB monolayers of fatty acids were also examined with contact angle measurements using water drops of varying size and at different pH values. The transferred LB monolayer of stearic acid exhibits good hydrophobicity and stability at the fluorite surface. The advancing contact angle was found to be 110 to 114 degrees and was not affected by the pH of the aqueous phase. A contact angle hysteresis of 10 to 20 degrees, depending on the pH value, was observed. The same advancing and receding contact angles were obtained when contact angle measurements were repeated at the same location on the transferred monolayer. It seems that carboxylate chemisorption causes immobilization of the transferred stearate molecules at a fluorite surface, thus providing the stability of this monolayer. Some slight instability of transferred LB chemisorbed stearate monolayers at a fluorite surface in water of alkaline pH requires further investigation.

The water advancing contact angles for the transferred LB monolayer of calcium distearate at the fluorite surface were found to be similar to those for the transferred LB monolayer of stearic acid. However, the contact angle hysteresis of the calcium distearate monolayer was larger, especially for acidic and alkaline solutions. It seems that after contact with water, some disorganization of the calcium distearate monolayer such as desorption and molecular reorientation occurred at the fluorite surface.

A considerable difference in the water receding contact angles between the transferred LB monolayer of stearic acid at the fluorite surface and the transferred LB monolayer of stearic acid at the calcite surface was observed. For example, at pH 5.8, the receding contact angles for the transferred LB monolayer of stearic acid at the calcite surface were only 13 to 15 degrees compared to 100 to 102 degrees for an LB stearate monolayer at the fluorite surface. Further, both the advancing and receding contact angles decreased significantly when the contact angle measurements were repeated at the same location of the monolayer. It seems clear that only some portion of the transferred LB monolayer of stearic acid might adsorb at the active sites of the calcite surface through

carboxylate chemisorption whereas the rest of the stearic acid monolayer remains unreacted and is adsorbed at the calcite surface through weaker interactions, possibly Coulombic interaction/hydrogen bonding. Interestingly, a similar contact angle/drop size relationship was obtained when a calcium distearate monolayer was transferred at the calcite surface. In view of these experimental results, it seems that the adsorption force(s) between the transferred LB monolayer of stearic acid and the calcite surface is similar in nature to the adsorption force(s) between the transferred LB monolayer of calcium distearate and the calcite surface.

The kinetics of destabilization of transferred LB monolayer films of fatty acid were also examined at fluorite and calcite surfaces by monitoring contact angle change with time. The results again agree with the previous observation that transferred LB monolayers of stearic acid are less stable at a calcite surface than at a fluorite surface. In addition, destabilization of the transferred LB monolayer of stearic acid by the aqueous phase was found to be even more pronounced at a quartz surface, indicating that choosing a proper surfactant is critical for hydrophobization of the surface.

Changes in the contact angles of self-assembled (SA) stearate monolayers at a fluorite surface were examined as a function of surface coverage (x). The results showed that good hydrophobicity and stability of the SA stearate monolayer can be obtained at $x > 0.7$. It is evident from the results of contact angle measurements for SA monolayers that formation of a SA stearate monolayer of structure and order equivalent to that surface created by a transferred LB monolayer does not occur, although the SA monolayer is still of fairly high quality.

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Table 1.

Polarizability of Fluorite and Calcite.

	Fluorite	Calcite
Molecular Weight (g/mole)	78.08	100.09
Density (g/cm ³)	3.18	2.71
Relative Dielectric Constant	7.36	8.5 (Parallel)
		8 (Perpendicular)
Polarizability (cm ³ /molecule)	6.61 x 10 ⁻²⁴	1.05 x 10 ⁻²³ for (Parallel)
		1.02 x 10 ⁻²³ for (Perpendicular)

Table 2.

Contact Angle Data for Transferred LB and SA Stearate Monolayers at a Fluorite Surface
(drop size varied from 2 to 6.5 mm, pH 5.8).(17)

Type	Adsorption density ($\times 10^{-10}$ mol/cm ²)	Molecular Orientation Angle (degrees)	Advancing Contact Angle (°)	Receding Contact Angle (°)
LB	8.1	13	110 to 114	100 to 102
SA	7.6	21	110 to 115	75 to 85

Figure 1. Oleate adsorption isotherms for fluorite (pH 9.5)⁽⁹⁾ and calcite (pH 9.2)⁽¹²⁾ as determined by in-situ FT-IR/IRS experiments (the original isotherms have been reconstructed using correction factors of 2.3 for fluorite and 1.2 for calcite, based upon sample area considerations⁽¹⁴⁾).

Figure 2. Advancing and receding contact angles for a transferred LB monolayer of stearic acid at fluorite (circles) and calcite (squares) surfaces as measured for a diiodomethane drop of varying size.

Figure 3. Advancing and receding contact angles for a transferred LB monolayer of oleic acid at fluorite (circles) and calcite (squares) surfaces as measured for a diiodomethane drop of varying size.

Figure 4. Advancing and receding contact angles for a transferred LB monolayer of stearic acid at a fluorite surface as measured for a water drop of varying size at different pH values (squares = pH 3.6, circles = pH 5.8, triangles = pH 11.0 and crosses = pH 12.0).

Figure 5. Advancing and receding contact angles for a transferred LB monolayer of stearic acid at a fluorite surface as measured for a water drop of varying size at pH 5.8. The measurements were performed for two runs at the same location on the LB monolayer surface (circles = first run, triangles = second run).

Figure 6. The effect of pH on receding contact angles of a transferred LB monolayer of calcium distearate at a fluorite surface as measured for water drops of varying size at different pH values (circles = pH 3.6, squares = pH 5.8, triangles = pH 11.0).

Figure 7. The effect of pH on advancing (open symbols) and receding (closed symbols) contact angles for a transferred LB monolayer of oleic acid at a fluorite surface as measured for water drops of varying size at different pH values (circles = pH 3.5, squares = pH 5.8, triangles = pH 11.1).

Figure 9. Advancing and receding contact angles for transferred LB monolayers of stearic acid (open symbols) and calcium distearate (closed symbols) at a calcite surface as measured for water drops of varying size at different pH values (circles = pH 3.6, squares = pH 5.8, triangles = pH 11.0).

Figure 10. Advancing contact angle for a transferred LB monolayer of oleic acid at fluorite (circles) and calcite (squares) surfaces as a function of time as measured for a water drop at pH 5.8.

Figure 11. Advancing contact angle for a transferred LB monolayer of stearic acid at fluorite (circles), calcite (squares) and quartz (triangles) surfaces as measured for a water drop (pH 5.8), as a function of time.

Figure 13. Receding contact angle changes for SA stearate adsorbed at a fluorite surface as measured for a water drop at pH 5.8 as a function of surface coverage (an adsorption density of 8.3×10^{-10} mol/cm² is equivalent to $x = 1$).