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A STUDY OF THE PHYSICAL-CHEMICAL MECHANISMS AND VARIABLES
WHICH AFFECT THE TRANSPORT OF INORGANIC AND ORGANIC
HETEROGENEOUS SYSTEMS

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FINAL REPORT FOR

A Study of the Physical-Chemical Mechanisms and Variables Which Affect the Transport of Inorganic and Organic Heterogeneous Systems

N O T I C E

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ABSTRACT

Our primary goal has been investigating the reaction mechanisms which affect microcontaminant partitioning between aqueous solutions and solid phase adsorbents, using goethite (α -FeOOH) as a model adsorbent. Cylindrical internal reflection - Fourier transform infrared (CIR-FTIR) spectroscopy has been developed as the primary technique for this study. Wet chemical adsorption studies, acoustophoresis and electrophoretic mobility have been used to obtain supporting information as needed.

Phenol and o-nitrophenol did not adsorb to goethite. Benzoate, phthalate and p-hydroxybenzoate all adsorbed via a bidentate mechanism to two adjacent iron atoms, while salicylate and 2,4-dihydroxybenzoate formed a chelate complex to single iron atoms. Phosphate adsorption was predominately bidentate, with a pK for deprotonation of the singly protonated surface complex of 4.6. A species involving monodentate phosphate adsorption to a single iron atom was also observed at higher pH values but always at low concentration.

Under certain conditions, CIR-FTIR can quantitate the suspension concentration which interacts with the evanescent wave from the internal reflection element (IRE) of the system. This concentration, as well as the ratio of the refractive index of the study medium to the refractive index of the IRE, can be calculated directly in two limiting cases: "thin films" and "semi-infinite thick films". Since many systems are of intermediate thickness, determination of suspension concentrations in these systems requires development of an intermediate layer model.

I. INTRODUCTION

In order to model transport of dissolved ions in subsurface environments, one should understand how these ions interact with solid phase adsorbents. There are very few techniques, however, which allow one to study such interactions directly. As a result, numerous models have been developed to describe these systems, but no one model has much better predictive capabilities than any other. The choice of an adsorption model is thus often a matter of individual preference as much as any other considerations.

Our efforts throughout this project have focused primarily on developing the methodology to use cylindrical internal reflection -Fourier transform infrared (CIR-FTIR) spectroscopy as an in situ probe of liquid-solid adsorption reactions. Initial studies were performed to determine the mechanisms of adsorption for several organic species and phosphate on a model adsorbent, goethite (α -FeOOH). As these studies proceeded, it became clear that CIR-FTIR was also providing information on water-goethite interactions near the internal reflection element (IRE) - the source of the probe signal in the technique. Further studies were carried out (studies that are still proceeding) with the aim of defining the conditions necessary to determine quantitatively both the index of refraction and the concentration of the suspension around the IRE. These parameters must be known before CIR-FTIR can be used to measure the surface concentrations of adsorbed species.

Another area of interest to us is the effect of particle-particle interactions on adsorption. As implied above, CIR-FTIR may prove very useful in studying this topic, but the requisite information base is not yet available to utilize CIR-FTIR in such studies. We turned instead to acousto-

phoresis, a technique which provides information about charge development on particles in concentrated suspensions, as a possible probe for these systems. Although our preliminary studies delineated the performance of the instrument, further work in this area was curtailed due to budget constraints.

II. ADSORPTION MECHANISMS

A. Organic Adsorbates

1. Non-Adsorbing Organics

Phenol and o-nitrophenol did not adsorb on aqueous suspensions of goethite when precautions were taken to avoid photodegradation, biodegradation and volatilization of the adsorbate. If these materials are reported to adsorb, one should check how well these factors were controlled.

2. Chelate Complexing Organics

Both salicylate and 2,4-dihydroxybenzoate anions form a strongly bound chelate complex on goethite crystals in which the phenol group and one oxygen of the carboxylic acid of the organic adsorbate bind to a single iron atom at the surface of the goethite (1,2). These complexes have the following general structure:

Due to steric constraints, only iron atoms along edges of the goethite crystal can form such complexes, which explains the low adsorption densities ($\approx 30 \mu\text{mol/g}$) exhibited by these two anions. Adsorption densities of phosphate on the same material can exceed $200 \mu\text{mol/g}$ under favorable conditions.

3. Bridging Organics

Benzoate, phthalate and p-hydroxybenzoate anions form bridging bidentate bonds between two adjacent iron atoms at the goethite surface (2,3). The resulting complexes have the following general structure:

Steric interactions between substituents of the organic anion and the crystal play a more important role in these systems than for chelate complexes. These interactions significantly affect both the bond strength of the complex and the adsorption density. The bond strength decreases in the order phthalate > p-hydroxybenzoate > benzoate, while the adsorption densities are p-hydroxybenzoate > phthalate >> benzoate.

B. Inorganic Adsorbates - Phosphate

Phosphate is the only inorganic anion whose adsorption was studied using CIR-FTIR (4). Its adsorption mechanism depended on both system pH (between pH 3.6 and 8, the pH range studied) and phosphate loading (adsorption densities

of 50, 100, 150 and 190 $\mu\text{mol/g}$, with Γ_{max} of approximately 200 $\mu\text{mol/g}$.

Spectra obtained in the 50 $\mu\text{mol/g}$ adsorption studies were very noisy, so few conclusions can be drawn for this system.

There is evidence for the existence of an unprotonated, monodentate surface complex $[\text{Fe-O-PO}_3]$ for all adsorption densities of phosphate studied, at pH values of 6 or higher (and possibly at pH 4 for 50 $\mu\text{mol/g}$ phosphate). However, the intensities of the IR adsorption bands for this complex are quite weak when compared to the other surface complexes, which indicates that very few phosphate ions adsorb to goethite by forming a monodentate complex.

Most phosphate ions adsorb on goethite by forming a bridging bidentate complex $[(\text{Fe-O})_2\text{PO}_2$ or $(\text{Fe-O})_2\text{PO}(\text{OH})]$ similar to that formed by the bridging organics discussed earlier. (Although protonated, monodentate surface complexes might have produced such spectra, IR studies of Fe(III)-phosphate complexes in solution strongly suggest to us that the spectra obtained in suspensions result from bidentate surface complexes.) The extent of protonation in these bidentate complexes increases, for a given pH, as the phosphate adsorption density increases.

Since the ratio of the concentrations of each surface complex (singly protonated bidentate and deprotonated bidentate) can be determined in each system, it is possible to obtain an apparent pK value for deprotonation of the bridging bidentate surface complex. However, this value is affected by the goethite surface charge which is a function of pH. Electrophoretic mobility measurements were performed to obtain the zeta potential of each phosphated goethite system. When the zeta potential is used to correct the apparent pK for electrostatic effects, the resulting intrinsic pK value for deprotonation of the surface complexes is 4.6, on average, for all systems studied.

III. SUSPENSION DISTRIBUTION AROUND CIR CRYSTALS

Although a pK value for deprotonation of surface complexes was obtained in the phosphate adsorption study described above, this procedure did not require true quantitative analysis of the phosphate adsorption by using CIR-FTIR since only ratios of peak heights for each species were measured. Wet chemical techniques were employed to measure total phosphate adsorption densities for each system. The utility and power of using CIR-FTIR as an in situ probe of interfacial reactions in suspensions would be tremendously enhanced if quantitative measurements of the adsorption density of each type of surface species present could be obtained directly by using only CIR-FTIR.

The first requirement for employing CIR-FTIR as a technique for quantitative analysis is that the concentration of suspended particles which are exposed to the IR beam around the internal reflection element (IRE) must be known. While performing our CIR-FTIR studies, we have noted that the intensities of IR absorption bands are often not proportional to the formal concentrations of goethite in suspension. In addition, ratios of band intensities attributed to goethite vary in a manner which suggests that the goethite particles are not uniformly distributed around the IRE for many suspension conditions. (Such variations in the distribution of goethite particles under different conditions contributed to the variation in intrinsic pK values measured for phosphate adsorption. In this case, however, such variations were minimized because the IR absorption bands which were analyzed covered only a small part, about 150 cm^{-1} , of the total spectral range sampled, some 3000 cm^{-1} .)

Consequently, conditions were determined under which the concentration of a suspension being sampled near the IRE could be quantitated (5). The method employed requires the use of a solid such as goethite which has at least two detectable absorption bands attributed to the bulk solid. We found that the suspension concentration surrounding the IRE, as well as the average index of refraction of this medium, could be calculated in two cases. For a "semi-infinite thick film" (either a very high solid concentration or a situation in which the solid and the IRE have the same charge), the computed suspension concentration is roughly 20% larger than the formal suspension concentration. For a "thin film" (low solid concentration with the solid and the IRE having opposite charges), the suspension forms a very thin layer around the IRE, and the suspension concentration in this film can be two orders of magnitude higher than the formal suspension concentration.

Several questions must still be addressed before CIR-FTIR can be utilized as a quantitative in situ probe for studying adsorption reactions in aqueous suspensions. Among these questions are:

1. Can suspension concentrations be determined for the intermediate cases not covered above, which constitute many of the situations of experimental interest?
2. Do IRE-particle interactions in general and particle-particle interactions in thin films affect the surface concentrations of adsorbed species?
3. Can a similar methodology be developed to study particles which only display one bulk absorption band (e.g., any pure metal oxide)?

IV. EFFECT OF PARTICLE-PARTICLE INTERACTIONS ON ADSORPTION

The question of the effect of particle-particle interactions on adsorption reactions, as raised above, is one which has concerned us for several years. Although CIR-FTIR is not yet developed enough to be used as a primary technique for studying this question, we have explored the use of other techniques (potentiometric titration, electrophoretic mobility, light scattering) in such studies. Our final area of interest in this project was to apply acoustophoresis as a probe of particle-particle interactions.

The principle which underlies this technique is that, if a sound wave (a mechanical pressure wave) is applied to a suspension, the pressure wave will induce the colloidal particles and ions in the suspension to move relative to each other. Due to their different inertias, the resulting distribution of charges in the "ionic cloud" surrounding the particles will not be symmetric. Thus, an oscillating electric dipole exists which sets up an alternating electric field at the same frequency as the applied ultrasound wave. The amplitude of the potential of this field is called an ultrasonic vibration potential (UVP).

An inverse effect is also detectable. The electrosonic amplitude (ESA) is the amplitude of the pressure wave induced by applying an alternating electric field to a suspension of charged colloidal particles. Because the magnitudes of the ESA and UVP depend on interactions between charged particles and the surrounding medium, ESA and UVP measurements provide information similar to electrophoretic mobilities. In general, strong signals can only be obtained in concentrated suspensions, which makes acoustophoresis an obvious probe for studying particle-particle interactions. Commercially available

instruments which utilize this technique (we use the Matec System 8000) also perform pH and conductivity measurements as well as potentiometric titrations.

Budget constraints limited our use of this technique to very basic experiments designed to familiarize us with the operation of the apparatus and to define its operational constraints. These studies indicate several areas which must be addressed before acoustophoresis can be further employed.

1. Required sample volumes are quite large, ≈ 200 mL, which limits our ability to study either expensive materials or solids available only in small amounts.

2. Values of ESA and UVP are not directly convertible to either zeta potentials or mobilities, which limits the applicability of this technique for studies of the electrical double layer. Ongoing theoretical studies by other investigators are addressing this problem. Theoretical studies of the effect of ionic strength and particle concentration, density, shape and polydispersity on ESA and UVP would also be helpful in determining the applicability of the technique to various systems.

3. The phase delay of the ESA or UVP signal must be properly calibrated before using the instrument, but it is not always obvious that this calibration has been performed correctly. In our initial titrations, even when the phase calibration was correct, drifting of the phase from the initial zero value was a problem. Although this difficulty was due primarily to temperature changes during the titrations, the problem was still present when good temperature control had been established. Since phase drift is most severe at high ionic strength, we feel that this problem is related to the ESA and UVP signals which are produced by the ions themselves in suspensions. Thus, there appears to be an upper limit on the concentration of background electrolyte

which can be employed for this technique. The relation between this maximum ionic strength and the concentration of solid present must be better defined, both experimentally and theoretically.

4. Although suspension equilibration during titrations was a problem for us, in terms of the time allowed between titrant additions by the software, this problem is related more to the material employed than the instrument itself.

5. Optimal stirring of the suspensions during measurements was also a concern. In many systems, particles settle from suspension easily, making the system nonhomogeneous. We used a separate magnetic stirrer in addition to the stirrer provided with the instrument but attributed two difficulties to the extra stirrer. First, the heat it produced made the temperature control less accurate. Second, friction between the magnetic stir bar and the Teflon cell was damaging the cell. Although these problems can be minimized, they should be recognized by investigators. A third problem with stirring was also noted. Although measured values in equilibrated systems are not significantly affected by varying the stirring speed, resulting titration curves are not smooth if the stirring speed is changed during the experiment. We attribute this observation to the different rates of reaction caused by different stirring speeds. Note that the stirring speed employed also affects the equilibration time mentioned in the above paragraph.

These areas of concern need to be addressed before acoustophoresis can be utilized to study particle-particle interactions and their effects on adsorption reactions.

V. SUMMARY

Our major project effort was devoted to developing CIR-FTIR spectroscopy as a useful technique for the in situ study of adsorption reactions in aqueous suspensions. It is clear that CIR-FTIR can be used to provide important information about the mechanisms of adsorption reactions, although methodology must still be developed for using CIR-FTIR for quantitative studies of these systems. The technique also serves as a useful probe of particle-solvent interactions. At present, attempts to use acoustophoresis to study particle-solvent interactions and adsorption reactions have been much less successful, but some of the problems associated with employing this technique have been delineated.

LIST OF PUBLICATIONS ASSOCIATED WITH THIS PROJECT

(as referenced in the Final Report)

1. Yost, E.C., M.I. Tejedor-Tejedor and M.A. Anderson, "In Situ CIR-FTIR Characterization of Salicylate Complexes at the Goethite/Aqueous Solution Interface", Environ. Sci. Technol. 24 (1990) 822-828.
2. Yost, E.C., M.I. Tejedor-Tejedor and M.A. Anderson, "Characterization of Benzoic and Phenolic Complexes at the Goethite/Aqueous Solution Interface Using CIR-FTIR Spectroscopy. Part 2. Bonding Structures", to be submitted to Langmuir.
3. Tejedor-Tejedor, M.I., E.C. Yost and M.A. Anderson, "Characterization of Benzoic and Phenolic Complexes at the Goethite/Aqueous Solution Interface Using Cylindrical Internal Reflection Fourier Transform Infrared Spectroscopy. Part 1. Methodology", Langmuir 6 (1990) 979-987.
4. Tejedor-Tejedor, M.I. and M.A. Anderson, "Protonation of Phosphate on the Surface of Goethite As Studied by CIR-FTIR and Electrophoretic Mobility", Langmuir 6 (1990) 602-611.
5. Tickanen, L.D., M.I. Tejedor-Tejedor and M.A. Anderson, "Quantitative Characterization of Aqueous Suspensions Using ATR-FTIR Spectroscopy: Influence of Internal Reflection Element-Particle Interactions on Spectral Absorbance Values", submitted to Langmuir.

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