**THE INFLUENCE OF INTERFACIAL PROPERTIES ON
THE TWO-PHASE LIQUID FLOW OF ORGANIC
CONTAMINANTS IN GROUNDWATER**

Final Report
Covering Period
July 1, 1989 through June 30, 1992

by

Avery H. Demond, Fred N. Desai and Kim F. Hayes

Environmental and Water Resources Engineering
Dept. of Civil and Environmental Engineering
The University of Michigan
Ann Arbor, MI 48109-2125

Prepared for

THE U.S. DEPARTMENT OF ENERGY
AGREEMENT NO. DE-FG02-89ER60820
Office of Health and Environmental Research
Subsurface Science Program

RECEIVED
AUG 04 1993
OSTI

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

EXECUTIVE SUMMARY

DOE's waste sites are contaminated with a variety of organic liquids such as trichloroethylene at Savannah River and carbon tetrachloride at Hanford. Because of their low solubility in water, organic liquids such as these will persist as separate liquid phases and be transported as such in the subsurface. Thus, an improved understanding of the factors influencing the movement of a separate organic liquid phase in the subsurface is important to DOE's efforts to control groundwater contamination. Wettability is sometimes cited as the most important factor influencing two-phase flow in porous media. The wetting phase migrates preferentially through the smaller pores, whereas the nonwetting phase is concentrated in the larger pores. Typically, aquifers are thought of as strongly water-wet, implying that the organic liquid preferentially occupies the larger pores. But in fact, that state depends on the properties of the three interfaces of the system: between the organic liquid and water, water and the solid, and the organic liquid and the solid. Characteristics of the system which affect the interfacial properties also impact the wettability, such as the nature of the aquifer solids' surfaces, the composition of the groundwater and the properties of the organic contaminant. The alteration of wettability at DOE waste sites may be dominated by the presence of co-contaminants such as organic acids and bases which behave as surface-active agents or surfactants. Because of their physicochemical nature, surfactants will sorb preferentially at the interfaces of the system, thereby impacting the wettability and the distribution of the liquids in the porous medium.

The overall objective of this research was to determine how changes in interfacial properties affect two-phase flow. Specifically, the objective was to examine the effect of surfactant sorption on capillary pressure relationships by correlating measurements of sorption, zeta potential, interfacial tension and contact angle, with changes in the capillary pressure-saturation relationships. To enable quantitative predictions of the impact of surfactant

sorption on multiphase flow, the goal was to develop a methodology to predict capillary pressure-saturation relationships for systems containing organic liquids and surfactants from the capillary pressure-saturation relationships for simpler air-water systems. Such a methodology would benefit personnel involved with the remediation of waste sites by providing a means of estimating the impact of surfactant sorption on multiphase flow.

This research concentrated on an ideal system composed of water, o-xylene as the organic liquid, quartz as the solid, and cetyltrimethylammonium bromide (CTAB), a C₁₆ quaternary ammonium cationic surfactant, as the surface-active species. Most of the experiments were performed at pH 6 and 9 with a NaCl concentration of 0.01 M. The main experimental effort was divided into three parts:

- (1) Surface chemical measurements (sorption and zeta potential measurements),
- (2) Interfacial tension and contact angle measurements, and
- (3) Capillary pressure saturation measurements.

Sorption experiments were done in small batch reactors to determine the equilibrium amounts of CTAB sorbed on quartz as a function of pH and surfactant concentration. Quartz has a point of zero charge in the vicinity of pH 2. Above this pH, quartz is negatively charged and a cationic surfactant like CTAB exhibits a strong affinity for the surface. The sorption density of CTAB as a function of equilibrium aqueous phase concentration showed an "S"-shaped isotherm, characteristic of systems in which the solute sorbs strongly. At low CTAB concentrations, the sorption was characterized by electrostatic attraction between the negative sites on the surface and the positively-charged CTAB head groups. As the CTAB concentration increased, the slope of the isotherm increased resulting from the aggregation of surfactant molecules on the surface. The sorption density became constant at about 9×10^{-4} M, beyond the critical micelle concentration (CMC) determined from surface tension (air-water) or interfacial tension (o-

xylene-water) measurements of 3×10^{-4} M or 2×10^{-4} M, respectively. As the pH increased, the CTAB sorption density increased because of the increased negative charge density on the quartz surface.

The zeta potential for the systems was measured as a function of pH, ionic strength, and surfactant concentration using an electrokinetic sonic amplitude (ESA) apparatus. These measurements showed that the quartz surface was initially negatively charged. As sorption increased, the surface charge increased, passing through an isoelectric point at a CTAB concentration of 1.8×10^{-4} M at pH 6 and 6×10^{-5} M at pH 9. In order to insure accurate derivation of values of zeta potential from the signal produced by the ESA apparatus, the signal due to the background electrolyte had to be subtracted. A new technique developed during the course of this research involving vector subtraction improved the ability to discount the background signal.

Interfacial tension and contact angle measurements were made for the air-water-CTAB-quartz and xylene-water-CTAB-quartz systems for pH 6 and 9 and NaCl concentration of 0.01M using a state-of-the-art automated pendant/sessile drop instrument. The surface tension of the CTAB solutions dropped sharply in the first few minutes after the drop was formed and then continued to decrease gradually for at least an hour. This time dependence was attributed to trace levels of highly surface-active impurities present in the CTAB. The interfacial tension between the CTAB solutions and xylene reached a constant value within 20 minutes after the drop was formed, suggesting that whatever impurities were present had a lesser effect at the xylene-water interface.

The surface tension for the air-water system and the interfacial tension of the xylene-water system at both pH 6 and 9 decreased log-linearly up to the CMC, after which there was little change. The effectiveness of CTAB, defined as $\Pi_{CMC} = \gamma^0 - \gamma^{CMC}$ where γ^0 is the

surface or interfacial tension in the absence of surfactant, and γ^{CMC} is the surface tension or interfacial tension in the presence of surfactant, was 36.4 dynes/cm in the air-water system and 32.9 dynes/cm in the xylene-water system. The proportional reduction, however, was greater in the xylene-water system, suggesting that CTAB has a greater impact in the xylene-water system than in the air-water system at the same aqueous phase concentration. The surface tension and interfacial tension were independent of pH.

Both the advancing and receding contact angles (reported as measured through the aqueous phase) were measured at pH 6 and 9 in the air-water and the xylene-water systems. In both systems, the contact angle was small at very low CTAB concentrations, indicating that the systems were strongly water-wet or hydrophilic. As the CTAB concentration increased, the contact angle increased and passed through a maximum close to the isoelectric point of the quartz surface, implying that the surface was most hydrophobic when a CTAB monolayer was present on the surface. For concentrations at and above the CMC, the air-water and xylene-water systems showed different behavior: the former system reverted to strongly hydrophilic, indicated by the decrease in the contact angle to about 20° at about 4×10^{-4} M, whereas the latter remained hydrophobic, indicated by the fact that the contact angle remained in the range of 155° - 180° . Since the formation of a surfactant bilayer would result in a positively charged or hydrophilic surface, it appears that xylene droplet was able to disrupt the top layer of the CTAB bilayer. This explanation is consistent with the empirical observations that a lagtime occurred prior to the spreading of the xylene and that the xylene droplets had to be of sufficient size to spread. The values of contact angles at a particular CTAB concentration increased with pH. The maximum value of 64° in the air-water was, however, independent of pH, whereas the maximum value in the xylene-water system was 155° at pH 6 and 180° at pH 9.

Primary drainage and spontaneous imbibition capillary pressure-saturation relationships

v

were measured for the air-water-CTAB-quartz and the xylene-water-CTAB-quartz systems at pH 6 and NaCl concentration of 0.01M for several CTAB concentrations selected to span the range of observed contact angles. The imbibition relationship showed a greater change than the drainage relationship, implying a greater dependence on interfacial conditions. At very low concentrations of CTAB, the aqueous phase imbibed strongly in the air-water system. As the contact angle increased with CTAB concentration, the aqueous phase imbibed less. At the isoelectric point, corresponding to the maximum value of the contact angle of 64° , the aqueous phase showed the least imbibition. As the CMC was approached and the contact angle decreased, the aqueous phase once again imbibed strongly. For the xylene-water system, spontaneous imbibition occurred when CTAB was absent and the contact angle was 15° . However, the amount of spontaneous imbibition that occurred at the other two CTAB concentrations was minimal, at $[\text{CTAB}] = 1 \times 10^{-5} \text{ M}$ when the system was intermediately-wet ($\theta = 91^\circ$), as well as at $[\text{CTAB}] = 5 \times 10^{-5} \text{ M}$ when the system was organic-wet ($\theta = 139^\circ$). The measurements of capillary pressure were confined to pH 6, since the maintenance of the capillary pressure cells at pH 9 over the length of the capillary pressure measurements proved infeasible due to contamination with atmospheric CO_2 .

To predict organic liquid-water capillary pressure-saturation relationships from air-water relationships, Leverett's function is commonly used. However, this method proved inadequate in the estimation of the capillary pressure relationships measured here. To simulate the trends observed here, particularly the lack of imbibition at the high contact angles, Leverett's function was modified to include the operational contact angle. The operational contact angles were derived from the measured contact angles by correcting them for roughness and for interfacial curvature using correlations obtained from the literature. Using this modified Leverett's function, reasonable estimates of the capillary pressure-saturation relationships were obtained for systems containing both xylene and

CTAB based on measurements made with only air and water. In addition, estimates were generated for the pH 9 systems for which capillary pressure data were not available. These estimates suggested that the capillary pressure will be impacted by pH, especially at $[\text{CTAB}] = 1 \times 10^{-5} \text{ M}$ where the system reverses wettability between pH 6 and pH 9. The modified Leverett's function proposed here showed less success in predicting the capillary pressure-saturation relationships for the air-water-CTAB system, particularly at high contact angles, than for organic liquid-water systems both with and without CTAB over the entire range of contact angles.

Thus, this research suggests that the presence of surface-active co-contaminants at DOE waste sites may strongly impact the flow pathways of the organic liquid contaminant. By sorbing to the interfaces of the system, co-contaminants will affect the capillary pressure-saturation relationship, a key constitutive relationship in the modeling of multiphase flow. The changes that occur in the capillary pressure relationship can be predicted on the basis of the contact angle and liquid-liquid interfacial tension.

ACKNOWLEDGEMENTS

The authors thank Dr. Frank J. Wobber, Program Manager, Subsurface Science Program, Office of Energy Research, U.S. Dept. of Energy, for his support. This research was possible due to funding provided by the U.S. Dept. of Energy under Grant #DE-FG02-89ER60820. The authors also thank the students who contributed to the research effort (in alphabetical order): Guan-Ru Duh, Haza Hammad, Susan Lindquist, Linda Timmer Verhulst, and Benjamin Witherell.

TABLE OF CONTENTS

Executive Summary	i
Acknowledgements	vii
List of Tables	x
List of Figures	xi
1.0 INTRODUCTION	1
2.0 BACKGROUND	4
2.1 Two-Phase Liquid Transport	4
2.2 Relationship Between Interfacial Properties and Two-Phase Liquid Flow	6
2.3 Definition of Wettability	8
2.4 Effect of Sorption on Wettability	9
2.4.1 Liquid-Liquid Interfacial Tension	10
2.4.2 Solid-Liquid Interfacial Tension	12
2.5 Quantifying the Effects of Sorption	13
2.6 Effect of Wettability on Capillary Pressure-Saturation Relationships	14
3.0 OVERVIEW OF APPROACH	18
4.0 EXPERIMENTAL MATERIALS AND METHODS	20
4.1 Materials	20
4.2 Methods	22
4.2.1 Surface Chemical Measurements	23
4.2.1.1 Sorption Measurements	23
4.2.1.2 ESA Apparatus	24
4.2.1.3 Zeta Potential	26
4.2.2 Interfacial Tension and Contact Angle Measurements	26
4.2.2.1 ADSA Apparatus	26
4.2.2.2 Air-Water-CTAB-Quartz System	27
4.2.2.3 o-Xylene-Water-CTAB-Quartz System	31
4.2.3 Capillary Pressure-Saturation Measurements	32

5.0	RESULTS AND DISCUSSION	35
5.1	Surface Chemical Measurements	35
5.2	Interfacial Tension and Contact Angle Measurements	41
5.2.1	Air-Water-CTAB-Quartz System	41
5.2.2	o-Xylene-Water-CTAB-Quartz System	49
5.3	Capillary Pressure-Saturation Measurements	56
5.3.1	Air-Water-CTAB-Quartz System	56
5.3.2	o-Xylene-Water-CTAB-Quartz System	58
5.3.3	Scaling of Capillary Pressure-Saturation Relationships	60
6.0	CONCLUSION AND RECOMMENDATIONS	70
7.0	REFERENCES	72
APPENDICES		
A	Standard Operating Procedures	A-1
A.1	Cleaning of Quartz	A-1
A.2	CTAB Purification	A-6
A.3	Surface Chemical Measurements	A-7
A.3.1	Sorption Measurements	A-7
A.3.2	ESA Measurements	A-8
A.4	Interfacial Tension and Contact Angle Measurements	A-11
A.4.1	Cleaning of Materials	A-11
A.4.2	Axisymmetric Drop Shape Analysis (ADSA) Apparatus	A-13
A.5	Capillary Pressure-Saturation Measurements	A-18
A.5.1	CTAB Analysis by Two-Phase Titration	A-18
A.5.2	Capillary Pressure-Saturation Experiments	A-20

LIST OF TABLES

TABLE		PAGE
2.1	Roughness Corrections for Contact Angles on Well-Roughened Surfaces	16
5.1	Surface Tension for Air-Water-CTAB System	45
5.2	Measured Contact Angles for Air-Water-CTAB-Quartz System	47
5.3	Interfacial Tension for o-Xylene-Water-CTAB System	50
5.4	Measured Contact Angles for o-Xylene-Water-CTAB-Quartz System	54
5.5	Calculated Scaling Factors for Air-Water-CTAB-Quartz System at pH 6	63
5.6	Calculated Scaling Factors for o-Xylene-Water-CTAB-Quartz System at pH 6	65
5.7	Calculated Scaling Factors for o-Xylene-Water-CTAB-Quartz System at pH 9	68

LIST OF FIGURES

FIGURE		PAGE
4.1	Schematic of the Axisymmetric Drop Shape Analysis (ADSA) instrument	28
4.2	Computer images of pendant and sessile drops	29
4.3	Schematic of the capillary pressure-saturation measurement system	33
5.1	Desorption of CTAB from quartz	36
5.2	Sorption of CTAB on quartz for different total CTAB concentrations	36
5.3	Sorption of CTAB on quartz as a function of pH	38
5.4	Particle-size distribution for #40 quartz	38
5.5	Sorption and zeta potential of CTAB on quartz as a function of pH	39
5.6	Surface tension for air-water-CTAB system as a function of time	42
5.7	Surface tension for air-water-CTAB system as a function of concentration	45
5.8	Contact angles for air-water-CTAB-quartz system as a function of time	46
5.9	Contact angles for air-water-CTAB-quartz system as a function of concentration	48
5.10	Interfacial tension for o-xylene-water-CTAB system as a function of time	51
5.11	Interfacial tension for o-xylene-water-CTAB system as a function of concentration	51
5.12	Contact angles for o-xylene-water-CTAB-quartz system as a function of time	53
5.13	Contact angles for o-xylene-water-CTAB-quartz system as a function of concentration	55
5.14	Measured capillary pressure-saturation relationships for air-water-CTAB-quartz system	57
5.15	Measured capillary pressure-saturation relationships for o-xylene-water-CTAB-quartz system	59
5.16	Comparison of measured and predicted capillary pressure-saturation relationships for air-water-CTAB-quartz system	64
5.17	Comparison of measured and predicted capillary pressure-saturation relationships for o-xylene-water-CTAB-quartz system	66
5.18	Comparison of predicted capillary pressure-saturation relationships for o-xylene-water-CTAB-quartz system at pH 6 and pH 9	69

1.0 INTRODUCTION

An improved understanding of the factors influencing the movement of a separate organic liquid phase in the subsurface is important to DOE's efforts to control groundwater contamination. Many organic compounds used in DOE operations such as carbon tetrachloride at Hanford and trichloroethylene at Savannah River have a low solubility in water. As a result, these compounds, if introduced into the subsurface, may persist as a separate phase and be transported as such. Thus, DOE's efforts to alleviate contamination from its waste sites will benefit from a better understanding of the principles governing the subsurface migration of a separate organic liquid phase.

Wettability is sometimes described as the most important factor influencing two-phase flow in porous media (Moore and Slobod, 1956). The liquid phase which preferentially wets the solid tends to move through the smaller pores, whereas the nonwetting liquid moves through the larger pores. Such a separation of flow has a profound effect on the relative transport of the organic phase. Typically, aquifers are thought of as strongly water-wet, implying that the organic liquid preferentially occupies the larger pores. But in fact, that state depends on the properties of the three interfaces of the system: the interfaces between the two liquids, and between the solid and each liquid. Thus, characteristics of the system which affect the interfacial properties also impact the wettability, such as the nature of the aquifer solids' surfaces, the composition of the groundwater and the properties of the organic contaminant. In addition, the presence of co-contaminants such as organic acids and bases, which act as surface-active agents or surfactants, may play a large role in the alteration of the native wettability of waste sites. Because of the dependence of wettability on interfacial properties and the dependence of transport pathways on wettability, the two relationships must be examined in tandem to gain a better understanding of how the physicochemical interactions of the aquifer solids, groundwater and contaminants affect two-phase flow.

The purpose of this research is to investigate how changes in interfacial chemical properties caused by the introduction of contaminants affect the capillary pressure-saturation relationship, a constitutive relationship used in multiphase flow modeling. If organic contaminants are introduced into the subsurface, they will sorb differentially at the various interfaces of the system: water-organic liquid, solid-organic liquid, and solid-water. The exact degree of sorption will be influenced by the pH and ionic strength of the aqueous solution. The sorption will, in turn, alter the interfacial tensions and the contact angle of the system, consequently impacting the capillary pressure-saturation relationship.

Previous studies have focused on various aspects of the relationship between sorption and capillary pressure-saturation relationships. For example, a number of studies have related surfactant sorption or zeta potential to the magnitude of the contact angle in air-water-mineral systems (Ginn, 1970; Aronson and Princen, 1978; McGuiggan and Pashley, 1987; Fuerstenau and Herrera-Urbina, 1991) as well as in organic liquid-water-mineral studies (Gaudin and Decker, 1967; Buckley et al., 1989). Yet in these cases, only the effects of sorption on wettability were demonstrated and the implications of these changes with respect to capillary pressure were not explored.

On the other hand, Morrow (1976, 1978) and Demond (1988) have looked at the effects of interfacial tension and contact angle on capillary pressure-saturation relationships. However, in these studies, the changes in contact angle and interfacial tension were accomplished through the use of different organic liquids and the role of co-contaminants in determining capillary pressure-saturation relationships was not considered.

Thus, previous studies have focused on the relationship between sorption and contact angle, or on the relationship between contact angle and capillary pressure. The purpose of

this research is to integrate these foci and examine the effects of surfactant sorption on capillary pressure by correlating measurements of sorption, electrophoretic mobility, interfacial tension and contact angle, with changes in the capillary pressure-saturation relationship for air-water-mineral and organic liquid-water-mineral systems. Because sorption has a direct effect on wettability and wettability impacts capillary pressure relationships, it should be possible to develop a relationship among sorption, wettability, and capillary pressure.

To make the correlation between sorption and capillary pressure as utilitarian as possible, it should enable quantitative predictions of capillary pressure-saturation relationships.

Leverett's (1941) relationship has been frequently used (Rose and Bruce, 1949; Lenhard and Parker 1987a) to estimate organic liquid-water relationships from air-water data.

Demon (1988) suggested that the discrepancies between measured relationships and those estimated using Leverett's function might be resolved by introducing an operational contact angle. However, such a tactic was not actually applied to organic liquid-water systems and its possible utility in systems where the wettability changes are governed by sorption has yet to be demonstrated. The development of a means of estimating changes in capillary pressure-saturation relationships due to sorption would prove useful to personnel involved in the remediation of waste sites by providing a means of estimating the impact of co-contaminants on multiphase flow.

2.0 BACKGROUND

2.1 Two-Phase Liquid Transport

The presence of a separate organic liquid phase at spill and waste disposal sites is not uncommon. In fact, there are many documented instances of its occurrence (Williams and Wilder, 1971; Roberts et al., 1982; Villaume, 1985; Feenstra and Coburn, 1986). Despite the observation of a separate organic liquid phase at many sites, little work has been devoted to understanding the movement of this phase in the subsurface. Most of the work has emphasized mathematical modeling. Early models focused on infiltration and spreading of hydrocarbons on the water table (van Dam, 1967; Mull, 1971; Dracos, 1978). Later models, such as those of Abriola and Pinder (1985a, 1985b), Faust (1985), Osborne and Sykes (1986), Corapcioglu and Baehr (1987), and Kuppusamy et al. (1987), are more comprehensive and multipurpose. For example, Faust's model describes the movement of an aqueous and an organic phase under saturated and unsaturated conditions, whereas Abriola and Pinder's model handles the contaminant in three phases simultaneously: as an organic phase, as a solute in the aqueous phase, and as a mobile fraction in the vapor phase.

These models describe the movement of the liquid phases using mass balance equations, written here for a system composed of a rigid, non-deformable, homogeneous porous medium, and two mutually saturated, incompressible liquid phases, with no internal sources or sinks (Peaceman, 1977):

Liquid 1:

$$\nabla \cdot \left[\frac{\rho_1 k k_{r1}}{\mu_1} (\nabla P_1 - \rho_1 g \nabla h) \right] = \frac{\partial(\phi \rho_1 S_1)}{\partial t} \quad (2-1)$$

Liquid 2:

$$\nabla \cdot \left[\frac{\rho_2 k k_{r2}}{\mu_2} (\nabla P_2 - \rho_2 g \nabla h) \right] = \frac{\partial(\phi \rho_2 S_2)}{\partial t} \quad (2-2)$$

where:

- ρ = density,
- k = intrinsic permeability,
- k_r = relative permeability,
- μ = viscosity,
- P = pressure,
- g = gravitational acceleration constant,
- h = height above a datum,
- ϕ = porosity,
- S = saturation, and
- t = time.

To obtain a solution, additional information must be provided in the form of constitutive relationships:

$$P_c \equiv P_1 - P_2 = f(S) \quad (2-3)$$

in which capillary pressure, defined as the difference between the pressures in the two liquids averaged over a representative elementary volume, is expressed as a function of saturation, and:

$$k_{r1} \equiv k_i/k = f(S) \quad (2-4)$$

in which the relative permeability to a particular liquid, defined as the ratio of the effective permeability to a particular phase to the intrinsic permeability, is expressed as a function of saturation.

Despite the sophistication of current mathematical models, their use is hindered by the lack of information for key constitutive relationships such as Eqns. (2-3) and (2-4) (Faust, 1985; Pinder and Abriola, 1986). Some recent studies (Lenhard and Parker, 1987a, 1987b; Parker and Lenhard, 1987; Parker et al., 1987; Demond, 1988) aim at alleviating this lack. Nevertheless, this work is still primarily oriented towards developing models for these constitutive properties, rather than towards understanding the fundamental principles governing the behavior of these relationships. Ultimately, to understand the behavior of these macroscopic relationships, it is necessary to examine the microscale parameters influencing them. Since relative permeability is often estimated from capillary pressure-saturation relationships (Burdine, 1953; Mualem, 1976), the emphasis here is on capillary pressure-saturation relationships.

2.2 Relationship Between Interfacial Properties and Two-Phase Liquid Flow

Although Eqn. (2-3) is macroscopic, it represents the effect of pore-level interfacial properties. At the level of a single pore, the capillary pressure is related to interfacial forces by two fundamental equations of capillarity. The first equation, the Young-Laplace equation, states:

$$P_c = \gamma_{L_1 L_2} (1/R_1 + 1/R_2) \quad (2-5)$$

where:

$\gamma_{L_1L_2}$ = interfacial tension between the two liquid phases, and

R_1, R_2 = principal radii of curvature of the meniscus.

If the meniscus is spherical, $R_1 = R_2 = R$. In a cylindrical capillary tube, this radius of curvature, R , may be related to the capillary tube radius, r , by the equation, $R = r/\cos\theta$ where θ is the contact angle. Substituting this relationship into Eqn. (2-5) yields:

$$P_c = 2\gamma_{L_1L_2} \cos \theta / r \quad (2-6)$$

The second equation, Young's equation, states:

$$\cos \theta = \frac{\gamma_{L_1S} - \gamma_{L_2S}}{\gamma_{L_1L_2}} \quad (2-7)$$

where:

γ_{LS} = interfacial tension between the solid and a liquid phase.

In turn, these interfacial tensions are affected by the sorption density at the three interfaces of the system. According to the Gibbs adsorption equation:

$$d\gamma = -RT \left(\sum_i \Gamma_i d(\ln a_i) \right) \quad (2-8)$$

where:

a_i = activity of species i in solution,

R = gas constant,

T = temperature, and

Γ_i = sorption density of species i at a given interface.

Eqns. (2-5) through (2-8) illustrate that, on the scale of an individual pore, the capillary pressure is a direct function of preferential sorption at the interfaces of the system. But flow in porous media is usually modeled on a macroscale rather than on the level of individual pores, using volume-averaged equations such as Eqns. (2-1) and (2-2). Thus, the relationship between sorption and migration of a separate organic liquid phase cannot be deduced directly from these equations. However, they suggest that to understand this relationship, one should examine the effect of sorption on the interfacial properties of the system and, in turn, their effect on the constitutive relationship between capillary pressure and saturation.

2.3 Definition of Wettability

The effect of interfacial properties on two-phase flow is frequently posed in terms of the effect of wettability. Wettability qualitatively describes the degree to which a liquid spreads on a solid and is often defined on the basis of the contact angle. If the contact angle measured through the droplet liquid is $< 90^\circ$, then the droplet liquid wets the solid; conversely, if the angle formed is $> 90^\circ$, then the ambient liquid wets the solid. If the wetting liquid is water, the surface is referred to as water-wet or hydrophilic; in contrast, if the wetting liquid is an organic liquid, the surface is termed organic-wet or hydrophobic.

Unfortunately, the contact angle is not always a unique function of the properties of the solid and the liquids making up the system, as Young's equation (Eqn. 2-7) implies. The contact angle in a porous medium is affected by the roughness of the surface, showing an enlarged angle while advancing and a diminished angle while receding. However, measurements of contact angles on rough surfaces demonstrate that, while hysteresis

increases with roughness and magnitude of the contact angle, these operational contact angles show a systematic dependence on those obtained on a smooth surface, or the intrinsic contact angle defined by Young's equation (Morrow, 1975; Zografí and Johnson, 1984).

For systems containing surface-active solutes, contact angle hysteresis can occur even when the contact angle is measured on a smooth, homogeneous solid (McCaffery and Cram, 1971; McGuiggan and Pashley, 1987). Because of the sorption and desorption of the surfactant, the condition of the surface differs depending on whether the liquid is advancing or receding. This phenomenon also leads to an enlarged angle while advancing and a diminished angle while receding.

Because of the difficulties of defining a single contact angle for a porous medium, other measures of evaluating wettability, such as the rate of spontaneous imbibition (Donaldson et al., 1969) and the amount of displacement (Amott, 1959), have been proposed. Yet, these measures often depend on other porous medium properties in addition to wettability, thus leading to the description of the contact angle as the only direct and unambiguous measure of wettability (Melrose and Brandner, 1974). Considering the correspondence between the operational contact angle and the intrinsic contact angle, and the problems of alternative measures, the best indicator of wettability in ideal systems appears to be the contact angle obtained on a smooth piece of representative mineral.

2.4 Effect of Sorption on Wettability

Wettability is influenced by sorption at the various interfaces of the system. Because wettability can be defined in terms of the intrinsic contact angle (Section 2.3), which, in turn, is defined by Young's equation (Eqn. 2-7) as a function of interfacial tensions,

understanding the effect of sorption on wettability implies understanding its effect on the interfacial tension at the three interfaces of the system: between the solid and each liquid, and between the two liquids.

2.4.1 Liquid-Liquid Interfacial Tension

When two slightly miscible liquids are brought into contact, the interface possesses a characteristic free energy, the interfacial free energy, denoted γ :

$$\left(\frac{\partial G}{\partial A}\right)_{T,P,n} = \gamma \quad (2-9)$$

where:

- G = Gibbs free energy,
- A = interfacial area,
- T = temperature,
- P = pressure, and
- n = chemical composition.

It is also common to find γ defined as an interfacial tension, the force per unit length necessary to stretch an interface. When dealing with Newtonian liquids, the distinction between the two is unimportant (Adamson, 1990). Thus, the informal practice of using the two terms interchangeably will be followed. The difference between interfacial tension and surface tension lies in whether a particular phase boundary is considered to be the division between two phases or to be solely the limit of that phase. The convention of using the word "interfacial" to apply to phase boundaries between two liquids and the word "surface" to apply to phase boundaries where one phase is air will be followed here.

Since interfacial tension arises from an imbalance of forces acting on molecules at the interface, its value depends on the interaction not only between the molecules of the two liquids, but also between the molecules of the individual liquids themselves. The magnitude of the interfacial tension reflects the relative difference between the intermolecular forces within the bulk liquid and between the liquids. Pairs of liquids having similar intermolecular properties, such as water and alcohols, have low interfacial tensions, whereas pairs having very different intermolecular properties, such as water and n-alkanes, have high interfacial tensions.

The effect of a solute on the interfacial tension between an organic liquid and water depends on the ability of the solute to reduce the intermolecular differences between the two liquids. Solutes that have a strong preference for one of the liquid phases have a relatively small effect on interfacial tension. For example, a 1 N KCl salt addition to a cetyl acetate-water system raises the interfacial tension from 15.9 to 17.0 dynes/cm (Dickinson, 1940). On the other hand, the addition of an organic solute that is miscible in water can lower the interfacial tension between water and an organic liquid substantially. For example, if ethanol is present at a concentration of 1.2% (by weight) in a system composed of water and benzene, the interfacial tension is reduced from about 35.0 to 17.2 dynes/cm (Sada et al., 1975). The effect of amphipathic solutes or surfactants is even more dramatic. Surfactants minimize the intermolecular repulsion forces that exist between the two liquids by orienting themselves in the interfacial region such that the polar head group resides in the aqueous phase and the nonpolar hydrocarbon tail resides in the organic phase. Thus, concentrations of 1×10^{-4} M can easily lower the interfacial tension by 30 dynes/cm (Rosen, 1989). Consequently, the interfacial tension between water and a relatively immiscible organic liquid is probably dominated by any surface-active species that may be present. This suggests that the presence of surface-active co-contaminants at DOE waste sites may control the interfacial tension between water and the organic liquid contaminant.

2.4.2 Solid-Liquid Interfacial Tension

The interfacial tension between a liquid and a solid results from the same intermolecular properties as those discussed for liquid-liquid pairs. Just as liquid-liquid interfacial tension depends on the chemical differences between the liquid phases, so does the interfacial tension between a solid and a liquid. For example, a mineral solid having polar surface functional groups in contact with a nonpolar liquid would have a relatively high interfacial tension compared to the same mineral surface in contact with water.

As with liquid-liquid interfacial tension, solid-liquid interfacial tensions can be modified by the sorption of solutes at the interface. The changes in interfacial tension caused by adsorption at the interface can be quite dramatic. In fact, such adsorption can cause a naturally hydrophilic surface to become hydrophobic as Jouany and Chassin (1987) discovered in their study of the adsorption of an organic coating onto montmorillonite. The change in the condition of the solid-liquid interface interfacial tension is heavily dependent on the system. For example, the adsorption of amphipathic molecules may result from a hydrophobic attraction to a hydrophobic surface in which the polar hydrophilic groups are oriented toward the liquid, or from ionic or coordinative interactions with a hydrophilic surface in which the hydrophobic parts of the molecule project into the solution (Ulrich et al., 1988). Solution characteristics such as pH and ionic strength may also have a sizeable influence on the interfacial tension between the solid and liquid phases. This type of effect was investigated by Holmes-Farley et al. (1985) who demonstrated that increasing the extent of surface ionization of a carboxylated polyethylene surface by changing pH resulted in a marked reduction of the interfacial tension between that surface and water.

2.6 Quantifying the Effects of Sorption

In order to assess the changes in interfacial tensions occurring due to sorption, the interfacial tensions of the three interfaces of the system need to be determined. A variety of methods are available for measuring liquid-liquid interfacial tension, including pendant drop method, Wilhelmy plate, and du Nouy ring (Adamson, 1990). For systems containing surfactants, the pendant drop method is the best for three reasons. First, both interfacial tension and the contact angle can be measured with one instrument. Second, there is no solid substrate involved and so no assumption must be made about the contact angle at the surface of the plate or ring as with the use of the Wilhelmy plate and du Nouy ring. Third, since the pendant drop method is a static method, it is possible to observe the same system over time, thus obtaining measurements as a function of time.

No satisfactory direct methods exist for the measurement of the interfacial tensions between solids and liquids (Benson and Yun, 1967; Parks, 1984). Consequently, some surrogate measure of the condition of the solid-liquid interface must be used in the determination of the effects of sorption. The contact angle is a composite measure, depending on both the liquid-liquid interfacial tensions and the solid-liquid interfacial tensions. It can be measured directly, using, for example, a pendant drop apparatus, but forming sessile drops instead. In as much as charge neutralization of a surface corresponds with adding hydrophobic groups on a surface, correlations between surface charge and wettability are expected. For example, Holmes-Farley et al. (1985) demonstrated a consistent correspondence between wettability and the extent of surface ionization and, on the basis of this, recommended the use of the contact angle as a measure of surface ionization. Thus, the change in the solid-liquid interfacial tensions may be correlated with changes in surface charge or zeta potential, and contact angle.

2.6 Effect of Wettability on Capillary Pressure-Saturation Relationships

The effect of interfacial tension and wettability on capillary pressure-saturation relationships has been examined to a limited extent in environmental engineering studies (Lenhard and Parker, 1987a; Demond, 1988) and to a greater extent in petroleum engineering research (Powers and Botset, 1949; Bethel and Calhoun, 1953; Killins et al., 1953; Morrow et al., 1973; Dumore and Schols, 1974; Morrow, 1976). Several of these studies have suggested that capillary pressure-saturation relationships for different organic liquid-water systems can be scaled using effective saturation, S_e , defined as:

$$S_e \equiv \frac{(S_w - S_{wr})}{(1 - S_{wr})} \quad (2-10)$$

where:

S_w = saturation of the wetting phase,

subscript e = effective, and

subscript r = residual,

and reduced capillary pressure, P_c^* , defined as:

$$P_c^* \equiv \frac{P_c}{\gamma_{L_1 L_2}} \quad (2-11)$$

as variables in an application of a modified Leverett's (1941) function (Morrow, 1976; Lenhard and Parker, 1987a; Demond, 1988).

Based on Eqns. (2-10) and (2-11), the capillary pressure for organic liquid-water systems

can be estimated if the corresponding relationship for air and water is known:

$$P_{CORG/H2O} = \frac{\gamma_{ORG/H2O}}{\gamma_{AIR/H2O}} P_{CAIR/H2O} \quad \text{at a given } S_e \quad (2-12)$$

The success of this scaling procedure in correlating capillary pressure-saturation measurements is dependent on the interfacial properties of the systems. As the interfacial tension decreases and the contact angle increases, or as the systems become less strongly water-wet, deviations from the common scaled curve become greater (Morrow, 1976; Demond, 1988). Furthermore, these deviations are greater for imbibition than for drainage.

Some of the discrepancies can perhaps be reduced by including the contact angle, θ , in the scaling coefficient:

$$P_c^* = \frac{P_c}{\gamma_{L_1 L_2} \cos \theta} \quad (2-13)$$

Yet, as Demond (1988) pointed out, use of the intrinsic contact angle does not resolve the problem. Calculations made by Melrose (1965) based on the ideal soil model, which treats a soil as a bed of uniform spheres, showed that the operational contact angles in drainage and imbibition may be significantly different from the intrinsic contact angle due to the differences in interfacial curvature between interfaces in a cylindrical tube and a pore. On the basis of his analysis, Melrose developed curvature correction functions, $Z(\theta)$, which could be applied to the intrinsic contact angle to yield the operational contact angles:

$$Z(\theta) = \left(\frac{P_c}{\gamma \cos \theta} \right) \left(\frac{\gamma}{P_c} \right)_{\theta=0} \quad (2-14)$$

Yet, this correction does not appear to be sufficient. Calculations using these functions showed that the corrections are qualitatively in the right direction, but quantitatively they are too small (Demond, 1988).

Not only will the differences in pore geometry affect the contact angle, but also the roughness of the solid surface. Measurements from studies such as those by Morrow (1975) and Zografí and Johnson (1984) showed that increased roughness resulted in increased hysteresis. This hysteresis displayed a systematic dependence on the intrinsic contact angle, becoming greater for larger angles. While it may be difficult to predict the impact of roughness on the contact angle theoretically, there exists a consistent empirical correlation between the operational and intrinsic contact angles. For example, the operational contact angles on well-roughened surfaces may be calculated as shown in Table 2.1 (Morrow, 1975):

Table 2.1. Roughness Corrections for Contact Angles on Well-Roughened Surfaces^a

Intrinsic Contact Angle	Operational Contact Angle	
	drainage (receding angle)	imbibition (advancing angle)
$0^\circ < \theta_{INT} < 21.6^\circ$	$\theta_R = 0^\circ$	$\theta_R = 0^\circ$
$21.6^\circ < \theta_{INT} < 87.6^\circ$	$\theta_R = 0.5\exp(0.05\theta_{INT}) - 1.5$	$\theta_R = 2(\theta_{INT} - 21.6)$

^a The subscripts INT = intrinsic and R = corrected for roughness.

Since Leverett's function serves as an accepted means of estimating the capillary pressure for organic liquid-water systems from the corresponding relationships for air-water systems, it needs to be examined to determine whether it can be modified to yield accurate results in systems containing organic liquids and sorbing solutes. To improve the accuracy

of Leverett's function, the contact angle may need to be included as a measure of the wettability. However, an operational contact angle is perhaps more appropriate for the systems of interest where large discrepancies between intrinsic contact angles and the operational contact angles are expected because of the magnitude of the intrinsic contact angle.

3.0 OVERVIEW OF APPROACH

The overall objective of this research is to estimate how changes in interfacial chemical properties affect two-phase flow relationships. Specifically, the objective is to examine the effects of surfactant sorption on capillary pressure-saturation relationships by correlating measurements of sorption, zeta potential, interfacial tension and contact angle, with changes in capillary pressure-saturation relationships.

This research concentrated on an ideal system composed of water, o-xylene as the immiscible organic solvent, quartz as the representative aquifer solid, and cetyltrimethylammonium bromide ($\text{CH}_3(\text{CH}_2)_{15}(\text{CH}_3)_3\text{N}^+\text{Br}^-$) (CTAB), as the surface-active co-contaminant. Most of the experiments were performed at pH 6 and 9 with a NaCl concentration of 0.01 M. The two systems examined were (i) air-water-CTAB-quartz, and (ii) o-xylene-water-CTAB-quartz. Although this study is limited to these specific systems, the methodology used and the results obtained are applicable to other two fluid-solute systems as well.

The research approach was divided into the following three parts:

- (1) **Determination of Effects of Sorption on Interfacial Properties.** Four types of measurements were made: (i) the CTAB sorption density as a function of aqueous phase concentration and pH, (ii) zeta potential as a function of aqueous phase CTAB concentration and pH, (iii) interfacial tension as a function of aqueous phase CTAB concentration at pH 6 and 9, and (iv) advancing and receding contact angles as a function of aqueous phase CTAB concentration at pH 6 and 9.
- (2) **Measurement of Capillary Pressure-Saturation Relationships.** Primary

drainage and spontaneous imbibition capillary pressure relationships were measured for several aqueous phase CTAB concentrations selected to cover the range of observed contact angles at pH 6 and 0.01M NaCl.

(3) Estimation of Capillary Pressure-Saturation Relationships. Leverett's function was modified to include the operational contact angle. The operational contact angles were calculated from the measured intrinsic contact angles using the correction for interfacial curvature developed by Melrose (1965) and for roughness developed by Morrow (1975). The capillary pressure-saturation relationships were estimated using this modified Leverett's function and then compared with the measured relationships.

4.0 EXPERIMENTAL MATERIALS AND METHODS

4.1 Materials

Quartz: The solid quartz (SiO_2) was selected as the mineral for this study because it represents one of the most commonly occurring minerals in groundwater environments and has surface properties representative of many other naturally occurring aluminosilicates. The surface of quartz is composed of silanol surface functional groups which are deprotonated at pH values above about 2, thus imparting a negative charge to the quartz surface over the range of pH normally encountered in subsurface environments. In addition, quartz is available in many forms, such as smooth flat plates necessary for contact angle measurements and different particle sizes necessary for capillary pressure, sorption and zeta potential measurements.

Several forms of quartz were purchased and prepared for these studies. Two size fractions of particles, #40 and F-65 (U.S. Silica, Berkeley Springs, WV), were used. The #40 quartz was used in the sorption and zeta potential experiments, while the F-65 quartz was used in the capillary pressure experiments. The #40 quartz had a particle size range of 1 to 15 μm with a median particle diameter of 5.1 μm as determined with the centrifugal particle size distribution analyzer (Capa-500, Horiba Instruments, Irvine, CA) and a surface area of 1.3 m^2/gm as determined by N_2 adsorption and the BET theory using an Autosorb-1 instrument (Quantachrome, Syosset, NY). The F-65 quartz had a particle size range of 106 to 425 μm , as specified by the manufacturer. The particles were cleaned by washing several times with 0.1 M HCl followed by several washes with 15% hydrogen peroxide at a pH of about 4, to remove metal ions and organic matter (Kunze and Dixon, 1986). This washing procedure is described in detail in Appendix A.1. Smooth quartz slides were used for the contact angle

measurements (Quartz Scientific, Fairport Harbor, OH); their cleaning is described in Section 4.2.2.1 on contact angle measurements.

Organic liquid: The organic liquid in the experiments was o-xylene. o-Xylene has been targeted as a compound for research by DOE due to its frequent presence at waste sites (Riley and Zachara, 1992). It is representative of a class of relatively nonpolar aromatic compounds that are less dense than water. It was purchased from Fluka (Ronkonkoma, NY) having a purity greater than 99% and was used without further purification.

Aqueous phase: Ultrapure water was obtained by passing deionized, distilled water through Milli-Q (Millipore, Bedford, MA) cartridge filters. This water is referred to as Milli-Q water in this report. The ionic strength was adjusted using sodium chloride (NaCl). The sodium chloride was purchased from Johnson Matthey (Seabrook, NH) with a purity of 99.999% and was used without further purification.

Co-contaminant: Cetyltrimethylammonium bromide (CTAB) ($\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$), a quarternary ammonium surfactant, was selected as the surface-active compound for these studies. Its choice was based on the fact that its solution chemistry is relatively simple, remaining as an unprotonated ammonium cation at all pHs examined in this study. As a cation, it was expected to sorb relatively strongly to the negatively charged quartz surface. Consequently, the surface condition of the quartz could be controlled in a predictable fashion through the addition of CTAB. Furthermore, CTAB is only slightly soluble in xylene; therefore, the sorption density of CTAB-coated quartz was not expected to change when the aqueous phase was displaced by xylene in the contact angle and capillary pressure-saturation experiments.

The purity of the CTAB, as purchased, was greater than 99% (Fluka, Ronkonkoma, NY). Based on electrical conductivity measurements with a CDM83 Conductivity Meter (Radiometer, Copenhagen Denmark), the critical micelle concentration (CMC) of the CTAB in pure water was 9.5×10^{-4} M, which is in close agreement with the literature values (Mukerjee and Mysels, 1971). The CTAB was further purified by recrystallizing three times from a 4:1 mixture by volume of acetone and methanol (MacRitchie, 1990). The CTAB purification procedure is described in detail in Appendix A.2. This cleaning procedure did not completely eliminate the time-dependent behavior of the surface tension measurements. Consequently, three other purification methods were tried: two recrystallizations from a nonpolar solvent, hexane saturated with ethanol (Pashley et al., 1988), foaming for several hours with ultrapure nitrogen (Mysels, 1986) and passing through a SepPak cartridge (Waters, Milford, MA) (Mysels, 1986). Despite the success of other researchers with these methods, these purification methods did not result in a significant improvement in the purity of CTAB in this study. Thus, they were not adopted as standard procedures. To determine the sorption density using a scintillation counter, radiolabeled cetyltrimethylammonium anion was also used. This was obtained from cetyltrimethylammonium iodide (CTAI), purchased from American Radiolabeled Chemicals (St. Louis, MO) and was used without further purification.

Solvents: All solvents used for cleaning procedures were HPLC grade (Mallinckrodt Specialty Chemicals, Paris, KY).

4.2 Methods

To examine the relationship between sorption and capillary pressure, five types of measurements were made: sorption, zeta potential, interfacial tension, contact angle and capillary pressure-saturation. For the purposes of describing the experimental effort, these measurements are divided into three parts: (i) surface chemical measurements, (ii) interfacial

tension and contact angle measurements, and (iii) capillary pressure-saturation measurements. Sodium chloride at a concentration of 0.01 M was used as the background electrolyte in all the experiments.

4.2.1 Surface Chemical Measurements

4.2.1.1 Sorption Measurements

CTAB sorption on quartz was measured in two ways. Initially, it was measured using series of reactor tubes, each adjusted to a particular pH, at room temperature ($23 \pm 2^\circ\text{C}$). At a particular total CTAB concentration, the quartz particles were mixed with appropriate amounts of water, CTAB, radiolabeled CTAI, NaCl and acid in 12 ml polypropylene centrifuge tubes, mixed end-over-end at 8 revolutions per minute on a Labquake shaker (Labindustries, Berkeley, CA) for 24 hours. The samples were then centrifuged at a relative centrifugal force (RCF) of 6555 using a Sorvall centrifuge (DuPont, Wilmington, DE) for 30 minutes and the supernatant analyzed for radiolabeled CTAI using a liquid scintillation counter (RackBeta Spectral, LKB Wallac, Turku, Finland) to give the equilibrium CTAB concentration in the aqueous phase and, by calculation, the sorption density of CTAB on quartz. Measurements aimed at assessing the significance of CTAB losses to the sample container walls showed that these losses were negligible (less than 0.5%) for aqueous phase surfactant concentrations in excess of 10^{-6} M. More details on the procedure are given in Appendix A.3.1.

Later, sorption density was measured in the electrokinetic sonic amplitude (ESA) apparatus (Section 4.2.1.2) in conjunction with zeta potential measurements. Here, sorption density was measured over a range of CTAB concentrations at pH 6 and 9 at a temperature of $25.0 \pm 0.2^\circ\text{C}$. At a particular total CTAB concentration, the quartz particles were mixed with appropriate amounts of water, CTAB, radiolabeled CTAI, NaCl and acid to give a total

volume of 250 ml, a NaCl concentration of 0.01M, and a pH close to 5.5. A nitrogen blanket was maintained above this solution in order to prevent contamination due to atmospheric carbon dioxide. The pH was then raised to 6 and the sample was allowed to equilibrate for 6 hours. A 10 ml aliquot of the sample was centrifuged and the supernatant analyzed for radiolabeled CTAI using the liquid scintillation counter to give the equilibrium CTAB concentration in the aqueous phase and, by calculation, the sorption density of CTAB on quartz. The pH of the sample was raised to 9 and the sorption density and the equilibrium CTAB concentration were again measured according to the above procedure.

4.2.1.2 ESA Apparatus

Zeta potential measurements were made using an electrokinetic sonic amplitude (ESA) apparatus (ESA-8000, Matec Applied Sciences, Hopkinton, MA). The procedure is described in Appendix A.3.2. In the ESA apparatus, an alternating current is applied to a colloidal suspension, causing the particles to undergo oscillatory motions due to the electrical forces on the charged particles. The resultant alternating pressure wave is a function of a number of factors including the volume fraction of the particles, the density difference between the particles and the solution, and the zeta potential of the particles. The relationship between ESA signal and dynamic electrophoretic mobility is given by:

$$ESA(\omega) = \frac{P}{E} = c \Delta\rho \phi G_f \mu_d \quad (4-1)$$

where:

- ω = angular frequency,
- P = pressure amplitude of the sound wave,
- E = amplitude of the applied electric field,
- c = sound velocity in suspension,

$\Delta\rho$ = density difference between the particles and the solvent,

ϕ = volume fraction of the particles,

G_f = geometric factor for electrode geometry, and

μ_d = frequency dependent dynamic electrophoretic mobility.

The zeta potential, ζ , can be determined from the dynamic electrophoretic mobility, μ_d , by (O'Brien, 1988):

$$\zeta = \frac{\mu_d \eta}{\epsilon} |G(\alpha) - 1| \quad (4-2)$$

where:

η = viscosity,

ϵ = dielectric permittivity, and

$\alpha = \frac{\omega a^2}{\nu}$, where a = particle radius and ν = kinematic viscosity,

for thin double layers, defined as situations where $\kappa a > 50$, where $1/\kappa$ = thickness of the double layer (Hiemenz, 1986).

For a solid suspension in an electrolyte solution, the measured ESA signal is a combination of two signals: one for the solid and the other for the background electrolyte. Under most operating conditions, the contribution from the background electrolyte is negligible compared to the ESA signal from the solid. However, the background signal can become significant when (i) the ionic strength is high, (ii) the pH is close to the isoelectric point (iep), (iii) the solid has a low charge density, (iv) the density difference between the solid and the liquid is small, or (v) the solid concentration is relatively low. For example, in ESA measurements conducted in this study utilizing silica at low pH and high ionic strengths, the background signal was sometimes as large or even larger than the solid signal (Desai et al., 1993a,b).

To minimize the impact of the background signal, the volume fraction of solid and ionic strength can be adjusted (Scales and Jones, 1992). Unfortunately, it is not always possible to reduce the background contribution by increasing the solid concentration while staying below 5% volume fraction necessary for the application of the theory relating the ESA signal to dynamic electrophoretic mobility. When the background is significant, this signal must be subtracted out in order to obtain an accurate electrophoretic mobility measurement. To correct for background, a technique was developed in which the background ESA signal was vectorially subtracted from the measured ESA signal for the slurry to give the ESA signal for the solid only. This technique was based on the methodology developed by Marlow et al. (1988) for the derivation of accurate colloid vibration potentials and is described in detail in two papers, Desai et al. (1993a,b).

4.2.1.3 Zeta Potential

At a particular total CTAB concentration, the quartz was mixed with appropriate amounts of water, CTAB, NaCl, and acid. A nitrogen blanket was maintained above this solution in order to prevent contamination due to atmospheric carbon dioxide and the temperature was maintained at $25.0 \pm 0.2^\circ\text{C}$. After each increase in pH, the sample was allowed to equilibrate for 6 hours before measuring the ESA signal. The zeta potential was then calculated from the ESA signal using Eqns. (4-1) and (4-2).

4.2.2 Interfacial Tension and Contact Angle Measurements

4.2.2.1 ADSA Apparatus

The interfacial tension and the contact angle were measured for the air-water-CTAB-quartz and the o-xylene-water-CTAB-quartz systems over a range of CTAB concentrations at pH 6 and

9, at a temperature of $25.0 \pm 0.2^\circ\text{C}$. These measurements were made using an automated pendant/sessile drop instrument, shown in Figure 4.1, based on the Axisymmetric Drop Shape Analysis (ADSA) technique (Cheng et al., 1990). The use of the apparatus is outlined in Appendix A.4.2. This method of analysis has advantages over other pendant drop techniques in that the interfacial tension or contact angle can be calculated from the location of a group of randomly selected points on the liquid interface, unlike other variations which require a knowledge of the location of specific points (Andreas et al., 1938). A droplet was formed with a microsyringe (Gilmont, Great Neck, NY). The droplet was then enlarged with a M3Z Plan S microscope (Wild Leitz, Heerbrugg, Switzerland). The enlarged droplet was photographed using a solid-state CCD monochrome camera (4810 Series, Cohu, San Diego, CA), and the image sent to a digitizer where the analog signal was converted to a digital signal containing the image data in the form of pixels. A microcomputer with a 80386 microprocessor acquired these data and performed the image analysis and computation. The computational analysis involved fitting Laplace's equation to an arbitrary array of coordinate points selected from the drop profile. An objective function that expresses the deviation of the physically observed curve from the Laplacian curve was minimized to give the best value for the interfacial tension or contact angle (Rotenberg et al., 1983). To damp vibrations, the apparatus was placed on a vibration-free table (Technical Manufacturing, Peabody, MA). Figure 4.2 shows a sampling of images of pendant and sessile drops along with the best-fit profiles.

4.2.2.2 Air-Water-CTAB-Quartz System

Surface Tension

The surface tension measurements were made by forming pendant drops of CTAB solution in air. These droplets were made using a Teflon tube attached to a microsyringe adjusted with a micromanipulator (World Precision, New Haven, CT) within an environmental chamber

Figure 4.1: Schematic of the Axisymmetric Drop Shape Analysis (ADSA) instrument.

Figure 4.2: Computer Images of Pendant and Sessile Drops

Pendant xylene droplet in water at pH 6, [CTAB] = 0 M

Sessile xylene droplet in water on quartz at pH 6, [CTAB] = 1×10^{-5} M

(Rame-Hart, Mountain Lakes, NJ) which had been flushed with high purity nitrogen saturated with Milli-Q water. The surface tension dropped sharply in the first 5 minutes after the pendant drop was formed. After about 10 minutes, the surface tension became fairly constant, dropping by less than 0.3 dynes/cm every 10 minutes. Therefore, the 10-minute values were used in subsequent analysis.

Contact Angle

For measuring the intrinsic contact angle, smooth quartz plates (Quartz Scientific, Fairport Harbor, OH) were used. Since the cleaning procedures influenced the reproducibility of the contact angle measurements, considerable attention was devoted to developing rigorous techniques. To clean the quartz slides, syringe barrels, quartz cell and other glassware, they were soaked for 20 minutes each in methanol, acetone, and Milli-Q water, followed by overnight soaking in Chromerge solution (VWR Scientific, Chicago, IL). These items were then again thoroughly rinsed in Milli-Q water. The syringe barrels and other glassware were oven dried at 110°C. The quartz slides were not dried, but were instead stored in Milli-Q water. The stainless steel needles and Teflon syringe plungers and stage were soaked for 20 minutes each in hexane, methanol, acetone, and Milli-Q water, after which the Teflon parts were soaked in Micro (International Products, Trenton, NJ). After rinsing thoroughly with Milli-Q water, the Teflon and steel parts were dried in the oven at 110°C. Additional details are given in Appendix A.4.1.

To make the measurements, the quartz slide was removed from the Milli-Q water and placed on a Teflon stage inside a quartz cell containing CTAB solution. The slide was allowed to equilibrate for 20 minutes with the CTAB solution. With an inverted stainless steel needle attached to the microsyringe, a sessile air droplet was formed on the underside of the quartz slide. Both advancing and receding contact angles were measured. The measurements were made 10 minutes after the droplet was advanced or receded. After this time, the contact angle

changed by less than 1° in 15 minutes. In all cases, the receding angle was more stable than the advancing angle.

4.2.2.3 o-Xylene-Water-CTAB-Quartz System

Interfacial Tension

The xylene and CTAB solution were preequilibrated by gently pouring water-saturated xylene over the aqueous CTAB solution followed by slow mixing on a magnetic stirring plate for at least 24 hours. Vigorous mixing was avoided in order to prevent emulsion formation. The interfacial tension measurements were made by forming inverted pendant drops of xylene in CTAB solution, according to the procedure discussed with respect to the air-water system (Section 4.2.2.2). The interfacial tension dropped sharply in the first 5 to 10 minutes, after which it remained constant. Therefore, the values measured at 20 minutes are reported.

Contact Angle

o-Xylene and CTAB solution were preequilibrated as described above. The CTAB solution was then poured into the quartz cell to completely submerge the quartz slide. A thin layer of xylene was placed on the CTAB solution to prevent pH drift due to contamination from atmospheric carbon dioxide. This was particularly important for the measurements at pH 9. If necessary, the pH of the aqueous phase was adjusted to the appropriate value, while gently stirring the aqueous phase on a magnetic stirrer using a tiny magnetic stirring bar. An inverted sessile drop of xylene was formed on the underside of the quartz slide using an inverted stainless steel needle attached to a microsyringe. Both the advancing and receding contact angles were measured. The contact angle changed noticeably within the first several minutes after the droplet was formed. The reported value was measured at about 20 minutes, at which point the contact angle was changing at the rate of about 1° every 15 minutes. In all cases, the receding angle was more stable than the advancing angle.

4.2.3 Capillary Pressure-Saturation Measurements

Capillary pressure-saturation measurements were made for the air-water-CTAB-quartz and the o-xylene-water-CTAB-quartz systems for different CTAB concentrations at pH 6 and 0.01 M NaCl concentration at $23 \pm 2^\circ\text{C}$ using the system shown in Figure 4.3. Standard plastic Tempe cells (Reginato and van Bavel, 1962) (Soil Moisture, Santa Barbara, CA) were used for the air-water-CTAB-quartz systems, whereas Teflon-coated stainless steel pressure cells with similar dimensions were custom made for the o-xylene-water-CTAB-quartz systems. The coreholders had a height of about 3.0 cm and an interior diameter of 5.5 cm. They were consistently packed with cleaned, dry F-65 quartz to a porosity of 0.34 ± 0.01 , in contact with a 1-bar porous ceramic plate (Soil Moisture, Santa Barbara, CA). The cell was evacuated and then an aqueous solution containing CTAB at a particular concentration was pumped through the cell at a rate of 1 ml/min until influent and effluent CTAB concentrations were the same, measured to an accuracy of 5% by a two-phase titration method using sodium dodecyl sulfate as the titrant (Rosen and Goldsmith, 1972), as described in Appendix A.5.1. To ensure that the system was at equilibrium, several additional pore volumes were pumped through the cell after this point.

The pressure in the wetting phase in the cell was maintained constant, close to atmospheric pressure. The pressure in the nonwetting phase was controlled by compressed air, passed through particulate and hydrocarbon traps, regulated by two regulators in series (Model 23, Scott Specialty Gases, Plumsteadville, PA; Model 40-7, Moore Products, Spring House, PA), and monitored by a low pressure gauge (Series 66-050, Wallace and Tiernan, Belleville, NJ). The drainage relationship was measured by incrementally increasing the nonwetting phase pressure. After each increment in this pressure, the cell was allowed to equilibrate for 24 hours or until the cell stopped draining. The decrease in wetting phase saturation within

Figure 4.3: Schematic of the capillary pressure-saturation measurement system

the porous medium was calculated based on the increase in weight of the cumulative effluent. This procedure was repeated until a negligible efflux was achieved in response to a step increment in pressure, suggesting that residual saturation had been achieved. This point served as the beginning of spontaneous imbibition. After each small reduction in nonwetting phase pressure, the system was allowed to equilibrate and the increase in saturation was calculated based on the weight loss of the effluent. Appendix A.5.2 gives additional details.

The CTAB concentrations at which the capillary pressure measurements were made were chosen to span the range of contact angles. In the xylene-water-quartz systems where xylene became the wetting phase, a slightly different procedure had to be adopted. To make the capillary barrier hydrophobic, a thin Teflon membrane filter with 1 μm pores (Gelman, Ann Arbor, MI) was placed on top of the porous ceramic plate. As with the water-wet systems, CTAB was sorbed onto the quartz by pumping CTAB solution through the pressure cell until the influent and effluent concentrations were equal. Then, most of the CTAB solution was removed by applying a vacuum to the bottom of the cell. The remaining liquid was drained out by applying high pressures, on the order of about 4 bars, to the top of the cell, followed again by the application of a vacuum. Next, several pore volumes of xylene which had been preequilibrated with the aqueous phase were introduced through the bottom of the cell at a rate of 1 ml/min. The reservoir was filled with the CTAB solution and the drainage and imbibition experiments were carried out as described above.

5.0 RESULTS AND DISCUSSION

5.1 Surface Chemical Measurements

CTAB was selected as the surfactant in this study because it was believed that it would sorb strongly and fairly irreversibly to quartz, thus providing a controlled means of altering interfacial properties. To verify this, reversibility studies were conducted to determine if the surfactant desorbed significantly into either surfactant-free water or xylene. These experiments involved replacing the supernatant with water whose pH and ionic strength were the same as that of the supernatant or with xylene. As shown in Figure 5.1, CTAB desorbed only slightly with each aqueous phase wash. When the centrifugate was washed with xylene instead of water, virtually all the CTAB remained on the quartz surface. Thus, it appeared that the sorption of CTAB was similar in both the air-water and xylene-water systems and CTAB was unlikely to desorb during the course of, for example, a capillary pressure experiment in which xylene displaced the aqueous phase.

Figure 5.2 shows the sorption of CTAB on quartz as a function of pH for several total CTAB concentrations. These data were used to obtain the sorption isotherms for CTAB on quartz as a function of pH (Figure 5.3). Quartz is negatively charged above its point of zero charge, which is in the vicinity of pH 2 (Parks, 1965). Therefore, above pH 2, a cationic surfactant such as CTAB will exhibit a strong affinity for quartz, giving an isotherm shape that has been previously noted as characteristic of sorption in these systems (Bijsterbosch, 1974; Stratton-Crawley and Shergold, 1981). Because the quartz surface is more negatively charged at higher pH values, CTAB sorbs more effectively at higher pHs.

Measurements of ESA as a function of CTAB concentration were conducted at pH 6 and 9. To convert the ESA signal to zeta potential using the theory of O'Brien (1988) requires a

Figure 5.1: Desorption of CTAB from Quartz

Figure 5.2: Sorption of CTAB on Quartz for Different Total CTAB Concentrations

value of the mean particle diameter. In absence of a measured value, the mean particle diameter was estimated to be $1.7\ \mu\text{m}$ based on a surface area of $1.3\ \text{m}^2/\text{gm}$ obtained using N_2 adsorption and BET theory and assuming that the particles are spherical. However, this approach was found to underestimate the actual mean particle size due to the disproportionately high weighting given to the smallest particles. To get a more accurate value, the actual particle size distribution was measured on a centrifugal particle size distribution analyzer (Capa-500, Horiba Instruments, Irvine, CA). These results showed that the diameter of the particles ranged from 1 to $15\ \mu\text{m}$ and the median particle diameter was $5.1 \pm 0.5\ \mu\text{m}$, significantly different from the value estimated on the basis of N_2 adsorption (Figure 5.4). When estimated from this measured mean particle diameter, the zeta potential was similar to values previously reported in the literature (Li and deBruyn, 1966; Allen and Matijevic, 1969).

Figure 5.5 gives the sorption density and the zeta potential for the sorption of CTAB on quartz at pH 6 and 9 over a wide range of CTAB concentrations. The sorption mechanism can be inferred from these data. The sorption isotherm can be divided into four regions (Figure 5.5). In region I, the sorption is characterized by electrostatic attraction between the negatively charged surface and the positively charged head group of isolated CTAB molecules. The negative values of the zeta potential measurements suggest that the surface had less than a monolayer coverage. In region II, the marked increase in sorption was probably due to hemimicelle or admicelle formation, a result of lateral interaction between the surfactant's hydrocarbon tails. Also in this region, the zeta potential became increasingly less negative and finally turned positive, with the isoelectric point occurring at an aqueous phase CTAB concentration of about $1.8 \times 10^{-4}\ \text{M}$ for pH 6 and $6 \times 10^{-5}\ \text{M}$ for pH 9. In region III, the slope in the isotherm decreased, suggesting a lessening tendency for a positively charged surfactant to adsorb onto an increasingly positively charged surface. The sorption that does occur in this region resulted primarily from the

Figure 5.3: Sorption of CTAB on Quartz as a Function of pH

Figure 5.4: Particle-Size Distribution for #40 Quartz

Figure 5.5: Sorption and Zeta Potential of CTAB on Quartz as a Function of pH

hydrophobic interaction between the hydrocarbon tails of the surfactant molecules. This strong hydrophobic interaction led to the formation of a more complete bilayer of surfactant molecules on the surface. Finally, the sorption isotherm reached a plateau in region IV at an aqueous solution concentration of about 9×10^{-4} M, when the maximum bilayer coverage was formed on the surface. Here, the sorption density on the quartz surface remained constant because the surface had become saturated at the maximum bilayer coverage..

Unlike some surfactant systems, the maximum coverage occurred at a CTAB solution concentration above the CMC, which occurred at 3×10^{-4} M in the presence of 0.01M NaCl. This observation is contradictory to the generally accepted fact that the sorption isotherm reaches a plateau in the vicinity of the CMC (Rosen, 1989). McCaffery and Cram (1971) characterized the sorption of CTAB on quartz above the CMC as extremely erratic. They also found that the sorption density increased with concentration beyond the CMC (1×10^{-3} M in the absence of salt), up to at least 5×10^{-3} M. Similarly, Rubio and Goldfarb (1971) observed that the sorption density for CTAB on Aerosil 200 colloidal silica increased with CTAB concentration above the CMC, at least up to 5×10^{-3} M. In contrast, others have examined the sorption of CTAB onto other types of silica (Bijsterbosch, 1974), on silica gel (Zhu et al., 1989), on hydroxyapatite and francolite (Hanna and Saleeb, 1980), on titania (Stratton-Crawley and Shergold, 1981), and observed that the isotherm reached a plateau in the vicinity of the CMC.

Thus, the various studies give conflicting results regarding the sorption of CTAB on various solids above the CMC. To resolve this question, a detailed investigation may be warranted. First, the studies outlined above were conducted under a variety of different conditions. If sorption above the CMC is dependent upon temperature, pH, ionic strength, or the solid surface's characteristics, a systematic study varying these conditions may

elucidate when such sorption may occur. Also above the CMC, the percent change in aqueous CTAB concentration due to sorption is small, conceivably introducing large errors in the calculation of sorption density. To avoid this problem, other techniques for CTAB analysis, such as two-phase titration or HPLC, might be tried.

5.2 Interfacial Tension and Contact Angle Measurements

A significant effort was devoted to the development of a methodology to give accurate results in the measurement of interfacial tension and contact angle. The ADSA system had been relatively recently developed when the apparatus was set up for this project. As far as we know, this represents its first application to surfactant systems.

5.2.1 Air-Water-CTAB-Quartz System

Surface Tension

Figure 5.6 gives the surface tension of CTAB solution in air as a function of time for a range of CTAB concentrations. The surface tension dropped sharply in the first 2 to 5 minutes after the drop was formed. After 10 minutes, the surface tension decreased by about 0.3 dynes/cm every 10 minutes, for at least an hour, the usual time frame of observation. There are two possible explanations for the slow decrease of surface tension with time:

(1) Reorientation of the CTAB molecules at the surface: The diffusion of CTAB molecules from the bulk solution to the air-water interface is relatively fast, on the order of 2 to 5 minutes. However, the reorientation or redistribution of CTAB molecules at the surface may be a slow process. Initially, the CTAB molecules may assume one configuration or distribution on the surface. But as time progresses, the configuration or distribution may

Figure 5.6: Surface Tension for Air-Water-CTAB System as a Function of Time

change, resulting in a slow decrease of surface tension over the time period of hours.

(2) Presence of highly surface-active impurities: The presence of trace concentrations of highly surface-active impurities, for example a C₂₀ or a C₂₄ chain amine, might result in lowering of the surface tension. Because of the lowness of the concentration and the size of the molecules, the movement of impurities to the surface might be slow.

The impact of impurities on surface tension has been observed by previous researchers. For example, Mysels (1986) compared the surface tension results he obtained for untreated solutions of sodium dodecyl sulfate (SDS) with samples he purified by passing through SepPak C₁₈ cartridges (Waters, Milford, MA) and by foaming. He observed that the surface tension of the unpurified samples decreased with time over a period of at least an hour, whereas those that were passed twice through SepPak cartridges and foamed dropped sharply in the first few seconds, and then remained virtually constant for at least an hour.

From our attempts to purify CTAB (Section 4.1; Appendix A.2), we concluded that trace amounts of highly surface-active impurities were the cause of the slow decrease in surface tension with time. Based on Mysels's (1986) experience and ours, a procedure was developed for handling the effects of trace impurities. The time period for measurement was defined so that it was of sufficient length to allow the surfactant to diffuse to the surface, yet short enough so that the impurities had not yet impacted the surface tension. Using this rule-of-thumb, measurements taken at 10 minutes were reported, noting that it appeared to take about 2 to 5 minutes for the surface and bulk solution to equilibrate with respect to CTAB.

The relationship between surface tension, aqueous phase CTAB concentration and pH

given in Table 5.1 and illustrated in Figure 5.7 is characteristic of aqueous solutions of surfactants (Rosen, 1989). The surface tension decreased log-linearly from a CTAB concentration of about 1×10^{-5} M to 3×10^{-4} M, after which the surface tension is almost constant. These data suggest that the critical micelle concentration (CMC) of CTAB for $[\text{NaCl}] = 0.01$ M is 3×10^{-4} M, which compares favorably with the value of 2.7×10^{-4} M reported by McCaffery and Cram (1971). The effectiveness of a surfactant, defined as $\Pi_{\text{CMC}} = \gamma^0 - \gamma^{\text{CMC}}$, where γ^0 is the surface tension in the absence of surfactant, and γ^{CMC} is the surface tension at the CMC of the surfactant (Rosen, 1989) is $72.3 - 35.9 = 36.4$ dynes/cm, giving a proportional reduction of 49.7%. Since the ionization of CTAB is independent of pH over the range examined, no dependence of surface tension on pH is seen.

Contact Angle

Figure 5.8 shows measurement of the advancing and receding contact angles as a function of time. Measurements such as these were used to determine the time at which measurements were taken (Section 4.2.2.2). Table 5.2 and Figure 5.9 show the measurements for solutions of CTAB on quartz as a function of CTAB concentration for pH values 6 and 9. The droplet phase was air. However, the contact angle was measured through the aqueous phase and the terms "advancing and receding" refer to the aqueous phase. The reproducibility of the contact angle measurements is $\pm 5^\circ$. Unlike the surface tension measurements, the contact angle depends on pH, showing a larger angle at pH 9 than at pH 6. This may be attributed to the greater amount of CTAB that sorbed to the quartz surface at pH 9 (Figure 5.3).

A comparison of Figures 5.5 and 5.9 shows the relationship between surface condition and contact angle. At low CTAB concentrations of about 1×10^{-6} M, the quartz surface is highly hydrophilic, corresponding to the region where the quartz is negatively charged. As

Table 5.1 Surface Tension for Air-Water-CTAB System

pH=6		pH=9	
[CTAB] (moles/liter)	Surface tension (dynes/cm)	[CTAB] (moles/liter)	Surface tension (dynes/cm)
1×10^{-6}	72.3	1×10^{-6}	70.7
1×10^{-5}	69.4	1×10^{-5}	65.8
5×10^{-5}	55.8	2×10^{-5}	66.4
8×10^{-5}	53.4	5×10^{-5}	55.9
1×10^{-4}	49.1	1×10^{-4}	50.1
2×10^{-4}	38.7	2×10^{-4}	43.9
4×10^{-4}	36.7	3×10^{-4}	39.1
1×10^{-3}	37.0	5×10^{-4}	37.4
2×10^{-3}	35.9	1×10^{-3}	39.4

Figure 5.7: Surface Tension for Air-Water-CTAB System as a Function of Concentration

Figure 5.8: Contact Angles for Air-Water-CTAB-Quartz System as a Function of Time

Table 5.2. Measured Contact Angles for Air-Water-CTAB-Quartz System

pH=6				pH=9		
[CTAB] (moles/liter)	Advancing θ (deg)	Receding θ (deg)	[CTAB] (moles/liter)	Advancing θ (deg)	Receding θ (deg)	
1×10^{-6}	13	125	1×10^{-6}	17	16	
1×10^{-5}	47	37	1×10^{-5}	59	56	
5×10^{-5}	57	51	2×10^{-5}	63	61	
8×10^{-5}	62	50	5×10^{-5}	64	59	
1×10^{-4}	64	47	1×10^{-4}	60	57	
2×10^{-4}	47	27	2×10^{-4}	44	39	
4×10^{-4}	14	13	5×10^{-4}	15	14	

All values of θ are given as measured through the aqueous phase.

Figure 5.9: Contact Angles for Air-Water-CTAB-Quartz System as a Function of Concentration

the CTAB concentration increases, the contact angle increases. The advancing contact angle goes through a maximum of about 64° at $[\text{CTAB}] = 1 \times 10^{-4}$ M at pH 6 and $[\text{CTAB}] = 5 \times 10^{-5}$ M at pH 9. This maximum occurs in the vicinity of the isoelectric point of quartz, which is about 1.8×10^{-4} M at pH 6 and 6×10^{-5} M at pH 9. At concentrations close to the CMC, the contact angle decreases, suggesting that the formation of a surfactant bilayer makes the surface strongly hydrophilic again.

The coincidence of the maximum contact angle of about 64° with the isoelectric point of the solid is not unilaterally corroborated by previous investigators. For a system of air-water-quartz-CTAB (in the absence of any background electrolyte), McCaffery and Mungan (1970) observed a maximum advancing contact angle of 60° , which occurred at a CTAB concentration of 7×10^{-4} M, slightly below the CMC, which for CTAB in pure water is 9.5

$\times 10^{-4}$ M. In the presence of NaCl as the electrolyte, Pashley et al. (1988) believed the maximum value to be around 95° , citing their earlier measured value of about 65° (Pashley and Israelachvili, 1981) to result from impurities removable by recrystallization from a 70:30 acetone-ether mixture. To decide whether this seemed a logical explanation, we also tried purifying CTAB by recrystallization from a mixture of methanol and acetone followed by recrystallization from hexane saturated with ethanol. However, our work showed no significant difference in values measured for the surface tension or the contact angle. Perhaps the discrepancies result from other differences in the experimental procedures. Pashley et al. (1988) measured the contact angle formed by a drop of CTAB solution in air, whereas we measured the contact angle formed by a captive air bubble inside the CTAB solution. Thus, we measured the water-receding angle first followed by the water-advancing angle, while the order was reversed in the first study by Pashley and coworkers. Furthermore, in our study, the quartz slide was allowed to soak in CTAB solution prior to making the measurements. Curiously enough, only the advancing angle is affected. In the case of the receding angle, our measured maximum value of near 50° is close to the value obtained by both McCaffery and Mungan (1970) and Pashley et al. (1988).

5.2.2 o-Xylene-Water-CTAB-Quartz System

Interfacial Tension

Figure 5.10 shows the interfacial tension for the o-xylene-water-CTAB system as a function of time for a range of aqueous phase CTAB concentrations. The interfacial tension dropped sharply in the first 5 to 10 minutes, after which it remained constant. For all CTAB concentrations, the interfacial tension was constant after 20 minutes equilibration time. Therefore, all measurements for this system were made after 20 minutes. The behavior of the interfacial tension over time for the o-xylene-water-CTAB system was decidedly different from that for the air-water-CTAB system, where the values decreased

continuously for at least a couple of hours. One possible explanation is that the trace impurities in the CTAB solution responsible for the slow decrease in surface tension were preferentially soluble in xylene, and simply partitioned into the bulk organic liquid phase rather than remaining at the interface.

The interfacial tension decreased log-linearly from 35.0 dynes/cm to 2.1 dynes/cm achieved at 2.0×10^{-4} M, after which the interfacial tension was essentially constant (Figure 5.11; Table 5.3). Based on these data, $\Pi_{\text{CMC}} = 32.9$ dynes/cm, a value similar to the value of 36.4 dynes/cm observed in the air-water system. Here, however, the proportional decrease is larger: 94.0% versus 49.7% for the air-water system. The interfacial tension measurements also suggest a CMC value of 2×10^{-4} M, which is in good agreement with the value of 2.3×10^{-4} M reported by McCaffery and Cram (1971) for the dodecane-water-CTAB system. Furthermore, this value is close to that for the air-water system of 3×10^{-4}

Table 5.3 Interfacial Tension for o-Xylene-Water-CTAB System

pH=6		pH=9	
[CTAB] (moles/liter)	Surface tension (dynes/cm)	[CTAB] (moles/liter)	Surface tension (dynes/cm)
1×10^{-6}	35.0	1×10^{-6}	35.0
1×10^{-5}	18.2	1×10^{-5}	18.2
2×10^{-5}	14.3	2×10^{-5}	14.5
5×10^{-5}	8.2	5×10^{-5}	9.4
1×10^{-4}	5.6	1×10^{-4}	5.1
2×10^{-4}	2.1	2×10^{-4}	2.2
5×10^{-4}	2.1	5×10^{-4}	2.1

Figure 5.10: Interfacial Tension for o-Xylene-Water-CTAB System as a Function of Time

Figure 5.11: Interfacial Tension for o-Xylene-Water-CTAB System as a Function of Concentration

M, suggesting again that the replacement of the air phase with xylene has little impact on the aqueous phase behavior of CTAB. Like the surface tension for the air-water-CTAB system, the interfacial tension for the xylene-water-CTAB system is independent of pH.

Contact Angle

Despite the similarities in the interfacial properties of the air-water-CTAB and xylene-water-CTAB systems, the wettability behavior is distinctly different. Figure 5.12 shows values for the advancing and the receding contact angles as a function of time. Measurements such as these were used to determine the time at which measurements were made (Section 4.2.2.3). Table 5.4 and Figure 5.13 show the measured values for the advancing and the receding contact angles at pH values 6 and 9. The reproducibility of these measurements was $\pm 5^\circ$. At a concentration of 1×10^{-6} M, negligible CTAB was sorbed on the quartz surface and the contact angle was small, suggesting that the quartz was hydrophilic. As the CTAB concentration increased, the contact angle exceeded 90° , indicating that the quartz surface had become hydrophobic. At pH 6, the contact angle reached a maximum of 155° at about $[\text{CTAB}] = 1 \times 10^{-4}$ M, again close to the isoelectric point of the CTAB-coated quartz. At a particular CTAB concentration, the hydrophobicity of the quartz surface increased with pH, due to the increased sorption density. At pH 9, above $[\text{CTAB}] = 5 \times 10^{-5}$ M, the xylene drop spread on the quartz surface, giving a maximum contact angle of 180° .

As the CTAB concentration continued to increase, the contact angle remained greater than 90° . This result agrees with the observation of Menezes et al. (1989), but contradicts the work of McCaffery and Cram (1971), who observed that the receding contact angle dropped to about 10° at $[\text{CTAB}] = 1 \times 10^{-3}$ M in the presence of 0.01 M NaCl in a system composed of dodecane, water, quartz and CTAB. These conflicting observations are perhaps related to whether the integrity of the sorbed bilayer of CTAB on the quartz surface

Figure 5.12: Contact Angles for o-Xylene-Water-CTAB-Quartz System as a Function of Time

Table 5.4. Measured Contact Angles for o-Xylene-Water-CTAB-Quartz System

pH=6				pH=9		
[CTAB] (moles/liter)	Advancing θ (deg)	Receding θ (deg)	[CTAB] (moles/liter)	Advancing θ (deg)	Receding θ (deg)	
1×10^{-6}	15	15	1×10^{-6}	15	15	
1×10^{-5}	91	70	5×10^{-6}	49	48	
5×10^{-5}	139	118	1×10^{-5}	100	98	
8×10^{-5}	143	131	2×10^{-5}	143	131	
1×10^{-4}	155	146	5×10^{-5}	116	110	
2×10^{-4}	148	125	1×10^{-4}	180	180	
5×10^{-4}	150	135	2×10^{-4}	180	180	
1×10^{-3}	140	135	5×10^{-4}	180	180	

All values of θ are given as measured through the aqueous phase.

Figure 5.13: Contact Angles for o-Xylene-Water-CTAB-Quartz System as a Function of Concentration

was maintained. If an intact bilayer exists, the charged head groups of CTAB would be outermost, endowing the surface with hydrophilic properties. However, if the top layer of CTAB molecules is disturbed, the xylene may spread on the exposed nonpolar tails of the CTAB molecules whose charged heads are oriented towards the quartz surface. Indeed, in the process of making contact angles in this study, it was observed that when a drop of xylene was initially placed on a quartz slide, the contact angle was less than 90° for a couple of minutes. Then, the xylene droplet suddenly spread on the surface, indicating that the quartz surface had become hydrophobic. Furthermore, this behavior was limited to droplets of an adequate size: very small drops (too small for accurate measurements) did not spread on the surface, suggesting that a sufficient gravitational force was necessary to disrupt the bilayer.

5.3 Capillary Pressure-Saturation Measurements

Both primary drainage and spontaneous imbibition capillary pressure-saturation measurements were made for the air-water-quartz and the xylene-water-quartz systems for a range of CTAB concentrations, selected to span the range of observed wettabilities, at pH 6 and $[\text{NaCl}] = 0.01\text{M}$. Measurements were also attempted at pH 9. However, it proved infeasible to maintain a system at pH 9 over the weeks that it took to generate both drainage and imbibition relationships due to contamination with atmospheric CO_2 .

5.3.1 Air-Water-CTAB-Quartz System

Figure 5.14 shows the measured drainage and imbibition capillary pressure-saturation relationships for the air-water system in the absence of CTAB. Figure 5.14 also shows the corresponding relationships for various aqueous phase concentrations of CTAB. Duplicate and triplicate experiments gave a measure of the reproducibility of the measurements. The air-entry pressure, which is the pressure at which drainage essentially begins, did not show much deviation in replicate experiments. However, the residual water saturation varied by about 5% from one replicate experiment to another, particularly in the experiments where CTAB was present.

The imbibition relationship showed a greater range of behavior than the drainage relationship, implying a greater dependence on the surface conditions. At small contact angles, the aqueous phase imbibed strongly. As the contact angle increased, the aqueous phase imbibed less. At the isoelectric point of the CTAB-coated quartz, corresponding to the maximum value of the contact angle of 64° , the aqueous phase showed the least imbibition. The fact that there still was substantial imbibition at this value for θ_A was unexpected based on results reported in other studies. For example, Morrow (1976) and

Figure 5.14: Measured Capillary Pressure-Saturation Relationships for Air-Water-CTAB-Quartz System

Demond (1988) observed no imbibition above a contact angle of about 60° - 65° . Yet, these past studies generated a range of contact angles through the use of a variety of liquid pairs, rather than through the use of a surfactant. Perhaps the greater imbibition observed here resulted from the time-dependent behavior of the interfacial properties in the air-water-CTAB system. In the measurements made in this study, it was observed that the interfacial properties of the air-water-CTAB system showed greater changes over time than those of the xylene-water-CTAB system. Furthermore, the advancing angle, the operative angle in imbibition, showed more change than the receding angle. If the surface tension continued to decline slowly during the weeks that it took to complete a capillary pressure experiment, this drop may have decreased the contact angle according to Young's equation (Eqn. 2-7), resulting in greater imbibition than expected based on values of contact angles measured after 10 minutes. A similar reversion to a more strongly water-wet state was also noted by Morrow et al. (1973) who observed that imbibition was highly sensitive to variations in the contact angle in the range of 40° - 70° .

5.3.2 o-Xylene-Water-CTAB-Quartz System

Figure 5.15 gives the drainage and imbibition capillary pressure-saturation relationships for the o-xylene-water system as a function of aqueous phase CTAB concentration. When the CTAB concentration is 0.0 M or 1×10^{-5} M, the quartz is hydrophilic. Therefore, drainage refers to the displacement of water by xylene. On the other hand, when the CTAB concentration is 5×10^{-5} M, the quartz is hydrophobic and drainage refers to the displacement of the xylene by the aqueous phase. Replicate runs for 0.0 M and 5×10^{-5} M CTAB showed reasonable reproducibility; both the entry pressure and the residual saturation showed little deviation for replicate experiments. The drainage capillary pressure-saturation relationship for $[\text{CTAB}] = 1 \times 10^{-5}$ M (Figure 5.15) showed a gradually increasing slope, unlike the data obtained at other CTAB concentrations, which

Figure 5.15: Measured Capillary Pressure-Saturation Relationships for o-Xylene-Water-CTAB-Quartz System

showed an essentially flat region for saturations down to about 0.3, followed by a steep slope at low saturations. This characteristic was attributed to the lack of sufficient equilibration time for these measurements. The equilibration time between incremental pressure changes had been set at about one day, based on preliminary measurements with air-water systems. However, measurements as a function of time showed that the cells continued to drain over a time period of anywhere from one to three days under these experimental conditions.

Similar to the air-water system, the imbibition relationship showed a greater range of behavior than the drainage relationship, implying a greater dependence on the surface conditions. Imbibition occurred when the contact angle is small, i.e., for [CTAB] = 0.0 M. However, no imbibition occurred for the other two CTAB concentrations where the contact angle was large.

5.3.3 Scaling of Capillary Pressure-Saturation Relationships

Based on Eqn. (2-11), a number of modifications of Leverett's function were proposed:

$$P_c^* = \frac{P_c}{\alpha} \quad (5-1)$$

yielding for the prediction of capillary pressure-saturation relationships:

$$[P_c]_{CS} = \alpha [P_c]_{AIR/H_2O} \quad \text{at a given } S_e \quad (5-2)$$

where:

subscript cs = contaminated system, and

α is a scaling factor given by the following equations:

$$\frac{\gamma_{CS}}{\gamma_{AIR/H2O}} \quad (5-3)$$

$$\frac{[\gamma \cos \theta]_{CS}}{[\gamma \cos \theta]_{AIR/H2O}} \quad (5-4)$$

$$\frac{[\gamma \cos \theta Z(\theta)]_{CS}}{[\gamma \cos \theta Z(\theta)]_{AIR/H2O}} \quad (5-5)$$

$$\frac{[\gamma \cos \theta_R Z(\theta)]_{CS}}{[\gamma \cos \theta_R Z(\theta)]_{AIR/H2O}} \quad (5-6)$$

where:

$Z(\theta)$ = curvature correction functions defined by Eqn. (2-14), and

θ_R = contact angle corrected for roughness.

The scaling factors given in Eqns. (5-3) through (5-6) were initially tested using data from Demond (1988). The contact angles were corrected for roughness, using the correlations developed by Morrow (1975) for well-roughened surfaces (Table 2.1). The curvature correction functions were calculated using equations given in Melrose (1965) assuming that (i) the sample packing was a weighted average of a square array (open or simple cubic) and a triangular array (close or tetrahedral), where the weighting factor, x , was determined by the measured porosity of the sample:

$$x\phi_C + (1 - x)\phi_T = \phi_S \quad (5-6)$$

where:

ϕ_C = porosity of cubic packing = 0.4764,

ϕ_T = porosity of tetrahedral packing = 0.2595, and

ϕ_S = measured porosity of sample,

and (ii) the particular type of imbibition which occurred was reinvasion, as recommended by Melrose (1965) for liquid-liquid systems. The application of these equations to the data set in Demond (1988) and the calculations of the goodness of their predictive abilities are summarized in Demond and Roberts (1991). Based on this evaluation, the most accurate scaling factor appeared to be that given by Eqn. (5-6). In particular, this equation was able to predict the lack of imbibition observed in the organic liquid-water systems where the intrinsic contact angle was greater than 60° .

To determine whether the scaling factor defined by Eqn. (5-6) could also predict the trends observed in the systems containing surfactants, the appropriate scaling factors were calculated. The calculated scaling factors for the air-water-CTAB-quartz system are listed in Table 5.5. The intrinsic contact angles for drainage are the receding angles given in Table 5.2, whereas the intrinsic contact angles for imbibition are the advancing angles given in the same table. These angles were corrected for roughness using the equations given by Morrow (1975) for well-roughened surfaces (Table 2.1) and for interfacial curvature according to the method outlined in Melrose (1965), assuming that imbibition occurs under equilibrium conditions (as recommended by Melrose for gas-liquid systems). By multiplying the capillary pressures of the air-water-quartz system (Figure 5.14, [CTAB] = 0M) by the calculated scaling factors, the corresponding capillary pressures for the air-water-CTAB-quartz systems were estimated. A comparison of the measured and estimated capillary pressure relationships for drainage and imbibition is shown in Figure 5.16. Eqn. (5-6) did not yield as accurate predictions for the air-water-CTAB systems as was anticipated based on the experience with the data from Demond (1988) and reported in Demond and Roberts (1991). In particular, the equation predicted no imbibition at [CTAB] = 1×10^{-4} M when, in fact, the system imbibed substantially. Thus, the system acted

Table 5.5. Calculated Scaling Factors for Air-Water-CTAB-Quartz System at pH 6

Process	CTAB conc. (moles/liter)	γ (dynes/cm)	θ_{INT} (degs)	θ_R (degs)	$Z(\theta)$	Scaling factor
DRAINAGE	0.0	72	2	0	1.00	1.00
	2.5×10^{-5}	59	37	2	1.05	0.86
	1×10^{-4}	49	47	4	1.10	0.74
	4×10^{-4}	38	13	0	1.00	0.52
IMBIBITION	0.0	72	5	0	0.92	1.00
	2.5×10^{-5}	59	47	51	0.21	0.12
	1×10^{-4}	49	64	86	No imbibi- tion	0.00
	4×10^{-4}	38	14	0	0.78	0.44

significantly more water-wet than expected based on the contact angle and previous experience with organic liquid-water systems whose contact angles were in the vicinity of 65° .

Table 5.6 lists the scaling factors for drainage and imbibition for the o-xylene-water-CTAB-quartz system. To yield the correct scaling factors in situations where the system reverses its wettability, attention must be paid to determining the appropriate intrinsic contact angle. For drainage, the appropriate θ is the receding angle if water is the wetting phase, whereas it is the advancing angle if xylene is the wetting phase. For imbibition, the appropriate θ is the advancing angle if water is the wetting phase, whereas it is the receding angle if xylene is the wetting phase. Figure 5.17 compares the measured and predicted

Figure 5.16: Comparison of Measured and Predicted Capillary Pressure-Saturation Relationships for Air-Water-CTAB-Quartz System

Table 5.6. Calculated Scaling Factors for o-Xylene-Water-CTAB-Quartz System at pH = 6

Process	System	[CTAB] (moles/liter)	Interfacial tension (dynes/cm)	Measured θ (deg) ^b	θ through the wetting phase θ_{wet} (deg)	$\theta_{R_{wet}}$ (deg)	$Z(\theta_{wet})$	Scaling factor ^c
DRAINAGE ^a	air-water	0.0	72.3	2	2	0	1.00	1.00
	xylene-water	0.0	35.0	15	15	0	1.01	0.49
		1×10^{-5}	18.2	70	70	15.1	1.49	0.36
		5×10^{-5}	8.2	139	41	2.4	1.07	0.12
IMBIBITION ^a	air-water	0.0	72.3	5	5	0	0.92	1.00
	xylene-water	0.0	35.0	15	15	0	0.88	0.35
		1×10^{-5}	18.2	91	91	138.8	No imbibition	0.00
		5×10^{-5}	8.2	118	62	80.8	No imbibition	0.00

^a Drainage refers to the displacement of the wetting phase by the nonwetting phase, whereas imbibition refers to the displacement of the nonwetting phase by the wetting phase.

^b θ is given as measured through the aqueous phase. For drainage, the appropriate θ is the receding angle if water is the wetting phase, whereas it is the advancing angle if xylene is the wetting phase. For imbibition, the appropriate θ is the advancing angle if water is the wetting phase, whereas it is the receding angle if xylene is the wetting phase.

^c Scaling factor =
$$\frac{[\gamma \cos \theta_R Z(\theta_{wet})]_{ORG/H_2O/CTAB}}{[\gamma \cos \theta_{R_{wet}} Z(\theta_{wet})]_{AIR/H_2O}}$$
 as derived from Equation 3.

Figure 5.17: Comparison of Measured and Predicted Capillary Pressure-Saturation Relationships for o-Xylene-Water-CTAB-Quartz System

capillary pressure-saturation relationships. This figure shows that Eqn. (5-6) is capable of estimating the trends in the capillary pressure-saturation relationship induced by the sorption of surfactants in organic liquid-water systems. Specifically, Eqn. (5-6) can predict the lack of imbibition seen $[CTAB] = 1 \times 10^{-5} \text{ M}$ and $5 \times 10^{-5} \text{ M}$ even though the system is intermediate-wet in the former case and organic-wet in the latter.

Although the inability to prevent contamination with atmospheric carbon dioxide made it infeasible to obtain capillary pressure measurements at pH 9, the success in predicting the changes resulting from surfactant sorption in organic liquid-water systems at pH 6 suggests that Eqn. (5-6) may be used to estimate the changes that would result with an increase in pH. Table 5.7 lists the scaling factors necessary to generate the capillary pressure relationships at pH 9 and Figure 5.18 shows a comparison between the estimated capillary pressure relationships at pH 6 and pH 9. At $[CTAB] = 1 \times 10^{-5} \text{ M}$, the system reverses wettability between pH 6 and 9. Thus at pH 6, drainage refers to displacement of water by xylene and imbibition refers to the displacement of xylene by water; at pH 9, drainage refers to the displacement of xylene by water, and imbibition, the displacement of water by xylene. Based on the results shown in Figure 5.18, it appears that an increase in pH can result in substantial changes in the capillary pressure-saturation relationships at the same equilibrium surfactant concentration.

Table 5.7. Calculated Scaling Factors for o-Xylene-Water-CTAB-Quartz System at pH = 9

Process	System	[CTAB] (moles/liter)	Interfacial tension (dynes/cm)	Measured θ (deg) ^b	θ through the wetting phase θ_{wet} (deg)	$\theta_{R_{wet}}$ (deg)	$Z(\theta_{wet})$	Scaling factor ^c
DRAINAGE ^a	air-water	0.0	72.3	2	2	0	1.00	1.00
	xylene-water	0.0	35.0	15	15	0	1.01	0.49
		1×10^{-5}	18.2	100	80	25.8	2.36	0.53
		5×10^{-5}	9.4	180	0	0	1.00	0.13
IMBIBITION ^a	air-water	0.0	72.3	5	5	0	0.92	1.00
	xylene-water	0.0	35.0	15	15	0	0.88	0.35
		1×10^{-5}	18.2	98	82	120.8	No imbibition	0.00
		5×10^{-5}	9.4	180	0	0	1.00	0.14

^a Drainage refers to the displacement of the wetting phase by the nonwetting phase, whereas imbibition refers to the displacement of the nonwetting phase by the wetting phase.

^b θ is given as measured through the aqueous phase. For drainage, the appropriate θ is the receding angle if water is the wetting phase, whereas it is the advancing angle if xylene is the wetting phase. For imbibition, the appropriate θ is the advancing angle if water is the wetting phase, whereas it is the receding angle if xylene is the wetting phase.

^c Scaling factor = $\frac{[\gamma \cos \theta_R Z(\theta_{wet})]_{ORG/H_2O/CTAB}}{[\gamma \cos \theta_{R_{wet}} Z(\theta_{wet})]_{AIR/H_2O}}$ as derived from Equation 3.

Figure 5.18: Comparison of Predicted Capillary Pressure-Saturation Relationships for o-Xylene-Water-CTAB-Quartz System at pH 6 and pH 9

6.0 CONCLUSION AND RECOMMENDATIONS

This work showed that the capillary pressure-saturation relationship, a key relationship in the description of multiphase flow, can be significantly altered by sorption at the interfaces of a system. The impact of sorption on interfacial properties such as zeta potential, contact angle and interfacial tension, in systems composed of air, water, CTAB and quartz, and o-xylene, water, CTAB and quartz were quantified and used to correlate sorption with changes in capillary pressure. Sorption of a surface-active species such as CTAB can reduce the interfacial tension between the two fluid phases, as well as alter the interfacial tension between the quartz and the aqueous phase, as indicated by the increase in the zeta-potential. The maximum change in wettability, as indicated by the contact angle, occurred near the isoelectric point of the CTAB-coated quartz. The spontaneous imbibition capillary pressure relationship is more sensitive to the changes in the interfacial properties than the drainage relationship. At contact angles between the range of about 65° – 115° , little imbibition was generally observed. The impact of the sorption of CTAB was predicted through the use of a modified Leverett's function which included an operational contact angle derived from the intrinsic contact angle by correcting for interfacial curvature and surface roughness. The ability of this modified function to predict the capillary pressure-saturation relationships was predicated on the existence of a stable state of wettability. The modified function worked best in the organic liquid-water systems and worked less well in the air-water-CTAB-quartz systems near the maximum contact angle where there appeared to be a slow reversion to a more strongly water-wet state.

Although this study considered ideal systems, this work demonstrated the dependence of capillary pressure relationships on the presence of surface-active solutes. The immediate practical implication of this finding is that the presence of surface-active co-contaminants at DOE waste sites will likely impact the migration of organic solvents such as carbon

tetrachloride and trichloroethylene. Thus, if the actual composition of the waste is not considered and the movement of the organic solvent is modeled as if the organic liquid phase were pure, large errors might result. Furthermore, this work demonstrated the need to include a measure of the wettability, such as the contact angle, in the estimation of the capillary pressure relationships for waste systems. If these relationships are calculated based only on the interfacial tension, as is the usual practice, again, large errors might result.

In this work, the impact of a number of factors that might influence multiphase migration was minimized. To extend this work to more realistic systems, the effect of variables such as organic carbon coatings on the solid matrix, the presence of metals or additional organic solutes, and equilibration time must be considered. Organic coatings may allow the partitioning of hydrophobic compounds to the surface, thus impacting the wettability. Similarly, if metals are present, they may facilitate the sorption of organic compounds. Even in the simple system examined here, evidence of the importance of equilibration time in determining the wettability of a system was observed. Consequently, to develop a more accurate description of evaluation of the relationship between waste composition and migration of organic liquid solvents at DOE waste sites, the effect of these factors on the interfacial chemical properties of waste sites needs to be evaluated.

7.0 REFERENCES

- Abriola, L.M., and G.F. Pinder, 1985a. A multiphase approach to the modeling of porous media contamination by organic compounds, 1. Equation development. *Water Resources Research* 21(1):11-18.
- Abriola, L.M., and G.F. Pinder, 1985b. A multiphase approach to the modeling of porous media contamination by organic compounds, 2. Numerical simulation. *Water Resources Research* 21(1):19-26.
- Adamson, A.W., 1990. *Physical Chemistry of Surfaces*, 5th ed., Wiley, New York. 777pp.
- Allen, L.H., and E. Matijevic, 1969. Stability of colloidal silica, 1. Effect of simple electrolytes. *Journal of Colloid and Interface Science* 31(3):287-296.
- Amott, E., 1959. Observations relating to the wettability of porous rock. *Transactions of the AIME* 216:156-162.
- Andreas, J.M., E.A. Hauser, and W.B. Tucker, 1938. Boundary tension by pendant drops. *Journal of Physical Chemistry* 42:1001-1019.
- Aronson, M.P., M.F. Petko, and H.M. Princen, 1978. On the stability of aqueous films between oil and silica. *Journal of Colloid and Interface Science* 65(2):296-306.
- Benson, G.C., and K.S. Yun, 1967. Surface energy and surface tension of crystalline solids. In *The Solid-Gas Interface*, Vol. I, E.A. Flood, ed. Marcel Dekker, New York, pp. 203-269.
- Bethel, F.T. and J.C. Calhoun, 1953. Capillary desaturation in unconsolidated beads. *Transactions of the AIME* 198:197-202.
- Bijsterbosch, B.H., 1974. Characterization of silica surfaces by adsorption from solution: investigations into the mechanism of adsorption of cationic surfactants. *Journal of Colloid and Interface Science* 47(1):186-198.
- Buckley, J.S., K. Takamura, and N.R. Morrow, 1989. Influence of electrical surface charges on the wetting properties of crude oils. *SPE Reservoir Engineering* 4(3):332-340.
- Burdine, N.T., 1953. Relative permeability calculations from pore-size distribution data. *Transactions of the AIME* 198:71-78.
- Calhoun, J.C., Jr., M. Lewis, and R.C. Newman, 1949. Experiments on the capillary properties of porous solids. *Transactions of the AIME* 186:189-196.
- Cheng, P., D. Li, L. Boruvka, Y. Rotenberg, and A.W. Neumann, 1990. Automation of axisymmetric drop shape analysis for measurements of interfacial tensions and contact angles. *Colloids and Surfaces* 43:151-167.
- Corapcioglu, M.Y., and A.L. Baehr, 1987. A compositional multiphase model for groundwater contamination by petroleum products, 1. Theoretical considerations. *Water Resources Research* 23(1):191-200.

- Demond, A.H., 1988. Capillarity in two-phase liquid flow of organic contaminants in groundwater. Ph.D. dissertation, Department of Civil Engineering, Stanford University, Stanford, CA. 211 pp.
- Demond, A.H., F.N. Desai, and K.F. Hayes, 1993. Effects of surfactants on organic liquid-water capillary pressure-saturation relationships. Submitted for publication to Water Resources Research.
- Demond, A.H. and P.V. Roberts, 1991. Effect of interfacial forces on two-phase capillary pressure-saturation. Water Resources Research 27(3):423-437.
- Desai, F.N., A.H. Demond, and K.F. Hayes, 1992. Influence of surfactant sorption on capillary pressure-saturation relationships. In Transport and Remediation of Subsurface Contaminants: Colloidal, Interfacial, and Surfactant Phenomena, R. Knox and D. Sabatini, eds., ACS Symposium Series no. 491, American Chemical Society, Washington, D.C., pp. 133-148.
- Desai, F.N., H.R. Hammad, and K.F. Hayes, 1993a. Background electrolyte correction for electrokinetic sonic amplitude measurements. Submitted for publication to Langmuir.
- Desai, F.N., H.R. Hammad, and K.F. Hayes, 1993b. ESA measurements for silica and alumina: background electrolyte corrections. In Electroacoustics for Characterization of Particles in Suspension, National Institute of Standards and Technology, U.S. Dept. of Commerce. Accepted for publication.
- Dickinson, W., 1940. The effect of certain potassium salts on the electrophoretic mobility of cetyl acetate emulsions and on the interfacial tension between cetyl acetate and water. Transactions of the Faraday Society 36:839-846.
- Donaldson, E.C., R.D. Thomas, and P.B. Lorenz, 1969. Wettability determination and its effect on recovery efficiency. Society of Petroleum Engineers Journal 9(1):13-20.
- Dracos, T., 1978. Theoretical considerations and practical implications on the infiltration of hydrocarbons in aquifers. Proceedings of International Symposium on Groundwater Pollution by Oil Hydrocarbons, Prague, Czechoslovakia, June 5-9, 1978, pp. 127-137.
- Dumore, J.M., and R.S. Schols, 1974. Drainage capillary pressure functions and the influence of connate water. Society of Petroleum Engineers Journal 14:437-444.
- Faust, C.R., 1985. Transport of immiscible fluids within and below the unsaturated zone: a numerical model. Water Resources Research 21(4):587-596.
- Feenstra, S., and J. Coburn, 1986. Subsurface contamination from spills of denser than water chlorinated solvents. Bulletin California Water Pollution Control Association 23(4):26-34.
- Fuerstenau, D.W., and R. Herrera-Urbina, 1991. Adsorption of cationic surfactants and the flotation of minerals. In Cationic Surfactants, D.N. Rubingh and P.M. Holland, eds., Surfactant Science Series 37, Marcel Dekker, New York, pp. 407-447.
- Gaudin, A.M., and T.G. Decker, 1967. Contact angles and adsorption in the system quartz-water-dodecane modified by dodecyl ammonium chloride. Journal of Colloid

- and Interface Science 24:151-158.
- Ginn, M.E., 1970. In Cationic Surfactants, E. Jungermann, ed., Surfactant Science Series 4. Marcel Dekker, New York, pp. 341-367.
- Hanna, H.S., and F.Z. Saleeb, 1980. Adsorption and wetting behavior of precipitated hydroxyapatite and francolite in contact with cationic surfactants. Colloids and Surfaces 1:295-311.
- Hayes, K.F., 1993. Personal communication, Dept. of Civil and Environmental Engineering, University of Michigan, Ann Arbor, MI.
- Hiemenz, P.C., 1986. Principles of Colloid and Surface Chemistry, 2nd ed., Marcel Dekker, New York. 815pp.
- Holmes-Farley, S.R., R.H. Reamey, T.J. McCarthy, J. Deutch and G.M. Whitesides, 1985. Acid-base behavior of carboxylic acid groups covalently attached at the surface of polyethylene: the usefulness of contact angle in following the ionization of surface functionality. Langmuir 1:725-740.
- Jouany, C., and P. Chassin, 1987. Determination of the surface energy of clay-organic complexes by contact angle measurements. Colloids and Surfaces 27:289-303.
- Killins, C.R., R.F. Nielsen, and J.C. Calhoun, 1953. Capillary desaturation and imbibition in porous rocks. Producers Monthly 18(2):30-39.
- Kunze, G.W. and J.B. Dixon, 1986. Pretreatment for mineralogical analysis, In Methods of Soil Analysis, Part 1: Physical and Mineralogical Methods, A. Klute, ed., American Society of Agronomy, Madison, WI. p. 91-100.
- Kuppusamy, T., J. Sheng, J.C. Parker, and R.J. Lenhard, 1987. Finite element analysis of multiphase immiscible flow through soils. Water Resources Research 23(4):625-631.
- Lenhard, R.J., and J.C. Parker, 1987a. Measurement and prediction of saturation-pressure relationships in three-phase porous media systems. Journal of Contaminant Hydrology 1:407-424.
- Lenhard, R.J., and J.C. Parker, 1987b. A model for hysteretic constitutive relations governing multiphase flow, 2. Permeability-saturation relations. Water Resources Research 23(12):2197-2206.
- Leverett, M.C., 1941. Capillary behavior in porous solids. Transactions of AIME 142:152-169.
- Li, H.C., and P.L. deBruyn, 1966. Electrokinetic and adsorption studies on quartz. Surface Science 5:203-220.
- MacRitchie, F., 1990. Chemistry at Interfaces, Academic Press, San Diego, CA. 283pp.
- Marlow, B.J., D. Fairhurst and H.P. Pendse, 1988. Colloid vibration potential and the electrokinetic characterization of concentrated colloids. Langmuir 4:611-626.
- McCaffery, F.G., and P.J. Cram, 1971. Wetting and adsorption studies of the n-

- dodecane-aqueous solution-quartz system. Research Report RR-13, Petroleum Recovery Research Institute, Calgary, Canada. 43pp.
- McCaffery, F.G., and N. Mungan, 1970. Contact angle and interfacial tension studies of some hydrocarbon-water-solid systems. *Journal of Canadian Petroleum Technology* 9(3):185-196.
- McGuiggan, P.M., and R.M. Pashley, 1987. A study of surfactant solution wetting on mica. *Colloids and Surfaces* 27:277-287.
- Melrose, J.C., 1965. Wettability as related to capillary action in porous media. *Society of Petroleum Engineers Journal* 5:259-271.
- Melrose, J.C., and C.F. Brandner, 1974. Role of capillary forces in determining microscopic displacement efficiency for oil recovery by waterflooding. *Journal of Canadian Petroleum Technology* 13:54-62.
- Menezes, J.L., J. Yan, and M.M. Sharma, 1989. The mechanism of alteration of macroscopic contact angles by the adsorption of surfactants. *Colloids and Surfaces* 38(4):365-390.
- Moore, T.F., and R.L. Slobod, 1956. The effect of viscosity and capillarity on the displacement of oil by water. *Producers Monthly* 20(10):20-30.
- Morrow, N.R., 1975. The effects of surface roughness on contact angle with special reference to petroleum recovery. *Journal of Canadian Petroleum Technology* 14(4):42-53.
- Morrow, N.R., 1976. Capillary pressure correlations for uniformly wetted porous media. *Journal of Canadian Petroleum Technology* 15(4):49-69.
- Morrow, N.R., P.J. Cram, and F.G. McCaffery, 1973. Displacement studies in dolomite with wettability control by octanoic acid. *Society of Petroleum Engineers Journal* 13(4):221-232.
- Morrow, N.R., and F.G. McCaffery, 1978. Displacement studies in uniformly wetted porous media, *In* *Wetting, Spreading, and Adhesion*, J.F. Padday, ed., Academic Press, New York, pp. 289-319.
- Mualem, Y., 1976. A new model for predicting the hydraulic conductivity of unsaturated porous media. *Water Resources Research* 12(3):513-522.
- Mukerjee, P., and K.J. Mysels, 1971. Critical micelle concentrations of aqueous surfactant solutions. *National Standards Reference Data*, National Bureau of Standards, Washington, DC.
- Mull, R., 1971. The migration of oil-products in the subsoil with regard to groundwater pollution by oil. *In* *Advances in Water Pollution Research*, Proceedings of 5th International Conference, 1970, Pergamon, Oxford, England, pp. HA-7(a)/ 1-8.
- Mysels, K.J., 1986. Surface tension of solutions of pure sodium dodecyl sulfate. *Langmuir* 2:423-428.
- O'Brien, R.W., 1988. Electro-acoustic effects in a dilute suspension of spherical particles.

Journal of Fluid Mechanics 190:71-86.

- Osborne, M., and J. Sykes, 1986. Numerical modeling of immiscible organic transport at the Hyde Park landfill. *Water Resources Research* 22(1):25-33.
- Parker, J.C., and R.J. Lenhard, 1987. A model for hysteretic constitutive relations governing multiphase flow, 1. Saturation-pressure relations. *Water Resources Research* 23(12):2187-2196.
- Parker, J.C., R.J. Lenhard, and T. Kuppusamy, 1987. A parametric model for constitutive properties governing multiphase flow in porous media. *Water Resources Research* 23(4):618-624.
- Parks, G.A., 1965. The isoelectric points of solid oxides, solid hydroxides and the aqueous hydroxo complex systems. *Chemical Reviews*. 65:177-198.
- Parks, G.A., 1984. Surface and interfacial free energies of quartz. *Journal of Geophysical Research* 89(B6):3997-4008.
- Pashley, R.M., and J.N. Israelachvili, 1981. A comparison of surface forces and interfacial properties of mica in purified surfactant solutions. *Colloids and Surfaces* 2:169-187.
- Pashley, R.M., P.M. McGuigan, R.G. Horn, and B.W. Ninham, 1988. Forces between bilayers of cetyltrimethylammonium bromide in micellar solutions. *Journal of Colloid and Interface Science* 126(2):569-578.
- Peaceman, D.W., 1977. *Fundamentals of Numerical Reservoir Simulation*, Elsevier, New York. 176 pp.
- Pinder, G.F., and L.M. Abriola, 1986. On the simulation of nonaqueous phase organic compounds in the subsurface. *Water Resources Research* 22(9):109s-119s.
- Powers, E.L., and H.G. Botset, 1949. Note on the relation between capillary pressure and interfacial tension. *Producers Monthly* 13(8):15-18.
- Reginato, R.J., and C.H.M. van Bavel, 1962. Pressure cell for soil cores. *Soil Science Society of America Proceedings* 26(1):1-3.
- Riley, R.G., and J.M. Zachara, 1992. *Chemical Contaminants on DOE Lands and Selection of Contaminant Mixtures for Subsurface Science Research*. DOE/ER-0547T, Office of Energy Research, U.S. Dept. of Energy, Washington, D.C. 77pp.
- Roberts, J.R., J.A. Cherry, and F.W. Schwartz, 1982. A case study of a chemical spill: PCBs, 1. History, distribution and surface translocation. *Water Resources Research* 18(3):525-534.
- Rose, W., and W.A. Bruce, 1949. Evaluation of capillary character in petroleum reservoir rock. *Transactions of the AIME* 186:127-142.
- Rosen, M.J., and H.A. Goldsmith, 1972. *Systematic Analysis of Surface-Active Agents*, 2nd ed. Wiley Interscience, New York, pp. 427-29.
- Rosen, M.J., 1989. *Surfactants and Interfacial Phenomena*, 2nd ed., John Wiley, New

York. 431pp.

- Rotenberg, Y., L. Boruvka, and A.W. Neumann, 1983. Determination of surface tension and contact angle from the shapes of axisymmetric fluid surfaces. *Journal of Colloid and Interface Science* 93(1):169-183.
- Rubio, J., and J. Goldfarb, 1971. Stability of colloidal silica in the presence of quaternary ammonium salts. *Journal of Colloid and Interface Science* 36(2):289-291.
- Sada, E., S. Kito, and M. Yamashita, 1975. Interfacial tensions of two-phase ternary systems. *Journal of Chemical Engineering Data* 20(40):376-377.
- Scales, P.J., and E. Jones, 1992. Effect of particle-size distribution on the accuracy of electroacoustic mobilities. *Langmuir* 8:385-389.
- Stratton-Crawley, R., and H.L. Shergold, 1981. Extraction of titanium dioxide into oil from cationic surfactant solutions. *Colloids and Surfaces* 2:145-154.
- Ulrich, H.-J., W. Stumm, and B. Cosovic, 1988. Adsorption of aliphatic fatty acids on aquatic interfaces. Comparison between two model surfaces: the mercury electrode and delta-Al₂O₃ colloids. *Environmental Science and Technology* 22:37-41.
- van Dam, J., 1967. The migration of hydrocarbons in a water bearing stratum. In *The Joint Problems of the Oil and Water Industries*, P. Hepple, ed., The Institute of Petroleum, Elsevier, New York, pp. 55-96.
- Villaume, J.F., 1985. Investigations at sites contaminated with dense non-aqueous phase liquids. *Groundwater Monitoring Review* 5(2):60-74.
- Williams, D.E., and D.G. Wilder, 1971. Gasoline pollution of a groundwater reservoir: a case history. *Ground Water* 9(6):50-54.
- Zhu, B.-Y., T. Gu, and X. Zhao, 1989. General isotherm equation for adsorption of surfactants at solid/liquid interfaces, Part 2. Applications. *J. Chemical Society, Faraday Trans. 1* 85(11):3819-3824.
- Zografi, G., and B.A. Johnson, 1984. Effects of surface roughness on advancing and receding contact angles. *International Journal of Pharmaceutics* 22:159-176.

APPENDIX A

STANDARD OPERATING PROCEDURES

A.1 CLEANING OF QUARTZ

Two size fractions, #40 and F-65 (U.S. Silica, Berkeley Springs, WV) were used in this study. The #40 quartz has a particle size range of 1 to 15 μm with a median particle diameter of 5.1 μm , whereas the F-65 quartz has a particle size range of 106 to 425 μm . The washing procedure involves acid and peroxide washes followed by thorough rinsing with water, as adapted from Kunze and Dixon (1986). The acid is to remove the metal ions and the peroxide is to oxidize the organic matter. The washing procedure is described separately for the two size fractions of quartz.

#40 Quartz

Acid Wash

- 1) Put 100 gm of #40 quartz in a 250 ml polypropylene (PP) centrifuge bottle. Add 150 ml of 0.1M HCl and shake on a mechanical shaker for 24 hours. Long-term (more than 3 days) exposure of quartz to the HCl must be avoided since the acid may, over a long period of time, change the surface characteristics of the quartz.
- 2) Centrifuge at 5,000 rpm for 30 minutes and carefully remove the supernatant with an aspirator, while ensuring minimal solid loss.
- 3) The supernatant may be brownish-yellow in color. After the acid wash, some liquid always remains trapped in the interstices between the particles. This trapped liquid can be removed by washing the solid with 0.01M HCl. It is important to use acid instead of water in this step because low pH keeps the metal ions in solution. The experimental steps are described in 4 and 5 below.
- 4) Add 150 ml of 0.1M HCl to the wet solid and shake it thoroughly by hand for a couple of minutes.

- 5) Centrifuge at 5,000 rpm for 30 minutes and carefully remove the supernatant with an aspirator.
- 6) Repeat the acid wash at least once more or until the supernatant is colorless.

Peroxide Wash

- 7) To the acid washed solid, add 75 ml of Milli-Q water and 75 ml of 30% hydrogen peroxide. Adjust the pH to about 2 by adding HCl. Allow the peroxide to react with the organic matter on the solid while mixing the contents every hour. Monitor the reaction carefully since the reaction is exothermic. Do not let the contents heat up for the following two reasons: first, an increase in temperature makes the reaction vigorous and, if unchecked, the contents may even start boiling. Second, PP is resistant to 15% hydrogen peroxide below about 30°C. (With 30% peroxide, PP is excellent at 20°C and good at 50°C [Nalgene Catalog 1991, p. 176]; PP is resistant to 30% peroxide at room temperature [Cole-Parmer Catalog]).
- 8) After allowing the contents to react for 24 hours, centrifuge for 30 minutes at 5,000 rpm and 20°C. (It is recommended that the temperature be less than 26°C during centrifugation [Nalgene Catalog 1991, p. 163]). Decant the supernatant with an aspirator.
- 9) Repeat this peroxide wash until there is no reaction. If there is a reaction, there will be lots of bubbles and also the supernatant will become brownish-yellow. There will always be some bubbles as a result of the decomposition of the peroxide.

Note: Iron is one of the major impurities. It is possible to find out if any iron is present in the supernatant by putting a small amount of the supernatant in a beaker and raising its pH to about 8. If iron is present, the solution will turn brownish and a brown solid will precipitate out.

- 10) Repeat steps 7 and 8 with one difference. Shake the solid/peroxide mixture on the mechanical shaker instead of allowing the reaction to occur without continuous mixing. Most of the impurities will have been removed and so the reaction should be mild, if it occurs at all. Repeat step 10 at least once or until the supernatant is colorless.

Acid Wash

- 11) Wash the solids once more with 0.1M HCl.

Milli-Q Wash

- 12) Wash the solids at least 8 times with Milli-Q water to remove all the acid. (Add 150 ml Milli-Q water, shake the contents for a couple of minutes, centrifuge, and decant.)
Monitor the pH at the end of each wash to ensure that all the acid has been washed off.

Drying

- 13) Place the wet solid in a wide pyrex dish and dry in an oven at 105°C.

F-65 Quartz

The cleaning procedure for the F-65 quartz involves acid and peroxide washes. Since the particles are large, they settle out easily and centrifugation is not required.

Acid wash

- 1) Take 2 liter of 0.1M HCl in a 1-gal polyethylene (PE) bottle. Add 750 gm of F-65 quartz and mix the contents with a high density polyethylene (HDPE) mechanical stirring paddle for 24 hours. Let the particles settle down and decant the clear supernatant. The supernatant will be green in color because of the presence of iron. After the acid wash, some liquid always remains trapped in the interstices between the particles. This trapped liquid can be removed by washing the solid once with 0.01M HCl. It is important to use acid instead of water in this step because low pH keeps the metal ions in solution. The experimental steps are described below.
- 2) Add 1000 ml of 0.01M HCl to the wet solid and shake it thoroughly by hand for a couple of minutes. Let the particles settle and decant the supernatant.
- 3) Repeat the acid wash at least once more or until the supernatant is colorless.

Peroxide wash

- 4) To the acid washed solid, add 500 ml of Milli-Q water and 500 ml of 30% hydrogen peroxide. Adjust the pH to about 2. Allow the peroxide to react with the organic matter on the solid while mixing the contents with HDPE mechanical stirring paddle. Monitor the reaction carefully since the reaction is exothermic. Do not let the contents heat up for the following reason: An increase in temperature makes the reaction vigorous and if unchecked the contents will get hot and may even start boiling.
- 5) After allowing the contents to react for 24 hours, let the particles settle and decant the supernatant with an aspirator.
- 6) Repeat this peroxide wash until there is no reaction. If there is reaction, there will be lots of bubbles and also the supernatant will become brownish yellow. There will always be some bubbles as a result of decomposition of the peroxide.

Note: Iron is one of the major impurities. It is possible to find out if any iron is present in the supernatant by taking a small amount of the supernatant in a beaker and raising its pH to about 8. If iron is present, the solution will turn brownish and a brown solid will precipitate out.

Acid Wash

- 7) Wash the solids once more with 0.1M HCl as described earlier.

Milli-Q Wash

- 8) Wash the solids at least 8 times with Milli-Q water to remove all the acid. (Add 2000 ml Milli-Q water, shake the contents for a couple of minutes and decant). Monitor the pH at the end of each wash to ensure that all the acid has been washed off.

Drying

- 9) Place the wet solid in a wide pyrex dish and dry in an oven at 105°C.

Precautions

- 1) Wear gloves, lab coat, and safety glasses when working with hydrogen peroxide.
Work in the hood.
- 2) The peroxide reaction will result in an increase in pressure. Always open the PP bottle slowly and gently release the pressure.

A.2 CTAB PURIFICATION

CTAB (Biochemika Microselect >99%) is purified by multiple recrystallizations from an acetone-methanol (4:1 by volume) mixture.

Solubility of CTAB in acetone-methanol (4:1 by vol) mixture:

T= 5°C 1 gm CTAB in 20 gm solvent

= 21.3°C 1 gm CTAB in 10 gm solvent

= 40°C 1 gm CTAB in 4.2 gm solvent

- 1) Put 10 gm each of solid CTAB in three 250 ml polypropylene centrifuge bottles. Add 70 gm of the solvent to each of the bottles and dissolve the solid completely by warming the bottles with warm tap water. Measure the weights of the bottle, CTAB and the solvent.
- 2) Let the CTAB crystallize out slowly by keeping the solution at room temperature (22-26°C) overnight. Slow recrystallization results in nice long crystals which are expected to be pure. Furthermore, larger crystals settle down easily and the solid can be separated from the liquid by decantation.
- 3) Decant the supernatant after the crystals have settled out. The liquid remaining in the interstices can be removed by gently adding 30 ml of acetone and carefully decanting the supernatant.
- 4) Weigh the beaker along with the wet solid to get a rough idea of the amount of solid remaining.
- 5) Repeat this procedure two times for a total of three washes using the appropriate amount of the solvent to give the same concentration as before.
- 6) Freeze dry the CTAB until completely dry (about 4 hours) in freeze dryer (Virtis, Gardiner, NY).

A.3 SURFACE CHEMICAL MEASUREMENTS

A.3.1 Sorption Measurements

The aim of this experiment is to obtain the sorption isotherm for CTAB on quartz as a function of pH with NaCl as the background electrolyte. The experimental procedure is described below.

- 1) Prepare a recipe that gives the amounts of quartz, CTAB, radiolabeled (C-14) CTAB*, NaCl, HCl, NaOH, and water that need to be mixed together in order to cover the pH range 4 to 9.5 and equilibrium CTAB concentration from 1×10^{-6} to 3×10^{-3} M at an NaCl concentration of 0.01 M. The solid can be added to the centrifuge tubes in one of two ways: in the first method, a concentrated stock slurry is prepared and appropriate amount used in each centrifuge tube. This method works well for small particles (less than 20 μm). In the second method, the exact amount of the solid is weighed and added to each centrifuge tube. This is recommended for large particles (greater than 20 μm) whose slurry cannot be pipetted out easily.
- 2) To each centrifuge tube, add appropriate amounts of NaCl solution, HCl or NaOH, water, CTAB, and radiolabeled CTAB. Mix the contents and add the concentrated quartz slurry. It is important to add the quartz slurry last so that it comes in contact with uniformly-mixed CTAB and radiolabeled CTAB.
- 3) Place the tubes on a rotator and let the samples equilibrate for at least 24 hours.
- 4) Centrifuge the samples at 10,000 rpm for one hour.
- 5) Determine the CTAB concentration in the supernatant using the liquid scintillation counter.
- 6) Calculate the amount of CTAB sorbed on quartz from the change in CTAB concentration in the supernatant.

* Radiolabeled CTAI (cetyltrimethylammonium iodide) was used instead of radiolabeled CTAB because this was a relatively inexpensive stock chemical.

A.3.2 ESA Measurements

The Matec ESA-8000 (Matec Applied Sciences, Hopkinton, MA) can be used to determine the surface charge and the zeta potential of charged solids in solution. This instrument is capable of making five kinds of measurements of which the "Single Point Measurement" and "Potentiometric Titrations" were used in this study. The measured quantities are the magnitude and the phase angle of the ESA signal, pH, temperature, electrical conductivity, and the amount of acid or base added. The "Single Point Measurement" makes just one measurement, whereas the "Potentiometric Titration" makes several measurements over a range of pH values. The standard operating procedure for the ESA is described below.

I. Instrument Startup

1. Turn on the computer and type STESA or change directory to ESA and type ESA.
2. Turn on the power to the system by turning on the following components:
 - a) Wavetek
 - b) MBS 8000 (watch overload button)
 - c) Oscilloscope
 - d) Pipetter (for titrations).

II. ESA probe calibration

1. Screw the gold cap onto the ESA probe. Tighten the left screw first. Do not overtighten the screws.
2. Use 10% by volume of Ludox TM as a phase reference. This is prepared by mixing one part (volume) of Ludox TM stock solution with two parts of Milli-Q water.
3. Make a Single Point Measurement for the Ludox TM. The ESA signal should be -3.67 ± 0.1 at 25°C. The ESA signal depends on the gap between the ESA probe and the gold cap; therefore, a small change in the position of the cap would give a substantial error in the ESA signal. It may be necessary to readjust the cap position until it gives the correct ESA value. Alternatively, it is possible to multiply the calibration constant in the software in order to get the right ESA value. (The calibration constant should be changed only as a last resort if repeated attempts to adjust the gold cap position fail to give the correct ESA value for the Ludox TM.)

4. Rinse the Teflon beaker and the probes at least 6 times with Milli-Q water so that all the Ludox is removed. Use a squirt bottle to remove any solid that may be sticking onto the Teflon cover or the probes.
5. After completing the experiment (or a set of experiments), measure the ESA signal for the Ludox TM to ensure that the probe calibration is accurate.

III. pH Calibration

The software is set up to utilize a two-point pH calibration between pH 4 and pH 7 or pH 7 and pH 10. In order to measure pH over this range, three buffers are calibrated during the pH electrode calibration.

1. Place the pH probe in the pH 4 buffer at 25°C. Ensure that the thermocouple is also at 25°C. Wait for about 3 to 5 minutes for equilibration. Repeat for pH 7 and pH 10 buffers.
2. Make sure that the pH calibration is accurate by measuring the pH of the buffers in the Single Point Mode. The measured pH of the buffers should be correct to ± 0.01 pH unit.

IV. Phase Calibration

The ESA measurement process generates an electrical signal which has a particular magnitude and phase. Because the system cannot, a priori, determine whether the polarity of the signal corresponds to positive or negative electrophoretic mobility, it is necessary to calibrate the polarity with a sample of known surface charge. In addition, Phase Calibration must be performed to scan the frequencies of the electro-acoustic frequency generator to ensure that the maximum signal amplitude is measured.

Ludox TM may be used as the phase reference in some cases. If the phase angle of the sample with reference to Ludox TM is between -10° and $+10^\circ$, the sample is said to have the same charge as the reference (i.e., negative in the case of Ludox). If, on the other hand, the phase angle is around 180° or -180° ($\pm 10^\circ$), the sample has opposite charge. If the phase angle is between 10° and 170° , the material is not completely in phase or out of phase with the phase reference and a new phase reference should be used.

Once the charge on the sample solid is known, this sample should be used as the phase reference. The phase angle for this sample solid (referenced against itself)

will be close to zero. As the titration progresses the phase angle may change a little. At the isoelectric point (iep), the phase angle will jump from zero to about 180° , indicating that the charge on the solid has reversed. All these measurements must be made at constant temperature since the magnitude and phase angle of the ESA signal change with temperature.

V. Single Point Measurement

1. Fill the sample cell with the sample to be measured.
2. Keep a blanket of CO_2 -free nitrogen gas on top of the liquid surface.
3. Connect the constant-temperature bath and wait until the sample reaches the desired temperature.
4. If the charge on this sample solid is known, go to the phase calibration and use this reference solid as the phase reference as described in the previous section.
5. Make a single point measurement.

VI. Potentiometric Titration

The computer must not be in Turbo mode when performing potentiometric titrations.

1. Fill the acid and base bottles with the standardized solutions.
2. Wash the syringes in the automatic titrator by selecting the POTENTIOMETRIC TITRATION mode and then selecting WASH from the command list. Press the space bar to terminate the washing cycle for the left dispenser. The syringe on the right will then begin the washing cycle. Press the space bar to terminate washing.
3. Select the SETUP mode and enter the appropriate parameter values. Save this as a file named POTxxx, where xxx is the file generation number. The output file from the potentiometric titration is POTNxxx.ESA.
4. Perform the potentiometric titration.

A.4 INTERFACIAL TENSION AND CONTACT ANGLE MEASUREMENTS

A.4.1 Cleaning of Materials

QUARTZ SLIDES:

Wash with deionized water.

Soak in methanol for 20 minutes.

Soak in acetone for 20 minutes.

Wash with Milli-Q water.

Soak in Chromerge overnight.

Soak in 0.1M NaOH for 20 minutes.

Rinse thoroughly with Milli-Q water and store in Milli-Q water (do not let the slide dry and avoid any contact with air).

Precautions:

- 1) Never touch the clean quartz slide with bare hands, always use clean, water-washed gloves.
- 2) Use fresh Milli-Q water everyday and collect it directly in a clean container without going through the carboy.
- 3) Use HPLC grade solvents.
- 4) Change the Chromerge at least once a month or sooner if it turns greenish.

MICROMETER SYRINGE:

Glass barrel:

Procedure is the same as that for quartz slides.

Teflon parts (includes Teflon tubing) and stainless steel needle:

Wash with deionized water.

Soak in hexane for 20 minutes.

Soak in methanol for 20 minutes.

Soak in acetone for 20 minutes.

Soak the Teflon pieces in 50% "Micro" for at least 4 hours. Do not soak the stainless steel needle in Micro.

Rinse thoroughly with Milli-Q water.

Wrap in aluminum foil or place in a clean dry beaker and cover with aluminum foil in order to avoid contaminating the cleaned pieces. Dry in an oven at 105°C.

Note: Disassemble the syringe parts before cleaning.

TEFLON STAGE:

The procedure is the same as that for the Teflon parts of the syringe.

A.4.2 Axisymmetric Drop Shape Analysis (ADSA) Apparatus

Version 9/5/91

WARNING! DO NOT OPERATE THIS APPARATUS UNLESS YOU HAVE PERMISSION TO DO SO AND HAVE BEEN SHOWN HOW. THIS APPARATUS IS EXPENSIVE. DOES NOT HAVE A HARDWARE MANUAL AND IS NOT SELF-EXPLANATORY. THE INSTRUCTIONS BELOW SERVE AS A REMINDER ONLY. AND ARE FOR USE BY THOSE WHO ALREADY HAVE BEEN SHOWN HOW TO USE THE APPARATUS.

I. COMMONLY USED COMPUTER COMMANDS

mkdir "name"	--creates a directory with specified name
rmdir "name"	--removes specified directory if empty
dir	--lists files in the directory
getimg "name"	--takes a picture with specified name
getimg	--puts camera's view on the monitor
putimg "name"	--puts specified picture on the monitor screen
edlin "name"	--enters line editor to edit specified file
utlsp	--enters a program which can mark certain parts of pictures for use in input files
apen	--batch file which runs the apendant program if a proper input file is created and called input.
asess	--batch file which runs the asessile program if a proper input file is created and called input.
sess	--batch file which runs the sessile program if a proper input file is created and called ses.
ss	--batch file which runs both the asessile and sessile programs, displays the result, and then returns the screen to camera's view.

II. WEEKLY CHORES

A. Change water in the temperature bath.

- B. Change water in the humidity bottle.
- C. Make up fresh Chromerge solution for the slides and syringe barrels.
- D. Copy files to the PICTURES directory to keep.
- E. Clean out directories in the computer.
- F. Clean other items (see sheet entitled "Cleaning Procedures").

III. PENDANT DROPS

A. Preparation

1. Turn on the constant temperature bath. Two switches need to be flicked. Standard temperature is 25°C. The heater/cooler should run at least 20 minutes before starting measurements and should run continuously throughout the experiments.
2. Turn on the humidity bottle nitrogen supply (for liquid/air systems only). This should run 20 minutes before starting experiments and should be turned off after the environmental chamber is sealed. The right pressure is an exit pressure of about 15 psi and should produce gentle bubbling.

NOTE: Steps 3-11 need to be done only when a new system is being started.

3. Set magnification. About 10-11 works well for droplets of aqueous solutions of CTAB. Slightly more magnification is needed for solvents or for the smaller teflon tube size.
4. Check leveling of table. Check underneath the table to make sure that the small supports on springs near the red knobs are in contact with the table.
5. Level the environmental chamber and camera. Use the Starrett 98 level. Leveling should be done on the stand, on top of the chamber, because the weight of the heating unit causes the chamber to tilt if it is not taken into consideration. Set the level diagonally on the chamber. Keep rotating level and adjusting the leveling screws until the level indicates that the chamber is indeed level.
6. Turn on power. Turn on power supply to light source. Turn on video monitor and computer. Plug in Cohu camera.
7. Take a picture of a plumbline. The plumbline is the fishing line with nut attached. Set the environmental chamber to one side. Hang the plumbline from the micromanipulator mounted on the ringstand. The nut can be submerged in water to steady it more quickly. The camera can be adjusted (physically twisted) to make the plumbline

appear vertical before the picture is taken. Focus the camera until the line of light is seen in center of the image of the plumbline. Take picture by typing "getimg plumb."

8. Take a picture of the grid. Select the appropriate grid for the degree of magnification you intend to use. Usually the 0.025 cm grid is used for pendant drops. The grid should be placed perpendicular to the lens, mounted in a vise. Care should be taken to make sure that light is distributed evenly over the entire grid to minimize errors. The lighting can be changed by turning the light source to one side or the other, or by raising or lowering it. Making sure the blinds on the windows are shut often makes a difference. Taking pictures with the room lights off often enhances contrast. The cleanest part of the grid that can be found should be used, and it should be cleaned periodically. Dirt give computer errors. Focus the camera. Take picture by typing, "getimg grid."

9. Take a picture of chrome bar. This step is only necessary when using two liquid systems to take into account the distortion caused by viewing through a liquid. The bar should be submerged in the surrounding liquid, not the drop liquid. Take the 3mm (usually) chrome bar (Van Keuren) and stand it on end in the quartz cell in the environmental chamber filled with the correct liquid. Focus the camera by focusing the reflection line running the length of the bar. Take picture by typing, "getimg bar."

10. Type UTLSP. To run the software associated with this apparatus, see the ADSA-P manual. The program, UTLSP, is used to create data files with the location information needed for the input file. The command "Image Storage and Retrieval" is used to bring the picture on screen, and "Restore Image" and "ADSA Digitization" are used to choose the necessary points on the pictures. To select the rectangle from the grid that the computer will work with, see p. 30 in the manual. The points must be selected in the correct order. Data files are stored with a .d ending, ie plumb.d, grid.d, bar.d .

11. Create an input file following the steps outlined in the manual. If the file is named 'input' the open batch file can be used. See p. 21 under "apendant."

B. Taking pictures

1. For non-inverted drops:

Fill the syringe (Gilmont, w/teflon plunger) with the correct liquid. Attach teflon tube (instead of a needle). Discharge any air from the syringe barrel and teflon tube. This is especially important for two-liquid systems. Refill so that you start with a full syringe. Thread the metal sleeve through the septum in the top of the environmental chamber and clamp to the micromanipulator so that minor adjustments can be made. Clamp syringe to the ring stand, and guide the teflon tube down the metal sleeve until about 1/8 inch is visible on the video screen.

For inverted drops:

The J-hook needle is used on the syringe instead of the teflon tube. The septum on top of the environmental chamber will have to be removed. In some cases, the whole top of the chamber may have to be removed. The syringe should be clamped into position on a ring stand so the tip of the needle can be seen about 1/8 inch from the bottom of the video screen.

2. Form a test drop. Make a test droplet by screwing the syringe barrel. Take picture of the droplet. The x-coordinate of the starting position must be determined in UTLSP for the input file. The start position of the drop must be within the grid boundaries for the program to run. This is the point at which the computer begins analyzing the drop surface. This drop should hang for 20 minutes before a fresh drop is made and the actual measurements are begun. This removes many of the impurities that gather on the liquid surface or interface.

3 Begin measurements. Make new droplet. Take pictures over a twenty minute period at five-minute intervals. Measurements taken over a 20 minute time period will help ensure that the surface tension is not dropping too rapidly over time indicating impurities.

IV. SESSILE DROPS

A. Preparation

1. Steps 1 and 2 are the same as for the pendant drops.
3. Set magnification. For sessile drops the magnification should be as low as possible to ensure the biggest drop picture. Use 6.5-7.
4. Level the environmental chamber. See III.A.3.
5. Tilt the microscope. For inverted sessile drops, it should be tilted 2-3 degrees upward; for non-inverted, the tilt should be downward. The tilting allows the reflection of the drop to be seen in the solid surface. Without a definite reflection, the software often make errors in calculating the contact angle.
6. Take a picture of the grid. See III.A.6. The 0.025cm grid is quite small at this magnification, and if a good picture cannot be taken, a larger grid size should be used.
7. Take a picture of the bar. See III.A.7.
7. Type UTLSP. See III.A.8.
8. Create input files. Follow the steps in the ADSA software manual; see "assessile" p. 25. If the file for the assessile program is named "input" the batch file "assess"

can be used. If the file for the sessile program is called "ses", the "ss" and "sess" batch files can be used.

B. Taking pictures.

1. Soak the slide in the surrounding liquid prior to forming a droplet on the surface. The optimal length of time for soaking is not established at this time.

2. For non-inverted drops:

The slide is placed in the quartz cell in the environmental chamber. The drop can be placed on the slide by use of a stainless steel needle, or teflon tube. The needle of the syringe is placed close to the slide surface and a droplet is formed. The droplet should not fall onto the surface. The droplet is released by pulling the needle back off the video screen. Problems have been encountered with the non-inverted drops and the use of inverted drops is recommended at this point.

For inverted drops:

The special slides with side notches, central hole and numbered need to be used. The slide should be placed on the teflon stage. The septum should be placed with teflon side up on the other side of the stage, snug without air space. The ambient liquid should be poured into the quartz cell and the stage, with the slide and septum attached, should be eased into the cell at an angle. The syringe and needle should be assembled as with the pendant drops. The needle should be positioned in the hole of the slide, and should not appear in the camera's view. The drop should be formed slowly to allow equilibrium. A level slide is most important, so leveling is recommended between drops. The teflon stage is assumed to have the same slant as the environmental chamber, so the environmental chamber is what is leveled.

3. Advancing and receding contact angles can be made by increasing and decreasing the size of the drop.

4. The sessile program should be run on every drop picture to make sure the program is reading the drop edge properly.

A.5 CAPILLARY PRESSURE-SATURATION MEASUREMENTS

A.5.1 CTAB Analysis by Two-Phase Titration

Cetyltrimethylammonium bromide (CTAB) can be analyzed by titrating it against an anionic surfactant like sodium dodecyl sulfate (SDS) using the two-phase titration method with mixed indicators (Rosen and Goldsmith, 1972, pp. 427-429).

- Reagents:**
- 1) CTAB
 - 2) SDS
 - 3) Chloroform
 - 4) Acid Indicator (dimidium bromide, disulphine blue VN, ethanol, sulfuric acid)

Preparation of acid indicator

- 1) Weigh 0.5 ± 0.005 gm dimidium bromide into a 50 ml beaker.
- 2) Weigh 0.25 ± 0.005 gm disulphine blue VN into a second 50 ml beaker.
- 3) Add between 20 and 30 ml of hot 10% (vol.) ethanol in water to each beaker and dissolve.
- 4) Transfer both solutions to a 250 ml volumetric flask. Rinse each beaker with the same solvent and dilute to mark with it.
- 5) Add 200 ml of Milli-Q water, 20 ml of the above indicator, and 20 ml of 2.5 M sulfuric acid into a 500 ml volumetric flask. Dilute to 500 ml with Milli-Q water. This is the acid indicator.

Titration Procedure

- 1) Add the following compounds to a 100 ml Erlenmeyer flask:
 - 10 ml of the unknown CTAB sample ($[CTAB]_{sam}$),
 - 10 ml (approx.) of Milli-Q water,
 - 10 ml (approx.) of chloroform, and
 - 10 ml (approx.) of the acid indicator.Mix well on a magnetic stirrer and observe that the chloroform phase is blue.
- 2) Titrate the CTAB against SDS of about the same concentration as the CTAB. The end point is when the color changes from blue to pink. Record the volume of SDS consumed.

Note: 1) The concentration of SDS should be such that the buret reading is somewhere between 50 and 100% of the buret volume.

- 2) Use 25 ml of CTAB if the CTAB concentration is less than $5 \times 10^{-5} M$.

- 3) If the CTAB concentration is low (less than $2.5 \times 10^{-5} \text{M}$), the color change is gradual and the end point is not sharp. In such a case, it is best to be consistent in the color change from one titration to another.

Calculations

$$\begin{aligned} \text{Moles of CTAB} &= \text{Moles of SDS} \\ [\text{CTAB}] V_{\text{CTAB}} &= [\text{SDS}] V_{\text{SDS}} \end{aligned}$$

where

$[\text{CTAB}]_{\text{sam}}$ = concentration of the unknown CTAB sample

$[\text{SDS}]$ = concentration of the SDS

V_{CTAB} = volume of the unknown CTAB sample

V_{SDS} = volume of SDS consumed.

A.5.2 Capillary Pressure-Saturation Experiments

Version 12/24/91

1. CLEANING

All parts of the tempe cell apparatus except porous ceramic plates should be soaked in 2% Micro solution for 24 hours, scrubbed with nylon brush and rinsed thrice with Milli-Q water and air dried. Ceramic plates should be sonicated in ethanol or methanol, rinsed in Milli-Q and dried in the drying oven (105°C) overnight to remove residual moisture.

2. PACKING

A. Preparing cell

Insert viton o-ring (small) in bottom of cell and place ceramic plate on top of o-ring. Insert large viton o-rings in side grooves of cell, both top and bottom. Insert sample holder (ring) by rotating while pushing in to meet ceramic plate. The sample ring must sit firmly against plate. Using 1/2"x1" strips of vinyl tape, tape over gap between sample holder and bottom of tempe cell to prevent solid from lodging in cavity above o-ring on outside of sample holder.

B. Weighing cell

Weigh complete cell [including wing nuts (and washers if plastic cell)] empty. **Be sure that wing nuts (and washers) remain dedicated to the cell throughout experiment.** The wingnuts and washers exhibit a large variability in weight.

C. Packing

Equipment needed for packing includes: large palate knife, brick-size lead weight, wooden block with hole drilled in center, aluminum extension sleeve, 100-150 ml of soil per cell in small beaker, vibrating table (located basement in Eng. 1-A), small test tube rack for storing cells before and after vibrating.

Step 1. Deposit $\approx 1/2$ centimeter of solid in an even horizontal layer.

Step 2. Rotate cell 3 or 4 revolutions while tapping with a small wrench.

Step 3. Repeat steps 1 and 2 until cell is 3/4 full.

Step 4. Gently attach aluminum sleeve and repeat steps 1 and 2 until level of solid

is at least 1 cm above top of Tempe cell.

- Step 5. Place cell with aluminum sleeve on wooden block then on vibrating table. Center lead weight on top of aluminum sleeve. Vibrate on lowest setting for ten minutes.
- Step 6. Gently remove lead weight and aluminum sleeve, taking care not to jar cell. Using large palate knife, gently remove excess solid from top of sample holder. A smooth horizontal surface should result as the solid becomes flush with the sample holder.
- Step 7. Gently place top of Tempe cell on packed cell. Add appropriate wingnuts (and washers). Slowly tighten down top of cell by alternately tightening the three wingnuts 1-3 turns at a time.
- Step 8. Remove excess solid from outside of cell by first, scraping it off with a spatula and small brush. Then remove the rest of the excess solid using compressed air. Keep tape on throughout.

D. Reweigh cell

Calculate bulk density by:

$$\rho_b = \frac{\text{weight of soil}}{\text{volume of sample}}$$

and porosity by:

$$\phi = 1 - \frac{\rho_b}{\rho_s}$$

Using a piece of tape, label cell with porosity.

3. SATURATING CELL (for experiments not involving adsorption of surfactants)

A. Prepare solutions

Prepare 1 liter of 0.01N NaCl per cell to be saturated. Check pH. If needed, adjust pH to 6.0 ± 0.1 using aliquots of acid or base. Solution should then be deaerated by pulling a vacuum with faucet aspirator (approx. 26" Hg) until boiling stops. Deaerating 2-3 liters of solution may take 20-30 minutes. Label and parafilm deaerated solution.

B. Evacuation and Saturation

- Step 1. Seal top of Tempe cell using a Swage-Lok plug (or vacuum gauge, see below). Attach three-way valve to bottom of cell via 1/8" stainless steel tubing. Three-way valve also attached to deaerated saturating solution (through HPLC pump) and faucet aspirator.
- Step 2. Turn faucet aspirator on first, then open valve to faucet. This procedure will pull a vacuum on the bottom of the Tempe cell without letting stale water left in aspirator lines into cell. It should take 2-5 minutes to evacuate the cell to ≈ 26 " Hg. One may also exchange the plug on the top of the cell for a vacuum gauge to monitor the vacuum pressure. This is especially helpful for step 2.
- Step 3. Turn valve to off position and turn faucet off slowly. Remove parafilm from deaerated solution and crack stopper. Turn faucet to deaerated solution (HPLC pump). Saturating solution will enter cell under vacuum. Wait at least 15 minutes for solution to enter cell under vacuum alone. It may be necessary to pump (5 ml/min) the last few ml of solution into cell.
- Step 4. To insure complete saturation, let cell sit for 1-2 hours then flush three pore volumes of deaerated solution through cell at a low flow rate (5ml/min). Repeat.

4. ADSORPTION OF SURFACTANTS

Prepare about 6 liters of appropriate surfactant solution for the experiment. Connect cell to HPLC pump as you would for saturating a cell. To initially saturate cell, follow steps 1, 2, and 3 in Section 3.8. Attach tubing to top of cell instead of vacuum gauge. Pump solution through cell at 1 to 5 ml/min. **Do not** exceed 5 ml/min or disruption of the packing may occur. Use the titration method to check the concentrations of the effluent and the influent every 1/2 liter or so. Pump through an additional liter after sample appears to be saturated with surfactant. This is a safety measure to insure equilibrium at the desired concentration. Collect and save 150-200 ml of both the influent and the effluent for interfacial tension and contact angle measurements. Additionally, collect and save 50 ml of effluent if you intend to measure imbibition.

5. EQUILIBRIUM AND CONNECTION TO SYSTEM

Fill two collection vials with solution that is present in cell. Place saturated cell on wooden stand and connect to one collection vial via Swage-Lok and Teflon or stainless steel tubing. Keep the other collection vial capped. The distance between the bottom of the sample (top of ceramic plate) and the solution level in the collection vial should be minimized. Cell should remain with no applied pressure in the nonwetting phase for 24 hrs. to equilibrate with collection vial. It is not necessary to weigh or record a height change in solution level for this first collection vial used for equilibration.

Step 1. Air-liquid system: Connect top of cell to pressure regulator.

Xylene-water system: Connect top of cell to xylene reservoir using steel tubing already in place. To insure hydraulic connectivity, apply small pressure to xylene reservoir until xylene begins to drip. Pressure can be applied using a specially fitted plastic syringe or by using the Moore regulator.

Daily measurements:

Step 2. Prior to weighing unconnected vials, achieve an appropriate liquid level in the vial. That is, during drainage you may need to pour off some of the liquid and during imbibition you may need to add some solution to the vial. Weigh unconnected collection vial and record **initial** temp. and weight, for the next day. Date, time, final applied pressure and any significant ($>1/16"$) change in solution level within attached collection vial should also be recorded.

Step 3. Switch collection vials.

Step 4. Weigh collection vial just disconnected from cell and record **final** temp. and weight. These **final** values correspond to the initial values measured on the previous day.

Step 5. Weigh evaporation control vial and record temp. and weight. Since the control vial should not be opened during an experiment, the initial reading for any given day will be the same as the final reading for the previous day.

Step 6. Increase pressure (drainage) or decrease pressure (imbibition).

Step 7. The pressure increment for each measurement depends on (1) what system is being studied and (2) what section of the pressure-saturation curve is being measured at the time. Previous experiments and/or the literature should be used to adjust the pressure increment.

5. PRESSURE MONITORING SYSTEM

Regulators and gauges:

Figure 4.3 shows a schematic of the capillary pressure system for use with organic liquids. If an air/liquid system is being studied, the organic reservoir is removed. The house air is initially regulated with a two-stage Scott regulator* (0-30 psi) which should be set at 12 psi for the low pressure (50" H₂O) system and 22 psi for the 7 psi system. The current system may be operated with one of two regulator/gauge systems. For low pressures (0-50" H₂O) Model 40-2 Moore regulator should be used in series with the Wallace and Tiernan 5 psi gauge. Care should be taken not to open the Moore regulator to exceed 50" of water. Pressure increases as the regulator knob is turned clockwise. For higher pressures (0-7 psi) Model 40-7 Moore regulator should be used in series with the Wallace and Tiernan 30 psi gauge. Again, one should avoid operating the Moore regulator above 7 psi. The Wallace and Tiernan gauges are very sensitive and expensive so PLEASE avoid using them with any regulator that could overpressurize the gauges.

Traps and filters:

Molecular sieves with Drierite may not need to be replaced unless moisture content of the air is a problem. The hydrocarbon traps should be replaced after 365 days of experiments involving organic liquids. Refills are available from Anspec (Ann Arbor, MI) for both traps and filters.

*User's Note: Anyone using the pressure equipment described above should first read the manuals for all regulators and gauges. Failure to do so may result in costly (\$\$\$) damage.

END

**DATE
FILMED**

10 / 22 / 93