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

Progress Report

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ABSTRACT

The purpose of this project is to investigate how changes in interfacial chemical properties affect two-phase transport relationships. Specifically, the objective is to develop a quantitative means that will enable the prediction of changes in the capillary pressure-saturation relationship, a fundamental constitutive relationship in multiphase flow, from changes in interfacial properties, such as adsorption and electrophoretic mobility, through a knowledge of their effect on wettability.

The information presented here summarizes the progress we have made in the past eight months of the second project period. Working with a system composed of air-water-silica -cetyltrimethylammonium bromide (CTAB), we have obtained a relationship between degree of adsorption and the surface charge of silica (as measured by electrophoretic mobility), and the drainage and imbibition capillary pressure relationships of the system. As the adsorption of CTAB increases, the naturally negatively-charged silica surface becomes positively charged. This change is reflected in the contact angle whose functional dependence on CTAB concentration passes through a maximum at the isoelectric point of the silica surface. The imbibition capillary pressure relationship is more sensitive to changes in surface properties than the drainage relationship. The system shows no imbibition at the maximum contact angle. The surface tension and contact angle can be used to predict both the drainage and imbibition relationships of air-water-silica-CTAB systems from that of the air-water-silica system. The prediction is accomplished through scaling using the value of surface tension and the operational contact angle, which can obtained from the intrinsic angle through the incorporation of corrections for roughness and interfacial curvature. Thus, the capillary pressure of an aquifer undergoing remediation with surfactants need not be measured for each concentration of surfactant; it can be estimated from a knowledge of the capillary pressure of the aquifer in its native state and information about the surface properties of the system.

The bulk of this report describes the completed set of measurements for the air-water-silica -CTAB system at pH 6. We are currently working on a comparable set of measurements for the xylene-water-silica-CTAB system at pH 6. Described here are the interfacial tension, contact angle and preliminary drainage capillary pressure measurements. Our work to date shows a dependence of surface properties on pH. Consequently, in the coming year, we will also complete a set of measurements at another pH value to show the effect of pH on capillary pressure relationships.

INTRODUCTION

An improved understanding of the factors influencing the movement of a separate organic liquid phase in groundwater aquifers is important to the U.S. Department of Energy's efforts to alleviate groundwater contamination by many common solvents. The overall objective of this project is to investigate how changes in interfacial chemical properties affect two-phase flow relationships. Specifically, the objective is to develop a quantitative theory that will enable the prediction of changes in the capillary pressure-saturation relationship, a fundamental constitutive relationship in multiphase flow modeling, from changes in interfacial properties through a knowledge of their effect on wettability.

The work over the past eight months of the project summarized here shows the interrelationship between the surface chemical properties of sorption, electrophoretic mobility, contact angle, surface tension and capillary pressure, and how the effects on capillary pressure might be predicted on the basis of surface tension and contact angle. If a surface active compound, such as a surfactant, is added to or naturally occurs in the subsurface, this compound will adsorb differentially at the three interfaces of the system: organic liquid-water, water-solid, and organic liquid-solid. Through the sorption at these interfaces, the three interfacial tensions of the system will change: $\gamma_{ORG/H2O}$, $\gamma_{H2O/SOLID}$ and $\gamma_{ORG/SOLID}$. In turn, the changes in the interfacial tensions will be reflected in the capillary pressure-saturation relationships. $\gamma_{ORG/H2O}$ can be measured directly. However, $\gamma_{H2O/SOLID}$ and $\gamma_{ORG/SOLID}$ must be measured indirectly through the quantification of properties such as electrophoretic mobility and sorption. In addition, the changes in $\gamma_{H2O/SOLID}$ and $\gamma_{ORG/SOLID}$ can be monitored through changes in the contact angle, which can be measured directly.

The model system we have been examining consists of o-xylene, water, silica sand, and cetyltrimethylammonium bromide (CTAB), in which all three interfacial tensions of the system change. To get a handle on this system, we have completed an investigation of a system consisting of silica-water-CTAB, in which only two interfacial tensions change: $\gamma_{H2O/SOLID}$ and $\gamma_{AIR/H2O}$. That investigation is reported in detail here. In addition, we completed a series of interfacial tension and contact angle measurements for o-xylene, water, silica sand, and CTAB, which shows that the wettability changes are more dramatic in systems containing an organic liquid.

AIR-WATER-SILICA-CTAB

SURFACE CHEMICAL MEASUREMENTS

The protocol for sorption and electrophoretic mobility measurements was described in the progress report covering the period 07/01/89-12/31/90. Figure 1 shows the sorption of

CTAB onto silica as a function of pH. Silica has a point of zero charge at pH=2. Consequently, as the pH increases, the degree to which CTAB, a cationic surfactant, can sorb increases. For example, at the aqueous phase concentration of 2x10^{-4} moles/liter, the sorption density increases by a factor of 2 from pH=5 to pH=7. By influencing the sorption density, the pH of a subsurface system will play an important role in determining changes in wettability.

Figure 2 shows the electrophoretic mobility of silica to which CTAB has been sorbed as a function of solution phase concentration. Electrophoretic mobility is an indicator of the charge of the particle's surface. Thus, Figure 2 shows that at low CTAB coverages, silica is negatively charged. As the aqueous phase concentration increases (corresponding to an increase in sorbed CTAB), the silica reaches an isoelectric point. This point corresponds to a monolayer coverage of CTAB on the silica. As the aqueous phase concentration increases further, a bilayer of CTAB is formed and the silica becomes positively charged. The aqueous phase concentration at which the solid becomes positively charged is also a function of pH, with the transition occurring at lower concentrations with increasing pH.

SURFACE TENSION AND CONTACT ANGLE MEASUREMENTS

The technique for measuring surface tension and contact angles using the ADSA (Axisymmetric Drop Shape Analysis) apparatus was described in the last progress report. Figure 3 summarizes the data for the surface tension of the aqueous phase as a function of CTAB concentration in the aqueous phase at pH 6. The functional dependence shown in this figure is characteristic of aqueous solutions of surfactants. Initially, the surface tension decreases rapidly with small increases in surfactant concentration. But when the concentration of CTAB is sufficiently high that a monolayer of CTAB is formed at the water-air interface, the decrease in surface tension falls off dramatically.

Figure 4 shows the measured advancing and receding angles as a function of CTAB concentration in the aqueous phase at pH 6. This graph show that at low CTAB concentrations, the silica surface is highly hydrophilic. A comparison of Figures 2 and 4 shows that this portion corresponds to the region where the silica is negatively charged. As the CTAB concentration increases, the contact angles increase. At a aqueous phase concentration of about 1x10^{-4} moles/liter, the advancing contact angle passes through a maximum of 64° corresponding to the isoelectric point of the silica surface. As the silica surface becomes positively charged, the contact angle decreases, implying that the silica surface becomes strongly hydrophilic again.

CAPILLARY PRESSURE-SATURATION MEASUREMENTS

The protocol for the capillary pressure-saturation measurements was described in the previous progress report. Figure 5 shows drainage and imbibition measurements at various concentrations of CTAB. These relationships are affected by both the surface tension and the contact angle. The imbibition relationship shows a greater dependence on surface forces than the drainage relationship. At small contact angles, the aqueous phase imbibes strongly. As the contact angle increases, the wetting phase imbibes less. At the maximum value of the contact angle of 64°, the wetting phase does not imbibe. As the contact angle decreases, the wetting phase again imbibes. The changes observed in the capillary pressure-saturation relationships can be predicted on the basis of the surface tension and the contact angle. According to Leverett (1941), the capillary pressure of one fluid-fluid pair in a porous medium may be predicted from the capillary pressure of another fluid-fluid pair in the same porous medium using the following equation:

$$P_c(S_c)_2 = P_c(S_c)_1 \, (\gamma_2/\gamma_1) \qquad [1]$$

where P_c = capillary pressure,

S_e = effective saturation = $(S_w - S_{wr})/(1 - S_{wr})$,

S_w = saturation of the wetting phase, and

S_{wr} = residual saturation of the wetting phase.

According to Equation [1], the capillary pressure at one CTAB concentration can be calculated from the capillary pressure at another CTAB concentration by multiplying by the ratio of the surface tensions of the systems. While adequate in some situations (Demond and Roberts, 1991), such a formulation cannot predict the changes in the imbibition relationships seen here. To predict this behavior, one must include an operational contact angle. It appears that appropriate operational contact angles may be derived from the intrinsic contact angle, measured on a flat, smooth, rigid, homogeneous solid surface, by correcting for interfacial curvature and roughness.

Through a theoretical analysis of uniform packings of spheres, Melrose (1965) developed a means of calculating a curvature correction factor, Z(θ), determined so that:

$$P_c = (2\,\gamma \cos \theta / r)\, Z(\theta) \qquad [2]$$

Morrow (1975) developed empirical equations for correcting the contact angle for the effects of roughness (Table 1):

Table 1. Roughness Corrections for Well-Roughened Surfaces

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

To include the effects of roughness and interfacial curvature, Equation [1] may be amended to yield:

$$P_c(S_e)_2 = P_c(S_c)_1 \ \{[\gamma \cos\theta_r \ Z(\theta)]_2/[\gamma \cos\theta_r \ Z(\theta)]_1\} \qquad [3]$$

where θ_r = contact angle corrected for roughness.

Table 2 gives the calculated scaling factors, the quantity contained within the brackets in Equation [3], for the systems for which the capillary pressure relationships were measured. By multiplying the capillary pressures of the air-water-silica system by these factors, the corresponding capillary pressures for the air-water-silica-CTAB systems were calculated.

Table 2. Calculated Scaling Factors

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
	1.0×10^{-4}	59	37	2	1.05	0.86
	2.5×10^{-5}	49	47	4	1.12	0.68
	3.0×10^{-4}	45	17	0	1.01	0.60
IMBIBITION	0.0	72	5	0	0.94	1.00
	1.0×10^{-4}	59	47	51	0.21	0.12
	2.5×10^{-5}	49	64	85	No imbibition	0.00
	3.0×10^{-4}	45	22	1	0.68	0.31

A comparison of the measured and calculated capillary pressure relationships is shown in Figure 6. This comparison demonstrates the methodology outlined here and described in more detail in Demond and Roberts (1991) has the capability of predicting the effect of surfactant concentration on both drainage and imbibition capillary pressure-saturation relationships.

XYLENE-WATER-SILICA-CTAB

The experimental measurements for the xylene-water-silica-CTAB system at pH 6 are currently underway. Figure 7 shows digitized images of pendant drops generated using the Axisymmetric Drop Shape Analysis (ADSA) apparatus set up in the last project period. A comparison of Figures 7a and 7b shows the effect of the increase in CTAB concentration in the pendant drop profile. As the CTAB concentration increases and the interfacial tension decreases, the maximum size of a pendant droplet decreases. Since the shape of the pendant drop is determined by the relative magnitude of the buoyancy and interfacial tension forces, the interfacial tension can be determined if the density of the fluids are known.

Figure 8 shows digitized images of sessile drops generated using the ADSA apparatus. A comparison of Figures 8a and 8b shows the effect of the increase in CTAB concentration on the contact angle at low CTAB concentrations. By adding CTAB in small quantities to the aqueous phase, the system can be altered from hydrophilic to hydrophobic. To determine the exact contact angle, the computational technique incorporated into the ADSA apparatus fits Laplace's equation to an arbitrary number of coordinate points along the drop's profile. By minimizing an objective function expressing the deviation of the physically observed curve from the Laplacian curve, the best value for the contact angle is calculated. The ADSA was originally developed for single-liquid systems. Figures 7 and 8 show our adaptation of the technique to two-liquid systems is successful.

Figure 9 and Figure 10 shows measurements of interfacial tension and contact angles, respectively, as functions of CTAB concentration for the xylene-water-silica-CTAB system. A comparison of Figure 10 with Figure 4 shows that contact angle in the xylene-water-silica-CTAB system varies over a larger range than in the air-water-silica-CTAB system. First the contact angle is 15° (as measured through the aqueous phase), indicating that the surface is strongly hydrophilic. As the CTAB concentration increases, the contact angle increases, indicting a decrease in the hydrophilicity of the silica surface. The surface becomes neutrally wetted at a CTAB concentration of about 1 x 10^{-5} M, after which the surface becomes xylene-wet. The corresponding capillary pressure-saturation relationships are currently being measured. The drainage capillary pressure-saturation relationship for a xylene-water-silica system (conc. of CTAB = 0.0 M) is shown in Figure 11.

REVISED EXPERIMENTAL WORK PLAN AND FUTURE WORK

The revised experimental work plan is outlined in Table 3. We have completed the set of experimental measurements of air-water-CTAB-silica at pH 6. That work is summarized in this report. We are in the midst of the xylene-water-silica-CTAB measurements at pH 6. The work to date is presented above. Since the CTAB desorption measurements (see the progress report for the period 07/01/89-12/31/90) indicate that CTAB does not desorb significantly in the presence of xylene, we will use the electrophoretic mobility and sorption data measured in the absence of xylene, and additional measurements of electrophoretic mobility of xylene-water emulsions to characterize the interfacial properties of the xylene-water-silica-CTAB system. Our work on CTAB sorption and electrophoretic mobility has shown that interfacial properties are strongly influenced by pH. As such, we hope to illustrate the influence of pH by repeating the measurements of contact angle, interfacial tension and capillary pressure for both systems at pH 9. The methodology of predicting capillary pressure-saturation relationships based on a knowledge of surface tension and contact angle is presented here. In the next project period, we intend to apply it to the measurements of the xylene-water-silica-CTAB system as well. In addition, we will use surface complex models to show how the wettability of a surface changes by the formation of certain complexes at the solid-liquid interface.

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Leverett, M. C., 1941, Capillary behavior in porous solids, *Trans. AIME, 142*, 152-169.

Melrose, J. C., 1965, Wettability as related to capillary action in porous media, *Soc. Petroleum Eng. J.*, *5*, 259-271.

Morrow, N. R., 1975, The effects of surface roughness on contact angle with special reference to petroleum recovery, *J. Canadian Petroleum Technol.*, *14*(4) 42-53.

LIST OF TABLES AND FIGURES

Table 3. Revised Project Work Plan

EXPERIMENTAL MEASUREMENTS

System	Adsorption	Electrophoretic mobility	Surface/interfacial tension	Contact angle	Capillary pressure
air/water/CTAB	pH 5-9 completed	pH 5-9 completed	pH 6 completed pH 9 needed	pH 6 completed pH 9 needed	pH 6 completed ph 9 needed

xylene/water/CTAB	influence of xylene is minimal (demonstrated)	EM of emulsions	pH 6 completed pH 9 needed	pH 6 completed pH 9 needed	pH 6: C_{eq}=0, C_{eq}=5 x 10^{-6} M ongoing pH 9 needed

MODELING

Both systems	Capillary pressure - saturation relationship scaling: completed Surface complexation modeling: needed Relationship between EM and θ: needed

Figure 1. Sorption of CTAB onto silica as function of pH.

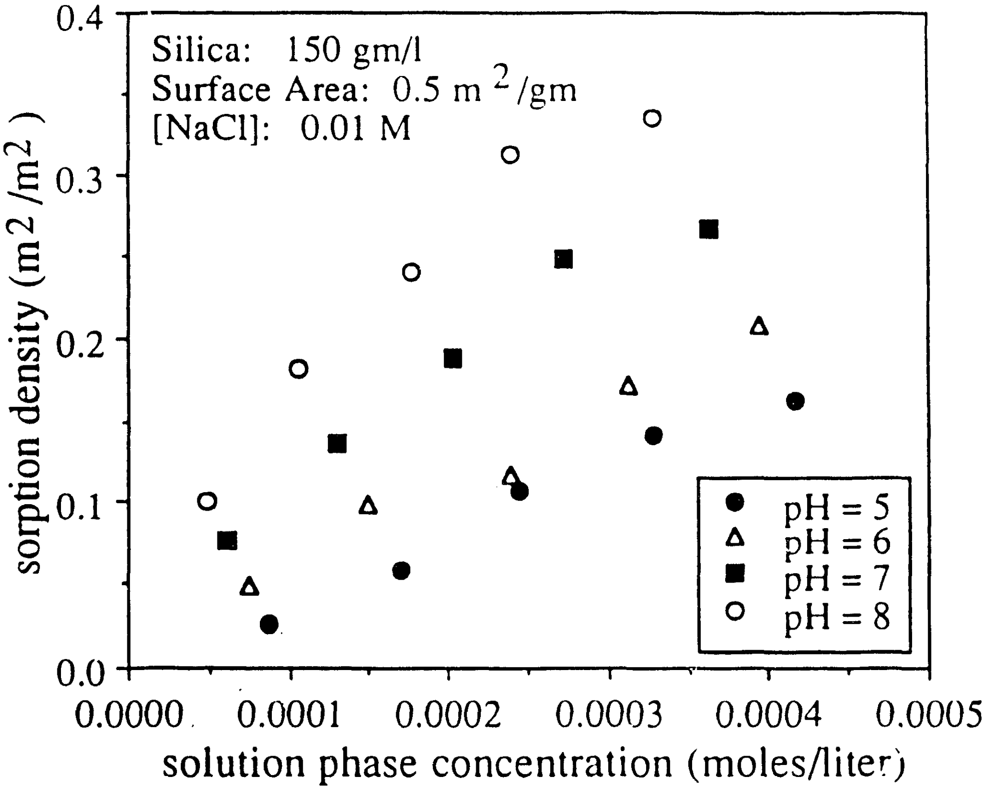


Figure 2. Electrophoretic mobility of CTAB-coated silica as function of pH

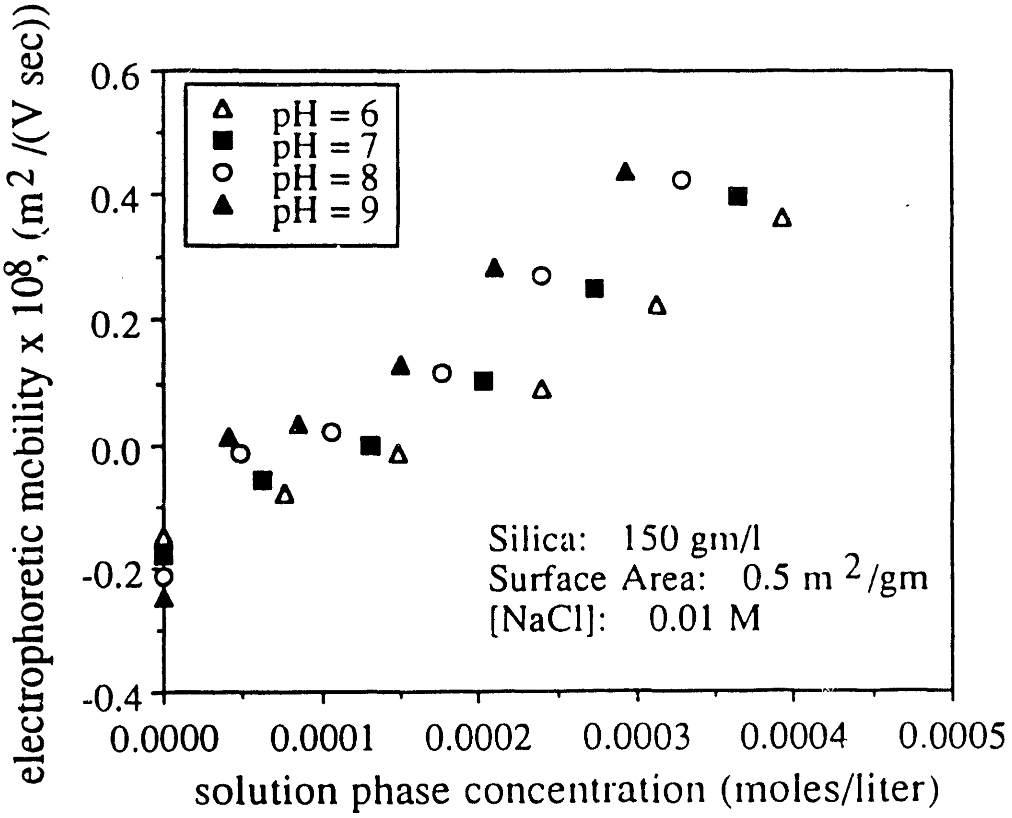


Figure 3. Surface tension of water as function of CTAB concentration.

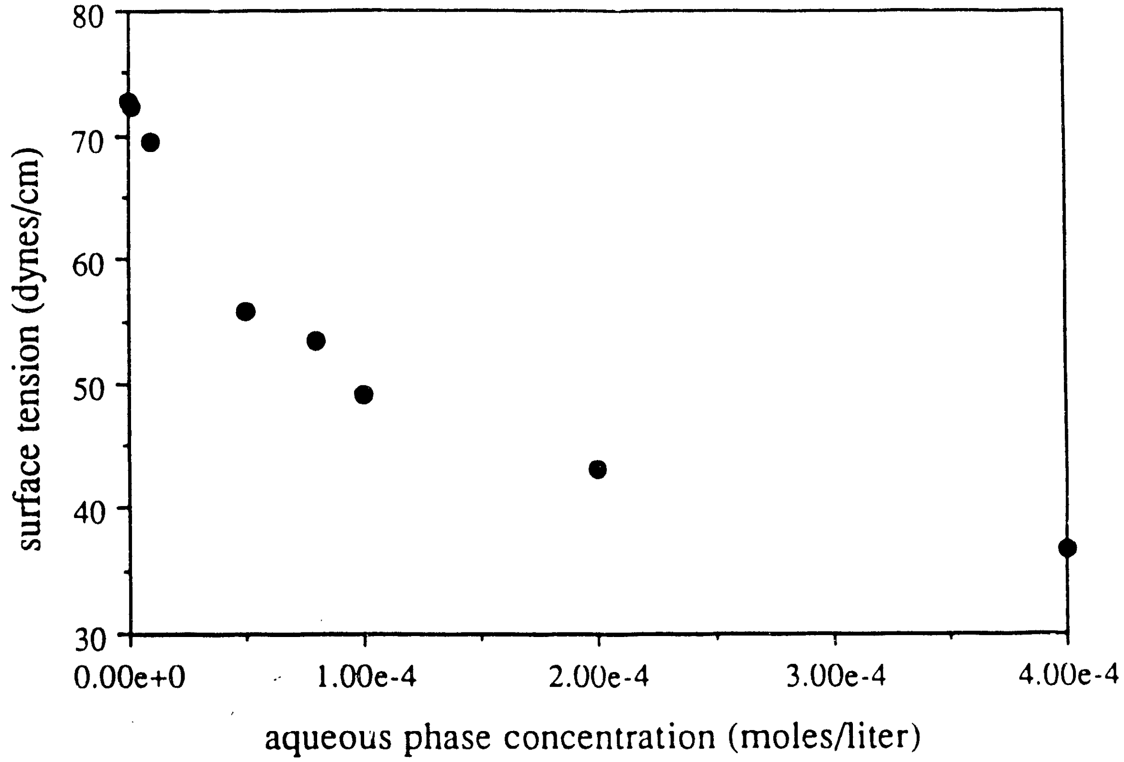


Figure 4. Advancing and receding contact angles of water as function of CTAB concentration.

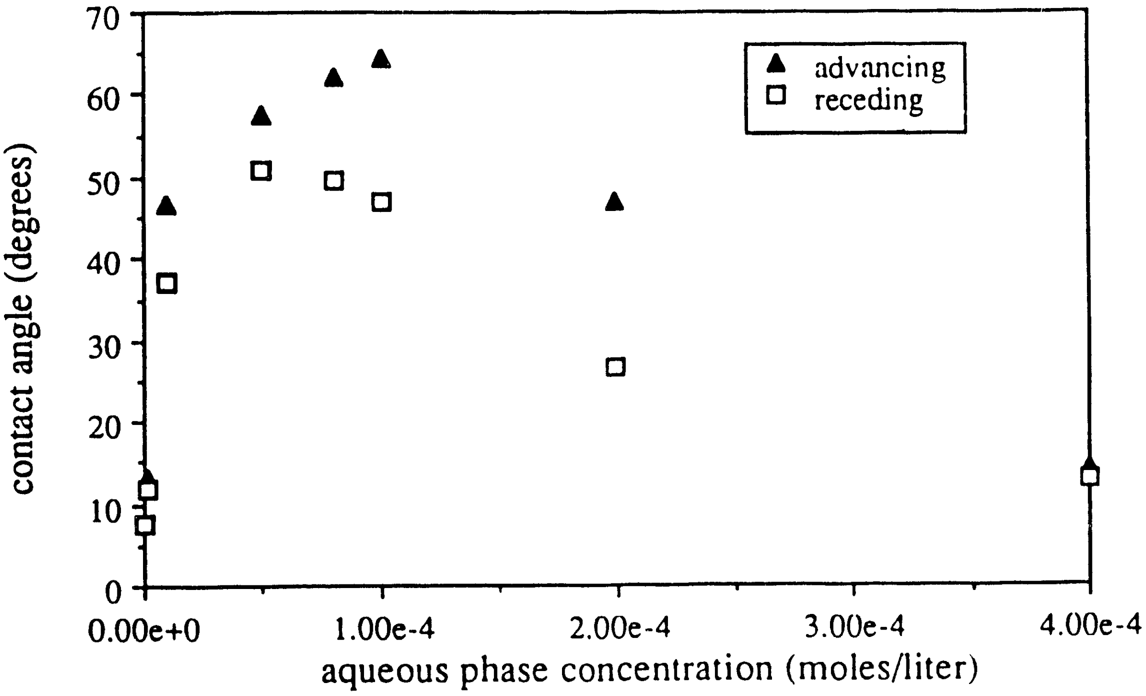


Figure 5. Drainage and imbibition capillary pressure-saturation relationships at various CTAB concentrations.

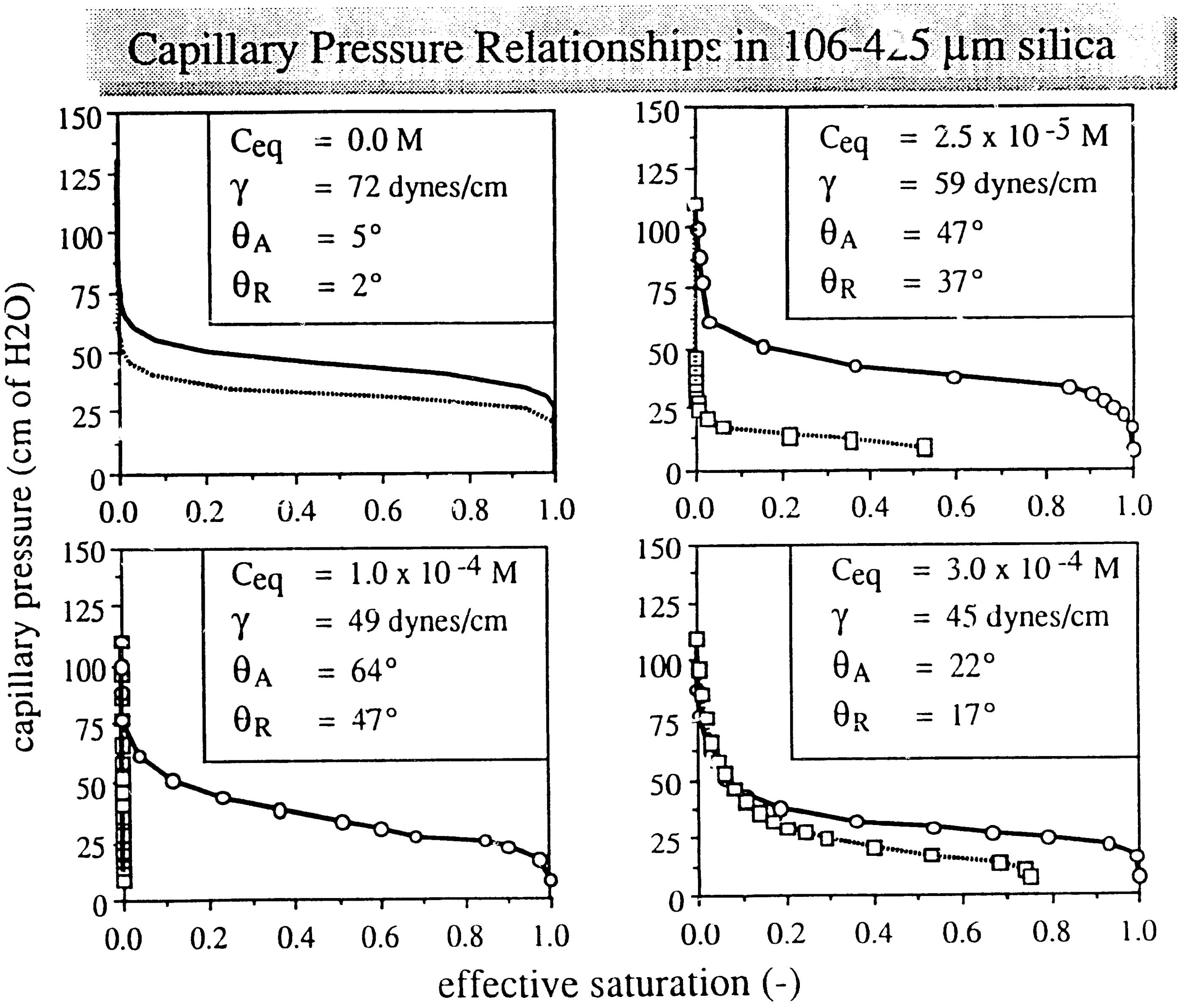
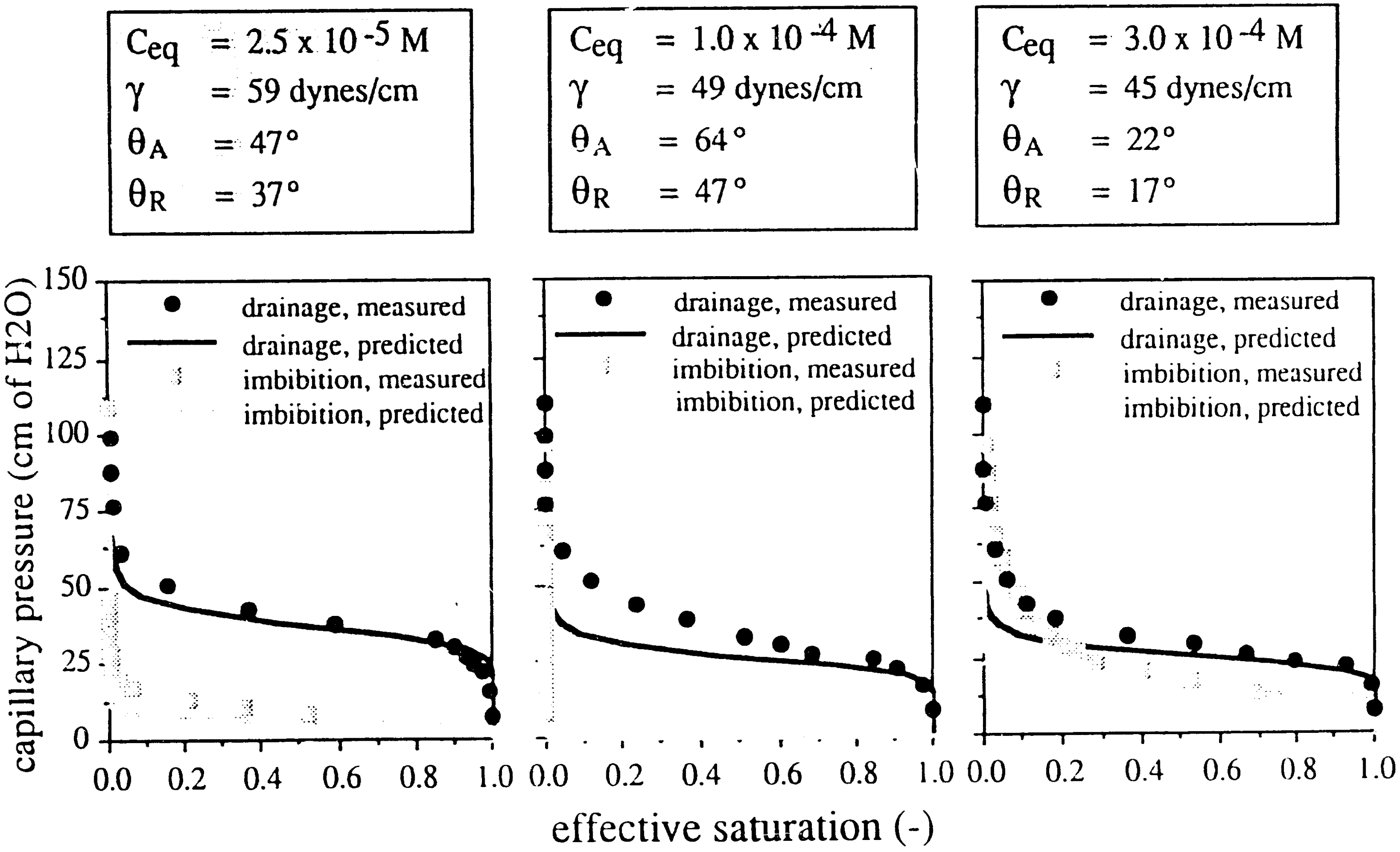


Figure 6. Comparison of measured and predicted capillary pressure-saturation relationships.



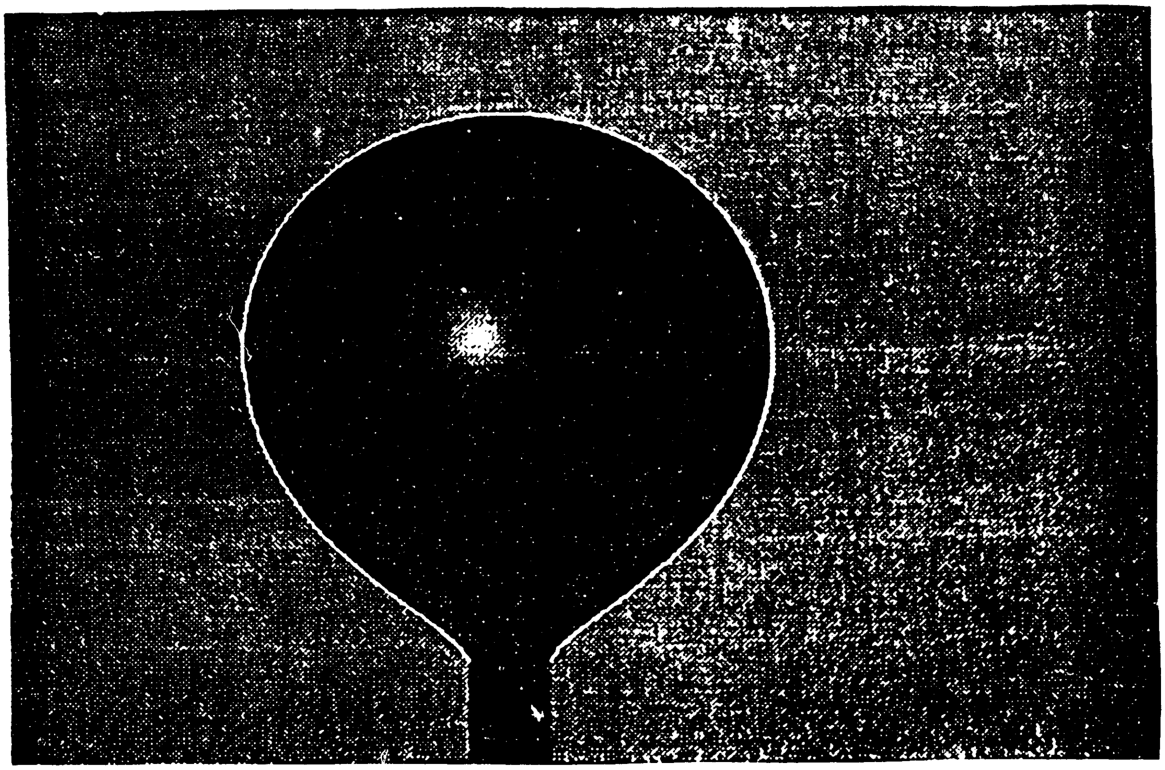
$C_{eq} = 2.5 \times 10^{-5}$ M
$\gamma = 59$ dynes/cm
$\theta_A = 47°$
$\theta_R = 37°$

$C_{eq} = 1.0 \times 10^{-4}$ M
$\gamma = 49$ dynes/cm
$\theta_A = 64°$
$\theta_R = 47°$

$C_{eq} = 3.0 \times 10^{-4}$ M
$\gamma = 45$ dynes/cm
$\theta_A = 22°$
$\theta_R = 17°$

Figure 7. Digitized images of pendant drops for interfacial tension determination

a. Xylene in pure water, $\gamma_{ORG/H2O}$ = 34.8 dynes/cm



b. Xylene in 8 x 10^{-4} M CTAB solution, $\gamma_{ORG/H2O}$ = 2.0 dynes/cm

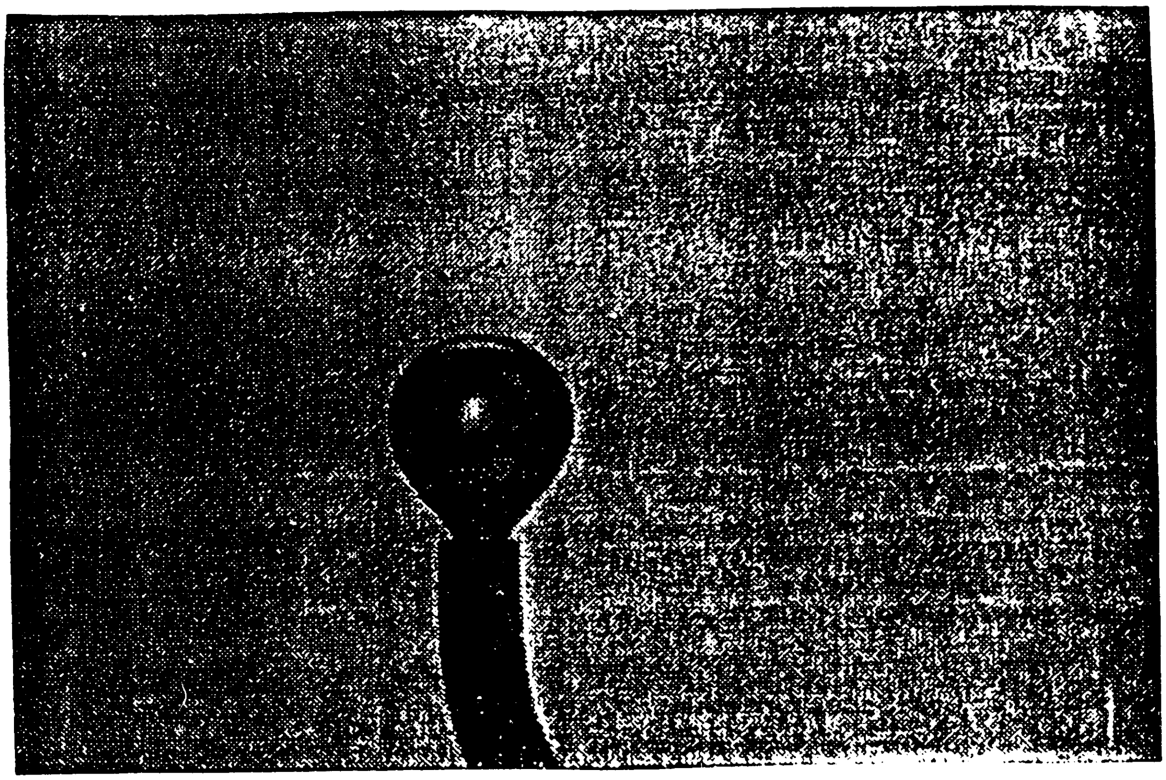
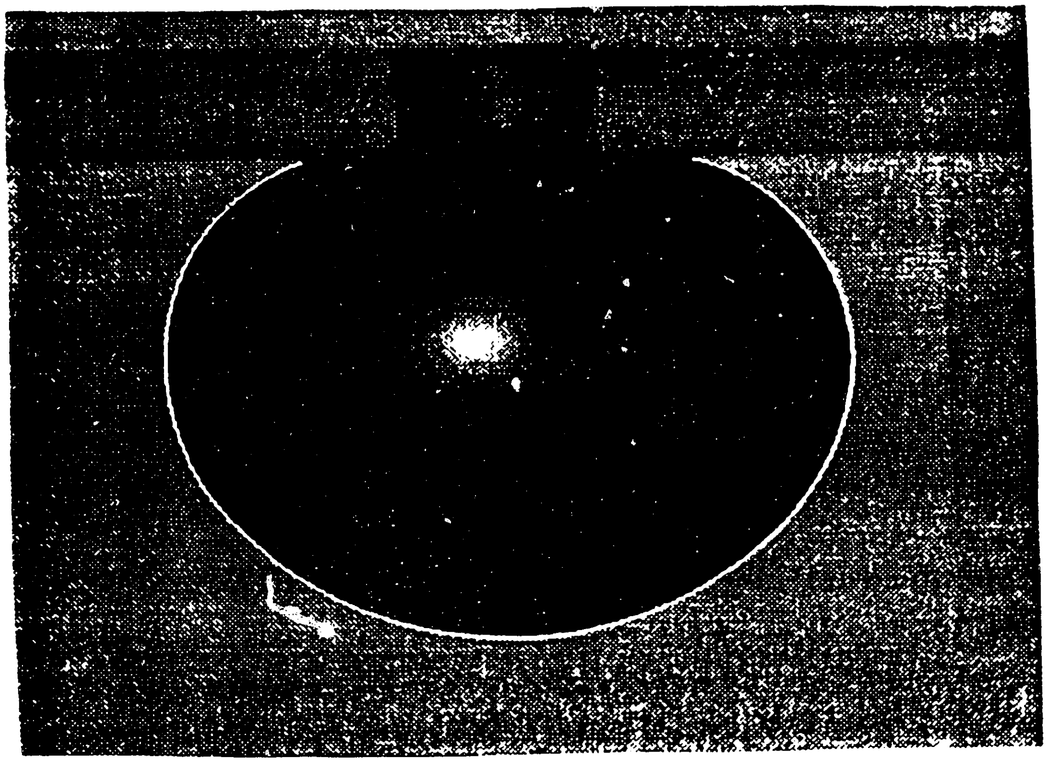


Figure 8. Digitized images of sessile droplets for contact angle determination

a. Xylene in pure water on quartz, θ = 20° (measured through aqueous phase)



b. Xylene in 1 x 10^{-5} M CTAB solution on quartz, θ = 90°

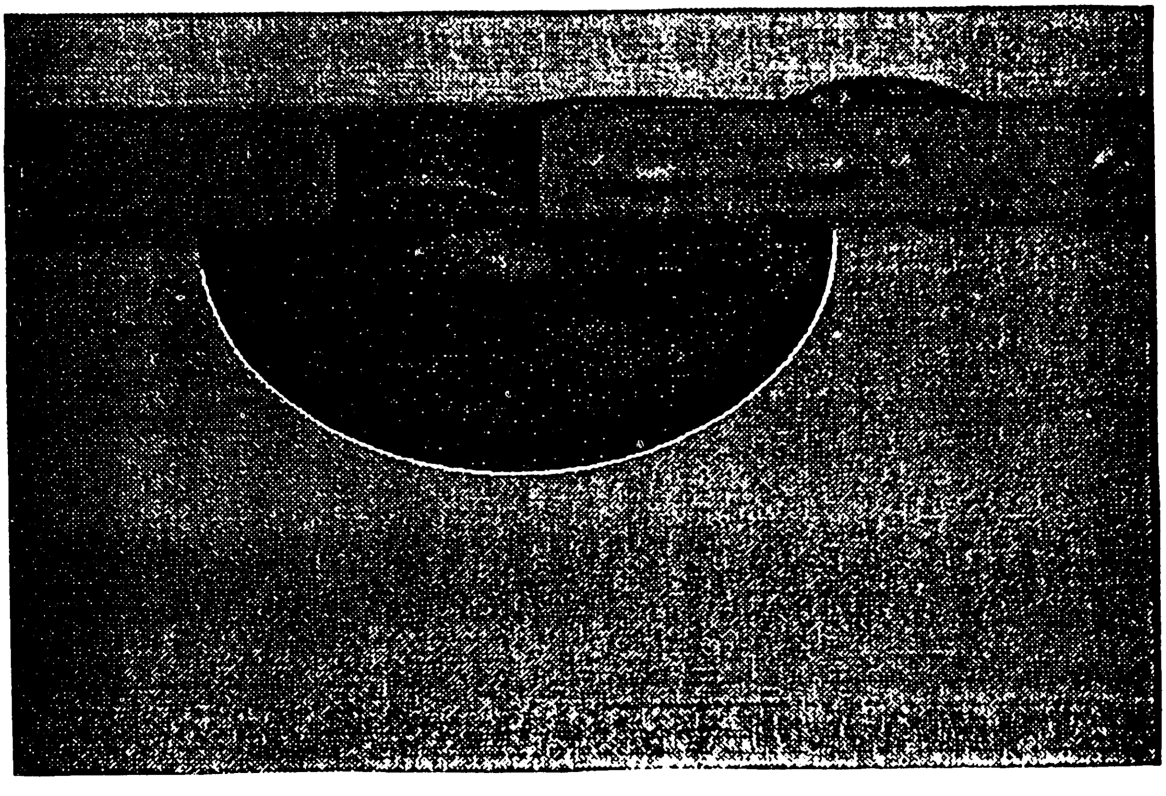


Figure 9. Interfacial tension of xylene-water as function of CTAB concentration.

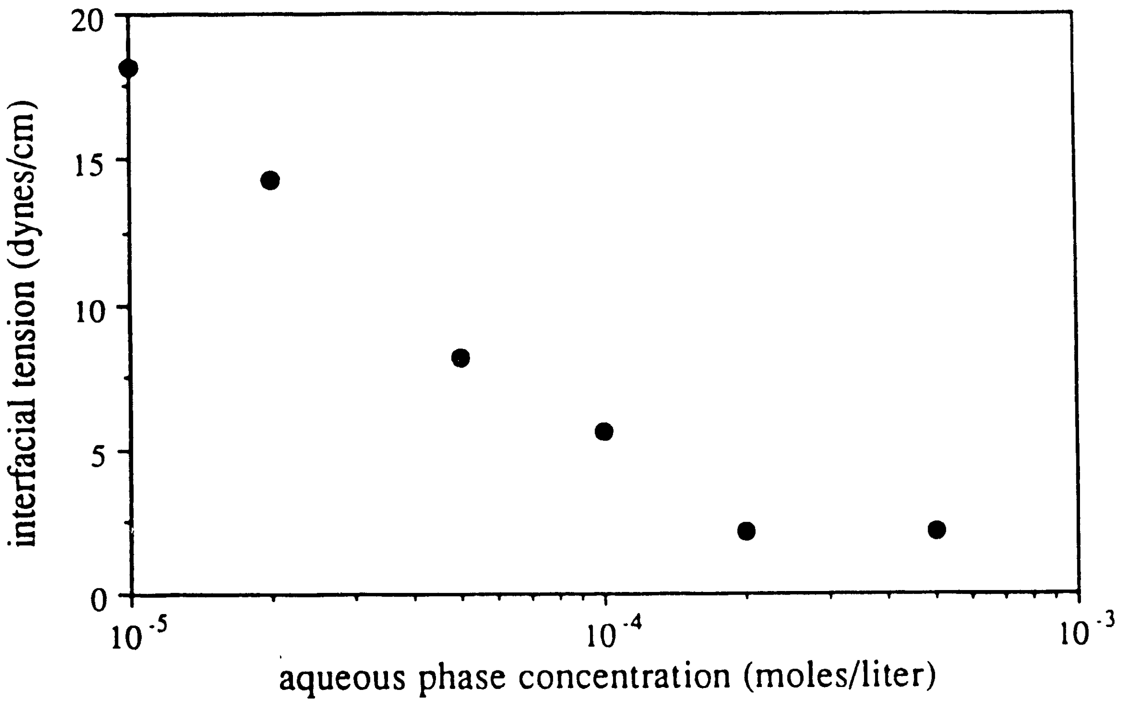


Figure 10. Advancing and receding contact angles of xylene-water as function of CTAB concentration.

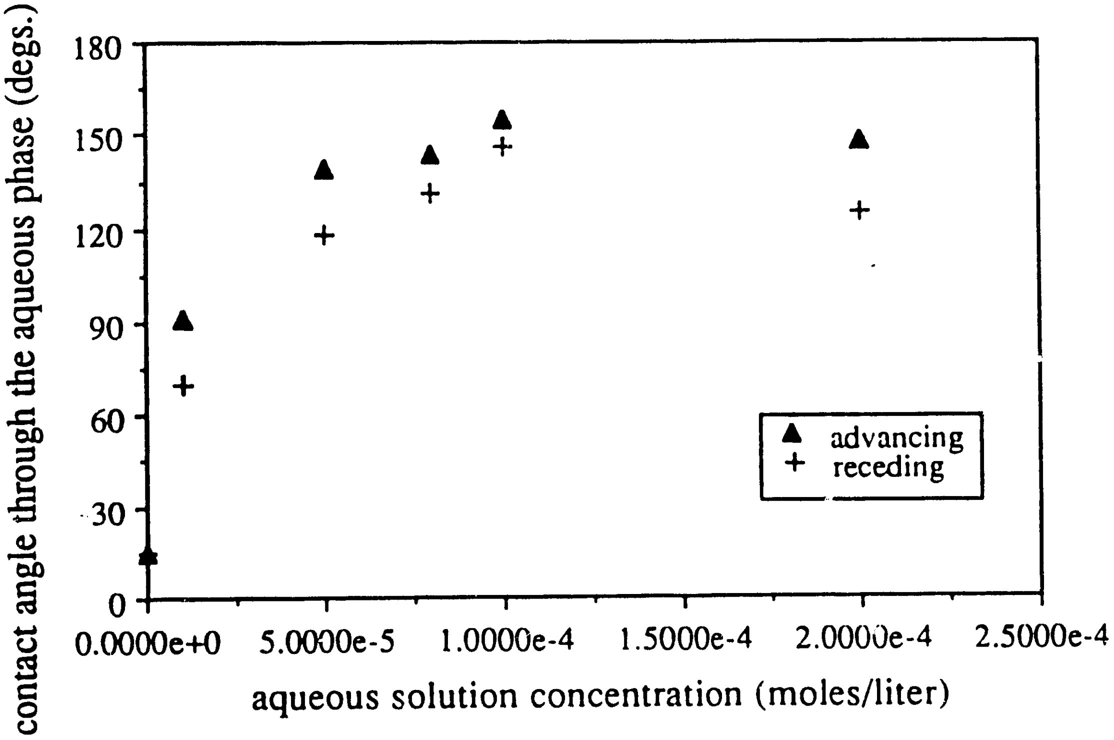
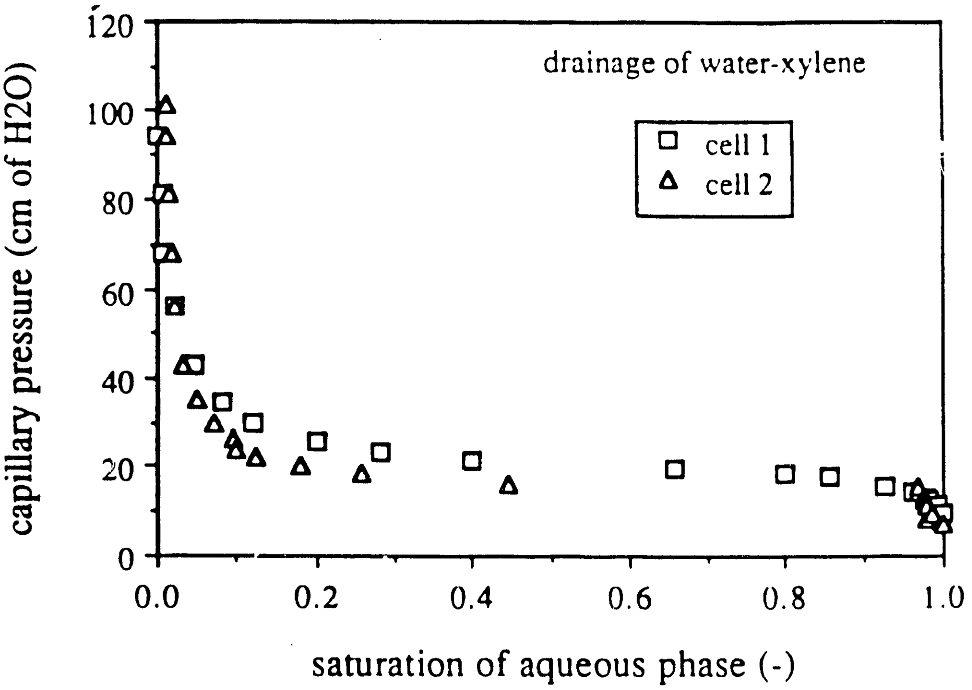


Figure 11. Drainage capillary pressure-saturation relationship for xylene-water-silica



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