Effects of Organic Base Chemistry on Interfacial Tension, Wettability, and Capillary Pressure in Multiphase Subsurface Waste Systems

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Abstract. The presence of surfactants may have profound effects on the transport of organic contaminants in multiphase systems. It is a common practice, however, to model the subsurface migration of liquids independently of the aqueous phase composition. As such, transport in these systems may not be adequately characterized. This study investigates the impact of pH on interfacial tension, wettability, and the drainage capillary pressure–saturation relationship in air–water–quartz and *o*-xylene–water–quartz systems containing dodecylamine, an organic base. In these systems, three mechanisms, speciation, partitioning, and sorption, are important in determining the interfacial tension and contact angle, and consequently, important in determining the capillary pressure. By adjusting the pH above and below, the pK_a of the base, the relative importance of these mechanisms was altered. Below dodecylamine's pK_a of 10.6, the base was primarily in a cationic form resulting in minimal partitioning into the nonaqueous liquid and greater sorption at the quartz surface. Above the pK_a, the base was primarily in a neutral form which did not sorb to the quartz, and, furthermore, partitioned into the organic liquid phase where its surface activity was minimized. The combination of these processes caused the capillary pressure to change in a manner consistent with pore-scale theory of capillarity. The utility in this approach lies in the possibility of predicting transport properties in multiphase systems while incorporating the direct effects of solution chemistry.

Key words: surfactant, dodecylamine, capillary pressure, interfacial tension, wettability, NAPL, organic base.

1. Introduction

The solution chemistry of surfactants may play an important role in determining nonaqueous phase liquid (NAPL) transport in the subsurface. Surfactants naturally concentrate at phase interfaces, and as a result, may affect surface tension, interfacial tension, and wettability, properties identified as critical to determining two-phase flow behavior in porous media (Moore and Slobod, 1956; Lenhard and Parker, 1987; Demond and Roberts, 1991). Many contaminated groundwater systems contain surface-active compounds, either resident in the waste mixture (Riley

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and Zachara, 1992; Barth and Borgund, 1994), added during remediation (Abdul *et al.*, 1990; West and Harwell, 1992), or produced from natural biological activity (West and Harwell, 1992). Realizing that the interfacial properties which govern multiphase flow in the subsurface may be influenced by the presence of surfactants commonly found in the subsurface, the adequate estimation of contaminant migration may first require an understanding of the relationship between solution chemistry of surfactants and interfacial properties in subsurface systems.

The objective of this work is to examine the impact of an organic base upon interfacial properties, and ultimately, transport properties, in multiphase subsurface waste systems. The results presented here are part of a broader study focused on the impact of surface-active waste constituents on multiphase migration (Desai *et al.*, 1992; Demond *et al.*, 1994; Lord *et al.*, 1997a,b). Through this study, the authors seek to identify the chemical mechanisms which affect contaminant transport in such systems. The ultimate goal is to generalize the principles elucidated here so that the behavior of similar systems may be predicted on the basis of the relevant mechanisms at work for given compound classes.

2. Background

Solution chemistry, and in particular, pH, may impact the interfacial properties of subsurface systems by at least two mechanisms: (1) the pH-sensitivity of aqueous speciation of surface-active co-contaminants; and, (2) pH-induced changes in the physicochemical nature of mineral surfaces. Organic bases assume two principal forms in aqueous solution depending on pH: a protonated acid form, as well as a deprotonated conjugate base form (Pankow, 1991; Porter, 1991). The relative concentrations of each may be calculated directly from the acid–base dissociation reaction, written here for an alkyl primary amine

$$RNH_3^+ = H^+ + RNH_2, \qquad K_a = 10^{-10.6}, \tag{1}$$
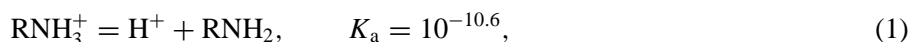
where R represents an alkyl group of arbitrary length and K_a denotes the acid dissociation constant for a typical alkyl primary amine. When the solution pH is below the pK_a, the protonated form is the prominent species in solution. Therefore, below pH 10.6, an alkyl primary amine will assume the cationic acid form, while above pH 10.6, it will assume the neutral conjugate base form.

The speciation may, in turn, impact the surface and interfacial tension because the surface activity of the various species present is governed by their molecular structure. For example, Lord *et al.* (1997a) observed that the surface tension of an aqueous solution of octanoic acid ($C_7H_{15}COOH$) decreased by 50% as the pH passed through the acid's pK_a (pH 4.9), although the total concentration remained constant at 3×10^{-3} M. Similarly, the surface tension of aqueous solutions containing fixed concentrations of dodecylamine ($CH_3(CH_2)_{11}NH_2$), an organic base, reached a distinct minimum near its pK_a of 10.6 (Somasundaran and Ananthapad-

manabhan, 1979). The existence of this minimum was attributed to the formation of a dimer complex

$$RNH_2 + RNH_3^+ = RNH_2 \cdot RNH_3^+, \qquad K_d = 10^{3.1}, \tag{2}$$

where K_d denotes the dimer formation constant (Somasundaran and Ananthapadmanabhan, 1979). According to speciation modeling results presented in that study, the peak activity of the dimer coincided with the experimentally determined minimum in surface tension. Therefore, the speciation of surface-active compounds in aqueous solution may play an important role in determining surface tension.

The interfacial tension of two-liquid phase systems also demonstrates a sensitivity to pH in the presence of organic bases (Gaudin and Decker, 1967). For two-liquid systems, not only must speciation be considered, but also the partitioning of the surfactant into the nonaqueous phase (Jafvert *et al.*, 1990; Rudin and Wasan, 1992a, b, c; Schwarzenbach *et al.*, 1993), as the relative concentrations of surfactant in each liquid phase may also impact the interfacial properties. The ratio of the concentration of surfactant in the nonaqueous liquid to the concentration remaining in the aqueous phase may be expressed as the distribution ratio D, a parameter which is strongly pH-dependent for organic bases (Schwarzenbach *et al.*, 1993)

$$D = \frac{(RNH_2)_o}{(RNH_3^+) + (RNH_2) + (RNH_3^+ \cdot RNH_2)}, \tag{3}$$

where ( ) and ( )$_o$ designate the concentrations of species in the aqueous and organic liquid phases, respectively. pH may therefore effect a significant impact on interfacial properties because interfacial tension is, in part, a function of the concentration of surface-active species assembled at the liquid–liquid interface, which is determined by the speciation and partitioning of the surfactant in the bulk phases.

While the aqueous speciation of surfactants may drive much of the pH-dependent surface-activity observed in mixed waste systems, the nature and charge density of the solid surface may also show a sensitivity to pH. The functional groups on a mineral surface may undergo an acid–base reaction, yielding net positively-charged surfaces at pH values below the surface's isoelectric point, and net negatively-charged surfaces above. For example, the charge density on quartz and the sorption density of cetyltrimethyl-ammonium bromide (CTAB) to quartz from aqueous solutions were shown to increase in parallel with pH above 2 (Desai *et al.*, 1992; Demond *et al.*, 1994), the isoelectric point for quartz in water (Parks, 1965). As the increase in charge density on the quartz surface induced a higher sorption density of CTAB, the quartz surface became more oil-wetting as the pH increased from 6 to 9 (Demond *et al.*, 1994). Therefore, the pH-sensitivity of the physicochemical properties of the solid surface may influence wettability.

The relationship between interfacial properties and NAPL transport in the sub-surface may be inferred, in part, through the properties' impact on the capillary

pressure–saturation relationship, a constitutive relationship often required in two-phase flow modeling. At the pore scale, the relationship among interfacial tension, contact angle, and capillary pressure is given by the Young–Laplace equation for a spherical meniscus in a cylindrical pore

$$P_c = \frac{2\gamma \cos \theta}{r}, \tag{4}$$

where P_c is the capillary pressure, γ is the interfacial tension, θ is the contact angle (a measure of wettability), and r is the radius of the pore. Although the pore geometry of natural soils is decidedly more complex than cylindrical, the basic dependence of P_c upon γ, θ, and r still holds (see Demond and Roberts, 1991, and references therein). Given that surfactant speciation may affect interfacial tension and contact angle, it follows that the capillary pressure will be affected as well.

Previous work in this context with an organic acid bears out this dependence. For example, the capillary pressure at a particular saturation in air–water–quartz and *o*-xylene–water–quartz systems was lowered by adjusting the pH to favor high aqueous phase concentrations of the nonionic form of octanoic acid (Lord *et al.*, 1997b). In this case, the capillary pressure was proportional to the corresponding surface or interfacial tension. As octanoic acid did not sorb to the solid, little change in contact angle was observed. Therefore, the reduction in capillary pressure was attributed to the surface or interfacial tension lowering resulting from changes in surfactant speciation and partitioning.

Sorption, however, is a significant mechanism by which the capillary pressure of a system may be altered. For example, Desai *et al.* (1992) and Demond *et al.* (1994) showed that CTAB, a cationic surfactant, sorbed strongly to a quartz surface. In the presence of *o*-xylene, sorption was sufficient to cause quartz to become oil-wetting, with a correspondingly dramatic consequence for the capillary pressure relationship. Yet, CTAB remained in a cationic form over the entire pH range examined; thus it failed to show any impact of speciation or partitioning. With an organic base, all three mechanisms may be operating. The complexities of the relationship between speciation, partitioning and sorption, and the capillary pressure–saturation relationship of systems containing organic bases have hitherto been examined piece meal: Gaudin and Decker (1967) and Shergold (1987) have looked at the impact of dodecylamine on interfacial tension or the contact angles, whereas Powers and Tamblin (1995) focused on the impact of dodecylamine on capillary pressure. Hence, this study seeks to elucidate both the effect of pH on the interfacial tension and contact angle, and its accompanying impact on the capillary pressure–saturation relationship, emphasizing the roles of speciation, partitioning, and sorption.

3. Methodology

3.1. MATERIALS

The relationship between the solution chemistry of an alkyl amine and the capillary pressure–saturation relationship was explored experimentally using model systems. In all systems, one fluid was water of ultrapure quality, obtained by passing deionized, distilled water through Milli-Q cartridge filters (Millipore, Bedford, MA). In the systems where the second fluid was an organic solvent, o-xylene was used as received (>99% purity, Fluka Chemical/BioChemika, Hauppage, NY). The surface-active organic base, dodecylamine ($CH_3(CH_2)_{11}NH_2$), (98% purity) (Aldrich, Milwaukee, WI), was purchased in its solid base form (M.P. = 28°C) and was used as received. The acidity constant, K_a, for dodecylamine was taken to be $10^{-10.6}$ (Gaudin and Decker, 1967). The critical micelle concentration (CMC) of dodecylamine is reported as 1.3×10^{-2} M at pH 6 (Ralston, 1948) and 1×10^{-4} M at pH 11 (Watson and Manser, 1968). In all systems, the solid was quartz. The porous medium was a packed bed of quartz particles with a particle-size range of 106–425 μm (F-65, U.S. Silica, Berkeley Springs, WV). The contact angles were measured on smooth quartz slides (Quartz Scientific, Fairport Harbor, OH). The agents used to control solution conditions, NaOH and HCl for pH, and NaCl for ionic strength, were all analytical reagent grade (Mallinckrodt, Paris, KY).

3.2. METHODS

A series of measurements were made on each system in order to characterize the relationship between speciation, sorption and partitioning, and the capillary pressure–saturation relationship. Surface or interfacial tension, contact angle, and capillary pressure–saturation measurements were made for all the systems considered. In addition, distribution measurements were made for the o-xylene–water–dodecylamine system. All measurements and sample preparations were conducted at room temperature, 23 ± 2°C. Sample preparation and glassware cleaning techniques were modeled closely after those described in Lord *et al.* (1997a).

3.2.1. *Surface and Interfacial Tension Measurements*

The Du Nouy ring tensiometer (Model K8, Kruss, Hamburg, Germany) was used to measure the surface tension in all of the air–water experiments. The surface tension was measured as a function of pH from 4 to 12 while the dodecylamine and sodium chloride concentrations were held constant at (DDA) = 3×10^{-5} M and (NaCl) = 0.01 M respectively.

The interfacial tension was measured using the axisymmetric drop shape analysis (ADSA) technique (Cheng *et al.*, 1990). Both NaCl and dodecylamine concentrations were held constant at $(NaCl)_T = 0.01$ M, and $(DDA)_T = 1 \times 10^{-3}$ M respectively, while pH was varied from 3 to 11. The subscript T indicates total number of moles of the given compound in a two-phase sample normalized by the

volume of the aqueous phase. See Lord *et al.* (1997a) for further details regarding sample preparation and measurement technique.

3.2.2. *Contact Angle Measurements*

The intrinsic contact angle was measured by imaging a sessile drop of the nonwetting fluid on a smooth quartz plate using the ADSA apparatus. Further description of the techniques used for cleaning the slides and conducting the measurements may be found in Lord *et al.* (1997b). All slides were immersed in the aqueous phase of systems for 48–72 h prior to the formation of a sessile drop of the nonwetting fluid. Up to a 10% increase in the magnitude in contact angle was observed during the first 30 min after the drop was formed, with additional increase of up to 10% observed over the ensuing five days. The contact angle reported here is the receding angle measured through the aqueous phase 30 min after the drop was formed.

3.2.3. *Distribution Measurements*

The distribution of dodecylamine between water and *o*-xylene was measured as a function of pH. Sample preparation and distribution measurement techniques were identical to those reported in Lord *et al.* (1997a), with several exceptions as follows. Dodecylamine was added as a solid to the aqueous phase to yield concentrations of either $(DDA)_T = 3 \times 10^{-4}$ M or 1×10^{-3} M. The pH of the aqueous phase was adjusted over a range from 3 to 11. The concentrations of dodecylamine present in both the aqueous and organic liquid phases were measured independently by first sampling the organic liquid phase for dodecylamine and then extracting the remaining dodecylamine from the aqueous sample using fresh xylene. In both sampling steps, the *o*-xylene was analyzed for dodecylamine on a gas chromatograph (HP 5890 Series II, Hewlett Packard, Novi, MI) outfitted with a DB-1 general purpose dimethylpolysiloxane column (Model 125–1032, J&W Scientific, Folsom, CA) and a nitrogen–phosphorus detector (NPD) (Hewlett Packard, Novi, MI).

The distribution coefficient, D (Equation 3), was determined directly from the results of the two sampling steps on the gas chromatograph. Assuming that only the neutral base monomer, RNH_2, was present in the *o*-xylene, the concentration of dodecylamine measured in the first sampling step was equated with $(RHN_2)_o$. Next, the total concentration of aqueous phase dodecylamine measured in the second sampling step was equated with $(RNH_3^+) + (RNH_2) + (RNH_3^+ \cdot RNH_2)$.

3.2.4. *Capillary Pressure–Saturation Measurements*

Table I summarizes the experimental conditions for the capillary pressure–saturation measurements conducted in this study. For both air–water and *o*-xylene–water systems, measurements were made at fixed dodecylamine concentrations at pH 6.5 and pH $\geqslant$ 10.6 to investigate the impact of pH below and above the pK_a of dodecylamine. Reference measurements were also made in the absence of surfact-

Table I. Experimental conditions for primary drainage capillary pressure–saturation measurements

Fluids	$(DDA)_T$ (M)	pH(± 0.2)	γ (mN/m)	$\theta_{RECEDING}$ (degrees)
Air–water	0.00	5.8	72	7
Air–water	3×10^{-5}	6.5	67	27
Air–water	3×10^{-5}	10.6	44	67
o-Xylene–water	0.00	5.7	39	17
o-Xylene–water	1×10^{-3}	6.5	24	62
o-Xylene–water	1×10^{-3}	11.3	37	10

ant. The measurements were obtained using a recently developed and more rapid version (Salehzadeh and Demond, 1999) of the traditional pressure cell apparatus. The pressure cell was wet-packed with F-65 silica and then flushed with at least 200 pore volumes of the aqueous phase in order to equilibrate the aqueous and solid phases. Upon completing the flushing process, the interfacial tension and contact angle were assumed to be constant throughout the duration of the experiment, with the values as given in Table I. Additional procedures used to clean the apparatus, prepare samples, and conduct the measurements are reported in Salehzadeh and Demond (1999) and Lord *et al.* (1997b).

4. Results and Discussion

4.1. AIR–WATER–QUARTZ SYSTEM

Figure 1 shows the surface tension of an aqueous solution containing $(DDA)_T = 3 \times 10^{-5}$ M as a function of pH. Titrating the solution through dodecylamine's pK_a of 10.6 induced a lowering in surface tension from 70 mN/m to roughly 45 mN/m. Raising the pH slightly further resulted in an increase in the surface tension back to nearly 70 mN/m. This behavior was explained by Somasundaran and Ananthapadmanabhan (1979) as resulting from the formation of a highly surface-active dimer complex, $RNH_3^+ \cdot RNH_2$, which exhibits peak activity near the pK_a. Apparently the neutral molecule, RNH_2, prevalent above pH 10.6, is not particularly surface-active at the air–water interface, as the surface tension of 65 mN/m is nearly that of pure water, 72 mN/m. The surface activity may be limited by the aqueous solubility above the pK_a, as Shergold (1987) reports the solubility limit of the neutral molecule as 2×10^{-5} M.

Figure 1 also shows the effects of pH on the receding contact angle in the same system. The cationic forms of dodecylamine, RNH_3^+ and $RNH_3^+ \cdot RNH_2$, present at pH values below the pK_a, reduced the hydrophilicity of quartz, as evidenced by an increase in contact angle to 70°. Raising the pH above the pK_a caused the receding
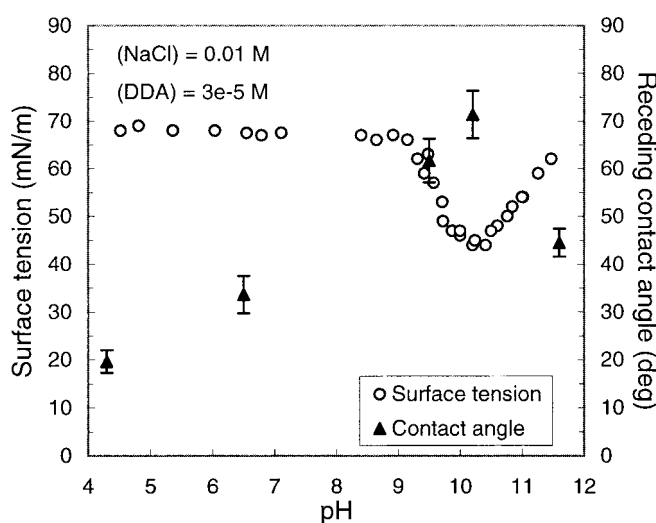
Figure 1. Surface tension and receding contact angle on quartz of aqueous solutions of dodecylamine, both as functions of pH. Total dodecylamine concentration was fixed at (DDA) = 3 × 10⁻⁵ M. Error bars on contact angle measurements represent 95% confidence intervals.

contact angle to return to about 45°, a phenomenon also reported by Shergold (1987). It is hypothesized that the cationic species sorb strongly to the negatively-charged quartz surface mainly due to electrostatic forces. As the charge density on quartz increased with pH, the degree of sorption increased and was reflected in the increasing contact angle from pH 4 to 10 (Figure 1). Above the pK_a, the cationic dodecylamine deprotonated and assumed its neutral form, with the total concentration in solution possibly limited by its solubility. As such, the degree of dodecylamine sorption to the quartz surface was reduced resulting in a reduction in the receding contact angle from 70 to 45°.

The alteration in surface properties of the system is reflected in the drainage capillary pressure relationship of this system, as Figure 2 shows. No discernible difference was observed between the reference system containing no dodecylamine and the system at pH 6.5 containing (DDA) = 3×10^{-5} M because the changes in surface tension and contact angle (Table I) were insufficient to cause a reduction in capillary pressure. However, for the same concentration of dodecylamine, raising the pH from 6.5 to 10.6 effected a decrease in surface tension of about 35% (Table I), a decrease in cos θ (Equation 4) of about 55% (Table I), and finally a decrease of more than 60% in capillary pressure (Figure 2). While capillary pressure is clearly lower at pH 10.6 than at pH 6.5 or in the absence of dodecylamine, the combined effect of surface tension and contact angle on the capillary pressure is not strictly proportional as suggested by Equation 4. The lack of proportionality may be attributable to differences in roughness (Morrow, 1975) and interfacial curvature (Melrose, 1965) between the smooth flat plate on which the contact angle was measured and the pores inside the porous medium. To account for the differences
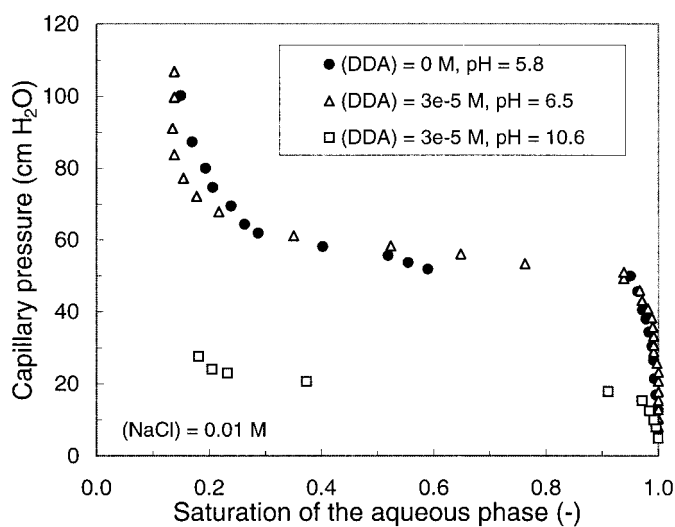
Figure 2. Primary drainage capillary pressure–saturation relationships for air–water system as a function of pH. Total dodecylamine concentration was fixed at (DDA) $= 0$ M and (DDA) $= 3 \times 10^{-5}$ M.

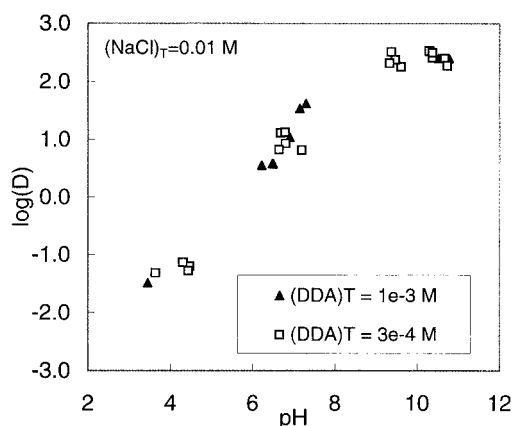*Figure 3.* Distribution coefficient for dodecylamine in *o*-xylene–water system as a function of pH. Total dodecylamine concentration was fixed at (DDA)$_T$ $= 3 \times 10^{-4}$ M and (DDA)$_T$ $= 1 \times 10^{-3}$ M, normalized by the volume of the aqueous phase.

in roughness and interfacial curvature, a correctional factor may need to be applied to the contact angle measured on a smooth plate (Demond and Roberts, 1991).

4.2. *o*–XYLENE–WATER–QUARTZ SYSTEM

The mass distribution of dodecylamine between the aqueous phase and *o*-xylene depended strongly upon pH (Figure 3). Log (*D*) measured greater than zero over most of the pH range examined because the neutral form of dodecylamine (RNH$_2$)
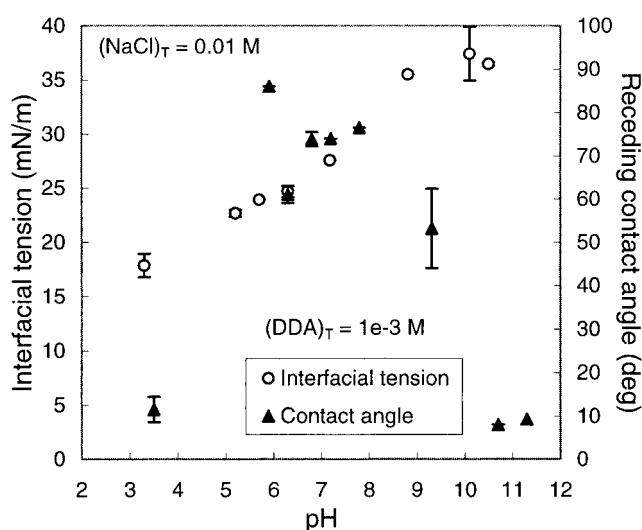
Figure 4. Interfacial tension between *o*-xylene and water and receding contact angle on quartz, both as functions of pH. Total dodecylamine concentration was fixed at $(DDA)_T = 1 \times 10^{-3}$ M, normalized by the volume of the aqueous phase. Error bars represent 95% confidence intervals.

partitioned strongly into the organic solvent. When the pH favored the cationic forms of dodecylamine, however, the compound partitioned into the aqueous phase of the two-liquid system, as evidenced by a decrease in *D* as pH was lowered from 10 to 3. The distribution coefficient above pH 11 was not quantified because the concentration of dodecylamine remaining in the aqueous phase fell below the detection limit for the analytical instrument used. Because of the strong partitioning into the xylene phase, the concentration in the aqueous phase remained below the CMC of 1×10^{-4} M at pH 11 even though the total concentration was $(DDA)_T = 3 \times 10^{-4}$ M.

The shifting mass distribution of dodecylamine is reflected in the magnitude of the interfacial tension as a function of pH (Figure 4). According to the distribution coefficient (Figure 3), the cationic species prevalent at low and neutral pH remain in the aqueous phase, resulting in an interfacial tension 10–15 mN/m lower than the value of 35.2 ± 2.4 mN/m measured in the absence of surfactant (Lord *et al.*, 1997a). As the pH neared the pK_a, however, the interfacial tension approached 36 mN/m, similar to the value for the system with no surfactant. Coupled with the observation that the distribution coefficient is much greater than unity above pH 7, it is apparent that upon partitioning into the *o*-xylene, the dodecylamine exhibits minimal activity at the *o*-xylene–water interface.

The receding contact angles for this system are also shown in Figure 4. The values pass through a maximum of about 80° near neutral pH, though remain fairly low, around 10°, at the endpoints, pH 3.5 and 11.5. This behavior reflects the combined processes of dodecylamine speciation in the aqueous phase, par-
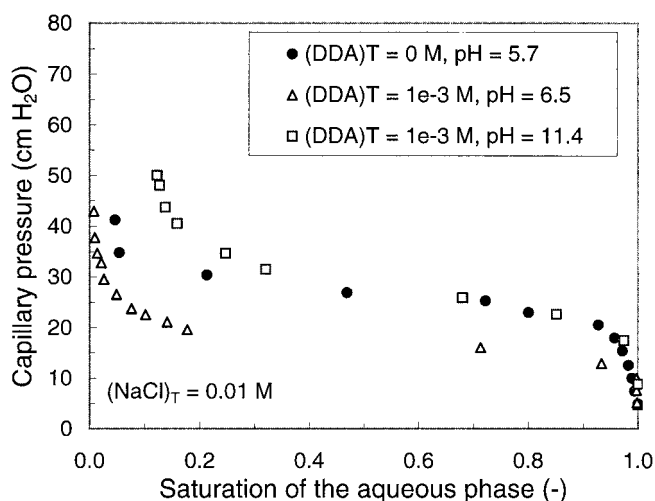
Figure 5. Primary drainage capillary pressure–saturation relationships for *o*-xylene–water system as a function of pH. Total dodecylamine concentration was fixed at $(DDA)_T = 0$ M and $(DDA)_T = 1 \times 10^{-3}$ M.

titioning between liquid phases, and dodecylamine sorption to the solid phase. Despite a high aqueous concentration of the cationic species at low pH, the low charge density on quartz precludes significant dodecylamine sorption. The contact angle, therefore, remains below 20°, comparable to the values of 10–15° reported for the same system at pH 6 and 9 in the absence of surfactant (Demond *et al.*, 1994). As the pH climbs into the neutral range, both the aqueous concentrations of the cationic species and the charge density on quartz are sufficiently large that the sorption of dodecylamine causes the contact angle to increase to about 80°. Finally, as the pH increases to near the pK_a, the dodecylamine is present primarily in its neutral form which partitions preferentially into the *o*-xylene phase. Thus, the sorption density on quartz declines, despite quartz's increased charge density. The result is a return to a strongly water-wetting state above pH 11.

The combination of these processes is also reflected in the capillary pressure relationships, shown in Figure 5. The capillary pressure at a given saturation is lower near neutral pH than at high pH due to both the reduction in interfacial tension from 37 to 24 mN/m and the increase in contact angle from 10 to 62° (Table I). Yet at pH 11.4, above the pK_a, the capillary pressure relationship looks similar to that for the *o*-xylene–water system in the absence of dodecylamine. The conversion of dodecylamine to the neutral form with its subsequent lack of sorption and increased partitioning into the *o*-xylene phase result in a minimal impact upon the capillary pressure.

5. Conclusion

The work presented here investigated the effect of pH on the capillary pressure–saturation relationship of model subsurface multiphase systems containing an organic base as a solute. pH was shown to impact interfacial tension, wettability, and consequently, capillary pressure, through its influence on three mechanisms: speciation, partitioning, and sorption of the solute. The systems considered here, however, are distinct from the systems employed in other portions of the broader study (Desai *et al.*, 1992; Demond *et al.*, 1994; Lord *et al.*, 1997a, b) because they exhibit the three aforementioned mechanisms simultaneously. For instance, adjusting the pH in air–water–quartz systems containing either an organic acid (Lord *et al.*, 1997a, b) or an organic base to favor the formation of the neutral species or dimer complex resulted in greater surface tension lowering than when the ionic species dominated. Yet here, the base also sorbed to the solid surface, resulting in significant wettability changes, while the acid failed to sorb. The observed reductions in capillary pressure were quantitatively related to changes not only in surface tension, but also in wettability, reflecting the combined effects of speciation and sorption of the organic base. Furthermore, adjusting pH in the *o*-xylene–water–quartz systems here to favor the neutral species caused the interfacial tension to increase to the value obtained in the absence of any surfactant. This resulted from strong partitioning of the neutral species into the *o*-xylene phase where it exhibited negligible surface activity. Yet, varying pH in a similar system containing the cationic surfactant CTAB had no measurable effect on interfacial tension because the CTAB neither exhibited changes in aqueous speciation nor significant solubility in the organic liquid phase (Demond *et al.*, 1994). Hence, the collective mechanisms of speciation, partitioning, and sorption exhibited in these systems containing an organic base served to enhance the effect of pH on capillary pressure, through their impact on interfacial tension and wettability.

Acknowledgements

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