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

Progress Report
for the period September 1, 1993 - August 31, 1994

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April 1994

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

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

ABSTRACT

Many organic liquid compounds that DOE has identified at its waste sites have a low solubility in water. As a result, these compounds may persist as separate phases and be transported as such in the subsurface. Thus, developing a better understanding of the principles governing the migration of a separate organic liquid phase in the subsurface is necessary to DOE's groundwater remediation efforts.

Wettability is sometimes described as the most important factor influencing two-phase flow in porous media. A groundwater aquifer is often thought of as water-wet. But that state, in reality, depends on the nature of the aquifer solids, the composition of the groundwater and the properties of the organic liquid contaminant. Furthermore, changes in wettability may be enhanced by the presence of co-contaminants such as metals and organic solutes. Because the recovery of organic liquid from the subsurface depends on the wettability of the system, an understanding of the important factors determining the wettability at a hazardous waste site may lead to the successful manipulation of wettability for the optimal extraction of organic liquid wastes.

The primary purpose of the research conducted here is to examine quantitatively the impact on wettability of a range of factors which may be critical at actual DOE waste sites. The goal is to understand how sorption at the various interfaces of the system modifies interfacial properties, primarily wettability, and then how, in turn, wettability determines the soil transport property of capillary pressure as a function of saturation. Specifically, this research seeks to 1) determine the range of wettability changes that may occur for DOE waste sites using wettability measures suitable for complex systems, 2) establish a correlation between these alternate measures of wettability and the contact angle, 3) establish the mechanism by which metals, organic solutes and soil particle coatings impact wettability, 4) evaluate whether the methodology developed in previous project periods among sorption, contact angle, and capillary pressure can be extended to more complex systems.

In this project period, emphasis was placed on goals 2-4. Major accomplishments include the adaptation of an apparatus for the measurement of capillary pressure-saturation relationships to produce the Amott and U.S. Bureau of Mines (USBM) indices, alternative measures of wettability. Preliminary measurements of the Amott and USBM indices for systems composed of o-xylene, water, silica and cetyltrimethyl ammonium bromide (CTAB) at various concentrations suggest that these indices correlate with the contact angle qualitatively. Work with organic acids as co-contaminants shows that the degree of sorption at the fluid-fluid interface is the major factor controlling the capillary pressure-saturation relationships in air-water-organic acid-quartz and xylene-water-organic acid-quartz systems. Since the speciation of the organic acid determines the degree of sorption at the fluid-fluid interface, variables which impact the speciation, such as pH and ionic strength, also impact the capillary pressure-saturation relationships. The relationship between wettability and sorption depends not only on sorption density, but also on the aggregate structure of the sorbed molecules. Atomic force microscope measurements made during this project period provide some of the first direct evidence of the structural changes that molecules sorbed at the solid interface undergo as the sorption density increases. This work elucidates the complexity of the relationship between sorption and wettability. Notwithstanding this complexity, this work continues to show that the methodology for the prediction of capillary pressure-saturation relationships of contaminated systems from the corresponding relationship for air-water systems developed in previous project periods is reasonable.

INTRODUCTION

Many organic liquid compounds that DOE has identified at its waste sites have a low solubility in water. For example, trichloroethylene, reported at Savannah River, and carbon tetrachloride, reported at Hanford, have solubilities on the order of 1 gram per liter (Demond and Lindner, 1993). As a result, these compounds may persist as separate phases and be transported as such in the subsurface. Thus, developing a better understanding of the principles governing the migration of a separate organic liquid phase in the subsurface is necessary to DOE's groundwater remediation efforts.

Wettability is sometimes described as the most important factor influencing two-phase flow in porous media (Moore and Slobod, 1956). A groundwater aquifer is often thought of as water-wet. But that state, in reality, depends on the nature of the aquifer solids, the composition of the groundwater and the properties of the organic liquid contaminant. Furthermore, changes in wettability may be enhanced by the presence of co-contaminants such as metals and organic solutes. The recovery of organic liquid from the subsurface depends on the wettability of the system, with weakly water-wet cited as the optimal wettability for the recovery of organic liquid (Morrow et al., 1986; Morrow, 1990). However, it is difficult to determine how to achieve such a wettability state if the mechanism by which wettability is determined is unknown. Thus, an understanding of the important factors determining wettability at hazardous waste sites may lead to the successful manipulation of wettability for the optimal extraction of organic liquid wastes.

The primary purpose of the research conducted in this project is to examine quantitatively the impact on wettability of a range of factors which may be critical at actual DOE waste sites. These include the presence of co-contaminants such as metals and organic acids and bases, the composition of the soil matrix, and the presence of organic and inorganic coatings. These factors have the potential for causing dramatic changes in soil wettability, but their effect on the wettability of systems representative of hazardous waste sites has yet to be explored. Through an examination of these factors, the quantitative relationships among sorption, wettability, and capillary pressure-saturation relationships that were developed in the first project period of this research (Demond and Hayes, 1990, 1991; Demond et al., 1992; Desai et al., 1992; Demond et al., 1994) will be extended to cover more complex waste and soil systems. Specifically, this research seeks to 1) determine the range of wettability changes that may occur for DOE waste sites using wettability measures suitable for complex systems, 2) establish a correlation between these alternate measures of wettability and the contact angle, 3) establish the mechanism by which metals, organic solutes and soil particle coatings impact wettability, 4) evaluate whether the methodology developed in previous project periods among sorption, contact angle, and capillary pressure can be extended to more complex systems. In this project period, emphasis was placed on goals 2-4. The work towards these goals is summarized in the next three sections.

ALTERNATE MEASURES OF WETTABILITY

Wettability is usually quantified in terms of the contact angle measured on a smooth, representative solid. The contact angle is sometimes regarded as the only direct and unambiguous measure of wettability (Melrose and Brandner, 1974). However, it is difficult to define an appropriate contact angle for a system where the effects of roughness, heterogeneity, and the geometry of the solid matrix are important (Neumann and Good, 1972). Consequently, the wettability of these systems must be characterized using alternative measures.

The quantitative methods commonly used in petroleum engineering are the Amott method

(Amott, 1959) and the U.S. Bureau of Mines (USBM) method (Donaldson et al., 1969). In the Amott method, the wettability of a system is determined by the volume of oil or water displaced in four steps: i) spontaneous imbibition of oil, ii) forced displacement of water by oil, iii) spontaneous imbibition of water, and iv) forced displacement of oil by water (Amott, 1959) (Figure 1). From this information, two ratios are calculated:

$$\delta_o = \frac{V_{wsp}}{V_{wt}} \quad (1)$$

where V_{wsp} = volume of water displaced by spontaneous oil imbibition,
 V_{wt} = total volume of water displaced by both imbibition and forced displacement, and

$$\delta_w = \frac{V_{osp}}{V_{ot}} \quad (2)$$

where V_{osp} = volume of oil displaced by spontaneous water imbibition,
 V_{ot} = total volume of oil displaced by both imbibition and forced displacement.

For a water-wet core, δ_w is positive and δ_o is zero, whereas the reverse is true for an oil-wet core. For fractional or mixed wettability cores, both indices may be positive. For neutrally-wet cores, the method is rather insensitive. In this region, neither liquid spontaneously imbibe and both displacement ratios are close to zero.

The USBM method compares the work done by one fluid to displace the other, as given by the capillary pressure relationships (Donaldson, 1969) (Figure 1). The USBM wettability index is defined by:

$$W = \log \frac{A_1}{A_2} \quad (3)$$

where A_1 = area under the secondary drainage curve, and
 A_2 = area under the forced imbibition curve.

For positive values of W , the core is water-wet; for negative values, the core is oil wet, and for W close to zero, the core is neutrally wet.

A recent modification allows both the Amott and the USBM indices to be calculated from the same data (Sharma and Wunderlich, 1985). To determine both of these indices, the primary drainage, spontaneous imbibition, and spontaneous drainage capillary pressure relationships are measured in addition to the forced imbibition and secondary drainage.

Although these indices are routinely measured in petroleum engineering studies, practical problems arise in their measurement for systems representative of hazardous waste sites. In petroleum engineering, measurements of capillary pressure-saturation relationship can be made expeditiously using a centrifuge. However, the use of a centrifuge is only appropriate with consolidated porous media where the force generated by the centrifuge will not disperse the solid. With unconsolidated soils common at hazardous waste sites, capillary pressure-saturation relationships are usually generated with porous plate apparatuses such as those used in soil science studies. However, our experience has shown that the measurement of a single capillary pressure curve can take on the order of a week with a conventional porous

plate apparatus. Thus, the generation of the five capillary pressure curves necessary to characterize the wettability of a single system would take on the order of five weeks, a daunting prospect.

To shorten the time frame for the measurement of these indices, an apparatus previously developed for the rapid measurement of capillary pressure-saturation relationships for air-water systems was modified. The original design of the apparatus, called the Soil Transport Property Measurement System (STPMS), and its testing with air-water systems are reported in Salehzadeh and Demond (1994). The adaptation of the apparatus for this project entailed modifying it so that it could handle two liquids and generate negative capillary pressures. To handle two liquids, a whole organic liquid monitoring and handling system similar to the extant one for water had to be constructed. Then, to generate negative capillary pressures, the pressure regulation system had to be altered so that the wetting phase could be maintained at higher pressures than the nonwetting phase. Through the use of this apparatus, we were able to reduce the time for the measurement of the necessary capillary pressure curves from about 5 weeks to about 8 days.

Figure 2 shows the five capillary pressure-saturation relationships, primary drainage, spontaneous imbibition, forced imbibition, spontaneous drainage, and secondary drainage, necessary for the calculation of the Amott and USBM indices for a system composed of o-xylene, water containing the cationic surfactant cetyltrimethyl ammonium bromide (CTAB) ($\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$), and quartz. The figure also gives the indices calculated from these relationships and the corresponding contact angles. The values of the contact angle and the Amott index suggest that this system is weakly water-wet. This correspondence between the contact angle and the Amott index observed here agrees with that reported by Sharma and Wunderlich (1985). However, the value of the USBM index of 1.2 calculated for this system is unexpectedly large. Based on Sharma and Wunderlich's work, a more appropriate value of the USBM index for a system whose advancing contact angle is 91° is 0.4; a USBM index of 1.2 corresponds to an advancing angle of about 30° . The high value of the USBM index is undoubtedly due to the forced imbibition curve. In our measurements, we observed a slow, but steady, imbibition at a capillary pressure of zero over the course of four to five days. This resulted in a small area underneath the forced imbibition curve. The capillary pressure relationships determined by Sharma and Wunderlich were measured using a centrifuge and the length of time the systems were allowed to equilibrate is unknown, but standard protocol does not call for an extended equilibration time.

RELATIONSHIP BETWEEN SORPTION DENSITY AND WETTABILITY

Figure 3 summarizes the surface chemical data for the o-xylene-water-quartz-CTAB system published in Demond et al. (1994). A comparison of graphs A and B shows that the system goes from being strongly water-wet ($\theta_{\text{ADV}} = 15^\circ$) at $[\text{CTAB}] = 10^{-6} \text{ M}$ to being neutrally-wet ($\theta_{\text{ADV}} = 91^\circ$) at $[\text{CTAB}] = 10^{-5} \text{ M}$, while the sorption density increases to under $0.1 \mu\text{mol}/\text{m}^2$, less than 4% of its maximum value. On the other hand, over the range of $[\text{CTAB}] = 1 \times 10^{-4} \text{ M}$ to $5 \times 10^{-4} \text{ M}$, the sorption density ranges from about 10% to 80% of the maximum, but the contact angle changes only 5° . Thus, the changes in wettability do not correlate proportionately with sorption density, with sorption occurring at low coverages having an incommensurately large impact on wettability.

To investigate this phenomenon, atomic force microscopy (AFM) measurements were made of the quartz surface in contact with aqueous solutions of CTAB. These measurements were made using a Digital Instruments Nanoscope III (Digital Instruments, Santa Barbara, CA)

scanning probe microscope with the fluid cell attachment. Degassed aqueous solutions of CTAB were continuously flowed through the fluid cell for 8-12 hours at 25-26°C. Imaging was performed in the contact mode using 200 μm SiN_4 Nanoprobes (Digital Instruments, Santa Barbara, CA) pyramidal tips with an estimated spring constant of 0.06 N/m, with forces ranging from 6-30 nN. Since the surface of interest was soft or malleable, images from only the first pass across a region of the surface were examined to avoid artifacts generated by extensively scraping the sample surface. More details concerning the sample preparation and measurement techniques are given in Hayes and Morton (1994a,b).

Figure 4 shows AFM images of CTAB sorbed to quartz at four aqueous phase concentrations of CTAB. Image A shows clean quartz in water containing no CTAB. By adjusting the contrast, the roughness of the clean quartz surface can be shown. In Image B, the contrast was adjusted to downplay the roughness of the quartz surface in order to reveal the hemimicelles that are already forming at aqueous CTAB concentrations as low as 5×10^{-7} M. Image C, taken at $[\text{CTAB}] = 1 \times 10^{-4}$ M, shows that large bilayer clusters are present, even though the sorption density is only 10% of the maximum. Image D shows a complete bilayer is never formed in this system, even at the maximum surface coverage. At CTAB concentrations as high as 1×10^{-3} M, the surface coverage remains patchwise with clusters comprising approximately 10,000 surfactant molecules (calculated assuming an average area per molecule of 0.26 nm^2).

The large changes in wettability occur at aqueous CTAB concentrations between 1×10^{-6} M and 1×10^{-5} M, in between the concentrations shown in Images B and C of Figure 4. To examine what occurs in that range, a region of the surface where no aggregate features were observed for $[\text{CTAB}] = 1 \times 10^{-5}$ M was enlarged (Figure 5). The image shown in Figure 5 suggests that the surface is effectively covered even at low sorption densities. The height of the molecular structures covering the surface, however, is lower than that of the prominent hemimicellular structures seen in Images B and C of Figure 4. This observation suggests that the molecules, then, are lying closer or more parallel to the surface. Thus, the large changes in wettability noted in this concentration range are due not to the sorption density (defined as number of molecules per unit surface area) per se but to the greater effective surface coverage (surface area covered per molecule). As a result, the relationship between sorption and wettability is complicated by the fact that molecular orientation and aggregate structure change as a function of surface coverage, making sorption density or zeta potential incomplete indicators of surface condition (Hayes et al., 1994c).

IMPACT OF ORGANIC ACID CO-CONTAMINANTS

In the work described in detail in Demond et al. (1992 and 1994) and Desai et al. (1992), CTAB, a quarternary ammonium surfactant, was selected to represent a surface-active co-contaminant. This compound was chosen because it remained as an unprotonated cation at all pHs examined and would sorb significantly to the negatively-charged quartz surface. Since there were no changes in the speciation with pH, no changes in interfacial properties were observed attributable to that. However, pH influenced the charge density on the quartz surface, and consequently impacted the amount of CTAB that could sorb to the surface. Thus, the surface tension and interfacial tension did not change as a function of pH, whereas the contact angle did (Figure 6).

The work completed in this project period complemented the research cited above. Here, we examined an anionic surface-active co-contaminant, octanoic acid ($\text{C}_7\text{H}_{15}\text{COOH}$), an organic acid which has been reported at DOE waste sites (Riley and Zachara, 1992). This compound

exists both in an unionized form, $C_7H_{15}COOH$, and in an anionic form, as $C_7H_{15}COO^-$, the relative concentrations of which are a function of pH:

as well as a function of ionic strength:

Neither the unionized or anionic form proved to sorb significantly to quartz. Thus, changes in the contact angle were insignificant (Figure 7). However, the relative speciation had a critical impact on both the surface tension in the air-water-octanoic acid-quartz system, and the interfacial tension in the o-xylene-water-octanoic acid-quartz system, which, in turn, impacted the capillary pressure-saturation relationships as a function of co-contaminant concentration.

At first, we speculated that the acid form (the unionized form, $C_7H_{15}COOH$) was the sole surface-active species. However, a plot of surface tension versus $[C_7H_{15}COOH]$ for the air-water system showed significant scatter at low concentrations of $C_7H_{15}COOH$ (Figure 8). Based on this information, it was then hypothesized that perhaps $C_7H_{15}COO^-$ also displayed some surface activity, but to a lesser degree. To test this hypothesis, a series of measurements were performed at pH 12, conditions under which the majority of octanoic acid would be present in the anionic form. As Figure 9 shows, $C_7H_{15}COO^-$ (in the ion-pair form $C_7H_{15}COO^- - Na^+$ [Equation (5)]) can indeed lower the surface tension as well. Since the degree of surface tension lowering was also a function of ionic strength, I (Figure 9), a composite variable, comprising $[C_7H_{15}COOH]$, $[C_7H_{15}COO^-]$ and I , was developed following the work of Lucassen-Reynders (1981). This variable:

$$V = [C_7H_{15}COOH] + 0.005 (I [C_7H_{15}COO^-])^{1/2} \quad (6)$$

served to correlate the surface tension data as Figure 10 shows.

In previous project periods, we showed that the key variables for predicting changes in the capillary pressure-saturation relationships were the surface tension (or interfacial tension) and the contact angle. Because the contact angle changed negligibly in these systems, its role in predicting capillary pressure was insignificant. In circumstances where only the surface tension is the operative variable, the scaling factor that we developed in previous project periods (Demond and Roberts, 1991):

$$\alpha = \frac{[\gamma \cos \theta_R Z(\theta)]_{cs}}{[\gamma \cos \theta_R Z(\theta)]_{AIR/H_2O}} \quad (7)$$

where γ = surface tension or interfacial tension,
 $Z(\theta)$ = curvature correction functions defined by Melrose (1965),
 θ_R = contact angle corrected for roughness using equations developed by Morrow (1975), and
subscript cs = contaminated system,

reduces to the scaling factor derived from Leverett's (1941) function:

$$\alpha = \frac{\gamma_{CS}}{\gamma_{AIR/H_2O}} \quad (8)$$

yielding for the prediction of capillary pressure, P_c :

$$[P_c]_{CS} = \frac{\gamma_{CS}}{\gamma_{AIR/H_2O}} [P_c]_{AIR/H_2O} \quad \text{at a given effective saturation.} \quad (9)$$

Figure 11 shows that Equation (9) performs reasonably for the prediction of capillary pressures for the air-water-octanoic acid-quartz system, despite the fact that the data were obtained at different pHs and changes in surface tension were attributable to more than one chemical species.

Parallel results showing the correlation of interfacial tension with a composite variable made up of $[C_7H_{15}COOH]$, $[C_7H_{15}COO^-]$ and I , and the prediction of capillary pressure-saturation relationships based on the value of interfacial tension, were also generated for the system comprised of o-xylene, water, octanoic acid and quartz. The results for both systems are currently being summarized in the form of two publications for submission to refereed journals.

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Amott Method: $\delta_o = \frac{\Delta S_{wsp}}{\Delta S_{wt}} = \frac{V_{wsp}}{V_{wt}} \quad \delta_w = \frac{\Delta S_{osp}}{\Delta S_{ot}} = \frac{V_{osp}}{V_{ot}}$

USBM Method: $W = \log \frac{A_1}{A_2}$

Figure 1: Capillary pressure-saturation curves for Amott/USBM method.

Quartz-Xylene-Water-CTAB (10^{-5} M)

Figure 2. Capillary pressure-saturation relationships for the determination of wettability in o-xylene-water-quartz-CTAB system.

Figure 3. Interfacial properties for o-xylene-water-CTAB-quartz system.
Upper graph (graph A): Sorption density and electrophoretic mobility.
Lower graph (graph B): Interfacial tension and contact angle.

Figure 4. AFM images of CTAB sorption quartz

**Figure 5. Enlargement of surface features
of CTAB sorbed to quartz ($[CTAB]=10^{-5}M$)**

Figure 6. Interfacial properties for o-xylene-water-CTAB-quartz system. Upper graph (graph A): Interfacial tension. Lower graph (graph B): Contact angle.

Figure 7. Contact angle in air-water-octanoic acid-quartz system.

Figure 8. Surface tension of aqueous solutions of octanoic acid as a function of [C7H15COOH].

Figure 9. Surface tension of aqueous solutions of octanoic acid as function of $[C_7H_{15}COO^-]$ at high pH.

Figure 10. Surface tension of aqueous solutions of octanoic acid as function of composite variable.

Figure 11. Comparison of predicted and measured capillary pressure-saturation relationships for air-water-octanoic acid-quartz system.

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