Influence of Aqueous pH on the Interfacial Properties of Coal Tar

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Coal tar is a dense nonaqueous phase liquid (DNAPL) of significant environmental concern due to its toxicity and persistence in the subsurface. The mobility and recoverability of subsurface coal tar is significantly influenced by its interfacial properties. This paper demonstrates the dependence of coal tar interfacial properties, such as interfacial tension and contact angle, on aqueous pH. Coal tar−water interfacial tension, quartz wettability, capillary pressure-fluid saturation relationships, and interfacial film presence or absence were experimentally determined in aqueous solutions of varying pH (3.4−12.4) at constant ionic strength (0.1 M). Interfacial tension varied as much as 25 dynes/cm, dramatically decreasing as pH was increased above 9. Contact angle results indicate that, as for most NAPLs, water wets quartz media under coal tar-advancing conditions over the entire pH range tested. However, unlike most NAPLs, coal tar wets quartz media under coal tar-receding conditions at acidic to neutral pH. At basic pH, quartz media remained water wet. These results were corroborated by capillary pressure versus saturation experiments, in which spontaneous imbibition of water— indicative of a water-wet system—occurred only at basic pH. In addition, interfacial films formed at acidic to neutral pH, but not at basic pH, and whenever films were present, coal tar was observed to strongly adhere to quartz. The effects observed in this study are postulated to occur due to the presence in coal tar of asphaltenes, compounds that are considered responsible for the pH-dependence of interfacial properties and formation of semisolid interfacial films in crude oil−water−rock systems.

Introduction

In the late 1800s and early 1900s, manufactured gas plants (MGP) in the U.S. and Western Europe used coal and oil to derive light-end hydrocarbons that were utilized for lighting and heating (*1*). A major byproduct of the gas manufacturing processes was coal tar, a dark-colored, dense nonaqueous phase liquid (DNAPL). Coal tar typically was disposed onsite (into wells, pits, lagoons or other bodies of water) until the development of distillation technology and refined-coal tar reuse in the late 19th century (*1, 2*). As a result of onsite disposal, coal tar-contamination of subsurface soil and groundwater is a common problem at former MGP locations.

Several long-standing issues regarding the environmental characterization and remediation of subsurface coal tar have continued to attract attention. First, coal tar is persistent in the subsurface and acts as a continuous source of ground-water contamination (*3, 4*). Second, due to the complexities associated with coal tar migration in subsurface media, many coal tar accumulations are difficult to locate (*4, 5*). Last, conventional remediation methods, such as excavation, direct pumping, and groundwater treatment, generally are not effective for removing coal tar from the subsurface (*4−9*). These issues point to a need for a more fundamental understanding of the interfacial phenomena that influence the mobilization of subsurface coal tar accumulations.

Coal tar is a compositionally complex DNAPL composed primarily of hundreds to thousands of monocyclic and polycyclic aromatic hydrocarbons such as benzene, naphthalene, and phenanthrene (*1, 2, 10−14*). Several of these aromatic compounds are suspected carcinogens (*15*). Coal tar is, therefore, a contaminant of significant concern. Various studies have also shown that coal tar contains some fraction of ill-defined, asphaltenic or high-molecular weight, polar compounds (*1, 2, 14*). Asphaltenes typically consist of aromatic compounds with heteroatoms (e.g., nitrogen, oxygen, sulfur) and/or aliphatic/cycloaliphatic substituents that are distributed throughout their structure (*16*).

Several studies in the petroleum literature have shown that asphaltenes and other high molecular weight polar components, which typically are amphiphilic, can alter mineral wettability in crude oil−water−rock systems (*17−19*). Wettability, a property that influences the subsurface flow and entrapment of nonaqueous phase liquids (NAPLs), is defined as the tendency of one fluid to spread over and adhesively coat a solid surface in the presence of another fluid. It is commonly expressed in terms of the contact angle at the water−NAPL−solid interface and measured through the water phase (*5, 20*). Contact angles less than 90° indicate that water is the wetting phase relative to NAPL. Contact angles greater than 90° indicate that NAPL is the wetting phase relative to water (*20*). The adsorption of asphaltenes and other polar compounds to mineral surfaces can change water wet systems to neutral or oil wet due to the formation of a strongly adhering film at the oil−solid interface (*21*). Benner and Bartell (*18*) and Brown and Neustadter (*22*) observed that mineral wettability varies in response to film formation, which in turn varies with pH. Oil−water interfacial tension has also been observed to vary with aqueous pH in crude oil−water systems that contain asphaltenes (*23, 24*).

Although coal tars are chemically different from crude oils, the interfacial properties of coal tar may be similarly affected by the presence of asphaltenic compounds. Luthy et al. (*25*) and Nelson et al. (*26*) observed that interfacial films do, in fact, form when coal tar is aged in water under quiescent conditions for a few days. Villaume et al. (*27*) and Powers et al. (*28*) showed that quartz wettability was altered from water wet to NAPL wet in the presence of coal tar. However, the effect of aqueous pH variation, which has been shown in crude oil studies to significantly influence film formation and alter interfacial properties, has not been investigated for coal tar systems. The objective of this study, therefore, was to demonstrate the effect of aqueous pH on coal tar interfacial properties, including interfacial tension and wettability, and the accompanying impact on capillary pressure-saturation relationships for a coal tar−water−quartz system. An additional objective of this research was to assess the effect of pH on interfacial film formation and correlate these results to interfacial property variations.

Experimental Methods

Interfacial properties of systems containing coal tar were characterized as a function of aqueous pH at a constant ionic

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strength by laboratory measurement of coal tar–water interfacial tension, wettability of quartz media as determined by contact angle, capillary pressure versus saturation experiments, and visual observations of interfacial film formation.

Coal Tar. The coal tar used in this study was obtained from a well completed in a free-flowing tar pool at a former MGP site located in Baltimore, MD. The coal tar collected from the well was brown/black in color and denser than water. Chemical and physical characteristics of the coal tar from this well have been described in detail by Ghosal et al. (29). The kinematic viscosity of the coal tar is 9.5 cSt (at 37 °C), and the specific gravity is 1.047 (at 25 °C). The average molecular weight is 226 g/mol based on vapor pressure osmometry. The general composition of the coal tar was determined using ASTM Method D2007. Aromatic compounds accounted for 98.4% (by weight) of the coal tar. Of these, naphthalene (as determined by EPA methods 8240 and 8270) was the most abundant individual constituent, accounting for 10% (by weight) of the coal tar. Asphaltenes and polar compounds accounted for 1.1% and 0.4% (by weight of the coal tar), respectively. By comparison, other coal tars as well as certain creosotes and crude oils are composed of as much as 10–15% polar compounds (12, 13).

Coal Tar–Water Interfacial Tension and Contact Angle Measurements. To evaluate the effect of aqueous pH on coal tar interfacial properties, interfacial tension and contact angle measurements for a coal tar–water–quartz system were obtained in aqueous solutions whose pH was varied from approximately 3.4 to 12.4 (at increments of approximately one pH unit) by dropwise addition of NaOH or HCl. Ionic strength was held constant at 0.1 M (with $NaClO_4$) throughout all experiments. Solution pH was measured with an Orion Model 520A pH meter equipped with a Ross Sure-Flow electrode.

Coal tar–water interfacial tension was determined (at 20 °C) using the pendant drop method, described by Ambwani and Fort (30). Coal tar pendants were formed by suspending droplets from a 2 mL micrometer syringe within a 30 mL aqueous solution of specified pH. A quartz crystal also was placed in the aqueous solution for subsequent contact angle measurements. The aqueous solution and quartz crystal were contained within an optically pure, 2.5 × 5 × 5 cm quartz cell. Each suspended coal tar droplet was viewed through the optical assembly of a contact angle goniometer (Rame-Hart, Inc.) and photographed with an attached Polaroid camera. Droplet dimensions were measured from the photograph and used to calculate the interfacial tension between coal tar and water. Prior to performing any measurements, the quartz crystals, quartz cells, and micrometer syringes were cleaned with acetone, washed with dilute Citronox, and then rinsed thoroughly with deionized water. For each set of experimental conditions, three duplicate pendants were measured, and the calculated interfacial tensions were averaged to obtain a mean interfacial tension. The reproducibility of the measurements was very good. The pooled standard deviation for interfacial tension was ±2.0 dynes/cm, ranging from ±0.3 to ±4.2 dynes/cm.

After each interfacial tension measurement, contact angle was measured in the same aqueous solution using the contact angle goniometer. The micrometer syringe was used to place coal tar droplets onto a prismatic facet of a hexagonal quartz crystal immersed in the aqueous solution. Static contact angles were measured on a flat, horizontal quartz facet using the sessile drop method described by Cohen and Mercer (5). Additionally, advancing and receding contact angles were measured by using the drop volume expansion and reduction technique described by Morrow et al. (21). For each type of contact angle measurement and each set of experimental conditions, three droplets of the organic liquid were placed on the quartz surface, and triplicate measurements of contact

angle were measured through the water phase on both sides of the droplets. All experiments were performed on the same crystal face to minimize the influence of surface variability on contact angle measurements. Preparation and cleaning procedures were identical to those used for interfacial tension measurement. Reproducibility of the contact angle measurements on the same crystal facet was also very good. The pooled standard deviation for all measurements on a single facet was ±1.2°, ranging from ±0.3° to ±3.1°. This is similar to standard deviations reported in the literature (31).

The experimental procedure for determining coal tar–water interfacial tension and contact angle as a function of pH involved filling the cell with an unbuffered aqueous solution of specified pH and ionic strength and then placing a quartz crystal and a small quantity of coal tar in the cell. The solution was gently stirred with a magnetic stir bar for 24 h to allow sufficient time for all phases to equilibrate (32). A coal tar droplet (presaturated with deionized water) was then suspended from the microsyringe, and droplet dimensions were recorded for calculation of interfacial tension. The suspended droplet of coal tar was then placed on the quartz crystal, and the static contact angle and solution pH were measured. Advancing and receding contact angles were subsequently measured by inserting the microsyringe back into the droplet and removing or adding coal tar. Most interfacial tension and contact angle measurements were recorded within 5 min of their introduction to the cell. In some cases, measurements were recorded over a 24-h period. A few static contact angles were observed for up to 1000 h.

Capillary Pressure versus Saturation Experiments. Capillary pressure-saturation curves were measured (at 20 °C) for a subset of the range of aqueous pH tested following the technique described by Demond and Roberts (33) with minor modifications. Drainage and spontaneous imbibition of water in the presence of coal tar were evaluated for aqueous solutions of pH 3, 7, and 12 using stainless steel capillary pressure cells (Soil Moisture Equipment) filled with quartz sand. The porous medium was composed of unconsolidated, medium-grained quartz sand with a mean grain diameter of 0.4 mm and a range of 0.075–2 mm. The base of the pressure cell was fitted with a porous ceramic plate (Soil Moisture Equipment) with an air entry pressure of 1 bar.

The cell was manually packed with oven-dried sand using a packing bar. The assembled cell was weighed to gravimetrically determine porosity and subsequently evacuated with CO_2 for a period of several hours to remove air from the sand pores. The evacuated cell was then saturated with water of specified solution chemistry. At least 10 pore volumes of water were flushed through the cell to solubilize the CO_2 and to completely saturate all pores. A reservoir containing coal tar was connected to the top of the pressure cell and used to displace the water in the cell. To measure the primary drainage curve of water, capillary pressure in the cell was increased initially by incrementally raising the reservoir of coal tar. The pressure at which significant water drainage began was noted and is referred to as the threshold pressure. Higher capillary pressures were achieved by connecting the coal tar reservoir to a compressed air tank and incrementally increasing the pressure in the reservoir. After each increase in pressure, the cell was allowed to equilibrate for 24 h, by which time drainage had ceased. This process was repeated until the water saturation in the cell reached an irreducible minimum. Spontaneous imbibition of water was then measured by incrementally decreasing the capillary pressure to zero (by reducing pressure on the coal tar reservoir). Water and coal tar saturation during primary drainage and spontaneous imbibition were calculated based on the incremental increase or decrease in the weight and volume of water expressed from the cell. Monitoring the weight and volume change of expressed water over time demonstrated that 24
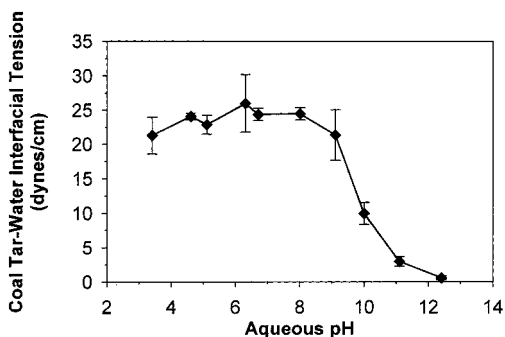
FIGURE 1. Measured coal tar–water interfacial tension (at 20 °C) as a function of aqueous pH at 0.1 M ionic strength (by addition of NaClO₄). Standard deviations of each data point were calculated from three duplicate measurements.
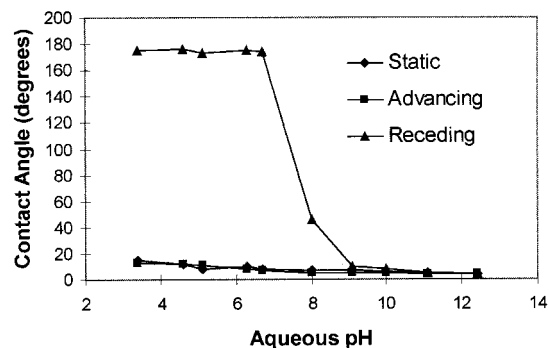

FIGURE 2. Measured static, advancing, and receding contact angles of coal tar on quartz (at 20 °C) as a function of aqueous pH at 0.1 M ionic strength (by addition of NaClO₄). Standard deviations, calculated from triplicate contact angle measurements on each side of three coal tar droplets, are smaller than the symbol size for each data point.

h was sufficient for the weight of the effluent to stabilize. The weight stabilization was assumed to indicate the achievement of equilibrium, although it is recognized that this apparent equilibrium is for the bulk liquid only and that minor discontinuous portions of the liquid may take orders of magnitude longer to equilibrate (*33*).

Qualitative Observations of Interfacial Films. The contact angle goniometer was used to detect the presence or absence of interfacial films at the coal tar–water and coal tar–quartz interfaces. At each pH value for which interfacial tension and contact angle were measured, the presence or absence of interfacial films was qualitatively assessed by deflating pendants suspended on the micrometer syringe and by deflating droplets on the quartz surface. In each case, deflation was performed by drawing coal tar back into the syringe. Interfacial films, if present, would appear as shriveled semisolid films at the contact between coal tar and water or coal tar and quartz.

Results and Discussion

Interfacial Tension as a Function of Aqueous pH. Interfacial tension between coal tar and water was determined as a function of aqueous pH (from pH 3.4 to 12.4) at constant ionic strength (0.1 M). These data are shown in Figure 1. No significant variation of interfacial tension was observed from pH 3.4 to 9.1; interfacial tension averaged 23.5 dynes/cm. However, above pH 9.1 interfacial tension decreased sharply, by approximately an order of magnitude, to a value of 0.6 dynes/cm at pH 12.4.

This observed reduction in coal tar–water interfacial tension with pH is similar to that reported for certain crude oils (*23, 24*) and hydrocarbons (*34–36*). In these studies, the interfacial tension reduction was ascribed to the presence of high molecular weight, polar organic compounds that exhibited acidic behavior in water. In explanation, the speciation of organic acids (neutral or anionic form) influences the molecular affinity of these constituents for the water and NAPL phases. When ionized as a result of increasing pH, anionic organic acid molecules become surface active— they migrate to and accumulate at the NAPL–water interface (*37*), thereby reducing interfacial tension.

The behavior observed for coal tar–water interfacial tension as a function of pH is in marked contrast to that observed for nonpolar DNAPLs. For DNAPLs such as tricholorethylene and carbon tetrachloride, interfacial tension was independent of pH over the pH range 4–10 (*38*). Additionally, the coal tar–water interfacial tensions observed over the entire pH range tested are considerably lower than the reported interfacial tensions between water and most pure DNAPLs, which typically range from 35 to 45 dynes/cm. This suggests that surface-active compounds affect coal tar–water interfacial tension over the entire range of pH

tested. As shown for crude oils, acidic organic compounds are likely responsible for the decrease in interfacial tension observed above pH 9. However, at lower pH, when these constituents are likely present in neutral form, other constituents such as basic organic compounds, which become ionized at lower pH, may be responsible for lowering the interfacial tension in the pH range 3–9. The results of this study suggest that coal tar–water interfacial tension is more sensitive to the presence of acidic organic compounds at high pH than to the presence of basic organic compounds at neutral to low pH.

Contact Angle as a Function of Aqueous pH. Static, advancing, and receding contact angles of coal tar measured on quartz as a function of pH (from pH 3.4 to 12.4) at constant ionic strength (0.1 M) are plotted in Figure 2. Static contact angles were indicative of strong water wetting conditions over the range of pH evaluated. However, a small, but measurable, decrease in static contact angle was observed as pH was increased; contact angles decreased approximately 10° over the pH range evaluated. Advancing contact angles, while slightly lower and therefore also indicative of strong water wet conditions, were not statistically different from the static contact angles. Receding contact angles were water wetting from pH 8.0 to 12.4, varying from 46.0° to 4.4°. However, from pH 3.4 to 6.7, receding contact angles varied from 173° to 176°, indicative of strong coal tar wetting.

When subjected to long term aging (up to 1000 h), static contact angles stabilized within 24 h at values roughly 20° higher than the recordings obtained within 5 min of coal tar introduction to the aqueous solution. However, since the long time frame values were still reflective of strong water wetting conditions, the shorter time frame measurements were considered representative of wetting conditions in a coal tar–water–quartz system.

The results shown in Figure 2 have broad implications regarding the wetting behavior of coal tar in water-saturated, quartz-dominated systems. Under low to neutral pH conditions, quartz-dominated systems are water wet as coal tar advances into the system, but become coal tar wet along its flow path after contact with the coal tar. Under basic pH conditions, however, the quartz-dominated system remains water wet.

During measurement of receding contact angle from pH 3.4 to 6.7, it was observed that coal tar strongly adhered to quartz over the contact area of the coal tar droplet. When the volume of a coal tar droplet was decreased, the contact area remained unchanged, and the receding contact angle proceeded to increase to coal tar wetting values. As a result, receding contact angles were highly dependent on the volume of decrease. The receding contact angles reported in Figure

2 are the maximum values observed after withdrawing nearly the entire droplet volume.

This observed sorption of coal tar to quartz in the low to neutral pH range and the resulting high receding contact angles corroborate the general findings of Villaume (*27*) and Powers et al. (*28*), who worked with coal tars from other MGP facilities. Each of the coal tars studied appears to alter quartz wettability from water wet to coal tar wet after some period of contact. However, the length of time required for the wetting reversal to occur appears to vary among studies and may be attributed to the variable composition of the different coal tars. Receding contact angles measured in this study suggest that coal tar wetting occurs nearly instantaneously upon contact with quartz surfaces. Powers et al. (*28*) observed similar wetting reversals in less than 48 h of coal tar contact with quartz in aqueous solutions of pH 7.2. Villaume (*27*), in contrast, found that coal tar wets quartz only after a lengthy equilibration time—hundreds to thousands of hours—in aqueous solutions of pH 4.6.

The presence of asphaltenic compounds in coal tar is likely responsible for the wetting behavior observed in this and other studies of coal tar. Comparable wetting behavior is reported in the petroleum literature for crude oils that contain asphaltenic compounds and other polar components (*17–19, 21*). Ionizable or polar constituents can sorb at NAPL–solid interfaces, leading to so-called adhesional wetting (*21*). Salathiel (*39*) referred to this type of behavior as mixed wettability, in that mineral surfaces in contact with NAPL are NAPL-wet, while the rest of the surfaces, not in contact with NAPL, remain water wet. Attempts to identify individual asphaltenic compounds responsible for altering wettability as well as other interfacial properties in crude oil–water–quartz systems (*40*) and coal tar systems (*25*) have proven unsuccessful. However, these compounds are believed to be high molecular weight, basic organic compounds, which have the capacity to ionize (at low to neutral pH) and become organic cations. Negatively charged surfaces, such as quartz, will preferentially adsorb compounds of the opposite polarity (cations). For example, significant changes in quartz wettability in hydrocarbon–water–quartz systems occurred in the presence of ionized organic bases or cationic surfactants (*41–43*) but not in the presence of ionized organic acids or anionic surfactants (*35, 41*).

The contact angle data presented in this study suggest that cationic organic compounds (for example, ionized basic organic compounds) are present below pH 8, resulting in sorption of coal tar onto quartz and, consequently, a coal tar wet system. At higher pH, the predominant form of basic organic compounds is the neutral species, which would not be expected to influence quartz wettability. The anionic species of acidic organic compounds believed to be present in coal tar above pH 9 (as evidenced by the decrease in interfacial tension observed at high pH) also would not be expected to lead to coal tar wetting.

Capillary Pressure versus Saturation Experiments. To evaluate the impact of interfacial tension and contact angle variation with pH on coal tar behavior in porous media, capillary pressure versus saturation curves were determined for coal tar and water in quartz sand. The drainage and imbibition capillary pressure versus saturation relationships for a coal tar–water–quartz sand system (at pH 7) and an air–water–quartz sand system (at pH 7) are presented in Figure 3a,b. The air–water–quartz sand experiment was performed to compare the capillary pressure versus saturation relationship of a system containing a well-understood, nonwetting fluid (that is, air) with that of a system containing coal tar. In both systems, drainage refers to the displacement of water by coal tar or air, and imbibition refers to the displacement of coal tar or air by water. Comparison of the imbibition curves presented in Figure 3a,b shows that little
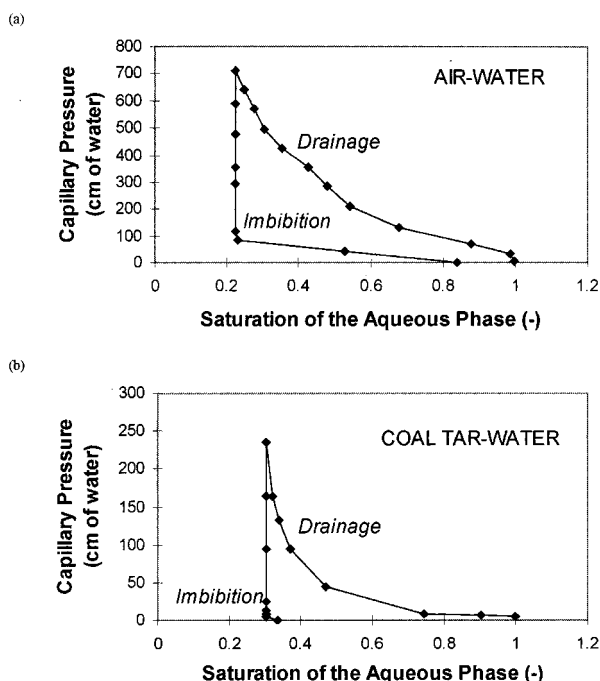

FIGURE 3. Primary drainage and spontaneous imbibition capillary pressure-saturation relationships (at 20 °C) for an air—water (a) and coal tar—water (b) system measured in a medium-grain, quartz sand at aqueous pH 7 and ionic strength 0.1 M ($NaClO_4$).

spontaneous imbibition occurs in the coal tar—water—quartz sand system relative to air—water—quartz sand system. Water saturation in the air—water system increases from 0.23 (the irreducible water saturation) to 0.84 as imbibition pressure is decreased from 100 to 0 cm of H_2O, a typical response in strongly water wet conditions (*42*). In contrast, water saturation for the coal tar—water system remains nearly constant (at the irreducible water saturation) over the same range of imbibition pressure. This difference is due to the tendency for coal tar to sorb to quartz, consequently altering the wetting character of the surface. A lack of spontaneous imbibition of water has been observed for other NAPL-wet systems, such as those containing *o*-xylene with a cationic surfactant (*43*), creosote, and coal tar (*28*). In explanation, once coal tar wetting occurs, capillary forces no longer act to spontaneously imbibe water into the media.

The occurrence or lack of spontaneous imbibition is pH dependent and resembles the dependence of contact angle on pH. The drainage and imbibition capillary pressure versus saturation relationships for coal tar—water—quartz sand systems at pH 3, 7, and 12 are shown in Figure 4a—c. Insignificant spontaneous imbibition of water was observed for a coal tar—water—quartz sand system at pH 3 and 7, implying that imbibition behavior is affected by coal tar wetting at pH ranging from acidic to neutral. At pH 12, however, spontaneous imbibition was quantifiable at very low imbibition pressures—an expected result considering that receding contact angles at pH 12 were indicative of strong water-wetting conditions.

The effect of pH on the interfacial properties of coal tar is also evident in the threshold pressures measured as a function of pH. Threshold pressure is the capillary pressure at which quantifiable water drainage begins during the drainage leg of a capillary pressure versus saturation experiment. The threshold pressures observed at pH 3 and 7, which averaged 9.4 and 6.3 cm of water, respectively, are approximately 8 to 12 times greater than those observed at pH 12, which averaged 0.8 cm of water (Table 1). Considering that threshold pressure is directly proportional to coal tar—
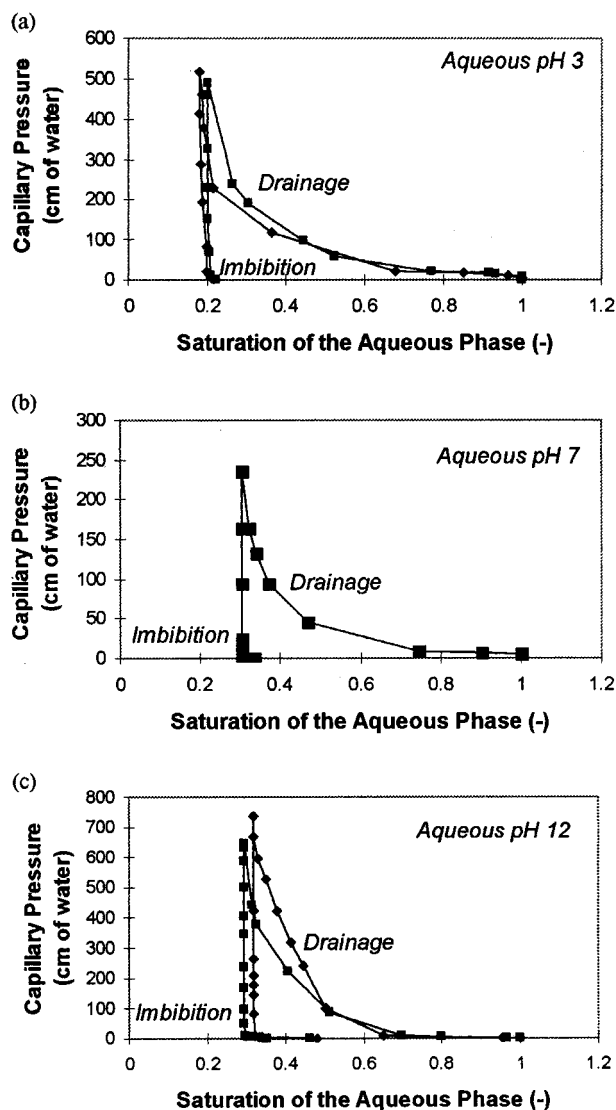
FIGURE 4. Primary drainage and spontaneous imbibition capillary pressure-saturation curves (at 20 °C) for a coal tar—water system measured in a medium-grain, quartz sand at aqueous pH 3 (a), 7 (b), and 12 (c) ($I = 0.1$ M ($NaClO_4$)).

TABLE 1. Measured[a] Values of Threshold Capillary Pressure for Entry of Baltimore Coal Tar into a Medium-Grain, Quartz Sand[b]

aqueous pH	measured threshold pressure[c] (cm of H_2O)
3.0	4.2−10.7
3.0 (replicate)	8.5−14.2
7.0	5.2−7.3
12.0	0.0−1.5
12.0 (replicate)	0.0−1.8

[a] Measured values were obtained from capillary pressure-saturation experiments. [b] Mean grain diameter of sand was 0.4 mm, ranging from 0.075 to 2.0 mm. [c] First value in range represents highest measured pressure with no drainage. Second value in range represents lowest measured pressure at which drainage is initiated.
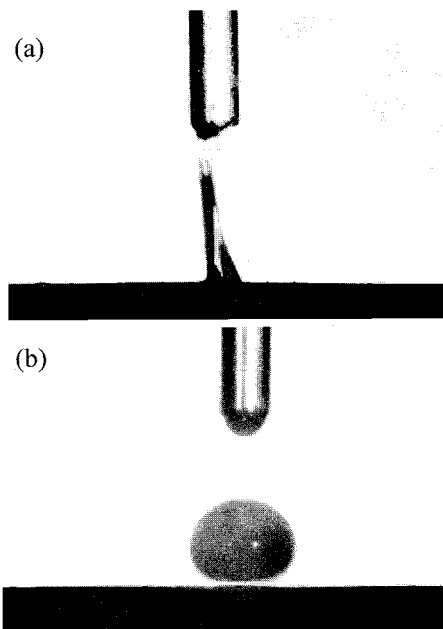

FIGURE 5. Photomicrographs of coal tar—water system at aqueous pH 7 (a) and pH 12 (b). At pH 7, the interfacial film of a deflated coal tar droplet strongly sorbs to a quartz surface. At pH 12, interfacial films were not present, and coal tar does not sorb to quartz, as evidenced by the thin veneer of water separating the droplet from the surface (needle size for scale: o.d. = 0.52 mm).

water interfacial tension (*44*), reasonably good agreement is expected and, indeed, exists between pH-induced changes in observed threshold pressure and coal tar—water interfacial tension. Both are significantly lower in aqueous solutions of basic pH. This is consistent with the findings of a number of other researchers who have shown that observed threshold pressures decrease with decreasing NAPL—water interfacial tension (*43, 45, 46*).

Interfacial Films. Qualitative assessments of the presence or absence of interfacial films indicate that interfacial film formation is dependent on aqueous pH over the pH range 3.4 to 12.4. Films formed in aqueous solutions of pH ranging from 3.4 to 8.0 but not in aqueous solutions of pH greater than 8. Reisberg and Doscher (*47*) reported a similar trend for a crude oil—water system, in which solid films formed at acid to neutral pH but not at basic pH. Coal tar films, when present, strongly adhered to quartz surfaces. Photomicrographs of coal tar droplets in aqueous solutions of pH 7 and 12 are shown in Figure 5a,b, respectively. In Figure 5a, coal tar has been removed from the interior of the droplet to expose the presence of a film. The film's tendency for tenacious sorption to quartz is evident in the picture. Conversely, at pH 12 (Figure 5b), no film formed. Addition-

ally, at pH 12, the droplet would not adhere to quartz, evident by the thin water layer separating the droplet from the surface. The thickness of the water layer is exaggerated due to distortion of the photographic image during digitization and reproduction. Lowering the pH reverses the observed interfacial effects. The correspondence between interfacial films and changes in wettability suggests that films likely play a critical role in altering wettability (from water wet to coal tar wet) in coal tar—water—quartz systems.

Implications of Findings. The results presented in this study show that aqueous pH can dramatically affect interfacial tension, wettability, and the accompanying capillary pressure-saturation relationships of coal tar—water—quartz systems. In addition, the presence of interfacial films, which form in response to pH, may affect interphase mass transfer from coal tar to water, as has been suggested by Luthy et al. (*25*). It is postulated that asphaltenic compounds in coal tar—even when these compounds comprise only a small fraction of the total mass—are responsible for the observed variations in coal tar interfacial properties as a function of pH. Both cationic compounds (at acidic to neutral pH) and anionic compounds (at basic pH) appear to be active in coal

tar over the pH range studied. Given the results of this study, it is likely that other coal and oil-derived NAPLs that contain an asphaltenic fraction, such as creosote, will exhibit interfacial phenomena similarly dependent on pH.

The mixed wetting observed in the coal tar−water−quartz system from pH 3.4 to 6.7 will likely impact the potential for coal tar recovery from subsurface accumulations. Indeed, Salathiel (39) has shown that the continuous crude-oil-wet pathways of mixed wettability systems yielded lower residual saturation than uniformly wetted systems. The reductions in interfacial tension observed at basic pH values indicate that coal tar in subsurface systems with groundwater pH greater than 8 may be significantly more mobile than coal tar in systems with neutral (or acidic) pH. These findings suggest that the ultimate selection of remedial strategies for sites with coal tar should carefully consider the mobility of coal tar in terms of the pH of the system. Additionally, alkaline flushing is a remedial strategy that may show promise for enhancing coal tar recovery.

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