

**INTERFACIAL PROPERTIES OF DENSE NON-AQUEOUS PHASE
LIQUIDS (DNAPLs) AS A FUNCTION OF ORGANIC
COMPOSITION AND AQUEOUS CHEMISTRY**

by

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A thesis submitted to the Faculty and Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Environmental Science and Engineering).

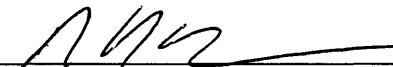
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ABSTRACT

This research was conducted to examine the influence of aqueous pH and ionic strength on interfacial properties that govern the subsurface migration, distribution, and recovery of DNAPLs containing pure, nonpolar organic compounds as well as those that contain both nonpolar and ionizable organic compounds. This study, regarding interfacial properties, was accomplished in stepwise fashion by first examining the effect of aqueous pH and ionic strength on DNAPL-water interfacial tension and quartz wettability for two pure, nonpolar DNAPLs: trichloroethylene (TCE) and carbon tetrachloride. Next, the effect of aqueous pH on interfacial tension, quartz wettability, and the accompanying capillary pressure-fluid saturation relationship was evaluated for coal tar, a multicomponent DNAPL known to contain ionizable organic components. Lastly, experiments were conducted to systematically evaluate the influence of organic base composition and concentration under varying aqueous pH and ionic strength on NAPL-water interfacial tension and quartz wettability for a series of controlled DNAPL mixtures containing TCE and an aliphatic/aromatic amine component or a pyridine component.

Experimental results show that DNAPL-water interfacial tension does not drastically vary with pH and ionic strength for DNAPLs composed of either pure nonpolar compounds or those containing the organic base components. Relatively minor, aqueous

chemistry-induced variations in wettability were observed for DNAPLs containing pure, nonpolar compounds: contact angles were observed to decrease slightly as pH and ionic strength were increased. Conversely, significant alteration of wettability—from water-wetting to DNAPL wetting-conditions—was observed for DNAPLs that contained cationic organic base components. Increasing DNAPL wetting showed a strong correlation with increasing base concentration, increasing base strength, and increasing base hydrophobicity.

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ACKNOWLEDGEMENTS

A great number of colleagues, friends, and family members have contributed in untold ways to this dissertation. Though I wish that each of you could be acknowledged herein, this document would be too expansive for binding. To those I cannot mention for the sake of brevity, I gratefully acknowledge all the support, friendship, and love you have provided through the years.

I would like to begin by thanking my Principal Advisor, Helen Dawson. Helen, has not only served as my mentor, she is one of my dearest friends. I am grateful and overjoyed to have had the opportunity to work closely with one whom I so admirably respect. I must give her credit for the original idea of this work. I developed and expanded this original research topic into related areas of my own interests to fulfill this dissertation. I would be remiss if I failed to mention that my writing skills are drastically improved as a direct result of her persistent guidance on technical writing. I am grateful for her advice, support, and assistance.

I would also like to acknowledge the assistance of my committee members: Bruce Honeyman, Donald Langmuir, Donald Macalady, Robert Siegrist, and Ivar Reimanis. The fact that several of my committee members are co-authors of journal articles developed from this dissertation is testament to their interest and involvement in this work..

Special thanks to the many people around the Environmental Science and Engineering Division for their much needed support and friendship. Over the years, I have been watching and waiting for the development of a Division culture. Reflecting back on the many enjoyable moments during my time here, I realize that we had one all along. I need

to specifically thank Eric and Andrew, who helped, no questions asked, whenever called upon. They know that I would do the same for them. Many thanks to Tim and Juanita, our unheralded support team for the Division. I could not have finished this dissertation without them.

Sincere thanks to my parents; out of their encouragement, patience, and support I have finally reached the terminal academic degree. Miles have separated us for years, but you are never far from my thoughts and dreams.

It is nearly impossible to find the words to thank my wife, Jean; she has made more compromises and concessions during the completion of this dissertation than one should rightfully have to endure. Jean has been a constant source of love and encouragement; the moral framework that kept me sane particularly toward the end of this work. Thanks also to my daughter Carolyn, who is patient with her father beyond her years. Daddy owes you, little one.

Finally, I would like to acknowledge the sources of financial support that made this work possible. Funding for this research was provided by the Baltimore Gas and Electric Company and the Environmental Science and Engineering Division at the Colorado School of Mines.

Chapter 1

INTRODUCTION

Problem Description

The capillary phenomena that govern the migration and distribution of dense nonaqueous phase liquids (DNAPLs), such as industrial chlorinated solvents, in porous media must be understood in order to adequately predict the subsurface mobility and recoverability of these environmental contaminants. The fundamental capillary characteristics of DNAPL movement are commonly described in terms of NAPL-water interfacial tension and mineral wettability. The interfacial tension that develops between NAPL and water is defined as the minimum amount of work required to create or expand the unit area of the interface between the two phases (1). Wettability, often measured as contact angle, is defined as the tendency of one fluid to spread over a mineral surface in the presence of another fluid. Interfacial tension and contact angle, when considered with pore geometry and NAPL saturation, define the capillary pressure of the NAPL-water system.

Although considerable attention has been paid in recent years to understanding the influence of NAPL-water interfacial tension, wettability and capillary pressure on the migration, distribution and recovery of NAPL contaminants, the influence of groundwater chemistry on these parameters has not been adequately studied. Many investigations have assumed that groundwater conditions, such as pH and ionic strength, have a negligible effect on the capillary phenomena that influence multiphase flow (2). For instance, it has routinely been assumed that strongly water-wetting conditions exist in aquifers regardless

of the chemistry of the groundwater or contaminants present. This assumption was based on the finding that common aquifer minerals are inherently hydrophilic (2). This assumption also has developed from the notion that DNAPLs comprised of nonpolar components do not significantly interact with the aqueous phase, regardless of solution pH and ionic strength (3, p.157). However, this assumption has not been formally evaluated for DNAPLs containing either nonpolar or polar components and may be questioned in particular for systems containing polar organic components, such as ionizable organic acids and bases. Such compounds, under certain aqueous pH and ionic strength conditions, have a charged functional group on an otherwise nonpolar chemical skeleton, rendering them amphiphilic and, therefore, capable of being surface interactive through adsorption at the DNAPL-water, DNAPL-solid and water-solid interfaces (3, p.291; 4). In turn, adsorption of these compounds at system interfaces may affect capillary properties, such as NAPL-water interfacial tension and wettability, which influence the mobility and distribution of DNAPL.

A review of the literature shows that a variety of chemically complex DNAPLs contain substituted aromatics and miscellaneous organic compounds, many of which behave as ionizable organic acids and bases (5). The major types of DNAPLs containing ionizable organic compounds are chlorinated solvent mixtures, coal tar, creosote and PCB oils. Commonly encountered organic acids in these DNAPLs include chlorophenols, nitrophenols, benzoic acid, and decanoic acid. Commonly-encountered organic bases include aromatic and aliphatic pyridines, amines, and anilines (6; 7).

The effect of aqueous pH and ionic strength on NAPL-water interfacial tension and wettability is reasonably well documented for NAPLs containing ionizable organic acids. Documented effects of aqueous pH and ionic strength on the capillary properties of NAPLs containing ionizable organic components are summarized in Table 1.1.

TABLE 1.1 Documented Effects of Aqueous pH and Ionic Strength on Capillary Properties of NAPLs Containing Ionizable Components

Reference	Parameters Measured and System Characteristics	Results and Conclusions	Implications for NAPL Mobility
(8)	IFT* measured as function of aqueous pH, ionic strength, and oleic acid concentration in water-benzene system	IFT decreased as function of increasing organic acid concentration, increasing aqueous pH and increasing ionic strength	IFT lowering represent a 24-, 219- and 875-fold reduction in Pc as function of increasing acid concentration, pH and ionic strength
(9)	IFT, visual interfacial film and emulsion tests measured as function of aqueous pH in distilled water and brine-crude oil-rock systems	IFT decreased as function of pH increase above 8; solid interfacial films (from adsorbed organic acids/bases) and emulsions unstable at high pH	pH important factor in affecting IFT lowering; observed changes correspond to a 30-fold reduction in Pc as pH raised
(10)	IFT and CA *measured as function of concentration of CTAB (cationic surfactant), Triton X-100 (nonionic surfactant), octadecanoic acid and octadecylamine (organic base) in water-benzene/n-dodecane-quartz systems	IFT decreased as CTAB, stearic acid, Triton X-100 concentrations increased; CA increased (from water-to NAPL-wetting) as CTAB and octadecylamine increased; no CA change as Triton X-100 or octadecanoic acid concentrations increased	2.9, 1.1, and 10-fold reduction in Pc as function of increasing concentration of organic acid, nonionic and cationic surfactants; cationic surfactants and organic bases promote NAPL-wetting on quartz (no restraining Pc)
(11)	IFT, CA and adsorption studies in a dodecane-water-quartz system containing the cationic surfactant CTAB	quartz reverted from initially hydrophobic in CTAB solutions to hydrophilic when aqueous ionic strength in these solutions increased	ionic strength affects cationic surfactant adsorption/desorption and wettability; high ionic strength leads to CTAB desorption and wettability reversal back to water-wetting (where positive Pc experienced)
(12)	CA in brine-crude oil-rock systems for 50 crude oils; measured primarily as a function of rock type with a few measurements as function of ionic strength	wettability of quartz reverted from water wet to oil wet (CA not available) for some crude oils with addition of 10 ppm of copper and nickel to synthetic formation water	ionic strength increases strongly affect the wettability of quartz in water-crude oil-quartz systems (although mechanism not examined); no restraining capillary force for NAPL-wet conditions
(13)	IFT of 164 crude oils in a water-crude oil system; measurements performed as a function of pH and ionic strength	IFT decreased as function of increasing pH; increasing ionic strength at high pH further decreased IFT	IFT results represent a 3000- and 30,000-fold reduction in Pc as function of increasing pH and I, respectively, in water-oil systems
(14)	ST* measured as function of pH in air-water system containing oleic acid and the organic base dodecylamine	ST decreased as function of increasing pH for oleic acid system (IFT minimum at pH 8) and for dodecylamine system (IFT minimum at pH 10); minimums coincide with peak concentration of aqueous complex of ionized and unionized species	surficially active organic acid and base species yield complex interfacial behavior as function of aqueous pH; observed max. to min. changes correspond to 1.5- and 3.1-fold reduction in Pc for acid and base, respectively
(15)	CA measured as function of pH and ionic strength (NaCl) in oil-water-silica systems	silica wetting strongly dependent on pH (NAPL-wetting at low pH and water-wetting at high pH) and ionic strength in the form of multivalent cations (water-wetting at low ionic strength and NAPL-wetting at high ionic strength)	no restraining Pc for NAPL-wet conditions (at high pH and ionic strength) in oil-water-silica systems studied

*IFT = NAPL-water interfacial tension, ST = surface tension, CA = contact angle, Pc = Capillary Pressure

TABLE 1.1 (Cont'd) Documented Effects of Aqueous pH and Ionic Strength on Capillary Properties of NAPLs Containing Ionizable Components

Reference	Parameters Measured and System Characteristics	Results and Conclusions	Implications for NAPL Mobility
(16)	CA qualitatively evaluated as function of ionic strength (transition metal ions, such as iron) in brine-crude oil-glass system	increasing ionic strength enhanced hydrophobicity (NAPL-wetting; no CA values) of glass surfaces; mechanism not examined but attributed to transition metal complexation to glass surface	No restraining Pc for NAPL-wet conditions
(17)	IFT in water-n-decane system containing oleic acid	IFT decreased as concentration of unionized acid increased ; IFT decreased as pH increased up to pka of acid; subsequent IFT increase as pH increased above pka	2.3-fold reduction in Pc as function of increasing acid concentration; 20,000-fold reduction in Pc as function of increasing aqueous pH up to acid pka
(18)	ST, CA, capillary pressure versus saturation, and electrophoretic mobility in air-water-silica system containing the cationic surfactant CTAB	decreased ST as function of increasing CTAB concentration; CA increased from strongly water-wetting to very weakly water-wetting as CTAB increased; no variation in ST and CA as function of aqueous pHs studied	ST and CA sensitive to CTAB concentration, but not sensitive to aqueous pH from 6 to 9; increasing CTAB concentration yielded 4.6-fold reduction in Pc
(19)	IFT, CA, capillary pressure versus saturation, adsorption density, and zeta potential in o-xylene-water-quartz system containing the cationic surfactant CTAB	decreased IFT, increased CA (from water-to NAPL-wetting) and decreased water imbibition as function of increasing CTAB concentration; no significant influence of pH on IFT or CA	IFT reduced an order of magnitude as function of increasing CTAB; no restraining Pc for observed NAPL-wetting conditions
(20)	IFT, CA, and capillary pressure versus saturation in water-coal tar-quartz system	decreased IFT, decreased advancing CA, decreased receding CA (from NAPL-wet to water-wet) and increased water imbibition as function of increasing aqueous pH	IFT and CA of water-coal tar systems are sensitive to solution pH due to presence of high-molecular weight, ionizable, polar impurities in coal tar; pH changes correspond to 23.5-fold reduction in Pc under NAPL advancing conditions
(21)	ST, IFT, CA, and capillary pressure versus saturation in water-air-quartz and water-o-xylene-quartz systems containing octanoic acid	increased ST and decreased IFT as function of increasing pH; decreased ST and IFT as function of increasing acid concentration; no pH or acid concentration affect on CA	ST and IFT (but not CA) of NAPLs containing organic acid components are sensitive to aqueous pH and organic acid concentration; observed changes in IFT as function of pH correspond to 1.8-fold reduction in Pc

*IFT = NAPL-water interfacial tension, ST = surface tension, CA = contact angle, Pc = Capillary Pressure

Studies with organic acids have shown that NAPL-water interfacial tension is dramatically decreased when acid functional groups are ionic rather than neutral (as a function of aqueous pH) or when acid concentration is increased (8; 17). The effect of organic acids on the wettability of common porous aquifer minerals, such as quartz, is not as dramatic. Organic acid speciation and concentration do not significantly alter quartz wettability in the presence of water because organic anions (the deprotonated conjugate base form of organic acids) have a low affinity for the mineral's net negatively-charged surface (10; 11; 21).

Much less can be said about the influence of aqueous pH and ionic strength on interfacial properties for NAPLs containing ionizable organic bases because they have been less adequately studied than organic acids, yet they are expected to yield quantifiable changes in both NAPL-water interfacial tension and wettability (10). NAPL-water interfacial tension, presumably, would be decreased when organic bases exist in ionized versus unionized form; the form being determined primarily by aqueous pH. This result would be similar to that observed for organic acids because ionized organic species, regardless of the sign of their charge, have a higher affinity for water than do neutral organic species. The influence of organic base ionization on the wettability of quartz is expected to be quantifiably greater than that of organic acid ionization. Studies have shown that organic cations (for example, cationic surfactants) strongly adsorb to negatively charged mineral surfaces (10; 19). As a result, quartz wettability likely will deviate from strong water wetting toward conditions of neutral or NAPL-wetting, depending on organic base concentration and speciation.

Such hypothesized changes of interfacial behavior will influence the subsurface migration, distribution and recoverability of DNAPLs. For instance, an organic base component may, under certain aqueous pH and ionic strength conditions, render the wettability of an aquifer intermediate wet by both water and DNAPL, thereby creating

more favorable conditions for displacement of trapped DNAPL by groundwater pumping techniques.

This research was conducted to confirm the interfacial conditions that support such hypotheses. To that end, the interfacial properties of DNAPLs containing polar and nonpolar components were evaluated and compared with the interfacial properties of DNAPLs composed solely of nonpolar components. Since aqueous pH and ionic strength govern the speciation and, consequently, the surface activity of ionizable organic compounds, the assessment of pH and ionic strength was an important component of the comparison between systems of varying DNAPL composition (that is, purely nonpolar organic components versus nonpolar and ionizable organic components).

Research Objectives

The goal of this research was to formally evaluate interfacial properties, such as interfacial tension and wettability, as a function of aqueous pH and ionic strength for DNAPLs composed of purely nonpolar components as well as for certain chemically complex DNAPLs containing ionizable organic bases, such as coal tar. Additionally, the influence of anthropogenic organic bases on interfacial properties of water-DNAPL-mineral systems was systematically evaluated in terms of organic base chemistry and concentration. The overall objectives of the research were to:

1. demonstrate that the interfacial properties of systems with DNAPLs containing purely nonpolar components do not significantly vary with aqueous pH and ionic strength relative to systems with nonpolar DNAPLs additionally containing ionizable organic components;
2. demonstrate that aqueous pH can significantly influence the interfacial properties of coal tar, a multicomponent DNAPL that contains ionizable organic components known to be surface active under certain aqueous conditions;

3. demonstrate, through the use of controlled binary DNAPL mixtures, that ionizable organic bases, when ionic, decrease NAPL-water interfacial tension and lead to significant deviations from strongly water wet conditions in water-DNAPL-quartz systems;
4. determine the compositions and concentrations of organic bases in controlled binary mixtures that can quantifiably influence interfacial properties of water-DNAPL-quartz systems.

The specific tasks required to meet the research objectives were as follows:

1. Experimentally determine the effect of aqueous pH and ionic strength on DNAPL-water interfacial tension and quartz wettability for the pure, nonpolar DNAPLs, trichloroethylene (TCE) and carbon tetrachloride.
2. Experimentally determine the effect of aqueous pH on coal tar-water interfacial tension, quartz wettability, and capillary pressure versus saturation for coal tar.
3. Experimentally determine the effect of aqueous pH, ionic strength, organic base concentration, organic base strength, and organic base hydrophobicity on NAPL-water interfacial tension and quartz wettability for a series of controlled DNAPL mixtures containing TCE and aliphatic/aromatic amines and pyridines.

Dissertation Organization

Each of the tasks described above are addressed in Chapters 2 through 4, which have been prepared in the format appropriate for the Research Section of *Environmental Science and Technology*, a peer-reviewed technical journal. Although there are multiple authors of each journal article, all work described in this dissertation was performed solely by Frank T. Barranco Jr. Each chapter contains an Introduction, Background, Experimental Methods, and Results and Discussion section. Chapter 5 provides

conclusions and implications that serve to bind the results presented in Chapters 2 through 4. Appendix A contains tabulated interfacial tension and contact angle data from Chapter 2. Appendix B provides the calculations used to estimate solid-water interfacial tension in Chapter 2.

Chapter 2 is titled “Influence of Aqueous pH and Ionic Strength on the Wettability of Quartz in the Presence of Dense Non-Aqueous Phase Liquids.” It was published in the March 1997 issue of *Environmental Science and Technology* (Volume 31, Number 3, pp. 676-681). The authors are Frank T. Barranco Jr., Helen E. Dawson, Jan M. Christener, and Bruce D. Honeyman, all of whom are associated with the Colorado School of Mines. This paper describes the experimental results of DNAPL-water interfacial tension and mineral wettability measurements performed as a function of aqueous pH and ionic strength for water-DNAPL-quartz systems containing pure TCE and carbon tetrachloride.

Chapter 3, “Influence of Aqueous pH and Ionic Strength on the Interfacial Properties of Coal Tar: Implications for Coal Tar Mobility in Water-Saturated Porous Media,” was submitted to *Environmental Science and Technology* in January 1998 and is currently being reviewed. The authors are Frank T. Barranco Jr. and Helen E. Dawson. In this paper, the influence of aqueous pH on coal tar-water interfacial tension, wettability, and the accompanying impact on capillary pressure-fluid saturation relationships, was experimentally determined for a water-coal tar-quartz system.

Chapter 4 is titled “Variation of Interfacial Tension and Quartz Wettability Induced by Anthropogenic Organic Base Components of Dense Non-Aqueous Phase Liquids.” It was prepared also for submission to *Environmental Science and Technology* by Frank T. Barranco Jr., Helen E. Dawson, and Donald L. Macalady (Colorado School of Mines). This paper describes the experimental results of interfacial tension and wettability

measurements of a water-DNAPL-quartz system containing pyridines and aliphatic/aromatic amines, anthropogenic organic bases often identified in chemically complex wastes. Interfacial properties were systematically evaluated as a function of organic base concentration, base strength, base hydrophobicity, aqueous pH and ionic strength.

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Chapter 2

**INFLUENCE OF AQUEOUS pH AND IONIC STRENGTH ON THE
WETTABILITY OF QUARTZ IN THE PRESENCE OF
DENSE NONAQUEOUS PHASE LIQUIDS**

Abstract

The location, distribution, and migration of non-aqueous phase liquids (NAPLs) in porous media are strongly influenced by the wettability of aquifer solids. Changes in wettability can significantly affect capillary pressure, relative permeability, residual saturation, and fluid displacement potential. In this study, mineral wettability by DNAPLs was evaluated as a function of aqueous pH and ionic strength for a water-DNAPL-quartz system. Contact angle and DNAPL-water interfacial tension, which is related to contact angle, were experimentally determined for trichloroethylene and carbon tetrachloride in aqueous solutions of varying pH and ionic strength. Both DNAPLs exhibited the following results: Contact angles were at a maximum near the pH of the point of zero surface charge of quartz (pH~2) and decreased as pH and ionic strength were increased. DNAPL-water interfacial tension was invariant with respect to pH and ionic strength (up to 0.1 M). Observed variations in contact angle yield calculated changes in capillary pressure as high as 10%, which may affect the mobility of DNAPLs in settings where capillary pressures are close to displacement entry pressures for porous media.

Introduction

The location, distribution, and migration of non-aqueous phase liquids (NAPLs) in porous media are strongly influenced by the wettability of aquifer solids with respect to the NAPLs (1). Wettability 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 is typically measured through the water phase (2, 3). Contact angles less than 90° generally indicate that water is the wetting phase relative to the NAPL. Contact angles greater than 90° indicate the NAPL is the wetting phase relative to water (2).

Subsurface systems can range from strongly water wet to strongly NAPL wet, depending on a number of variables, including aqueous chemistry, NAPL chemistry, aquifer mineralogy, and pore geometry (1). Early work regarding the wettability of NAPLs in aqueous systems focused on the variation of crude oil contact angle as a function of rock type and demonstrated that the contact angle of crude oil on quartz sandstone differs significantly from that on carbonate media (4). Subsequent studies of aqueous systems containing NAPLs have shown that changes in contact angle can significantly affect capillary pressure, relative permeability, residual saturation, and fluid displacement potential. Comprehensive reviews of these studies are presented by Anderson (1), who concentrated on crude oil, and Cohen and Mercer (3), who focused on DNAPLs common in environmental settings. Additional studies in which contact angle measurements for NAPLs are reported include those of Demond (5), Ethington (6), Demond and Roberts (7), and Dawson (8).

Several studies have considered the effect of solution chemistry on wettability. No discernible dependence of contact angle on solution ionic strength was observed for sodium chloride solutions (in contact with air) placed on treated glass (9). In contrast, brine ionic strength in brine-crude oil-rock systems was found to enhance sorption of

crude constituents on surfaces, thereby affecting contact angles (4, 10). Also, brine pH was found to influence wettability and other interfacial properties of crude oil in brine-crude oil-rock systems (11, 12). Benner and Bartell (13) and Brown and Neustadter (14) observed that contact angle variation resulting from aqueous chemistry changes in water-crude oil-silica systems is caused by activation of surfactant impurities present in oil. Villaume et al (15) reached a similar conclusion with regard to contact angles in water-coal tar-quartz systems. Comparable results were observed for alkane-water-quartz systems containing cationic surfactants (16, 17), in which aqueous pH and ionic strength were found to significantly affect wettability. Similarly, organic polymer-water-mica systems were observed to undergo changes in properties that affect wettability as a result of pH and ionic strength variation (18).

This paper begins with a theoretical evaluation of the influence of aqueous pH and ionic strength on the parameters that determine contact angle in a water-DNAPL-quartz system. Following the theoretical evaluation, we present the results of an experimental program where contact angle and DNAPL-water interfacial tension were determined for trichloroethylene and carbon tetrachloride in a water-DNAPL-quartz system over a broad range of aqueous pH and ionic strength. These experimental results are evaluated in terms of the theoretical framework. Finally, we discuss the significance of the experimental results with respect to capillary pressure and the potential mobility of these two DNAPLs.

Theory

Contact Angle. The contact angle a NAPL produces on quartz when at equilibrium with water is a function of the balance of interfacial tension forces, as expressed by Young's equation (2):

$$\gamma_{ow} \cos\theta = \gamma_{os} - \gamma_{ws} \quad (1)$$

where γ_{ow} is the NAPL-water interfacial tension, θ is the contact angle measured through the aqueous phase, and γ_{os} and γ_{ws} are the NAPL-quartz and water-quartz interfacial tensions, respectively. Although Young's equation has not been verified experimentally, it is extensively used (2) and widely accepted for rigid, non-deformable solids, such as quartz (19). Based on equation 1, a change in contact angle must be a function of change in one or more of the interfacial tensions (γ_{ow} , γ_{os} , or γ_{ws}).

NAPL-Water Interfacial Tension. NAPL-water interfacial tension (γ_{ow}) can be estimated from empirical and semi-empirical relationships (recently evaluated by Demond and Lindner (20)) based on the mutual solubilities of water and NAPLs (Donahue and Bartell (21) and Fu et al. (22)) and surface tensions (Antonov (23) and Girifalco and Good (24)). By considering the influence of pH and ionic strength on the parameters in these relationships, some insight is gained as to how aqueous chemistry will influence γ_{ow} .

Using Donahue and Bartell's relationship (21), γ_{ow} may be expressed as:

$$\gamma_{ow} = b - c \ln(S_{o(w)} + S_{w(o)}) \quad (2)$$

where b and c are empirically-derived constants, $S_{o(w)}$ is the mole fraction solubility of a NAPL in water, and $S_{w(o)}$ is the mole fraction solubility of water in a NAPL. Aqueous pH is expected to have little to no effect on $S_{o(w)}$ or $S_{w(o)}$ when considering nonionic organic compounds, such as trichloroethylene or carbon tetrachloride (25). Consequently, γ_{ow} is expected to be independent of pH. However, $S_{o(w)}$ is known to decrease as salt concentration increases, an effect commonly referred to as "salting out" (26). According to equation (2), this effect should result in an increase in γ_{ow} , if $S_{w(o)}$ remains constant, and suggests that γ_{ow} will increase with increasing ionic strength. Similar results are obtained with the estimation method of Fu et al. (22).

Antonov's relationship (23), in which γ_{ow} can be expressed in terms of NAPL and

water surface tensions (γ_o and γ_w , respectively),

$$\gamma_{ow} = |\gamma_o - \gamma_w| \quad (3)$$

may be similarly evaluated for the effects of ionic strength. The surface tension of water has been shown to increase when ionic strength is increased substantially above 0.1 M (2, 27). In such cases, the surface tension of water has been observed to increase approximately 2 dynes/cm per 1 M increase in ionic strength (2, 27). On a molecular scale, this phenomenon results from the stronger electrostatic attraction of aqueous ions to the bulk medium of high dielectric constant (i.e., the aqueous phase) than to the interface with a medium of low dielectric constant (i.e., DNAPL) (27). Considering that the surface tensions of organic liquids (~ 15 - 50 dynes/cm) are less than that of water (~ 73 dynes/cm at low ionic strengths), equation (3) suggests that increasing ionic strength above 0.1 M will result in an increase in NAPL-water interfacial tension, as was shown with equation (2).

The relationship derived by Girifalco and Good (24), which also expresses γ_{ow} in terms of NAPL and water surface tensions, allows us to consider the influence of solution pH and ionic strength on the intermolecular interactions across the NAPL-water interface. Using this method, γ_{ow} can be expressed as:

$$\gamma_{ow} = \gamma_o + \gamma_w - 2\Phi[\gamma_o\gamma_w]^{0.5} \quad (4)$$

where Φ represents the contributions of attractive interactions across the interface. Girifalco and Good (24) originally considered that only dispersion forces contribute to Φ . Good (28) and Fowkes (29) later considered modifications to equation (4) to compensate for polar interactions at the NAPL-water interface. While perhaps counterintuitive, polar interactions, such as dipole-dipole and dipole-induced dipole, are important for some NAPLs and water (30, 31). Since γ_{ow} increases with increasing ionic strength (as

estimated by equations (2) and (3)), it may be inferred that the net forces contributing to attraction are decreasing. Changes in pH, however, are not expected to influence γ_{ow} (as discussed earlier). This implies that the intermolecular forces acting at the NAPL-water interface are not strongly dependent on pH.

A marked increase in NAPL-water interfacial tension, γ_{ow} , (as is expected with a large increase in ionic strength) may have the effect of increasing contact angle in Young's equation. However, since ionic strength and pH may affect γ_{os} and γ_{ws} as well, contact angle (as defined by Young's equation) will depend on the relative influence of all liquid-solid and liquid-liquid interfacial tensions.

Liquid-Solid Interfacial Tension. Estimation techniques for liquid-solid interfacial tensions (γ_{ws} and γ_{os} in equation (1)) rely on the use of thermodynamic principles (2, 32). Water-quartz interfacial tension (γ_{ws}) can be indirectly estimated by considering solute adsorption from aqueous solutions to quartz surfaces. Estimation of NAPL-quartz interfacial tension (γ_{os}), however, is hampered by a lack of information regarding the specific surface interactions between NAPLs and high-energy mineral surfaces, such as quartz (2).

When chemical species partition from a dilute, aqueous phase and adsorb on a solid surface, a change in surface free energy (or water-solid interfacial tension) occurs. This change can be estimated from the Gibbs adsorption equation, which relates the extent of adsorption to water-solid interfacial tension (2):

$$\partial\gamma_{ws} = -\sum\Gamma_i RT \partial\ln a_i \quad (5)$$

where Γ is the adsorption density of individual adsorbed ionic species (i), R is the universal gas constant, T is temperature, and a is the activity of the ionic species (i) in the bulk solution. Thus, water-quartz interfacial tension can be predicted for a system in which temperature, adsorption densities, and solution concentrations of the ionic species

are known. The Gibbs adsorption equation states that an increase in the adsorption density of any species must be accompanied by a decrease in the water-solid interfacial tension (33). Adsorption densities can be determined experimentally or often estimated through the application of surface complexation models (34).

Experimental studies with quartz have shown that adsorption density is dependent on aqueous chemistry and surface charge (35, 36). For amphoteric surfaces, such as quartz, the surface has a net negative charge at pHs greater than the point of zero charge (pH_{pzc}) of the mineral (37). At pHs less than the pH_{pzc} , the surface has a net positive charge. The reported pH_{pzc} for quartz (and silica) generally falls between 1.5 and 4 (38). The magnitude of surface charge and adsorption density increases both at pHs greater than and less than the pH_{pzc} and increases with increasing ionic strength (39). For example, Li (35, 36) showed that the adsorption density of sodium ions increased as solution pH increased to values greater than the pH_{pzc} and as ionic strength increased. Conversely, adsorption density of iodide ions increased as pH decreased and ionic strength increased. Adsorption densities were zero for sodium and iodide at the pH_{pzc} .

Employing Li's adsorption density data (35, 36), we can illustrate the influence of pH and ionic strength on water-quartz interfacial tension (γ_{ws}). When the Gibbs adsorption equation is applied to Li's data and numerically integrated (methodology suggested by Parks (33)), it is possible to solve for the change in γ_{ws} with pH and ionic strength. The integration was carried out graphically by plotting $-RT\Gamma_{\text{Na}^+}$ versus $\ln a_{\text{NaOH}}$ for pH values greater than the pH_{pzc} and $-RT\Gamma_{\text{I}^-}$ versus $\ln a_{\text{HI}}$ for pH values less than the pH_{pzc} . Results of the integration are presented in Figure 2.1 and show that γ_{ws} is at a maximum between pH 3 and 7 (in the range of pH_{pzc} reported for quartz) and decreases to each side of the maximum. 2.1 also shows that, at pHs greater than 7 or less than 3, higher ionic strength results in lower water-quartz interfacial tension.

Considering these calculated trends for water-quartz interfacial tension (Figure 2.1), Young's equation suggests a maximum in contact angle should occur near the pH_{pzc} .

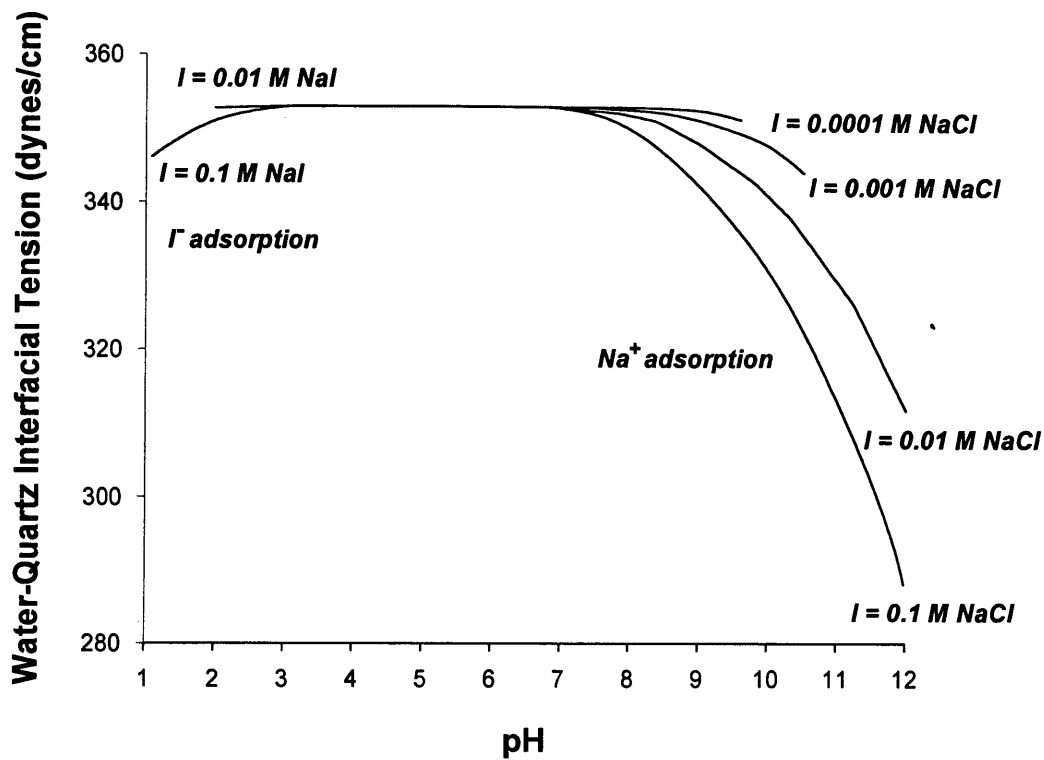


FIGURE 2.1 Computed water-quartz interfacial tension (γ_{ws}) as a function of aqueous pH and ionic strength at 20°C. This parameter was calculated by numerical integration of the Gibbs adsorption equation (methodology suggested by Parks (33) using experimentally-measured adsorption densities of Na^+ and I^- on quartz from Li (35, 36).

Additionally, increasing ionic strength should decrease contact angles when the pH is greater than 7 or less than 3. This analysis is based entirely on the observed changes in water-quartz interfacial tension as a function of pH and ionic strength. However, as described in the previous section, high values of ionic strength may have the tendency to increase NAPL-water interfacial tension (γ_{ow}) and consequently increase contact angle. Thus, actual changes in contact angle will depend on the relative influence of solution pH and ionic strength on all parameters in Young's equation.

Experimental Methods

Contact Angle Measurement. Contact angles were measured using a contact angle goniometer (Rame-Hart, Inc.) and the sessile drop method described by Cohen and Mercer (3). A 2 ml micrometer syringe was used to place trichloroethylene and carbon tetrachloride droplets onto prismatic facets of hexagonal quartz crystals in a 30 ml aqueous solution of specified pH and ionic strength. Each set of experiments used the same crystal face to minimize the influence of surface variability on contact angle measurements. The quartz crystals and aqueous solutions were contained within an optically pure, 2.5 x 5 x 5 cm, quartz cell. Prior to performing any measurements, the quartz crystals, quartz cells, and micrometer syringes were washed with dilute Citronox, then rinsed thoroughly with deionized water. (Chromerge acid washing was initially used but discontinued because of undesirable surface etching effects.)

For each set of measurements, three droplets of the organic liquid were placed on the quartz surface and triplicate measurements of contact angle were obtained from both sides of the droplets. Reproducibility of the contact angles measured in this study was very good for repeated measurements on the same crystal facet. (In contrast, contact angles for a given DNAPL measured on different crystal facets varied by as much as 10°.) The pooled standard deviation for all measurements on a single facet was $\pm 2^\circ$,

ranging from $\pm 1^\circ$ to $\pm 4^\circ$. This is in agreement with standard deviations reported in the literature (32).

Interfacial Tension Measurement. DNAPL-water interfacial tensions of trichloroethylene and carbon tetrachloride in aqueous solution were determined using the pendant drop method, described by Ambwani and Fort (40). DNAPL pendants were formed by suspending droplets from a 2 ml micrometer syringe within a 30 ml aqueous solution of set pH and ionic strength. Each droplet was viewed through the contact angle goniometer and photographed with an attached Polaroid camera. Droplet dimensions were measured from the photograph and used to calculate interfacial tension. Preparation and cleaning procedures were identical to those described in the contact angle section. For each set of experimental conditions, five duplicate pendants were measured. The calculated interfacial tensions were averaged to obtain a mean interfacial tension as a function of aqueous pH and ionic strength. Reproducibility of interfacial tension measurements was very good; the pooled standard deviation of the data was ± 2 dynes/cm, ranging from ± 1 to ± 5 dynes/cm.

pH Variation. Contact angle and interfacial tension measurements were obtained for trichloroethylene and carbon tetrachloride in aqueous solutions whose pH was typically varied from 5 to 10 (at increments of approximately one pH unit) by dropwise addition of NaOH or HCl. A series of experiments was also run in which pH was varied from 0.4 to 10. Solution pH was measured with an Orion model 520A pH meter equipped with a Ross Sure-Flow electrode. Aqueous solutions with three distinct ionic strengths were used for these experiments: 0.001 and 0.1 M for the solutions in which pH was varied from 5 to 10 and 0.4 M for the solutions in which pH was varied from 0.4 to 10. Ionic strength was held constant for the 0.001 and 0.1 M solutions with NaClO₄ and for the 0.4 M solution with HCl and NaOH.

The experimental procedure for determining contact angle as a function of pH

involved placing a quartz crystal and a small quantity of DNAPL in the quartz cell and filling the cell with an aqueous solution of specified ionic strength. The solution was then gently stirred with a magnetic stir bar for 24 hours to allow sufficient time for all phases to equilibrate (41). DNAPL droplets (presaturated with deionized water) were then placed on the quartz crystal and the contact angle and pH were measured. Subsequently, the pH was varied through appropriate additions of either NaOH or HCl, the system was allowed to equilibrate for 24 hours, and the measurements of contact angles and pH were repeated. The same protocol was followed for interfacial tension measured as a function of pH, except that droplets were suspended in solution rather than placed on the crystal.

Ionic Strength Variation. Contact angle and interfacial tension were measured for trichloroethylene and carbon tetrachloride in aqueous solutions ranging in ionic strength from 2×10^{-6} to 1 M. Sodium perchlorate was used to achieve ionic strengths above 2×10^{-6} M. The pH of the solutions remained relatively constant (approximately 5.7) for the entire range of ionic strengths tested. All other preparatory and procedural steps were similar to those employed for pH experiments, except ionic strength rather than pH was varied.

Results and Discussion

The results of DNAPL contact angle measurements on quartz as a function of pH and ionic strength are shown in Figures 2.2 and 2.3. Over the ranges of pH and ionic strength tested, contact angles varied as much as 20° , generally decreasing as pH or ionic strength increased. DNAPL-water interfacial tension was independent of pH over a range of 4 to 9.5 in a 0.1 M solution. DNAPL-water interfacial tension also was invariant with respect to ionic strengths up to values of 0.1 M, but increased markedly in a 1 M solution (Figure 2.4).

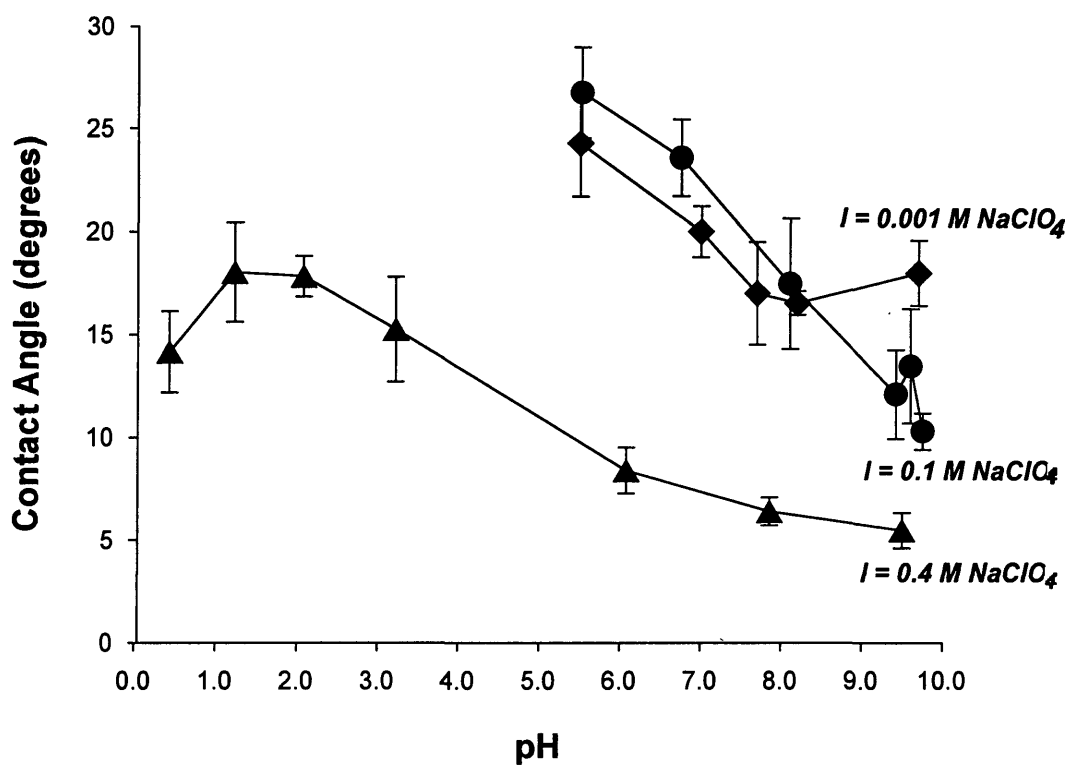


FIGURE 2.2 Measured trichloroethylene contact angles (θ) on quartz as a function of aqueous pH for several ionic strengths, at 25°C. Error bars represent the standard deviation of 18 measurements for each data point.

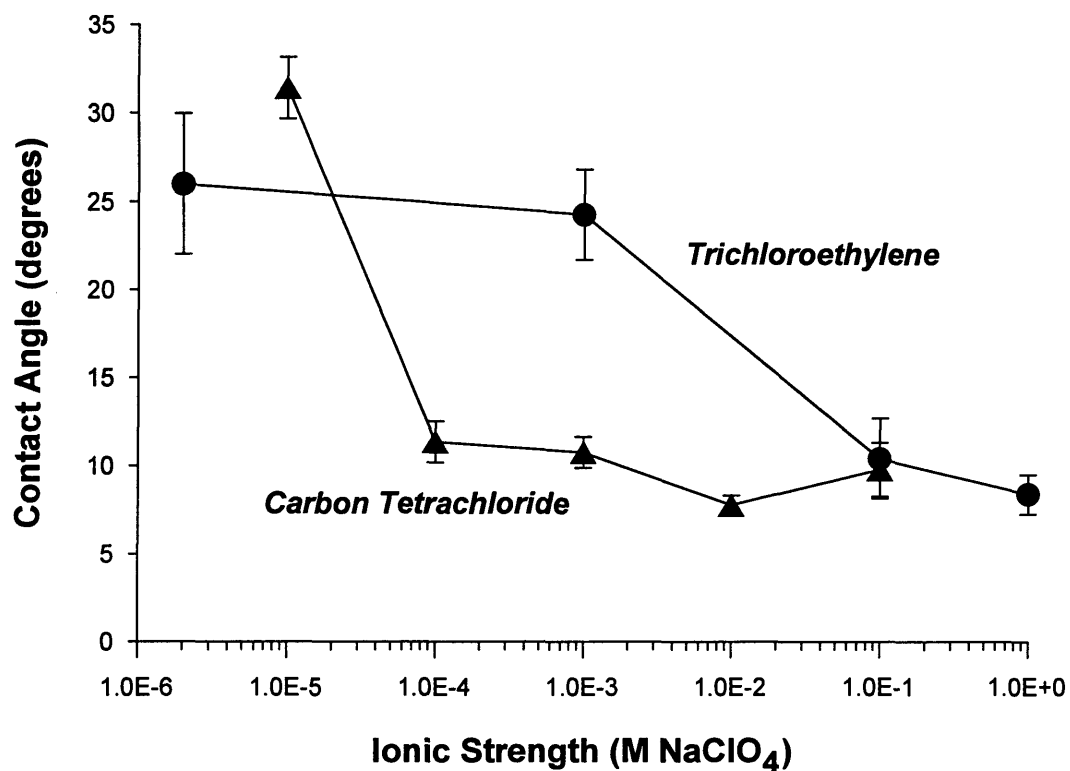


FIGURE 2.3 Measured trichloroethylene and carbon tetrachloride contact angles (θ) on quartz as a function of aqueous ionic strength, at 25°C and pH 5.7. Error bars represent the standard deviation of 18 measurements for each data point.

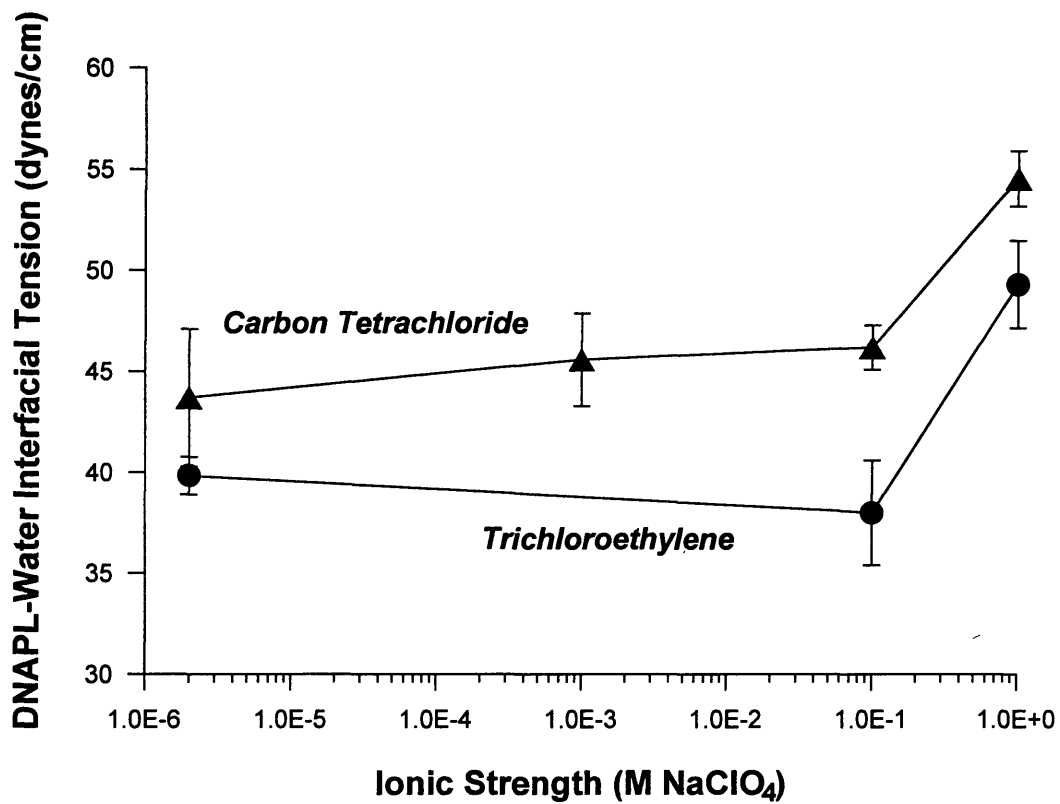


FIGURE 2.4 Measured DNAPL-water interfacial tension (γ_{ow}) for trichloroethylene and carbon tetrachloride as a function of aqueous ionic strength, at 25°C and pH 5.7. Error bars represent the standard deviation of five duplicate measurements for each data point.

Contact Angle as a Function of Aqueous pH. Trichloroethylene contact angles measured on quartz as a function of pH at several ionic strengths are plotted in Figure 2.2. A broad decrease in contact angle is observed with an increase in pH. However, a maximum in contact angle is observed between pH 1 and 2 for the 0.4 M solution. (Contact angles decreased below pH 1.) This maximum occurs near the pH_{pzc} of quartz. Lower contact angles are generally obtained for higher ionic strength solutions (although only above a pH of 8 when considering the 0.001 versus 0.1 M solutions). Similar trends were observed for carbon tetrachloride.

The overall trends shown in Figure 2.2 are commensurate with expectations from theory. As discussed earlier, a contact angle maximum should occur at the pH_{pzc} of quartz if pH-induced changes to water-quartz interfacial tension are significant relative to other Young's equation parameters. Also according to theory, ionic strength should influence contact angles, but only at pH values less than 3 or greater than 7 (Figure 2.1). Although our study employed perchlorate and chloride as the anionic electrolytes instead of iodide (as with Li's (35, 36) studies), this substitution should not affect the general arguments that we made regarding water-quartz interfacial tension.

The expected influence of ionic strength on contact angle is observed at pHs greater than 8 for the three ionic strengths tested (Figure 2.2). However, contact angles for the 0.4 M solution in the pH range of 3 to 7 were substantially lower than expected. In this region, the expectation was that contact angle curves should converge in response to the similarity of water-quartz interfacial tensions for all ionic strengths (Figure 2.1). The departure of observations from the expected trends suggests that high values of ionic strength must significantly change either DNAPL-water or DNAPL-quartz interfacial tension. DNAPL-water interfacial tension is expected from theory to increase with ionic strength, which in turn would have the effect of increasing contact angle. Since observed contact angles instead decrease, the apparent anomaly can be reasonably explained by changes in DNAPL-quartz interfacial tension. Variation of this parameter with pH and

ionic strength will be discussed further in a subsequent section describing the implications of the experimental results on DNAPL-quartz interfacial tension.

Contact Angle as a Function of Aqueous Ionic Strength. Contact angles measured for trichloroethylene and carbon tetrachloride on quartz as a function of aqueous ionic strength are plotted in Figure 2.3. The ionic strength of the solutions ranged from 2×10^{-6} to 1 M; the pH of the solutions remained constant at 5.7. Significant decreases in contact angles of both organic liquids were observed as ionic strength was increased; trichloroethylene and carbon tetrachloride contact angles decreased approximately 15° and 20° , respectively, over the ionic strength range tested. Theoretical analysis provided earlier suggested that a substantial increase in ionic strength would cause an increase in NAPL-water interfacial tension and, consequently, an increase in contact angle. However, an increase in ionic strength was also theoretically shown to decrease the water-solid interfacial tension, which would have the effect of decreasing the contact angle. Since observed contact angles decreased as ionic strength increased, contact angles appear to be more sensitive to changes in water-quartz (and potentially NAPL-quartz) than NAPL-water interfacial tension.

DNAPL-Water Interfacial Tension as a Function of Aqueous pH. DNAPL-water interfacial tensions were determined for trichloroethylene and carbon tetrachloride as a function of aqueous pH (from pH 4 to 10) at constant ionic strength (0.1 M). As expected from theory, no variation in γ_{ow} was observed. The average DNAPL-water interfacial tensions measured for trichloroethylene and carbon tetrachloride in this set of experiments were 39 and 43 dynes/cm, respectively.

DNAPL-Water Interfacial Tension as a Function of Aqueous Ionic Strength. DNAPL-water interfacial tensions for trichloroethylene and carbon tetrachloride, observed as a function of ionic strength (at a constant pH of 5.7), are presented in Figure 2.4. This parameter varied little for ionic strengths in the range of 2×10^{-6} M to 0.1 M.

Average DNAPL-water interfacial tension over this range was 39 and 45 dynes/cm for trichloroethylene and carbon tetrachloride, respectively. However, as predicted from estimation methods (equations (2), (3), and (4)), interfacial tensions increased sharply for ionic strengths greater than 0.1 M (an increase of approximately 10 dynes/cm from 0.1 to 1.0 M). These results suggest that in most aqueous systems (which have ionic strengths of 0.1 M or less), DNAPL-water interfacial tensions for trichloroethylene and carbon tetrachloride may be considered constant.

Implications of Experimental Results for DNAPL-Quartz Interfacial Tension.

NAPL-quartz interfacial tension (γ_{os}) is a parameter which is not directly amenable to measurement and thus was not quantified with the experimental methods employed in this study. However, the behavior of γ_{os} as a function of pH and ionic strength can be assessed by applying the results of this study to relationships containing γ_{os} . Two such relationships are considered here: Young's equation (1), which was described in the theory section, and a formulation developed by Neumann (32) that also relates γ_{os} to the water-quartz and DNAPL-water interfacial tensions. Neumann's relationship written for a water-DNAPL-quartz system is:

$$\gamma_{ws} = \frac{\gamma_{os} + \gamma_{ow} - 2\beta\sqrt{\gamma_{os}\gamma_{ow}}}{1 - 2\alpha\sqrt{\gamma_{os}\gamma_{ow}}} \quad (6)$$

where α and β represent constants that are a function of the liquids and solids analyzed. If water-quartz interfacial tension (γ_{ws}) varies with pH and ionic strength (as described in the theory section) and if DNAPL-water interfacial tension (γ_{ow}) is constant (as shown in the experimental results for all aqueous conditions studied except ionic strengths greater than 0.1 M), then equation (6) implies that DNAPL-solid interfacial tension (γ_{os}) must also vary as a function of pH and ionic strength.

Young's equation yields similar results. If DNAPL-quartz interfacial tension is

considered independent of pH and ionic strength, application of the calculated water-quartz interfacial tensions and the measured DNAPL-water interfacial tensions to Young's equation yields contact angles that are much lower than the observed values, in some cases less than zero. This result is clearly not possible. We thus conclude that the DNAPL-quartz interfacial tension also varies as a function of aqueous pH and ionic strength. To yield the contact angles observed in this study, DNAPL-quartz interfacial tensions for trichloroethylene and carbon tetrachloride must decrease substantially as pH increases to values greater than the pH_{pzc} and/or as ionic strength increases.

Such changes to DNAPL-quartz interfacial tension may result from an increase in the interfacial forces of attraction between DNAPLs and quartz as pH or ionic strength increase. This effect could result from dipole induction between DNAPL and the charged quartz surface, as has been observed for neutral organic compounds such as carbon tetrachloride and benzene (30). Moreover, water solubilized in the DNAPL may enhance the DNAPLs attraction to the charged mineral surface due to additional forces of hydrogen bonding and dipole-dipole interaction.

Implication of Experimental Results for Capillary Pressure. The observed changes in contact angle are related to changes in capillary pressure, a parameter that governs mobility of NAPLs in the subsurface. Capillary pressure (P_c), defined by (42):

$$P_c = \frac{2\gamma_{ow} \cos\theta}{r} \quad (7)$$

is a function of contact angle (θ), DNAPL-water interfacial tension (γ_{ow}), and pore radius (r).

Results of this study show that contact angle, and consequently capillary pressure, is a function of pH and ionic strength. Observed contact angle variations suggest that capillary pressure in a water-DNAPL-quartz system may increase by as much as 10% as pH varies from 5 to 10 in solutions of 0.1 M ionic strength. Smaller changes are

estimated for solutions of lower ionic strength. The calculated changes in capillary pressure are relatively small and, consequently, may not significantly affect DNAPL behavior in most subsurface systems. This conclusion is in agreement with findings of Morrow et al. (43), who showed that capillary pressure versus saturation relationships are fairly insensitive to contact angle for organic liquids with angles below 73° . The observed changes may, however, affect DNAPL mobility in systems with capillary pressure near the displacement entry pressure of particular porous media. For example, if mobilization of a subsurface accumulation of DNAPL in a water-saturated aquifer is desired, the critical hydraulic gradient (3) required to mobilize the DNAPL increases as capillary pressure increases, since hydraulic gradient is directly proportional to capillary pressure. Thus, a 10% increase in capillary pressure requires a 10% increase in the critical hydraulic gradient required to mobilize the DNAPL. Higher groundwater pH and/or ionic strength, consequently, may lead to potentially decreased recoverability of DNAPLs.

Nomenclature

- a activity of ionic species (moles/kg)
- b empirical constant (-)
- c empirical constant (-)
- P_c capillary pressure (dynes/cm²)
- R universal gas constant (8.3145 J/mol·K)
- r pore throat radius (cm)
- $S_{o(w)}$ mole fraction solubility of NAPL in water (-)
- $S_{w(o)}$ mole fraction solubility of water in NAPL (-)
- α empirical constant (-)
- β empirical constant (-)

- γ_w surface tension of water (saturated with NAPL) (dynes/cm)
- γ_o surface tension of NAPL (saturated with water) (dynes/cm)
- γ_{ow} NAPL-water interfacial tension (saturated with quartz) (dynes/cm)
- γ_{ws} water-solid interfacial tension (saturated with NAPL) (dynes/cm)
- γ_{os} NAPL-solid interfacial tension (saturated with water) (dynes/cm)
- Γ adsorption density (moles/cm²)
- Φ intermolecular interaction parameter (–)
- θ contact angle (degrees)

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Chapter 3

INFLUENCE OF AQUEOUS pH ON THE INTERFACIAL PROPERTIES OF COAL TAR. IMPLICATIONS FOR COAL TAR MOBILITY IN WATER- SATURATED POROUS MEDIA

Abstract

Dense nonaqueous phase liquids (DNAPLs), such as coal tar, represent a significant environmental concern due to their toxicity and persistence in the subsurface. This paper demonstrates the dependence of coal tar interfacial properties such as interfacial tension and contact angle—properties that can significantly influence the mobility of DNAPLs in the subsurface—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 to 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 water wets quartz media under coal tar-advancing conditions over the entire pH range tested. However, coal tar wets quartz media under coal-tar-receding conditions at acidic to neutral pH, but not at basic 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 semi-solid 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 non-aqueous 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 nineteenth 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 groundwater 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). Lastly, 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 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.

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 NaClO₄) 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 x 5 x 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, 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.

Subsequent to 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 very good. The pooled standard deviation for all measurements on a single facet was $\pm 1.2^\circ$, ranging from $\pm 0.3^\circ$ to $\pm 3.1^\circ$. 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 hours 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.

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 to 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 CO₂ 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 CO₂ 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 hours, 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.

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 semi-solid 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 Table 3.1 and Figure 3.1. 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 non-polar DNAPLs. For DNAPLs such as trichloroethylene and carbon tetrachloride, interfacial tension was independent of pH over the pH range 4 to 10 (38). Additionally, the coal tar-water interfacial tensions

TABLE 3.1 Experimentally-Determined Values of Coal Tar-Water Interfacial Tension^{a,b,c} for Baltimore Coal Tar as Function of Aqueous pH^{d,e}

Aqueous pH	Interfacial Tension (dynes/cm)
3.4	21.3 (2.7)
4.6	24.1 (0.5)
5.1	22.9 (1.4)
6.3	26.0 (4.2)
6.7	24.4 (0.9)
8.0	24.5 (0.9)
9.1	21.4 (3.7)
10.0	10.0 (1.6)
11.1	3.0 (0.7)
12.4	0.6 (0.3)

a. All measurements performed at 20°C.

b. Standard deviations are shown in parentheses following mean value of parameter.

c. Interfacial tensions represent the mean value of three duplicate measurements.

d. Aqueous pH adjustment performed with HCl or NaOH.

e. Ionic strength adjustment performed with NaClO₄.

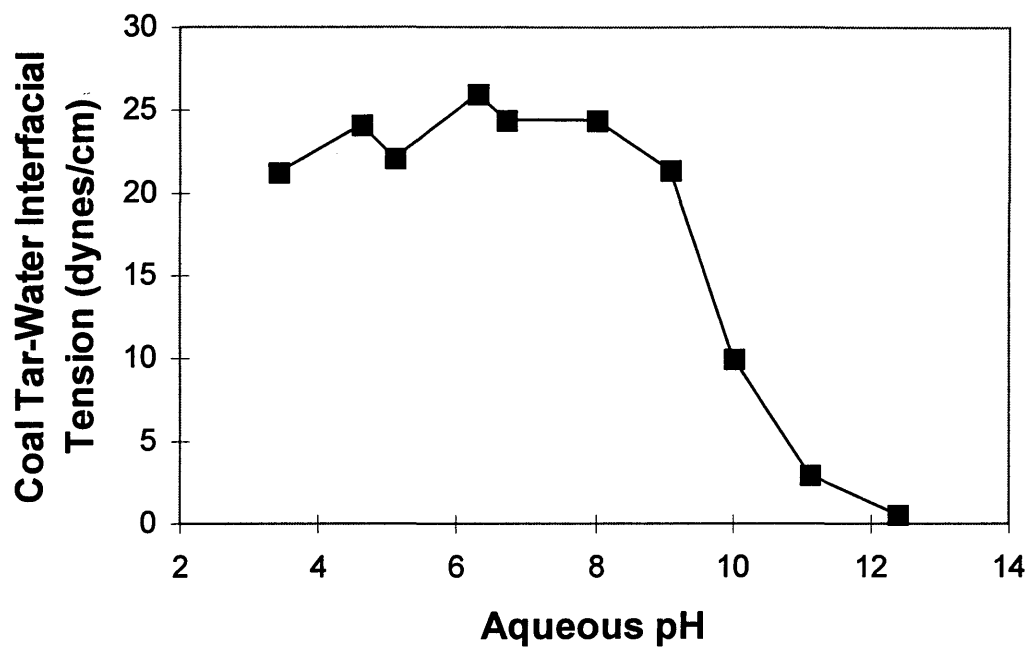


FIGURE 3.1 Measured coal tar-water interfacial tension (at 20°C) as a function of aqueous pH at 0.1 M ionic strength (by addition of NaClO₄). Standard deviations of each data point, shown in Table 3.1, were calculated from three duplicate measurements.

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 to 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 given in Table 3.2 and plotted in Figure 3.2. 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. When subjected to long term aging (1000 hrs), static contact angles stabilized roughly 20° higher than the instantaneous recordings reported herein. Advancing contact angles, also indicative of strong water wetting, were 1 to 2° lower than static contact angles for a given pH. 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 coal tar wetting. These results have broad implications regarding the wetting behavior of coal tar in water-saturated, quartz-dominated systems. Under low to neutral pH condition, 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-

TABLE 3.2 Experimentally-Determined Values of Advancing, Static, and Receding Contact Angle^{a,b,c} for Baltimore Coal Tar as Function of Aqueous pH^{d,e}

Aqueous pH	Advancing (degrees)	Static (degrees)	Receding (degrees)
3.4	13.1 (1.0)	15.1 (1.1)	175.2 (1.9)
4.6	12.3 (1.3)	12.3 (0.9)	176.4 (2.5)
5.1	10.5 (1.4)	8.5 (0.8)	173.3 (2.8)
6.3	8.4 (0.9)	10.0 (0.9)	175.1 (3.1)
6.7	6.6 (0.8)	7.7 (0.9)	174.2 (1.7)
8.0	5.4 (1.2)	7.0 (0.3)	46.0 (1.9)
9.1	5.0 (1.5)	6.8 (0.5)	10.1 (1.5)
10.0	4.6 (1.0)	5.9 (0.5)	8.2 (2.5)
11.1	4.0 (1.3)	4.7 (0.7)	5.1 (2.2)
12.4	3.7 (1.4)	4.4 (0.7)	4.4 (1.7)

a. All measurements performed at 20°C.

b. Standard deviations are shown in parentheses following the mean value of parameter.

c. Contact angles represent mean value of triplicate measurements on each side of three coal tar droplets.

d. Aqueous pH adjustment performed with HCl or NaOH.

e. Ionic strength adjustment performed with NaClO₄.

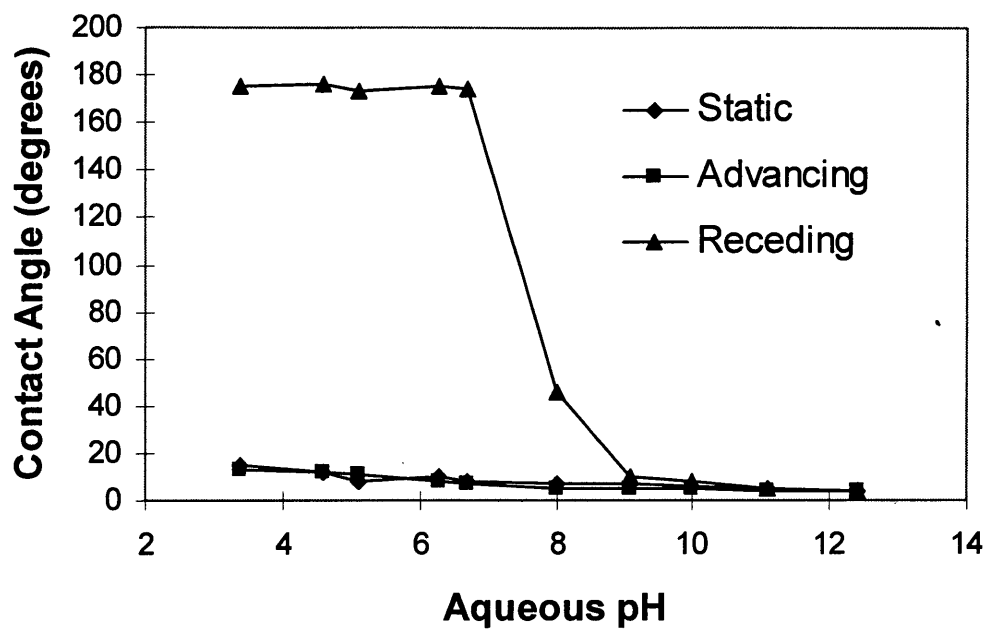


FIGURE 3.2 Measured static, advancing, and receding contact angles of coal tar on quartz (at 20° C) as a function of aqueous pH at 0.1 M ionic strength (by addition of NaClO₄). Standard deviations of each data point, shown in Table 3.2, were calculated from triplicate measurements on each side of three coal tar droplets.

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. Receding contact angles reported in Table 3.2 and Figure 3.2 represent 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 hrs 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.

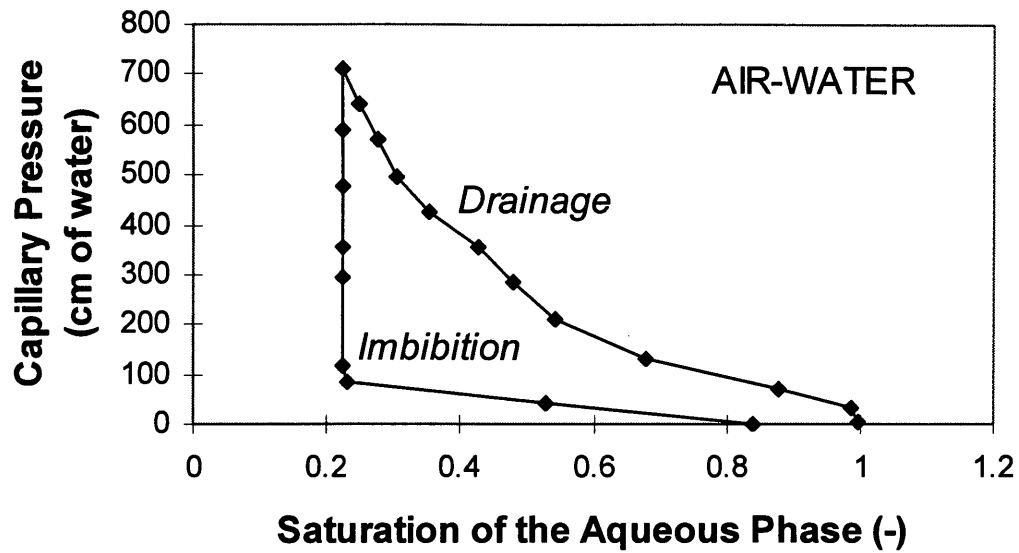
The presence of asphaltenic compounds in coal tar is likely responsible for the wetting behavior observed in this and other studies of coal tar. Comparable wetting behavior is reported in the petroleum literature for crude oils that contain asphaltenic compounds and other polar components (17-19, 21). 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. In order 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 3.3 (a) and (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)

(a)



(b)

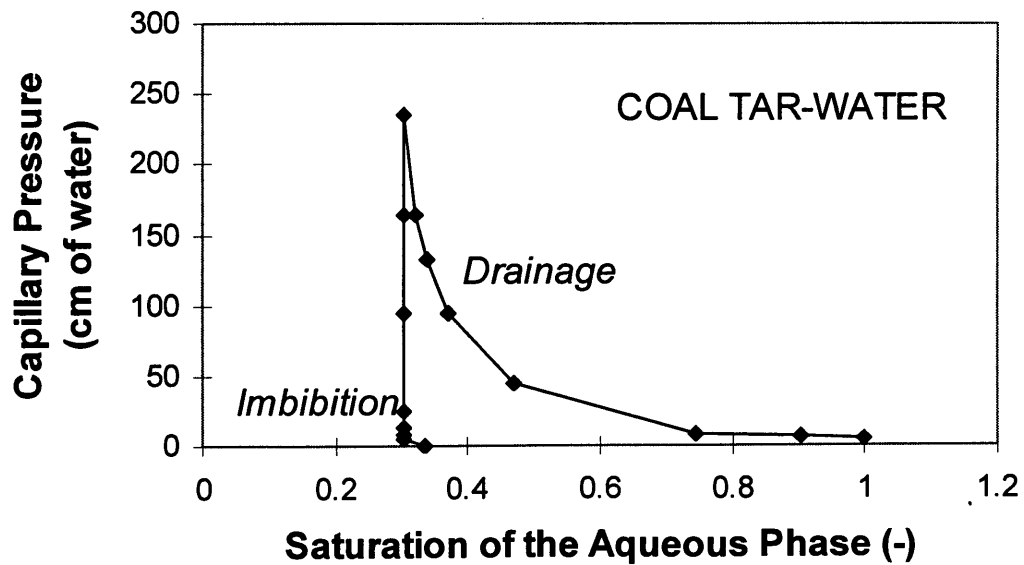


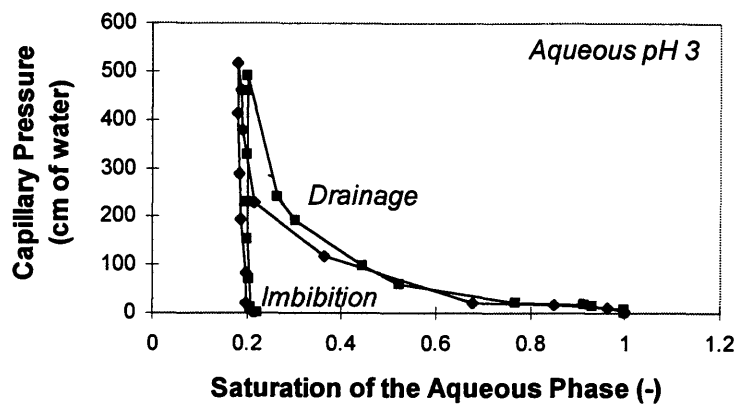
FIGURE 3.3 Primary drainage and spontaneous imbibition capillary pressure-saturation relationships (at 20° C) for an air-water (a) and coal tar-water (b) system measured in a medium-grain, quartz sand at aqueous pH 7 and ionic strength 0.1 M (NaClO₄).

by water. Comparison of the plots presented in Figure 3.3 (a) and (b) shows that spontaneous imbibition is insignificant in the coal tar-water-quartz sand system relative to air-water-quartz sand system. Spontaneous imbibition of water occurs in the system with air as a result of strong water wetting conditions (42). Conversely, minimal spontaneous imbibition of water occurs in the system with coal tar as a result of the tendency for coal tar to sorb to quartz. 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.

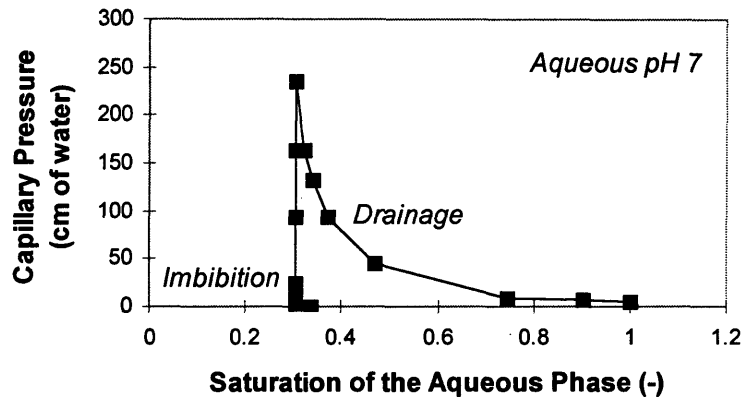
The occurrence or lack of spontaneous imbibition is pH dependent and resembles the dependence of contact angle on pH. The drainage and imbibition capillary pressure versus saturation relationships for coal tar-water-quartz sand systems at pH 3, 7 and 12 are shown in Figure 3.4 (a), (b), and (c). Insignificant 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 3.3). Considering that threshold pressure is directly proportional to coal tar-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

(a)



(b)



(c)

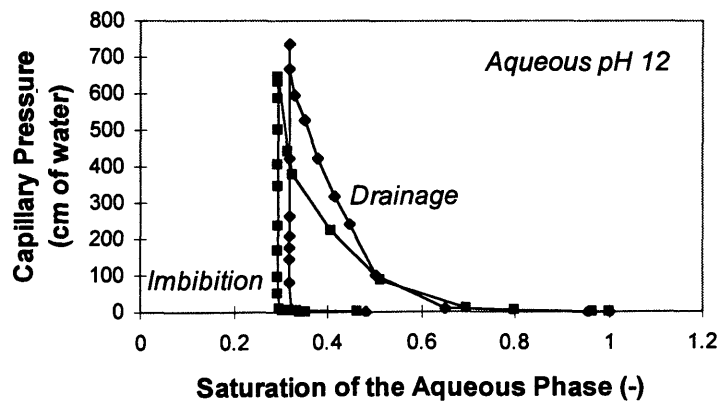


FIGURE 3.4 Primary drainage and spontaneous imbibition capillary pressure-saturation curves (at 20° C) for a coal tar-water system measured in a medium-grain, quartz sand at aqueous pH 3 (a), 7 (b), and 12 (c) ($I = 0.1 \text{ M (NaClO}_4\text{)}$).

TABLE 3.3 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 ₂ O)
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 0.4mm, 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.

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 3.5 (a) and (b), respectively. In Figure 3.5 (a), coal tar has been removed from the interior of the droplet to expose the presence of a film. The film's tendency for tenacious

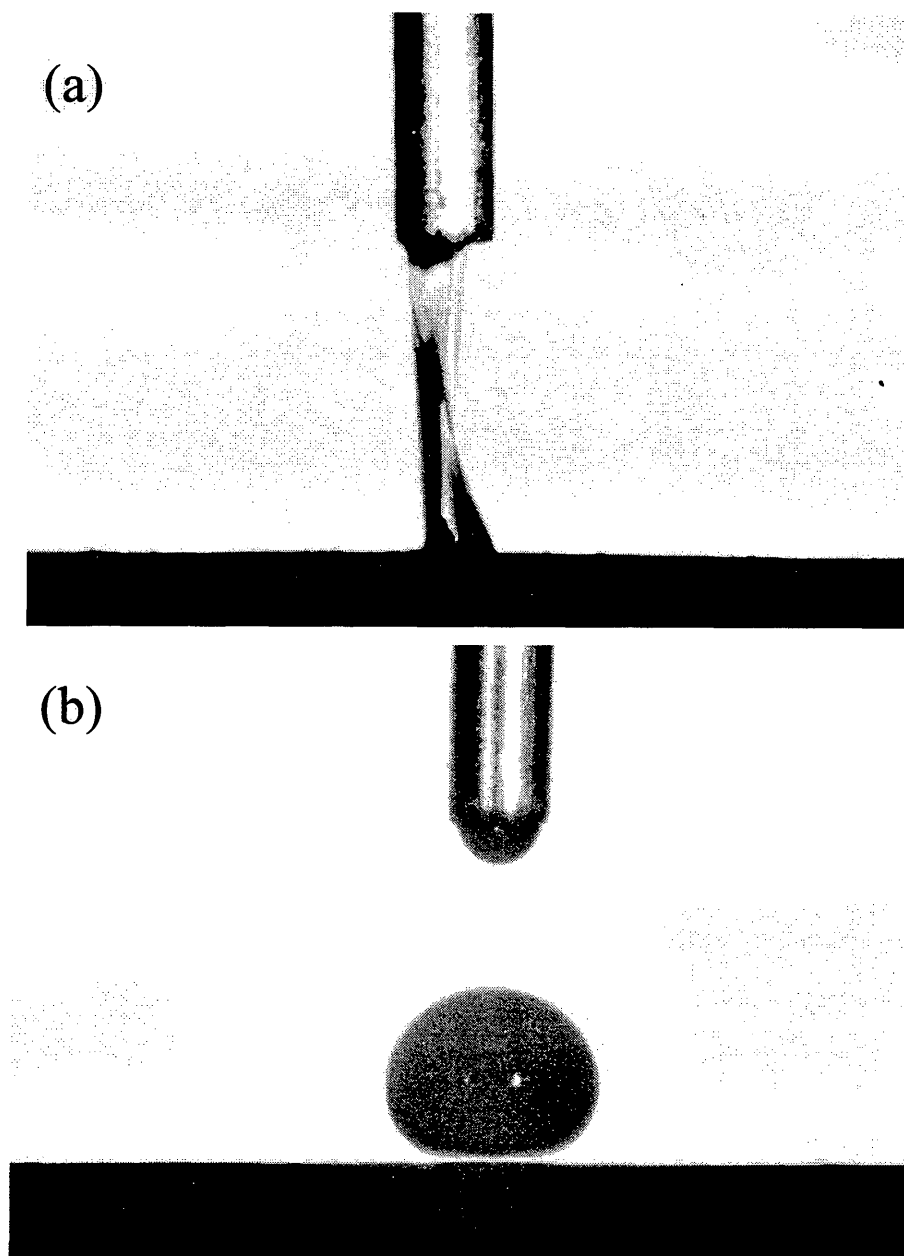


FIGURE 3.5 Photomicrographs of coal tar-water system at aqueous pH 7 (a) and pH 12 (b). At pH 7, the interfacial film of a deflated coal tar droplet strongly sorbs to a quartz surface. At pH 12, interfacial films were not present and coal tar does not sorb to quartz, as evidenced by the thin veneer of water separating the droplet from the surface (Needle size for scale: o.d.=0.52 mm).

sorption to quartz is evident in the picture. Conversely, at pH 12 (Figure 3.5 (b)), no film formed. Additionally, at pH 12, the droplet would not adhere to quartz, evident by the thin water layer separating the droplet from the surface. Alternately raising and lowering pH could reverse the observed effects. The correlation 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. 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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Chapter 4

VARIATION OF INTERFACIAL TENSION AND QUARTZ WETTABILITY INDUCED BY ANTHROPOGENIC ORGANIC BASE COMPONENTS OF DENSE NONAQUEOUS PHASE LIQUIDS

Abstract

A variety of dense nonaqueous phase liquids (DNAPLs) identified in the subsurface at hazardous wastes sites reportedly contain substituted aromatic and miscellaneous organic components, many of which behave as ionizable organic bases. This study demonstrates the dependence of interfacial tension and mineral wettability—properties that can significantly influence the mobility of DNAPLs in the subsurface—on the presence of anthropogenic organic base components in a water-DNAPL-quartz system with trichloroethylene (TCE) as the predominant DNAPL component. DNAPL-water interfacial tension and quartz wettability were experimentally determined as a function of organic base strength (pKa range: 4.6-9.4), organic base hydrophobicity (alkyl chain length: 1-18 carbons), organic base concentration in TCE (10^{-6} - 10^{-2} M), aqueous pH (2.3-12.0) and ionic strength (10^{-4} - 10^{-1} M) for a suite of aliphatic/aromatic amines and pyridines. Interfacial tension and wettability variation showed a strong correlation between solution pH and pKa. Interfacial tension and contact angle were invariant with respect to factors evaluated when the neutral form of the organic base was abundantly present relative to the cationic form (aqueous pH \gg pKa). Even with abundant cationic organic base present, interfacial tension was observed to vary only slightly with pH, ionic

strength, base concentration and hydrophobicity— a maximum change from 40.5 to 32.4 dyn/cm as octadecylamine concentration was increased from 10^{-5} to 10^{-2} M— and negligibly with base strength. Conversely, significant alteration of quartz wettability, from strongly water wetting (for pure TCE) to DNAPL wetting, was observed as a function of increasing base concentration, base strength, and base hydrophobicity when the cationic form was abundantly present relative to the neutral form (aqueous $\text{pH} \ll \text{pK}_a$).

Introduction

Many dense nonaqueous phase liquids (DNAPLs) identified in the subsurface at hazardous waste sites reportedly contain more than one compound, resulting from the release of codisposed pollutants or from subsurface mixing of organic liquids (1, 2). Denser-than-water organic liquid mixtures, commonly referred to as multicomponent DNAPLs, also may be created by chemical and biological degradation reactions resulting from natural and remedial processes (3, 4). Often found mixed with nonpolar chlorinated solvents, such as trichloroethylene (TCE), in multicomponent DNAPLs are a variety of substituted aromatics and miscellaneous organic compounds, many of which behave as ionizable organic acids and bases. Commonly encountered organic acids in waste mixtures include chlorophenols, nitrophenols, benzoic acid, and decanoic acid. Commonly encountered organic bases include pyridines and aliphatic/aromatic amines (2, 5). Such compounds, under certain aqueous pH and ionic strength conditions, contain a charged functional group on an otherwise nonpolar chemical skeleton, rendering them amphiphilic (having both hydrophilic and hydrophobic moieties) and, therefore, capable of being surface active through sorption at the DNAPL-water, DNAPL-solid and water-solid interfaces (6, 7). In turn, sorption of these compounds at system interfaces may

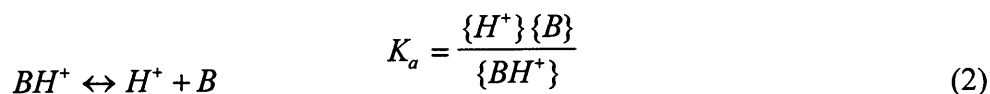
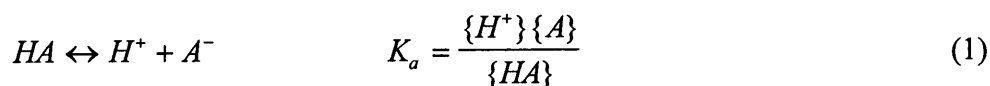
affect capillary properties, such as DNAPL-water interfacial tension and wettability, which influence the mobility and distribution of nonaqueous-phase contaminants.

To accurately assess the migration, distribution and recovery of multicomponent DNAPLs containing ionizable organic acids and bases, their complex chemistry should be considered. Yet, most assessments of subsurface DNAPL migration have treated the organic phase as a pure, nonpolar compound (1). As a result, little specific information exists about how the presence of ionizable organic constituents in DNAPLs composed primarily of nonpolar compounds affect important capillary phenomena in subsurface environments. Realizing that the mobility and entrapment of these DNAPLs will depend on interfacial properties, which are a function of the composition of the organic and aqueous phases, it becomes increasingly apparent that the relationship between DNAPL composition and aqueous conditions (for example, pH and ionic strength) must be examined to adequately predict the migration of chemically complex DNAPLs.

Previous studies have demonstrated that ionized organic acid components reduce NAPL-water interfacial tension (8-10), but have no effect on the wettability of commonly encountered, negatively charged minerals, such as quartz (10, 11). The influence of organic base components on interfacial properties has not been systematically evaluated, yet they are expected to yield quantifiable changes in both interfacial tension and wettability of water-DNAPL-mineral systems. The purpose of this study, therefore, was to evaluate the effect of anthropogenic organic bases, such as pyridines and aliphatic/aromatic amines, on interfacial tension and wettability of a controlled water-DNAPL-quartz system by analyzing a number of bases that vary in concentration, base strength, and molecular hydrophobicity. An additional objective of this work was to examine the relationship between aqueous conditions (pH and ionic strength) and interfacial properties for a controlled water-DNAPL-quartz system containing an amine compound that exhibited a high degree of interfacial property variation as a function of the component's concentration in the DNAPL studied.

Background

Speciation of Organic Acids and Bases. The interfacial properties of a water-DNAPL-mineral system may be influenced by the ability of amphiphilic DNAPL components to concentrate (or adsorb) at fluid-fluid and fluid-solid interfaces, thereby reducing the differences between the phases' intermolecular interactions. Amphiphilic behavior of organic acid and base components is largely controlled by their ability to, first, diffuse from the DNAPL phase to the DNAPL-water interface and to, then, undergo a dissociation/association reaction to an extent governed by the aqueous pH (12). For instance, a neutral organic base can become amphiphilic when functional groups, undergoing an association reaction, develop a positive charge (7, 13). The dissociation/association reaction and equilibria expression for organic acids and bases to form ionic species in the presence of water are shown below:



where { } is the activity of each species in aqueous solution, HA is the neutral acid, A⁻ is the deprotonated conjugate base, H⁺ is the proton, BH⁺ is the protonated conjugate acid, and B is the neutral base. Neutral organic acids undergo deprotonation to form anions, whereas neutral organic bases undergo protonation to form cations. The speciation of organic acids and bases will influence their distribution within the DNAPL and aqueous phase and also the degree to which fluid-fluid and fluid-solid surface activity is manifested; the ionic form (rather than neutral form) is the more interfacially active (7).

Effect of Organic Acids and Bases on NAPL-Water Interfacial Tension.

Effect of Acid and Base Concentration. Several studies with chemically complex NAPLs composed collectively of nonpolar and ionizable components have considered the effect of the ionizable component concentration on NAPL-water interfacial tension. Controlled experiments with a water-dodecane system containing stearic acid (11) and a water-o-xylene system containing octanoic acid (10) demonstrated that interfacial tension decreases as a function of increasing ionized acid concentration. Furthermore, small additions of ionic surfactants to systems with an aqueous phase and an aliphatic hydrocarbon phase have been shown to substantially lower interfacial tension (13-15). Additionally, studies in the petroleum literature have shown that high-molecular weight, ionizable acidic and basic compounds, residing in the asphaltene and resin fractions of certain crude oils, reduce interfacial tension of brine-crude oil systems by several orders of magnitude (16-19).

Effect of Aqueous pH and Ionic Strength. The effect of aqueous pH on NAPL-water interfacial tension is well-documented for water-benzene and water-n-decane systems containing oleic acid (8, 9) as well as a water-o-xylene system containing octanoic acid (10). Dramatic decreases in NAPL-water interfacial tension were observed when acid species were ionic (high aqueous pH) versus neutral (low aqueous pH). A few studies have identified more complex interfacial and solution behavior in which interfacial tension was at a minimum when the aqueous pH coincided with the acids' pK_{as} (9, 20). These phenomena, occurring as a function of pH, are in marked contrast to that observed for nonpolar DNAPLs. Studies with trichloroethylene and carbon tetrachloride in water-DNAPL-quartz systems have shown that interfacial tension is independent of pH over the pH range 4 to 10 (21).

The ionic strength of the aqueous phase has also been observed to affect NAPL-water interfacial tension in systems containing ionizable organic acids and bases. Studies of a

benzene-water system containing oleic acid (8), a crude oil-water system (19) and a coal tar-water system (22) have shown that significant reduction in NAPL-water interfacial tension occurs as a function of increasing aqueous-phase ionic strength. This phenomenon presumably occurs because an increase in the concentration of aqueous ions promotes more favorable interactions with the relatively polar functional groups of constituents in the NAPL phase.

Effect of Organic Acid and Base Speciation on Mineral Wettability.

Effect of Acid and Base Concentration. Wettability, the tendency of one fluid phase to spread over a mineral surface in the presence of another phase, will depend on the characteristics of the mineral, such as surface charge, and the composition of the fluids that make contact with these surfaces. Components, dissolved in either a NAPL or water phase, may have the potential to sorb to mineral surfaces and, consequently, alter the surface's wetting state. Sorption of nonpolar or neutral organic compounds to charged mineral surfaces is energetically unfavorable and, therefore, has limited effect on the wettability of charged minerals, such as quartz (21). However, polar or ionizable organic compounds have the potential to sorb to mineral surfaces of opposite sign through electrostatic interactions and/or chemical bonding with charged surface sites (7, 13). For instance, protonated forms of atrazine (23) and aliphatic amines (24) have been observed to sorb strongly to negatively charged mineral surfaces, such as quartz and smectite. McCaffrey and Mungan (11) observed that sorption of protonated octadecylamine, when present in n-dodecane at concentrations higher than 10^{-3} M, resulted in wettability alteration of quartz media from strong water wetting to NAPL wetting. Furthermore, researchers in the petroleum industry have recognized for decades that high-molecular weight, nitrogen-containing organic bases in crude oil strongly adhere to mineral surfaces, altering wettability from strong water-wetting to oil-wetting conditions (16, 25-27). High-molecular weight organic bases similar to those present in crude oil may be

responsible for wettability alterations observed in coal tar-water-quartz systems (22, 28-29).

Effect of Aqueous pH and Ionic Strength. Studies with chemically complex NAPLs containing polar or ionizable organic components illustrate that wettability can be affected by aqueous pH and ionic strength, which influence the speciation of ionizable organic constituents (ionic or neutral form) as well as the charge of mineral surfaces present. Aqueous pH and ionic strength influence both the sign and magnitude of surface charge of most common aquifer minerals. For instance, quartz surfaces have a net negative charge in aqueous systems with pH greater than about 2 and the magnitude of charge increases as pH increases above this value (30). The magnitude of quartz surface charge also increases as ionic strength increases. If mineral surface charge is of opposite sign to that exhibited by an ionizable functional group of an organic compound, then electrostatic and chemical forces may lead to adsorption of the organic molecule to the surface (either directly at the surface or in the thin film of surrounding water). As a result, marked changes in quartz wettability (changes from water- to oil-wetting) of water-hydrocarbon-quartz systems have occurred in the presence of cationic surfactants and ionized organic bases (11, 15, 31). Conversely, ionizable organic compounds with the same sign of charge as the surface will be repulsed from the near-surface water and, consequently, will sorb minimally. As a result, neither anionic surfactants nor ionized organic acids significantly alter the wettability of such systems (10, 11).

The studies cited above allude to interfacial phenomena associated with water-NAPL-mineral systems that contain ionic organic constituents. However, many questions remain as to how interfacial tension and wettability vary as a function of ionic component concentration and aqueous chemistry. Furthermore, these potential influences have been largely unexplored for systems containing organic base components. To that end, this study was performed to evaluate the influence of organic base compositional variation and aqueous chemistry changes on a water-DNAPL-quartz system.

Experimental Methods

To examine the dependence of interfacial properties on DNAPL composition and aqueous conditions, a number of laboratory experiments with different system conditions were performed. First, interfacial properties of a water-trichloroethylene (TCE)-quartz system amended with two sets of organic bases, one varying in organic base strength and the other varying in organic base hydrophobicity, were characterized by laboratory determination of DNAPL-water interfacial tension and wettability of quartz media. Next, interfacial tension and quartz wettability were evaluated as a function of aqueous pH and ionic strength for an organic base that promoted significant changes in wettability during the hydrophobicity experiments. Wettability was determined in terms of contact angle at the water-DNAPL-quartz interface and measured through the water phase. All measurements and sample preparations were performed at room temperature, 21 ± 2 °C. The next two sections summarize the sample preparation and measurement procedure common to all experiments. Following sections describe experimental conditions for the factors evaluated.

Interfacial Tension Measurements. DNAPL-water interfacial tension was determined using the pendant drop method, described by Ambwani and Fort (32). DNAPL pendants were formed by suspending droplets from a 2 ml micrometer syringe within a 30 ml aqueous solution of specified base concentration, pH, and ionic strength. 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 x 5 x 5 cm quartz cell. Each suspended DNAPL 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 DNAPL and

water. Prior to performing any measurements and after each measurement of a specified condition, the quartz crystal, quartz cell, and micrometer syringe were cleaned with 0.1 M NaOH, followed with acetone cleaning, then washed with dilute Citronox, and finally 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 all interfacial tension measurements was ± 1.1 dynes/cm, ranging from ± 0.3 to ± 2.2 dynes/cm.

Contact Angle Measurements. Contact angle was measured subsequent to each interfacial tension measurement in the same aqueous solution using the contact angle goniometer. The micrometer syringe was used to place DNAPL 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 (*1*). Additionally, advancing and receding contact angles, which provide an indication of surface wetting before and after contact with DNAPL, were measured by using the drop volume expansion and reduction technique described by Morrow et al. (*26*). 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. Contact angles were allowed to equilibrate prior to measurement. Contact angle equilibration throughout all experiments was relatively fast: angle stabilization occurred within 10 minutes of droplet placement on the surface. 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 very

good. The pooled standard deviation for all measurements on a single facet was $\pm 1.2^\circ$, ranging from $\pm 0.3^\circ$ to $\pm 9.6^\circ$, the higher standard deviations correlating with receding angles. These standard deviations are similar to those reported in the literature (33).

Organic Base Strength Experiments. To evaluate the effect of organic base strength on interfacial properties, interfacial tension and contact angle measurements were obtained for a water-TCE-quartz system containing individual aliphatic/aromatic amines and pyridines of similar molecular size and structure, but different base strength (expressed as the acidity constant (or pKa) of the base's conjugate acid). Compound selection was based on association with identified organic base wastes (2, 5), commercial availability, compound similarity (except for factor to be varied), and appropriate base strength. The compounds evaluated (in order of increasing pKa) were aniline, pyridine, 2,4-dimethylpyridine, 2,4-dichlorobenzylamine, and benzylamine. The pKa's of the preceding compounds, respectively, are 4.63, 5.42, 6.95, 8.43, and 9.39 (34). Aniline, a compound with a low pKa will be present in ambient pH water predominantly as a neutral base. Conversely, benzylamine, a compound with a high pKa (9.39), will be present in ambient pH water predominantly as a cation. Each organic base was evaluated over the concentration range 10^{-5} to 10^{-2} M (molar concentration within the DNAPL phase), the concentration range observed for interfacial property variation in previous studies of organic acids and bases (10, 11). Measurements with each organic base were made at approximately two pH units below (base present predominantly in cationic form) and two pH units above (base present predominantly in neutral form) the compound's pKa in order to evaluate the influence of organic base speciation on interfacial tension and contact angle. Ionic strength was held constant at 10^{-2} M (with NaClO_4) throughout the measurements. The influence of the cationic organic base on ionic strength was minimal, even at high base concentrations, considering that a total of only 50 microliters of DNAPL was added to the cell for each experimental condition.

Organic Base Hydrophobicity Experiments. To evaluate the effect of organic base hydrophobicity on interfacial properties, interfacial tension and contact angle measurements were obtained for a water-TCE-quartz system containing individual aliphatic/aromatic amines of similar molecular size/structure and similar organic base strength (pK_a range: 9.39-10.60), but different hydrophobicity (expressed as the length of the aliphatic chain connected to the amine functional group). Compound selection was based on criteria similar to organic base strength experiments; however, hydrophobicity rather than base strength was considered. Compounds evaluated (in order of increasing hydrophobicity) were benzylamine, phenylethylamine, phenylbutylamine, and octadecylamine. As with organic base strength measurements, each compound was evaluated from 10^{-5} to 10^{-2} M (molar concentration within the DNAPL phase) at approximately two pH units below and two pH units above the compound's pK_a . Ionic strength was held constant at 10^{-2} M (with NaClO_4) throughout the measurements. The influence of the cationic organic base on ionic strength was, again, minimal for reasons explained in the previous section.

Aqueous pH Experiment. To evaluate the effect of aqueous pH on interfacial properties, interfacial tension and contact angle measurements were obtained for a water-TCE-quartz system containing 5×10^{-3} M (molar concentration within the DNAPL phase) phenylbutylamine, a compound that promoted large changes in contact angle as a function of compound concentration and hydrophobicity. Aqueous pH was varied from 2.3 to 12.4 (at increments of approximately one pH unit) by dropwise addition of NaOH or HCl. Solution pH was measured with an Orion model 520A pH meter equipped with a Ross Sure-Flow electrode. Ionic strength was held constant at 10^{-2} M (with NaClO_4) throughout the measurements.

The experimental procedure for determining interfacial tension and contact angle as a function of pH involved filling the cell with an aqueous solution (presaturated with TCE)

of specified pH and ionic strength, and then placing a quartz crystal in the cell. The solution was gently stirred with a magnetic stir bar for 1 hour to allow sufficient time for liquid-solid phase equilibration (35). A DNAPL droplet (TCE presaturated with deionized water and amended with a specified concentration of organic base) was then suspended from the microsyringe and droplet dimensions were recorded for calculation of interfacial tension. This procedure was repeated in triplicate. The three suspended droplets of DNAPL, for interfacial tension measurement, were placed consecutively 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 each droplet and removing or adding DNAPL. Subsequently, the cell and all utensils were cleaned, a new solution to evaluate the next specified pH was prepared, and the measurements of interfacial tension and contact angle were repeated.

Aqueous Ionic Strength Experiment. To evaluate the effect of aqueous ionic strength on interfacial properties, interfacial tension and contact angle measurements were obtained for a water-TCE-quartz system containing 5×10^{-3} M (molar concentration within the DNAPL phase) phenylbutylamine, selected for similar reasons as the pH experiment. Aqueous solution ionic strength was varied from 10^{-4} to 10^{-1} M (with NaClO_4), a range inclusive of most natural and remedial systems. For reasons explained in previous Experimental Method sections, the effect of cationic phenylbutylamine on ionic strength was minimal. Aqueous pH was held constant at 6.28 (phenylbutylamine present predominantly in cationic form) throughout the measurements. All preparatory and procedural steps were similar to those employed for pH experiments, except ionic strength rather than pH was varied.

Results and Discussion

Interfacial Tension as a Function of Organic Base Strength and Concentration.

DNAPL-water interfacial tension was determined as a function of organic base strength (pKa ranging from 4.63 to 9.39 for series including aniline, pyridine, 2,4-dimethylpyridine, 2,4-dichlorobenzylamine, and benzylamine) and base concentration (10^{-5} to 10^{-2} M in DNAPL phase) at approximately two pH units below and above each compound's pKa in a 10^{-2} M NaClO₄ aqueous solution. These data are listed in Table 4.1. When pH conditions dictated the predominance of the cationic base species, a slight but quantifiable reduction of interfacial tension with increasing base concentration occurred for all compounds analyzed. No significant variation (as indicated by analysis of variance (ANOVA) at the 95% significance level) of interfacial tension occurred as a function of increasing pKa for the compounds analyzed. The interfacial tension of aniline and benzylamine, the respective endmembers of base strength, decreased from 37.9 to 35.3 and 40.7 to 36.6 dyn/cm, respectively, as base concentration was increased from 10^{-5} to 10^{-2} M in the DNAPL phase. When pH conditions dictated the predominance of the neutral base form (that is, when pH was 2 units above the base's pKa), no significant change of interfacial tension (compared with pure TCE (21)) with increasing organic base strength or concentration occurred.

The observed reduction of interfacial tension with increasing base concentration, when compounds were present predominantly in cationic form (pH approximately 2 units less than the base's pKa), is similar to that reported for certain crude oils (17, 19) and hydrocarbons (8-10). In these studies, interfacial tension reduction was ascribed to the presence of ionizable organic compounds that exhibited acidic and/or basic behavior in water. In explanation, the speciation of acids and bases (ionic or neutral form) influences the constituent's molecular affinity for the water and NAPL phases. When ionized as a result of aqueous pH, ionic organic molecules become surface active—they migrate to

TABLE 4.1 Experimentally-Determined Values of Trichloroethylene-Water Interfacial Tension^{a,b,c} as Function of Organic Base Strength^d and Concentration

Interfacial Tension Measurements of Cationic Organic Base Form^e					
Base Conc. (M)	Aniline (pKa=4.63)	Pyridine (pKa=5.42)	2,4-Dimethyl- pyridine (pKa=6.95)	2,4-Dichloro- benzylamine (pKa=8.43)	Benzylamine (pKa=9.39)
0.00001		40.3 (1.8)	39.6 (0.8)	38.8 (1.6)	40.7 (0.4)
0.0001	38.4 (0.4)	38.7 (0.3)	38.3 (1.2)	37.3 (0.7)	39.2 (1.7)
0.001	36.2 (0.8)	36.2 (0.3)	37.0 (0.5)	35.1 (1.1)	38.4 (0.6)
0.005		34.3 (0.3)	35.8 (0.6)	34.6 (0.3)	38.0 (0.7)
0.01	34.5 (0.8)	34.0 (0.6)	34.8 (0.6)	34.7 (0.8)	36.6 (0.7)

Interfacial Tension Measurements of Neutral Organic Base Form^f					
Base Conc. (M)	Aniline (pKa=4.63)	Pyridine (pKa=5.42)	2,4-Dimethyl- pyridine (pKa=6.95)	2,4-Dichloro- benzylamine (pKa=8.43)	Benzylamine (pKa=9.39)
0.00001		39.1 (1.3)	39.8 (0.8)	38.8 (1.2)	41.0 (1.4)
0.0001	38.8 (0.8)	39.5 (1.1)	40.2 (1.1)	40.5 (0.4)	41.6 (1.8)
0.001	38.3 (1.2)	40.2 (0.8)	39.2 (0.6)	40.3 (0.9)	40.5 (0.5)
0.005		38.7 (1.0)	38.6 (0.7)	39.9 (1.4)	40.1 (0.9)
0.01	38.3 (1.2)	39.5 (0.6)	39.8 (1.3)	39.0 (2.2)	39.9 (1.5)

^a All measurements performed at 21°C. Ionic strength set at 10⁻² M with NaClO₄.

^b Standard deviations are shown in parentheses following mean value of parameter.

^c Interfacial tensions represent the mean value of three duplicate measurements.

^d Organic base strength expressed as pK_a of the conjugate acid.

^e All measurements performed at aqueous pH approximately two pH units below the base pK_a.

^f All measurements performed at aqueous pH approximately two pH units above the base pK_a.

and accumulate at the NAPL-water interface (13), thereby reducing interfacial tension. Conversely, when present predominantly in neutral form, ionizable organic molecules are not surface active (7) and, therefore, do not lower interfacial tension. Because the observed reductions of interfacial tension are small relative to the reductions induced by commercial surfactants (13), it can be concluded that the aliphatic/aromatic amines and pyridines studied lack the degree of surface activity required for marked NAPL-water interfacial tension alteration. This may result from their lack of a long-chain hydrocarbon, hydrophobic group common to surfactants (13) that efficiently reduce interfacial tension at the compound concentrations assessed.

Quartz Wettability as a Function of Organic Base Strength and Concentration.

Advancing, static, and receding contact angles were measured on quartz (in a 10^{-2} M NaClO_4 aqueous solution) as a function of organic base strength (pKa ranging from 4.63 to 9.39 for series including aniline, pyridine, 2,4-dimethylpyridine, 2,4-dichlorobenzylamine, and benzylamine) and base concentration (10^{-5} to 10^{-2} M in DNAPL phase) at approximately two pH units below and above each compound's pKa. Advancing, static, and receding angles versus organic base strength and concentration are shown in Figure 4.1 for the condition where pH was less than the pKa (abundance of cationic organic base form). Dramatic increases in advancing, static, and receding contact angles were observed for all compounds, except aniline. The degree of increase in contact angle was more substantial as organic base strength and concentration increased. For instance, Figure 4.1 shows that as base concentration was increased, the increase in receding contact angle of benzylamine (23.4 to 114.3°) was substantially greater than that of aniline (15.4 to 21.4°). These results show also that quartz wettability, under receding conditions, can be reversed (from strongly water wetting to DNAPL wetting) by the addition of aliphatic/aromatic amines (such as, benzylamine) to TCE in millimolar concentrations. Addition of millimolar concentrations of pyridine-

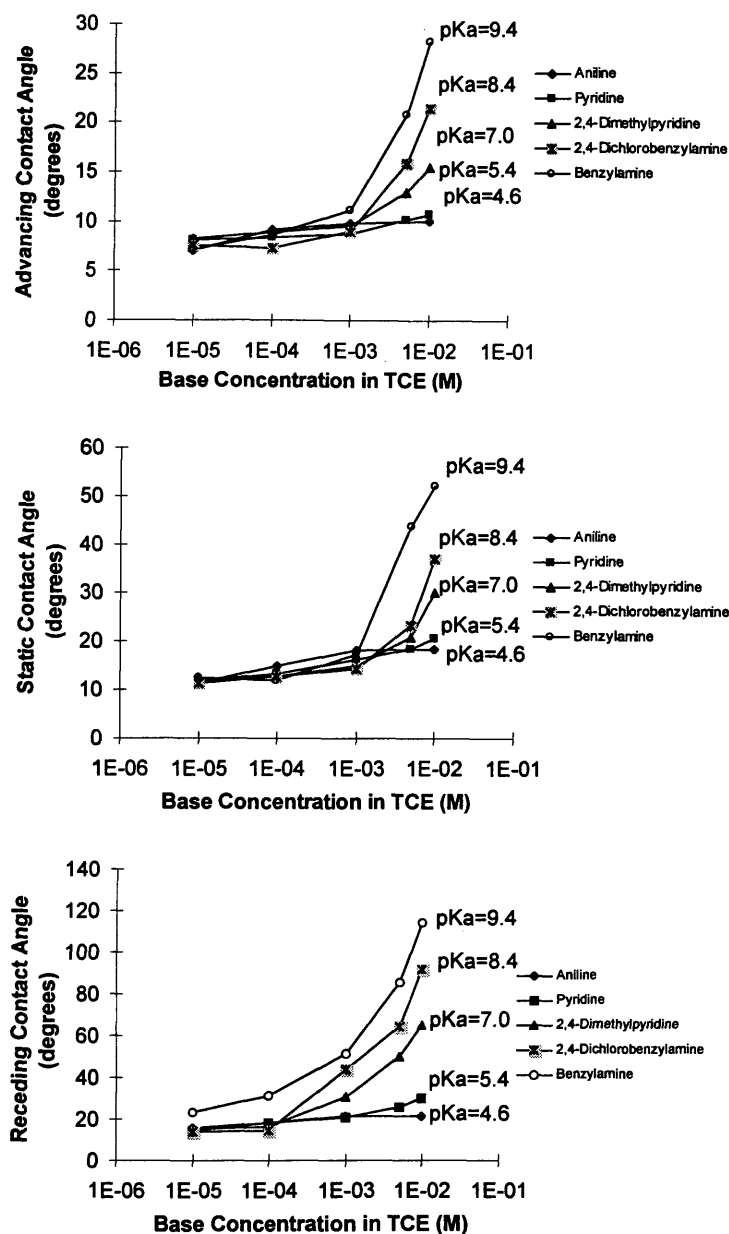


FIGURE 4.1 Measured advancing, static, and receding contact angles (at 21° C) of trichloroethylene containing organic bases varying in base strength (pKa 4.63 to 9.39). Contact angles were measured on quartz in the presence of a 10^{-2} M ionic strength (with NaClO_4) aqueous solution. Aqueous pH was set for each organic base at approximately two pH units below the compound's pKa. Each data point represents the average of triplicate measurements on each side of three DNAPL droplets. The pooled standard deviation for all data is 1.8.

type compounds of intermediate base strength (such as, and 2,4-dimethylpyridine) appear to alter quartz wettability, under receding conditions, from strongly water wetting to intermediate wetting. Contact angles were indicative of adhesional-type wetting (26): receding contact angles were substantially higher than advancing and static contact angles for a given compound. However, advancing and static angles increased as well with increasing base strength and concentration. At aqueous conditions in which the organic base was present predominantly in neutral form, advancing, static, and receding contact angles were strongly water wetting (7.4° to 15.6°) and invariant with respect to organic base strength and concentration for all bases tested.

The observed trends have broad implications regarding the influence of organic base sorption on the wetting behavior of quartz-dominated systems. Weak bases have a tendency to protonate only in aqueous solutions of low pH. At these conditions, quartz surfaces exhibit a net negative charge that is insignificant (or even zero) relative to higher pH. The reported pH of zero point of charge for quartz (and silica) is approximately 2 (30). In the absence of electrostatic and chemical forces resulting from a significantly charged quartz surface, adsorption of charged organic base molecules to surface sites and consequent alteration of wettability is not expected. Conversely, strong bases have a tendency to remain protonated even in aqueous solutions at high pH. At these conditions, a relatively high density of net negatively charged surface sites is expected for oxide minerals, such as quartz. Thus, the sorption of strong base cations to quartz at high pH appears to be more favorable than for weak base cations at low pH. Consequently, the impact of organic base sorption on quartz wettability is more significant for strong bases than weak bases.

Interfacial Tension as a Function of Organic Base Hydrophobicity. DNAPL-water interfacial tension was determined as a function of organic base hydrophobicity (increasing aliphatic chain length from 1 to 18 carbons for series including benzylamine,

phenylethylamine, phenylbutylamine, and octadecylamine) and base concentration (10^{-5} to 10^{-2} M in DNAPL phase) at approximately two pH units below and above each compound's pKa in a 10^{-2} M NaClO₄ aqueous solution. Results are reported in Table 4.2. As observed with the data from organic base strength experiments, a slight but quantifiable reduction of interfacial tension with increasing base concentration occurred for all bases analyzed when pH conditions promoted the predominance of the cationic form. Changes to interfacial tension as a function of hydrophobicity were not statistically significant (as indicated by ANOVA at the 95% significance level), except for greater reduction associated with octadecylamine. Greater interfacial tension reduction for octadecylamine (relative to other compounds evaluated) was expected considering that its hydrophobic portion (18 aliphatic carbons) is significantly longer in chain length than that of the other compounds (1 to 4 aliphatic carbons). The interfacial tension of the system containing octadecylamine decreased from 40.5 to 32.4 dyn/cm as base concentration was increased from 10^{-5} to 10^{-2} M in the DNAPL phase. No significant change of interfacial tension (from pure TCE values) occurred with increasing base concentration or organic base strength when pH conditions were such that the neutral organic base was abundantly present.

Quartz Wettability as a Function of Organic Base Hydrophobicity. Advancing, static, and receding contact angles were measured on quartz (in a 10^{-2} M NaClO₄ solution) as a function of organic base hydrophobicity (increasing aliphatic chain length from 1 to 18 carbons for series including benzylamine, phenylethylamine, phenylbutylamine, and octadecylamine) and base concentration (10^{-5} to 10^{-2} M in DNAPL phase) at approximately two pH units below and two pH units above each compound's pKa. Results for solution pH less than the pKa are plotted in Figure 4.2. Significant increases in advancing, static, and receding contact angles were observed with increasing base concentration for all compounds assessed. Additionally, the amount of increase in

TABLE 4.2 Experimentally-Determined Values of Trichloroethylene-Water Interfacial Tension^{a,b,c} as Function of Organic Base Hydrophobicity^d and Concentration

Interfacial Tension Measurements of Cationic Organic Base Form^e				
Base Conc. (M)	Benzylamine (Alkyl C's=1)	Phenylethylamine (Alkyl C's=2)	Phenylbutylamine (Alkyl C's=4)	Octadecylamine (Alkyl C's=18)
0.000001				41.8 (0.8)
0.00001	40.7 (0.4)	39.5 (0.6)	39.3 (1.1)	40.5 (0.9)
0.0001	39.2 (1.7)	37.1 (1.6)	38.8 (0.5)	39.5 (0.9)
0.001	38.5 (0.6)	36.8 (1.0)	37.2 (1.1)	36.4 (1.4)
0.005	38.0 (0.7)	34.5 (0.6)	36.3 (0.4)	
0.01	36.6 (0.7)	34.0 (0.4)	36.0 (0.8)	32.5 (1.1)

Interfacial Tension Measurements of Neutral Organic Base Form^f				
Base Conc. (M)	Benzylamine (Alkyl C's=1)	Phenylethylamine (Alkyl C's=2)	Phenylbutylamine (Alkyl C's=4)	Octadecylamine (Alkyl C's=18)
0.000001				39.7 (0.9)
0.00001	41.0 (1.4)	39.3 (0.5)	40.0 (1.5)	38.8 (0.9)
0.0001	41.6 (1.8)	38.3 (2.2)	38.7 (1.7)	39.5 (0.5)
0.001	40.5 (0.5)	37.8 (1.7)	39.2 (1.3)	38.8 (0.6)
0.005	40.1 (0.9)	39.0 (0.8)	39.2 (1.3)	
0.01	39.9 (1.5)	38.2 (1.3)	40.1 (0.5)	38.5 (1.3)

^a All measurements performed at 21°C. Ionic strength set at 10⁻² M with NaClO₄.

^b Standard deviations are shown in parentheses following mean value of parameter.

^c Interfacial tensions represent the mean value of three duplicate measurements.

^d Organic base hydrophobicity expressed as alkyl carbon chain length. (pK_a varied from 9.4 to 10.6)

^e All measurements performed at aqueous pH approximately two pH units below the base pK_a.

^f All measurements performed at aqueous pH approximately two pH units above the base pK_a.

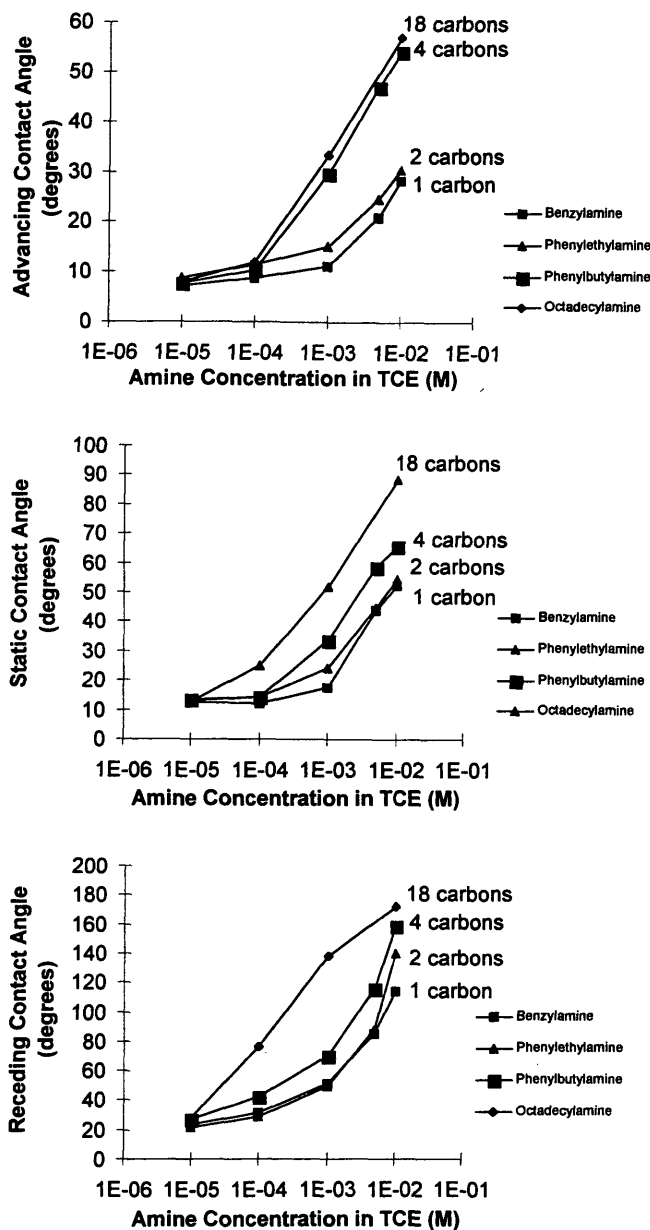


FIGURE 4.2 Measured advancing, static, and receding contact angles (at 21° C) of trichloroethylene containing organic bases varying in base hydrophobicity (alkyl chain length: 1 to 18 carbons). Contact angles were measured on quartz in the presence of a 10^{-2} M ionic strength (with NaClO_4) aqueous solution. Aqueous pH was set for each organic base at approximately two pH units below the compound's pKa. Each data point represents the average of triplicate measurements on each side of three DNAPL droplets. The pooled standard deviation for all data is 2.3.

contact angle with concentration was more substantial as organic base hydrophobicity increased. For instance, the system containing 10^{-2} M octadecylamine, a compound with 18 carbons per alkyl chain, exhibited strongly DNAPL wetting contact angles (171.8°), whereas the system containing 10^{-2} M benzylamine, a compound with only one carbon per alkyl chain, exhibited intermediate DNAPL wetting contact angles (114.3°). At aqueous pH in which the organic base was present predominantly in neutral form, advancing, static, and receding contact angles were strongly water wetting (6.6° to 19.3°) and exhibited no change with increasing base hydrophobicity or concentration.

The observed association between increasing amine hydrophobicity and increasing wettability alteration bears a striking resemblance to an observed association between increasing amine hydrophobicity and sorption from aqueous solutions to negatively charged clays (23) and quartz (36). Increased sorption, in these studies, was attributed to hydrophobic forces favoring chemical partitioning to near-surface water from bulk aqueous solutions, thereby augmenting electrostatic forces in the binding of these sorbates to particle surfaces. Presumably, similar forces decrease the aqueous solubility and increase the surface activity at the water-quartz interface of the more hydrophobic organic bases studied herein. It is also likely that longer alkyl chained molecules (that is, more hydrophobic) show a greater capacity for closely spaced, perpendicular orientation at the DNAPL-quartz interface; a characteristic important for surfactant-promoted wettability alteration (13).

Interfacial Tension as a Function of Aqueous pH. Interfacial tension between water and TCE containing 5×10^{-3} M phenylbutylamine (an aliphatic/aromatic amine that promoted substantial wettability alteration with increasing concentration in the hydrophobicity experiments), was determined as a function of aqueous pH (from pH 2.3 to 12.0) at a constant ionic strength (10^{-2} M). These data are shown in Figure 4.3. No significant variation of interfacial tension was observed from pH 2.3 to 9.7; interfacial

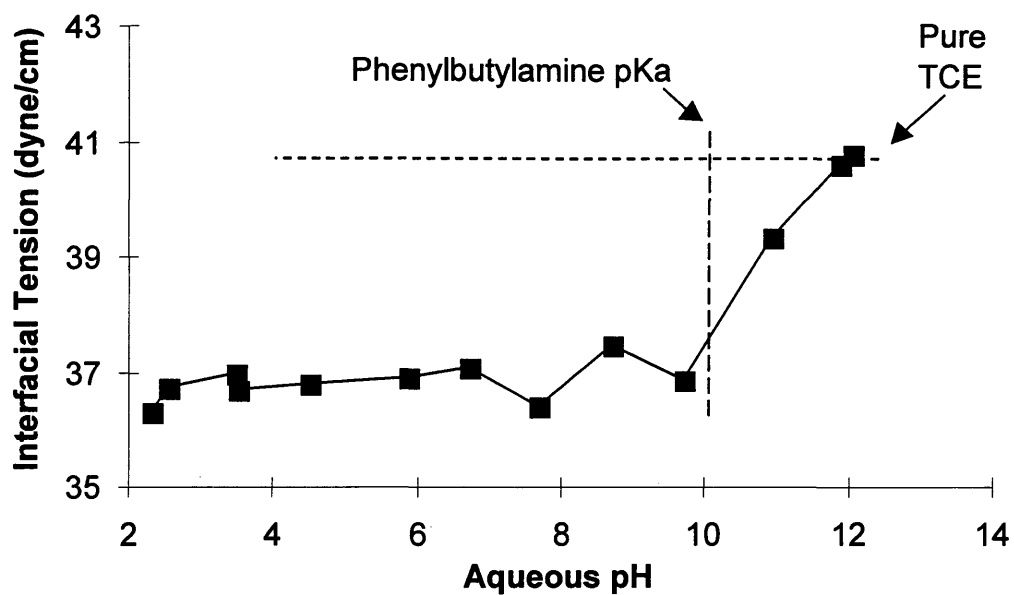


FIGURE 4.3 Measured interfacial tension (at 21° C), between water and trichloroethylene containing 5×10^{-3} M phenylbutylamine, as a function of aqueous pH (from pH 2.3 to 12.0) at a constant ionic strength (10^{-2} M NaClO_4). Each data point represents the average of triplicate measurements. The pooled standard deviation for all data is 0.7 dynes/cm.

tension averaged 36.8 dyn/cm. However, above pH 9.7 interfacial tension increased sharply, by approximately 4 dyn/cm (a statistically significant change at the 95% significance level as indicated by ANOVA), to a value of 40.8 dyn/cm at pH 12.0.

The aqueous pH at which interfacial tension increases coincides with the pKa of phenylbutylamine (pKa 10.2). In explanation, a reduction of interfacial tension results when phenylbutylamine is abundantly present in the surface active, cationic form. When present predominantly in neutral form (above approximately pH 12), phenylbutylamine is expected to partition almost entirely to the bulk DNAPL phase and, therefore, show little surface activity and, thus, the capacity to reduce DNAPL-water interfacial tension.

Quartz Wettability as a Function of Aqueous pH. Advancing, static, and receding contact angles of TCE containing 5×10^{-3} M phenylbutylamine, measured on quartz as a function of aqueous pH (from pH 2.3 to 12.0) at a constant ionic strength (10^{-2} M), are shown in Figure 4.4. Advancing, static, and receding contact angles significantly deviated from strongly water wetting conditions typical for pure TCE over most of the pH range evaluated. Static and receding angles sharply increased from pH 2.3 to 4.5. Gradual, but continued, increase in advancing, static, and receding contact angles occurred from pH 4.5 to 9.7. Wettability alteration was most dramatic under receding conditions, where contact angles were indicative of DNAPL wetting from pH 4.5 to 9.7, varying from 96.7 to 114.1°. Above pH 9.7, advancing, static, and receding contact angles sharply decreased to strongly water wetting values.

Elevated contact angles observed from pH 2.3 to 9.7 presumably result from sorption-induced wettability alteration by cationic phenylbutylamine. Conversely, the sharp decrease in contact angles observed above pH 9.7 coincides with phenylbutylamine's pKa and marks the pH above which the neutral, surface inactive form predominates. Less substantial wettability alteration occurred at acidic versus neutral pH; the potential result of fewer net negatively charged sites per unit area for sorption of cationic

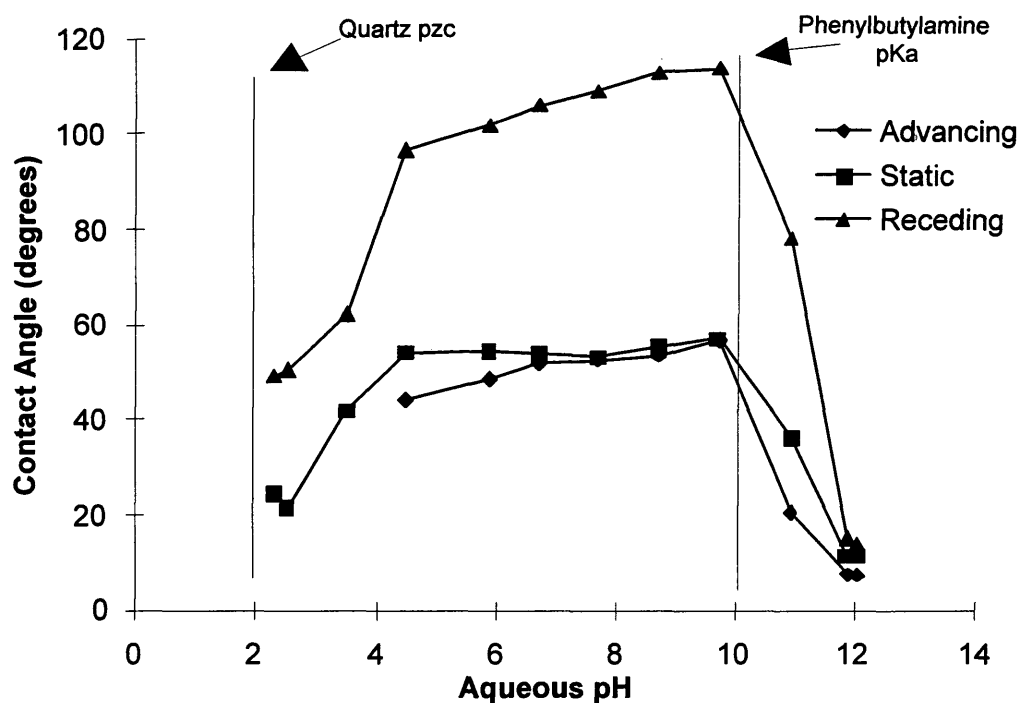


FIGURE 4.4 Measured advancing, static, and receding contact angles (at 21° C) of trichloroethylene containing 5×10^{-3} M phenylbutylamine. Contact angles were determined as a function of aqueous pH (from pH 2.3 to 12.0) at a constant ionic strength (10^{-2} M NaClO_4). Each data point represents the average of triplicate measurements on each side of three DNAPL droplets. The pooled standard deviation for all data is 3.5.

phenylbutylamine. These data suggest that the surface excess concentration of phenylbutylamine bound to quartz increases as a function of increasing aqueous pH and that this increase leads to greater wettability alteration.

Interfacial Tension as a Function of Aqueous Ionic Strength. Interfacial tension between water and TCE containing 5×10^{-3} M phenylbutylamine was determined as a function of aqueous ionic strength (from 10^{-4} to 10^{-1} M) at a constant pH (6.28). These data are shown in Table 4.3. A small decrease of interfacial tension was observed over the range of ionic strength tested; values decreased from 41.1 to 38.7 dyn/cm as ionic strength was increased.

The observed interfacial tension decrease suggests that increasing ionic strength to 10^{-1} M (at pH 6.28) slightly increases the attractive affinity between the DNAPL and water phases. Considering that phenylbutylamine will be present predominantly in cationic form at pH 6.28 and that ionic strength increases up to 10^{-1} M effectively lower activity coefficients of monovalent ions in water (37), an increase in the affinity of phenylbutylamine molecules, at the NAPL-water interface, for the water phase would be expected; thereby lowering interfacial tension.

Quartz Wettability as a Function of Aqueous Ionic Strength. Advancing, static, and receding contact angles of TCE containing 5×10^{-3} M phenylbutylamine measured on quartz as a function of aqueous ionic strength (from 10^{-4} to 10^{-1} M) at a constant pH (6.28) are given in Table 4.3. A small, but quantifiable, decrease in contact angles were observed from 10^{-4} to 10^{-2} M; advancing, static, and receding angles averaged 49.2° , 59.3° , and 106.3° , respectively. However, between 10^{-2} and 10^{-1} M advancing, static, and receding angles respectively decreased to 38.0° , 41.3° , and 76.3° .

Addition of strong electrolytes to systems containing ionic surfactants has been shown to decrease surfactant adsorption onto oppositely charged adsorbents (13). This effect

TABLE 4.3 Experimentally-Determined Values of Interfacial Tension^{a,b,c} and Contact Angle^{a,b,d} as Function of Aqueous Ionic Strength^{e,f} for TCE-Water System Containing Phenylbutylamine^g

DNAPL-Water Interfacial Tension (IFT)			
<u>Ionic Strength (M)</u>	<u>IFT (dynes/cm)</u>		
0.0001	41.1 (2.0)		
0.001	40.1 (0.1)		
0.01	39.0 (0.7)		
0.1	38.7 (0.5)		

Contact Angle			
<u>Ionic Strength (M)</u>	<u>Advancing</u>	<u>Static</u>	<u>Receding</u>
0.0001	50.9 (0.9)	60.5 (2.2)	109.3 (1.2)
0.001	49.6 (1.0)	58.8 (0.4)	106.3 (1.2)
0.01	47.1 (3.1)	58.7 (3.8)	103.3 (3.1)
0.1	38.0 (1.3)	41.3 (1.0)	76.3 (1.5)

^a All measurements performed at 21 °C.

^b Standard deviations are shown in parentheses following mean value of parameter.

^c Interfacial tensions represent mean value of three duplicate measurements.

^d Contact angles, measured in degrees, represent mean value of triplicate measurements on each side of three beads.

^e Aqueous pH constant at 6.28.

^f Ionic strength varied from 10^{-4} to 10^{-1} M with NaClO₄.

^g Phenylbutylamine concentration set at 5×10^{-3} M within TCE phase at start of experiment.

was attributed to decreased attraction between oppositely charged sorbates and sorbents and competitive adsorption at higher ionic strengths. This phenomena may explain the reduction of contact angles observed above 10^{-2} M ionic strength.

Implications of Findings. The results presented in this study show that anthropogenic organic bases, such as aliphatic/aromatic amines and pyridines, have only a minor influence on lowering DNAPL-water interfacial tension, but a significant influence on altering mineral wettability of water-DNAPL-quartz systems. These results show that intermediate to strong organic bases, but not weak organic bases, have the capacity to alter quartz wettability from strong water wetting to DNAPL wetting conditions, depending primarily on aqueous pH. Wettability alteration occurred only at pH conditions where the cationic organic base species was abundantly present. Although increasing the degree of hydrophobicity of an organic base tends to increase DNAPL wetting, even cationic organic bases with relatively low hydrophobicity (for instance, benzylamine) substantially impact quartz wettability. These observed wettability variations will significantly influence properties governing multiphase systems, such as capillary pressure, relative permeability, residual NAPL saturation, and NAPL recovery behavior. Additionally, these findings support the potential for remedial applications involving pH- and ionic strength-induced wettability alteration for enhanced subsurface recovery (or stabilization) of DNAPL wastes containing organic base components.

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Chapter 5

SUMMARY AND CONCLUSIONS

The primary objective of this dissertation was to demonstrate the effect of aqueous pH and ionic strength on the interfacial properties that influence the subsurface mobility and recovery of the following types of dense nonaqueous phase liquids (DNAPLs):

- Pure nonpolar chlorinated solvents (Chapter 2)
- Coal tar (a complex, multicomponent DNAPL) (Chapter 3)
- Controlled mixtures containing ionizable organic base components (Chapter 4)

An additional objective of this work was to determine the influence of organic base composition (that is, base strength and base hydrophobicity) and organic base concentration on the interfacial properties evaluated in controlled, binary mixtures. Observed variations of properties evaluated are summarized below for each type of DNAPL studied. Subsequently, the overall conclusions and implications regarding the mobility and recovery of DNAPLs from water-saturated, porous media are addressed.

Pure Nonpolar DNAPLs

DNAPL-water interfacial tension was invariant with respect to aqueous pH and ionic strength (up to 0.1 M) for the nonpolar DNAPLs, trichlorethylene and carbon tetrachloride. This data suggests that nonpolar DNAPLs maintain their hydrophobic character regardless of pH and ionic strength conditions. Static contact angles, which were water wetting over the entire range of pH and ionic strength evaluated, exhibited

maxima near the pH of the zero point of charge of quartz ($\text{pH} \approx 2$) and decreased as pH and ionic strength were increased. These changes are attributed primarily to the effect of water-quartz interfacial on contact angle, as expressed by Young's Equation.

Coal Tar

Coal tar-water interfacial tension varied as much as 25 dynes/cm over the pH range 3 to 12, dramatically decreasing as pH was increased above 9. Contact angle and capillary-pressure-versus-saturation results indicate that quartz media remains water wet under coal-tar-advancing conditions over the entire pH range tested. Quartz, however, becomes coal tar wet under receding conditions at acidic to neutral pH, but not at basic pH.

The behavior observed for coal tar-water interfacial tension and contact angle as a function of pH is in marked contrast to that observed for the nonpolar DNAPLs, trichloroethylene and carbon tetrachloride. The observed variations of coal tar interfacial properties with aqueous pH are speculated to be a function of the pH-promoted ionization, surface activation, and consequent sorption of ionizable organic components at the DNAPL-water, DNAPL-quartz, and water-quartz interfaces of the system studied. The reduction of coal tar-water interfacial tension with increasing pH is attributed to the adsorption of anionic species of acidic coal tar components at the DNAPL-water interface. The alteration of quartz wettability, from strongly water wetting (observed for the DNAPLs, trichloroethylene and carbon tetrachloride) to DNAPL wetting, with decreasing pH is ascribed to the sorption of cationic species of basic coal tar components at the DNAPL-quartz interface. The observed effects of aqueous chemistry on the interfacial properties of coal tar are postulated to occur due to the presence of acidic and basic asphaltenes, compounds reported as responsible for the pH-dependence of interfacial properties in crude oil-water-rock systems.

Controlled DNAPL Mixtures of Trichloroethylene and an Ionizable Organic Base Component.

DNAPL-water interfacial tension and quartz wettability were invariant with respect to organic base composition and aqueous chemistry when neutral species of organic bases' assessed were abundantly present relative to cationic species (aqueous $\text{pH} \gg \text{base pK}_a$). Conversely, significant variations of interfacial properties with organic base composition and aqueous chemistry were observed when cationic species were abundantly present relative to neutral species (aqueous $\text{pH} \ll \text{base pK}_a$). These observed trends show that base component fractional speciation, determined by aqueous pH, plays an important role in affecting interfacial tension and mineral wettability.

DNAPL-water interfacial tension was observed to decrease slightly (approximately 10%) with decreasing pH below the organic base component's pK_a . Interfacial tension also decreased slightly (approximately 10 to 20%) with increasing ionic strength, base concentration, and base hydrophobicity over the range of conditions studied. Contact angles on quartz were observed to dramatically increase with increasing base concentration, base strength, and base hydrophobicity when the cationic organic base form was abundantly present relative to the neutral form. Weak organic base aromatic amines, such as aniline (pK_a 4.6), and weak organic base heterocyclic compounds containing nitrogen, such as pyridine (pK_a 5.4), insignificantly altered wettability even when present in high concentrations. Conversely, strong organic base aliphatic/aromatic amines, such as benzylamine (pK_a 9.4), promoted alterations in quartz wettability from water wetting (observed for pure TCE) to DNAPL wetting. Although increasing the hydrophobicity of aliphatic/aromatic amines (by increasing the alkyl chain length) resulted in increasing contact angle, even amine compounds of low hydrophobicity, such as benzylamine (1 alkyl carbon), were capable of altering quartz wettability from water to DNAPL wet.

Wetting phenomena observed for the controlled DNAPLs studied are, in part, very similar to those observed for coal tar. The alteration of quartz wettability from strongly water wet to DNAPL wet with decreasing pH for DNAPLs containing organic base components is ascribed to the adsorption of cationic organic base species at the DNAPL-quartz interface. The observed results of DNAPL mixtures containing trichloroethylene and an organic base indicate that low- to moderate-molecular-weight aliphatic/aromatic amines and pyridines affect quartz wettability in a fashion similar to high-molecular-weight asphaltenic compounds that exhibit basic behavior in systems with coal tar.

Implications for DNAPL Mobility and Recovery

Based on the conditions examined in this research, the following overall conclusions regarding the mobility and recovery of those DNAPLs evaluated are evident:

1. The influence of aqueous pH on the interfacial properties of DNAPLs composed of nonpolar organic compounds is insignificant compared to this influence on those composed of nonpolar and ionizable organic compounds. Observed variations in contact angle with pH and ionic strength for the pure nonpolar DNAPLs studied yield calculated changes in capillary pressure no higher than 10%. Though quantifiable, these changes may not significantly affect the mobility of nonpolar DNAPLs, except in settings where capillary pressure is close to displacement entry pressure of porous media. Conversely, the order of magnitude decrease in DNAPL-water interfacial tension (observed with coal tar systems) and wettability reversals (observed with coal tar and controlled DNAPLs containing an organic base component) with pH will significantly influence the mobility, entrapment, and recovery potential of DNAPLs.
2. The impact of ionic strength on nonpolar DNAPLs is minimal relative to those that contain ionizable organic components. Ionic strength increases (up to 0.1 M) in systems that contain organic bases decrease DNAPL-water interfacial tension and decrease

wetting angles by influencing the surface activity and adsorption of cationic organic base components at the DNAPL-water, DNAPL-quartz, and water-quartz interfaces.

3. Quartz wettability, but not DNAPL-water interfacial tension, is significantly altered as a function of organic base concentration, base strength, and base hydrophobicity for DNAPLs that contain aliphatic/aromatic amines and pyridines in cationic form.

From the preceding conclusions, the following overall implications can be drawn:

1. Observations from this work suggest that the selection of remedial strategies for sites with DNAPLs that contain ionizable components, such as coal tar, should carefully consider the mobility of the DNAPL in terms of the pH of the system. The observed order-of-magnitude decrease of coal tar-water interfacial tension with increasing pH from 9 to 12 will increase the miscibility of coal tar and water, thereby improving the tendency for simultaneous two-phase flow. Moreover, the reversal of wetting conditions from coal tar wet to water wet above pH 8 will promote more efficient recovery of coal tar under waterflooding conditions. As a result of miscibility and wettability effects, alkaline flushing is a remedial strategy that may show promise for enhancing coal tar recovery. However, application of this technique should consider the effects of alkalinity on aquifer alteration, such as pore clogging as a result of mineral precipitation under basic pH conditions.
2. The major implication regarding the behavior of DNAPLs containing aliphatic/aromatic amines and pyridines is similar to that just described for coal tar: the mobility and recovery of DNAPLs containing amines and pyridines will be significantly influenced by mineral wettability, which, in turn, will be controlled predominantly by aqueous pH. As with coal tar, the potential for the recovery of DNAPLs containing amine- and pyridine-type compounds from water-saturated, porous media may be improved under alkaline, rather than acidic or neutral, conditions.

APPENDIX A**TABULATED INTERFACIAL TENSION AND CONTACT ANGLE
DATA FROM CHAPTER 2**

Experimentally-Determined Values of DNAPL-Water Interfacial Tension^{a,b,c} for Trichloroethylene and Carbon Tetrachloride

DNAPL-Water Interfacial Tension as a Function of Aqueous pH

<u>Trichloroethylene</u>		<u>Carbon Tetrachloride</u>	
<u>pH</u>	<u>I=0.1 M</u>	<u>pH</u>	<u>I=0.1 M</u>
5.8	41.4 (±4.9)	4.0	43.4 (±0.9)
7.0	38.0 (±2.6)	5.9	43.9 (±0.4)
9.3	40.3 (±2.6)	9.6	43.7 (±2.3)

DNAPL-Water Interfacial Tension as a Function of Aqueous Ionic Strength^d

<u>Trichloroethylene</u>		<u>Carbon Tetrachloride</u>	
<u>I (M)</u>	<u>pH=6</u>	<u>I (M)</u>	<u>pH=6</u>
0.000002	39.8 (±0.9)	0.000002	43.7 (±3.4)
0.1	38.0 (±2.6)	0.001	45.6 (±2.3)
1.0	49.4 (±2.2)	0.1	46.2 (±1.1)
		1.0	54.6 (±1.4)

- a. All measurements performed at 25°C.
 b. Interfacial tensions represent mean value of 5 duplicate measurements.
 c. Standard deviations are shown in parentheses following mean interfacial tension value.
 d. Ionic strength adjustment performed with NaClO₄.

Experimentally-Determined Values of Contact Angle^{a,b,c} for Trichloroethylene and Carbon Tetrachloride

Contact Angle on Quartz as a Function of Aqueous pH

<u>Trichloroethylene</u>					<u>Carbon Tetrachloride</u>						
pH	I=0.001 M	pH	I=0.1 M	pH	I=0.4 M	pH	I=0.001 M	pH	I=0.1 M	pH	I=0.4 M
5.5	24.3 (±2.6)	5.5	26.8 (±2.2)	0.4	14.2 (±2.0)	5.7	22.8 (±1.3)	6.0	24.0 (±2.1)	0.4	17.1 (±2.0)
7.0	20.1 (±1.2)	6.8	23.6 (±1.8)	1.2	18.0 (±2.4)	7.3	20.9 (±2.6)	6.5	23.0 (±3.0)	1.1	21.3 (±4.7)
7.7	17.1 (±2.5)	8.1	17.5 (±3.2)	2.0	17.0 (±1.0)	7.4	21.2 (±2.7)	7.1	14.7 (±1.3)	2.0	18.9 (±2.0)
8.2	16.6 (±0.6)	9.4	12.1 (±2.2)	3.2	15.3 (±2.6)	7.5	19.9 (±2.8)	8.4	17.3 (±1.1)	3.0	15.0 (±2.0)
9.7	18.1 (±1.6)	9.6	13.5 (±2.8)	6.1	8.4 (±1.1)	8.1	20.6 (±1.8)	9.3	13.9 (±1.8)	3.9	13.4 (±1.9)
		9.8	10.3 (±0.9)	7.9	6.4 (±0.7)	9.0	18.8 (±2.4)	9.8	14.4 (±1.6)	5.0	11.2 (±0.7)
				9.5	5.5 (±0.9)	9.4	21.6 (±1.4)	10.1	10.0 (±0.9)	5.8	9.6 (±1.2)
								10.2	9.9 (±1.4)	6.5	7.9 (±1.4)
										8.0	8.0 (±1.4)
										8.9	8.6 (±0.9)
										10.8	8.8 (±1.4)

Contact Angle on Quartz as a Function of Aqueous Ionic Strength^d

<u>Trichloroethylene</u>		<u>Carbon Tetrachloride</u>	
I (M)	pH=5.7	I (M)	pH=5.7
0.000002	26.0 (±4.0)	0.00001	31.4 (±1.7)
0.001	24.3 (±2.6)	0.0001	11.4 (±1.2)
0.1	10.4 (±2.3)	0.001	10.8 (±0.9)
1.0	8.4 (±1.1)	0.01	7.8 (±0.6)
		0.1	9.8 (±1.5)

a. All measurements performed at 25°C.

b. Contact angles represent mean value of triplicate measurements on each side of three beads.

c. Standard deviations are shown in parentheses following mean contact angle value.

d. Ionic strength adjustment performed with NaClO₄.

APPENDIX B**CALCULATION OF WATER-QUARTZ INTERFACIAL TENSION
FROM CHAPTER 2**

CALCULATION OF SURFACE FREE ENERGY OF SODIUM AND IODIDE ADSORBED TO QUARTZ (DATA FROM LI (1955))

Ionic Strength (0.1 M)		Na Adsorption		Na Adsorption (mol/cm ²)		Gas Constant (emp/mol*K)		Temp (K)		-RT(AdsDen) [*]		pOH		-pOH [*]		[OH]		[H]		[Na]		Ionic Strength		
pH	(mol/cm ² * E10)	(mol/cm ²)	(mol/cm ²)	(mol/cm ²)	(mol/cm ²)	(mol/cm ²)	(mol/cm ²)	(K)	(K)	(K)	(K)	(K)	(K)	(K)	(K)	(K)	(K)	(K)	(K)	(K)	(K)	(K)	(K)	(K)
6.62	0.885	8.85E-11	8.31E+07	298	-2.19278	7.18	-7.18	6.81E-08	1.51E-07	0.1	0.1	0.1	0.1											
7.67	1.5	1.5E-10	8.31E+07	298	-3.71658	6.33	-6.33	4.68E-07	2.14E-08	0.1	0.1	0.1	0.1											
11.98	5.63	3.4E-10	8.31E+07	298	-8.42425	4	4	0.0001	1E-10	0.1001	0.1	0.1001	0.1											
12.91	7.39	5.63E-10	8.31E+07	298	-13.70718	2.02	-2.02	0.00955	1.05E-12	0.10955	0.1	0.10955	0.1											
12.91	7.55	7.39E-10	8.31E+07	298	-18.3104	1.09	-1.09	0.081283	1.23E-13	0.181283	0.1	0.181283	0.1											
12.91	7.55	7.55E-10	8.31E+07	298	-18.7068	1.09	-1.09	0.081283	1.23E-13	0.181283	0.1	0.181283	0.1											

Ionic Strength (0.01 M)		Na Adsorption		Na Adsorption (mol/cm ²)		Gas Constant (emp/mol*K)		Temp (K)		-RT(AdsDen) [*]		pOH		-pOH [*]		[OH]		[H]		[Na]		Ionic Strength	
pH	(mol/cm ² * E10)	(mol/cm ²)	(mol/cm ²)	(mol/cm ²)	(mol/cm ²)	(mol/cm ²)	(mol/cm ²)	(K)	(K)	(K)	(K)	(K)	(K)	(K)	(K)	(K)	(K)	(K)	(K)	(K)	(K)	(K)	(K)
1.96	0.084	6.4E-12	8.31E+07	298	-0.15657	12.04	-12.04	8.12E-13	0.010965	0.01	0.01	0.015482	0.01										
1.96	0.087	6.7E-12	8.31E+07	298	-0.16601	12.04	-12.04	8.12E-13	0.010965	0.01	0.01	0.015482	0.01										
2.99	0.094	8.4E-12	8.31E+07	298	-0.23291	11.01	-11.01	9.77E-12	0.001023	0.01	0.01	0.010512	0.01										
2.99	0.094	9.4E-12	8.31E+07	298	-0.23291	11.01	-11.01	9.77E-12	0.001023	0.01	0.01	0.010512	0.01										
3	0.122	1.22E-11	8.31E+07	298	-0.30228	11	-11	1E-11	0.001	0.01	0.01	0.0105	0.01										
4.08	0.077	7.7E-12	8.31E+07	298	-0.19078	9.92	-9.92	1.2E-10	8.32E-05	0.01	0.01	0.010042	0.01										
4.08	0.102	1.02E-11	8.31E+07	298	-0.25273	9.92	-9.92	1.2E-10	8.32E-05	0.01	0.01	0.010042	0.01										
4.11	0.103	1.03E-11	8.31E+07	298	-0.25273	9.92	-9.92	1.2E-10	8.32E-05	0.01	0.01	0.010042	0.01										
5.42	0.139	1.39E-11	8.31E+07	298	-0.3444	8.58	-8.58	2.63E-09	3.8E-06	0.01	0.01	0.010039	0.01										
5.44	0.141	1.41E-11	8.31E+07	298	-0.3444	8.58	-8.58	2.63E-09	3.8E-06	0.01	0.01	0.010039	0.01										
5.48	0.147	1.47E-11	8.31E+07	298	-0.34936	8.56	-8.56	2.75E-09	3.63E-06	0.01	0.01	0.010002	0.01										
5.59	0.149	1.49E-11	8.31E+07	298	-0.36422	8.52	-8.52	3.02E-09	3.31E-06	0.01	0.01	0.010002	0.01										
5.59	0.153	1.53E-11	8.31E+07	298	-0.36918	8.41	-8.41	3.89E-09	2.57E-06	0.01	0.01	0.010001	0.01										
5.83	0.164	1.64E-11	8.31E+07	298	-0.37609	8.41	-8.41	3.89E-09	2.57E-06	0.01	0.01	0.010001	0.01										
5.99	0.158	1.58E-11	8.31E+07	298	-0.40635	8.07	-8.07	8.51E-09	1.17E-06	0.01	0.01	0.010001	0.01										
6.15	0.174	1.74E-11	8.31E+07	298	-0.39148	8.01	-8.01	9.77E-09	1.02E-06	0.01	0.01	0.010001	0.01										
6.4	0.157	1.57E-11	8.31E+07	298	-0.43112	7.85	-7.85	1.41E-08	7.08E-07	0.01	0.01	0.010001	0.01										
6.41	0.169	1.69E-11	8.31E+07	298	-0.389	7.6	-7.6	2.51E-08	3.98E-07	0.01	0.01	0.010001	0.01										
6.5	0.19	1.9E-11	8.31E+07	298	-0.41873	7.59	-7.59	2.57E-08	3.89E-07	0.01	0.01	0.010001	0.01										
6.5	0.197	1.97E-11	8.31E+07	298	-0.47077	7.5	-7.5	3.16E-08	3.16E-07	0.01	0.01	0.010001	0.01										
6.8	0.228	2.28E-11	8.31E+07	298	-0.48811	7.5	-7.5	3.16E-08	3.16E-07	0.01	0.01	0.010001	0.01										
7.34	0.517	5.17E-11	8.31E+07	298	-0.55996	7.2	-7.2	6.31E-08	1.58E-07	0.01	0.01	0.010001	0.01										
7.48	0.508	5.08E-11	8.31E+07	298	-1.29098	6.66	-6.66	2.19E-07	4.57E-08	0.01	0.01	0.010001	0.01										
7.68	0.422	4.22E-11	8.31E+07	298	-1.25373	6.52	-6.52	3.02E-07	3.31E-08	0.01	0.01	0.010001	0.01										
7.8	0.423	4.23E-11	8.31E+07	298	-1.0458	6.32	-6.32	4.79E-07	2.09E-08	0.01	0.01	0.010001	0.01										
8.37	0.813	8.13E-11	8.31E+07	298	-1.04808	6.2	-6.2	6.31E-07	1.58E-08	0.010001	0.01	0.010001	0.01										
8.37	0.808	8.08E-11	8.31E+07	298	-2.01439	5.63	-5.63	2.34E-06	4.27E-09	0.010002	0.01	0.010002	0.01										
9.8	1.81	1.81E-10	8.31E+07	298	-2.002	5.63	-5.63	2.34E-06	4.27E-09	0.010002	0.01	0.010002	0.01										
10.32	2.04	2.04E-10	8.31E+07	298	-3.68913	4.2	-4.2	6.31E-05	1.58E-10	0.010063	0.01	0.010063	0.01										
10.32	2.03	2.03E-10	8.31E+07	298	-5.05455	3.68	-3.68	0.000209	4.79E-11	0.010209	0.01	0.010209	0.01										
11.23	3.03	3.03E-10	8.31E+07	298	-5.02877	3.68	-3.68	0.000209	4.79E-11	0.010209	0.01	0.010209	0.01										
11.94	3.9	3.9E-10	8.31E+07	298	-7.50749	2.77	-2.77	0.001688	5.89E-12	0.011688	0.01	0.011688	0.01										
12	3.96	3.96E-10	8.31E+07	298	-8.66311	2.06	-2.06	0.00871	1.45E-12	0.01871	0.01	0.01871	0.01										
				298	-8.564	2	-2	0.01	1E-12	0.02	0.01	0.02	0.01										

Ionic Strength (0.001 M)		Na Adsorption		Na Adsorption (mol/cm ²)		Gas Constant (erg/mol ^o K)		Temp (K)		-RT(AdsDen) [*]		pOH		[H ⁺]		[Na ⁺]		[Cl ⁻]		Ionic Strength	
pH	$\frac{Na}{(mol/cm^2 \cdot E_{10})}$	Na Adsorption (mol/cm ²)	Gas Constant (erg/mol ^o K)	Temp (K)	-RT(AdsDen) [*]	pOH	[H ⁺]	[Na ⁺]	[Cl ⁻]	Ionic Strength											
3.54	0.018	1.8E-12	8.31E+07	298	-0.0446	10.48	3.47E-11	0.000288	0.001	0.001	0.001144										
4.08	0.026	2.6E-12	8.31E+07	298	-0.06442	9.92	1.2E-10	8.32E-05	0.001	0.001	0.001042										
5.6	0.036	3.6E-12	8.31E+07	298	-0.0892	8.4	3.98E-09	2.51E-06	0.001	0.001	0.001001										
5.72	0.037	3.7E-12	8.31E+07	298	-0.09168	8.28	8.28	5.25E-09	1.81E-06	0.001	0.001	0.001001									
6.15	0.052	5.2E-12	8.31E+07	298	-0.12884	7.85	7.85	1.41E-08	7.08E-07	0.001	0.001	0.001001									
6.35	0.056	5.6E-12	8.31E+07	298	-0.14371	7.65	7.65	2.24E-08	4.47E-07	0.001	0.001	0.001001									
7.2	0.093	9.3E-12	8.31E+07	298	-0.23043	6.8	6.8	1.56E-07	6.31E-08	0.001	0.001	0.001001									
8.47	0.285	2.85E-11	8.31E+07	298	-0.73093	5.53	5.53	2.95E-06	3.39E-09	0.001	0.001003										
9.03	0.487	4.87E-11	8.31E+07	298	-1.1571	4.97	4.97	1.07E-05	9.33E-10	0.001	0.001011										
9.97	0.935	9.35E-11	8.31E+07	298	-2.31667	4.03	4.03	9.33E-05	1.07E-10	0.001	0.001083										
10.51	1.256	1.26E-10	8.31E+07	298	-3.11202	3.49	3.49	0.000324	3.09E-11	0.001	0.001324										
10.51	1.223	1.22E-10	8.31E+07	298	-3.03025	3.49	3.49	0.000324	3.09E-11	0.001	0.001324										

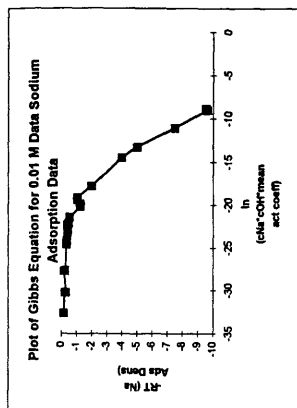
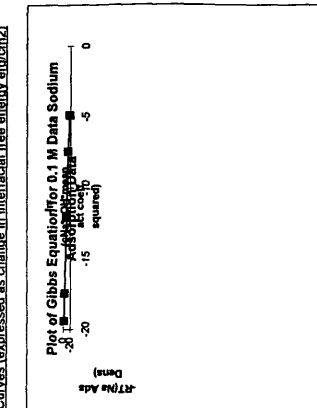
Ionic Strength (0.0001 M)		Na Adsorption		Na Adsorption (mol/cm ²)		Gas Constant (erg/mol ^o K)		Temp (K)		-RT(AdsDen) [*]		pOH		[H ⁺]		[Na ⁺]		[Cl ⁻]		Ionic Strength	
pH	$\frac{Na}{(mol/cm^2 \cdot E_{10})}$	Na Adsorption (mol/cm ²)	Gas Constant (erg/mol ^o K)	Temp (K)	-RT(AdsDen) [*]	pOH	[H ⁺]	[Na ⁺]	[Cl ⁻]	Ionic Strength											
5.7	0.019	1.9E-12	8.31E+07	298	-0.04708	8.3	8.3	5.01E-09	2E-06	0.001	0.000101										
7	0.022	2.2E-12	8.31E+07	298	-0.09451	7	7	1E-07	1E-07	0.001	0.0001										
8.1	0.041	4.1E-12	8.31E+07	298	-0.10159	5.9	5.9	1.26E-06	7.94E-09	0.001	0.000101										
9.1	0.188	1.88E-11	8.31E+07	298	-0.46581	4.9	4.9	1.28E-05	7.84E-10	0.001	0.000113										
9.58	0.281	2.81E-11	8.31E+07	298	-0.64669	4.42	4.42	3.8E-05	2.63E-10	0.001	0.000138										
9.82	0.259	2.59E-11	8.31E+07	298	-0.64173	4.38	4.38	4.17E-05	2.4E-10	0.001	0.000142										

CALCULATION OF SURFACE FREE ENERGY OF IODIDE ADSORBED ON QUARTZ (DATA FROM LI (1958))

Ionic Strength (0.1 M)		I Adsorption		I Adsorption (mol/cm ²)		Gas Constant (erg/mol ^o K)		Temp (K)		-RT(AdsDen) [*]		pOH		[H ⁺]		[Na ⁺]		[Cl ⁻]		Ionic Strength	
pH	$\frac{I}{(mol/cm^2 \cdot E_{10})}$	I Adsorption (mol/cm ²)	Gas Constant (erg/mol ^o K)	Temp (K)	-RT(AdsDen) [*]	pOH	[H ⁺]	[Na ⁺]	[Cl ⁻]	Ionic Strength											
1.09	1.1	1.1E-10	8.31E+07	298	-2.72549	12.91	12.91	1.23E-13	0.061283	0.1	0.181283	0.181283									
2.02	0.585	5.85E-11	8.31E+07	298	-1.44947	11.98	11.98	1.05E-12	0.00955	0.1	0.10955	0.10955									
3.08	0	0	8.31E+07	298	0	10.82	10.82	1.2E-11	0.000832	0.1	0.100832	0.100832									
4.11	0	0	8.31E+07	298	0	9.89	9.89	1.28E-10	7.76E-05	0.1	0.100078	0.100078									
6.14	0	0	8.31E+07	298	0	7.86	7.86	1.38E-08	7.24E-07	0.1	0.100001	0.100001									

Ionic Strength (0.01 M)		I Adsorption		I Adsorption (mol/cm ²)		Gas Constant (erg/mol ^o K)		Temp (K)		-RT(AdsDen) [*]		pOH		[H ⁺]		[Na ⁺]		[Cl ⁻]		Ionic Strength	
pH	$\frac{I}{(mol/cm^2 \cdot E_{10})}$	I Adsorption (mol/cm ²)	Gas Constant (erg/mol ^o K)	Temp (K)	-RT(AdsDen) [*]	pOH	[H ⁺]	[Na ⁺]	[Cl ⁻]	Ionic Strength											
2	0.0736	7.36E-12	8.31E+07	298	-0.18286	12	12	1E-12	0.01	0.11	0.065										
3	0.0853	8.53E-12	8.31E+07	298	-0.21135	12	12	1E-12	0.01	0.11	0.065										
3	0	0	8.31E+07	298	0	11	11	1E-11	0.001	0.01	0.056										
4.01	0	0	8.31E+07	298	0	9.89	9.89	1.02E-10	9.77E-05	0.01	0.100098	0.100098									

Measured Area Under Curves (expressed as change in interfacial free energy emJ/cm²)



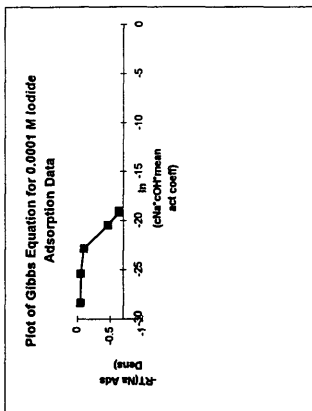
Debye Huckel Eqn AdtCoef. (Na)	Debye Huckel Equation AdtCoef. (OH)	Ionic Strength (0.1 M) Mean AdtCoef	Mean AdtCoef Squared	$\int \ln(CNa^+COH^+ZNaOH)$	$-RT(\Delta S_{Den})^*$
0.769568	0.761931	0.76574	0.586337	-19.369	-2.19276
0.769567	0.761931	0.76574	0.586337	-17.4116	-3.71656
0.769486	0.761855	0.765666	0.586245	-12.0459	-8.42425
0.76304	0.75496	0.756889	0.576064	-13.7018	-7.41413
0.72606	0.715234	0.720626	0.519303	-4.87278	-18.3104
	0.715234	0.720626	0.519303	-4.87278	-18.7068
Debye Huckel Eqn AdtCoef. (Na)	Debye Huckel Equation AdtCoef. (OH)	Ionic Strength (0.01 M) Mean AdtCoef	Mean AdtCoef Squared	$\int \ln(CNa^+COH^+ZNaOH)$	$-RT(\Delta S_{Den})^*$
0.882167	0.860192	0.861176	0.776476	-32.5813	-0.15657
0.882167	0.860192	0.861179	0.776476	-32.5813	-0.16601
0.899492	0.898059	0.898775	0.807797	-30.1701	-0.23281
0.899492	0.898059	0.898775	0.807797	-30.1701	-0.23281
0.899539	0.898107	0.898623	0.807882	-30.1469	-0.30228
0.901399	0.900019	0.900709	0.811276	-27.656	-0.19078
0.901399	0.900019	0.900709	0.811276	-27.656	-0.25273
0.90141	0.900031	0.900072	0.811257	-27.5869	-0.25521
0.901562	0.900188	0.900675	0.811575	-24.5701	-0.3444
0.901563	0.900188	0.900675	0.811576	-24.5241	-0.34836
0.901563	0.900189	0.900676	0.811577	-24.432	-0.36422
0.901565	0.90019	0.900677	0.81158	-24.1787	-0.36918
0.901565	0.90019	0.900677	0.81158	-24.1787	-0.37909
0.901568	0.900193	0.90068	0.811585	-23.9858	-0.40635
0.901568	0.900193	0.90068	0.811586	-23.2576	-0.39146
0.901569	0.900194	0.900681	0.811587	-22.8692	-0.43112
0.901569	0.900194	0.900681	0.811587	-22.8692	-0.43112
0.901569	0.900195	0.900682	0.811588	-22.3136	-0.389
0.901569	0.900195	0.900682	0.811588	-22.2906	-0.41873
0.901569	0.900185	0.900682	0.811588	-22.0833	-0.47077
0.901569	0.900185	0.900682	0.811588	-22.0833	-0.48811
0.901569	0.900195	0.900682	0.811588	-21.3825	-0.55696
0.901569	0.900195	0.900682	0.811588	-20.1491	-1.28098
0.901569	0.900194	0.900681	0.811587	-19.8268	-1.25373
0.901568	0.900184	0.900681	0.811586	-19.3662	-1.0456
0.901567	0.900183	0.90068	0.811585	-19.0899	-1.04808
0.90156	0.900186	0.900673	0.811572	-17.7773	-2.01439
0.90156	0.900186	0.900673	0.811572	-17.7773	-2.002
0.90131	0.89828	0.900619	0.811115	-14.4791	-3.88913
0.900713	0.899315	0.900014	0.810025	-13.2687	-5.05465
0.900713	0.899315	0.900014	0.810025	-13.2687	-5.02977
0.894921	0.893353	0.894137	0.799481	-8.89437	-7.50749
0.872906	0.871755	0.871755	0.759957	-8.98653	-6.86311
0.869519	0.867085	0.868306	0.753956	-8.78962	-8.564

Debye Huckel Eqn
ActCoeff (Na)
0.962746
0.964356
0.965014
0.965018
0.965028
0.96503
0.965031
0.964986
0.964858
0.963534
0.960114
0.960114

Debye Huckel Equation
ActCoeff (OH)
0.96255
0.964178
0.964841
0.964846
0.964858
0.964858
0.964859
0.964813
0.964899
0.964771
0.963347
0.95989
0.95989

Ionic Strength (0.001 M)
Mean ActCoeff Mean ActCoeff Squared
0.962648 0.926891
0.964267 0.929811
0.964927 0.931085
0.964832 0.931095
0.964842 0.931113
0.964844 0.931117
0.964845 0.931119
0.964899 0.931031
0.964771 0.930784
0.963344 0.928217
0.960002 0.921604
0.960002 0.921604

$\ln(\text{Na}^+\text{OH}^-\text{NaOH})$ $-\frac{RT}{\text{ActDen}}^*$
-31.0689 -0.0446
-29.8222 -0.06442
-26.3209 -0.0892
-26.0445 -0.09168
-25.0544 -0.12884
-24.5939 -0.14371
-22.6365 -0.23043
-19.7096 -0.73093
-18.4127 -1.1571
-16.1724 -2.31667
-14.7451 -3.11202
-14.7451 -3.03025

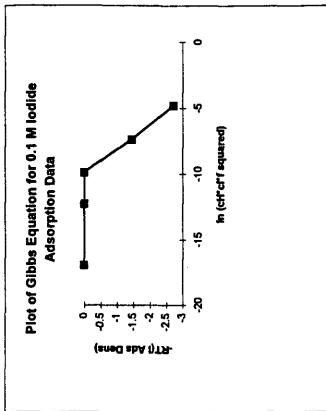


Debye Huckel Eqn
ActCoeff (Na)
0.98844
0.988469
0.988425
0.987807
0.986529
0.986355

Debye Huckel Equation
ActCoeff (OH)
0.988421
0.988469
0.988406
0.987787
0.986504
0.986329

Ionic Strength (0.0001 M)
Mean ActCoeff Mean ActCoeff Squared
0.98843 0.976985
0.988478 0.97709
0.988416 0.976966
0.987787 0.975743
0.986516 0.973214
0.986342 0.972871

$\ln(\text{Na}^+\text{OH}^-\text{NaOH})$ $-\frac{RT}{\text{ActDen}}^*$
-28.345 -0.04708
-25.3506 -0.05451
-22.8064 -0.10159
-20.399 -0.46581
-19.0927 -0.64669
-18.9747 -0.64173

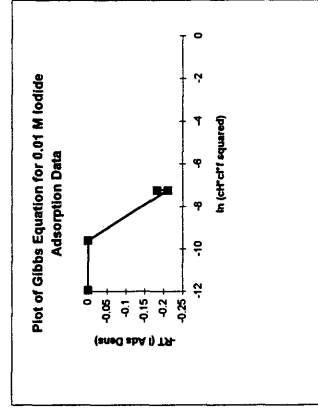


Debye Huckel Eqn
ActCoeff (I)
0.703527
0.746315
0.753102
0.753712
0.753775

Debye Huckel Equation
ActCoeff (H)
0.801668
0.821882
0.825287
0.825574
0.825605

Ionic Strength (0.1 M)
Mean ActCoeff Mean ActCoeff Squared
0.751004 0.564008
0.783187 0.613382
0.788359 0.62151
0.788625 0.622245
0.788673 0.62232

$\ln(\text{H}^+\text{I}^-\text{HI})$ $-\frac{RT}{\text{ActDen}}^*$
-4.7902 -2.72549
-7.35736 -1.44947
-9.86187 0
-12.2399 0
-16.9146 0



Debye Huckel Eqn
ActCoeff (I)
0.787508
0.787508
0.78954
0.789721

Debye Huckel Equation
ActCoeff (H)
0.843278
0.843278
0.823565
0.824495

Ionic Strength (0.01 M)
Mean ActCoeff Mean ActCoeff Squared
0.814916 0.664008
0.814916 0.664008
0.823565 0.67826
0.824495 0.679783

$\ln(\text{H}^+\text{I}^-\text{HI})$ $-\frac{RT}{\text{ActDen}}^*$
-7.22179 -0.18286
-7.22179 -0.21135
-8.58862 0
-11.9209 0

