BEHAVIOR OF DENSE NONAQUEOUS PHASE LIQUIDS IN SANDY AQUIFER MATERIAL: DEPENDENCE ON CHEMICAL AND PHYSICAL PROPERTIES

by

Jan Marie Lockhart Christner

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

Golden, Colorado

Date 8/23/93

Signed: Jan M Christner
Jan M. Christner

Approved: HED
Helen E. Dawson
Thesis Advisor

Golden, Colorado

Date 8/23/93

JA Cordes
John A. Cordes
Division Director
Environmental Science and Engineering

ABSTRACT

The purpose of this study was to determine the effect of varying organic liquid and porous medium properties on the organic liquid saturation of dense non-aqueous phase liquids in sandy aquifers. The migration of organic liquids in aquifers has been shown to depend on the wetting characteristics and density of the organic liquid, on the porosity, permeability and geometry of the porous medium, and on the velocity of the groundwater. A theoretical model which relates the organic liquid saturation to the relative magnitude of these properties was used to determine the anticipated effect of variations in wettability, porosity, and pore geometry on organic liquid saturation. Adhesion tension, defined as the product of the water-organic liquid interfacial tension and the cosine of the contact angle formed between the solid, water and organic liquid phases, was used to describe the wettability of the organic liquid. The model indicated that an increase in adhesion tension should cause an increase in the groundwater velocity required to reach the minimum residual saturation attainable by groundwater pumping. Higher aquifer porosity should result in a decrease in the groundwater velocity required to reach the minimum residual saturation. Porous media geometry should significantly influence the groundwater velocity required to reach minimum residual saturation.

Adhesion tension was an important factor in determining the groundwater velocity required to reach minimum residual saturation, therefore, experimental work was done to determine the effects of groundwater characteristics, pH and ionic strength, on adhesion tension. In this study, the dependence of contact angle on pH and ionic strength for two dense organic liquids, trichloroethylene and carbon tetrachloride, on two common minerals, quartz and corundum, was studied. The pH range investigated was from 5.3 to approximately 10. The ionic strength range was from 0 to 1M $NaClO_4$. The investigation showed variation in wettability with pH variation on corundum surfaces but not on quartz surfaces. A significant decrease in wettability with increasing ionic strength was observed.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGEMENTS

I would like to thank Helen Dawson for her assistance in selection this thesis topic, for the use of her displacement model, and for her assistance and encouragement in carrying the project through. I'd also like to thank Bruce Honeyman for his help with surface chemistry, Steve Marinello for adding perspective to the project, and to Frank Dunkle, Thesis Committee Chairman.

NOMENCLATURE

A - Area

c - Pore geometry constant

drn - Drainage

G - Gibbs free energy

g - Gravitational constant

imb - Imbibition

k - Permeability

k_{rw} - Relative permeability to water

L - Length

M - Mass

n - Mole fraction

n - Number of samples in statistical tests

N_{Ca} - Capillary Number

N_{Bo} - Bond Number

o - Organic liquid

P - Pressure

P_c - Capillary pressure

$P_{c,eq}$ - Equilibrium capillary pressure

$P^*_{c,eq}$ - Nondimensional equilibrium capillary pressure

p - Number of means in statistical tests

q - Darcy velocity

r, R - Radius

r_p - Statistical factor

R_p - Least significant range

R(X) - Rank of X value

s - Solid

s_x - Standard deviation of means

S_{or} - Residual saturation of organic liquid

S_w - Saturation of water

V - Volume

w - Water

v_w - Velocity of water

ϑw - Contact angle measured in water

ϕ - Porosity

γ - Interfacial tension

μ - Chemical potential

Ψ - Electrical potential

σ - Surface charge

ρ - Density

ρ - Spearman's rho in statistical tests

Γ - Surface excess of ions

υ - viscosity of water

INTRODUCTION

Organic liquid contamination in the subsurface can serve as a continuing source of pollutants to groundwater systems. Organic liquid that is insoluble or slightly soluble in water exists in the subsurface as non-aqueous phase liquid (NAPL). Left untreated, this liquid will slowly dissolve into the groundwater for many years. Even slight solubility of these chemicals can cause the concentration in groundwater to be above regulatory groundwater standards. However, the solubility is low enough (and mass transfer limitations in the subsurface cause actual concentrations to be even lower) so that dissolution is not a viable treatment approach.

When NAPL is introduced into the subsurface, it migrates downward through the vadose zone to the water table, leaving some liquid entrapped in the pore spaces due to capillary forces. A NAPL with density less than that of water (LNAPL, "light non-aqueous phase liquid") will spread out on top of the water table. A dense non-aqueous phase liquid (DNAPL, "dense non-aqueous phase liquid") has higher density than water, so penetrates the saturated zone and continues to migrate downward (See Figure 1).

Migration continues until the DNAPL is immobilized in the pore spaces in discontinuous blobs (Powers et al., 1989). The percentage of pore space occupied by the DNAPL is defined as the organic liquid saturation (See Figure 2).

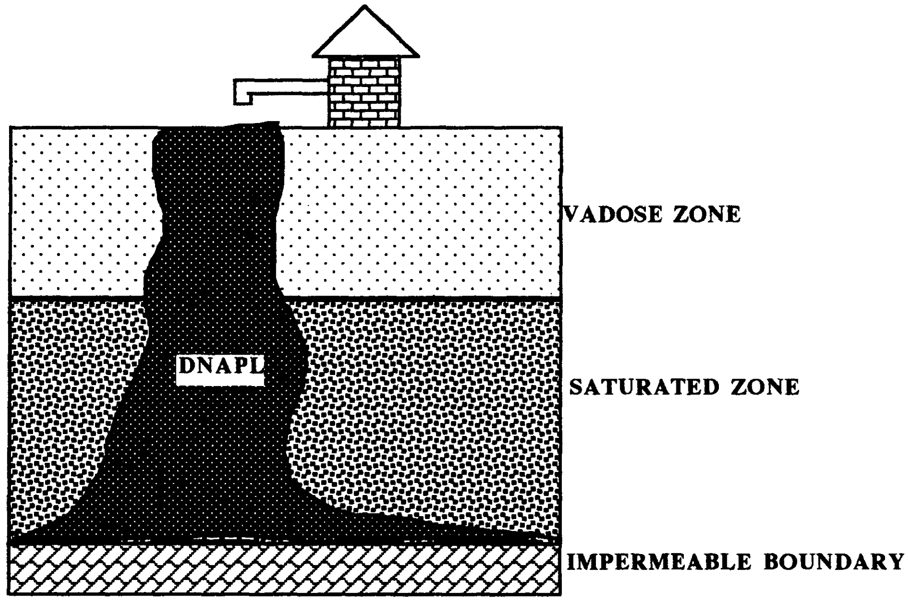


Figure 1 Spreading of DNAPL after penetrating the saturated zone. (After Schwille, 1967)

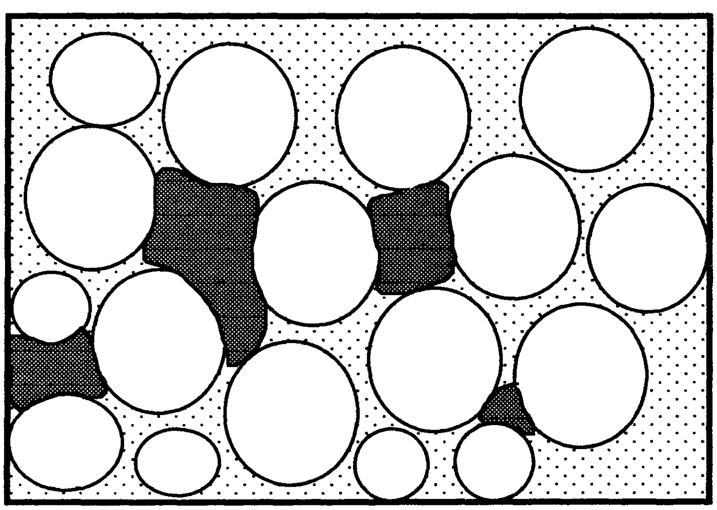


Figure 2 DNAPL (dark areas) trapped in pore spaces as discontinuous blobs. Water (light background) remains a continuous phase but DNAPL blobs are not connected so are a discontinuous phase.

The usual technique for removing organic chemicals from the subsurface is the so called pump and treat method. Pumping is very effective for chemicals soluble in water, but for sparingly soluble compounds pump and treat isn't efficient because it causes the contamination of large volumes of water without complete removal of the contaminant. To effectively remove DNAPL, the individual globules must be mobilized. Given sufficient water flow rate during groundwater pumping, much of the organic liquid can be mobilized and removed. However, a significant amount remains, the minimum residual saturation, beyond which the system cannot be cleaned by water flooding.

The organic liquid saturation has been shown to depend on the direction and velocity of the displacing water during pumping, the density of the organic liquid relative to that of water, the wetting characteristics of the organic liquid, and the porosity, permeability, and pore geometry of the porous medium (Anderson, 1987; Dawson, 1992; Lake, 1989; Mercer and Cohen, 1990; Stegemeier, 1977; Wilson et al.,1990).

The wetting characteristics of the organic liquid affect both the infiltration and removal of DNAPL in the subsurface (Anderson, 1987). A liquid will either wet (spread out on) a solid surface or bead up on the surface depending on the relative surface free energies of the liquid and solid. Organic liquid drops are non-wetting, so they bead up on most aquifer material. The wettability of a solid surface by an organic liquid can be described by the adhesion tension of the liquid on the solid material in the presence of water. The adhesion tension is defined as the interfacial tension between the organic liquid and water times the cosine of the contact angle measured in the wetting phase. An organic liquid with a high adhesion tension will likely penetrate only the largest pore spaces of the aquifer, allowing it to be more easily removed by groundwater pumping than an organic liquid with lower adhesion tension. Conversely, a liquid with a low adhesion tension will more likely wet the solid surfaces and invade the smaller pore spaces causing the liquid to be difficult to displace and therefore leave a higher residual saturation. However, the groundwater velocity at which the minimum residual saturation is reached may be lower in a low adhesion tension liquid than a higher adhesion tension liquid, since the low adhesion tension liquid located in the larger pore spaces is mobilized more easily. This will be discussed more thoroughly in the Displacement Model Analysis section of this paper.

Aquifer conditions which may affect the adhesion tension of an organic liquid contaminant are the aquifer material characteristics, pH, and ionic strength. An understanding of the effects of aquifer conditions on adhesion tension may be critical in predicting the effectiveness of remediation techniques such as pump and treat and determining the groundwater velocity required to achieve the minimum level of residual saturation.

This study will focus primarily on the effects of wettability on organic liquid saturation, but will also consider the effects of porous medium properties. The results may be used to determine the viability of pump and treat clean-up efforts when one or more DNAPL is present. It may also be the basis for study on methods to reduce residual saturation such as surfactant addition, alkalinity adjustment, or bioreclamation.

BACKGROUND AND DISCUSSION

Previous work has shown that wettability can affect the behavior of organic liquids in the subsurface (Anderson, 1987). Organic liquid saturation can depend on the relative wettability of the organic liquid and water and also on the porosity, permeability and geometry of the porous medium. The scientific basis for this will be discussed in this section.

Wettability

When a liquid contacts a solid and the liquid has a lower surface free energy than the solid, the liquid will spread out on the solid (wet the solid) to minimize the system's surface free energy. If, however, the liquid has higher surface free energy than the solid, it will bead up on the solid (not wet the solid) to minimize the system's surface free energy. In a three-phase system, the contact angle is a measure of the relative wettability of a solid by each of the two fluids in the system. It is defined as the angle formed at the fluid-fluid-solid interface (Figure 3). In this study, the contact angle was measured in the wetting phase (water).

Interfacial tension (called surface tension when a substance is in equilibrium with its own vapor) is a measure of the attraction of a molecule towards it's own kind relative to its attraction to another kind of molecule. The contact angle can be described as the result of three interactive interfacial tensions. Consider a drop of organic liquid on a solid surface immersed in water as shown in Figure 3. The interfacial tensions between the solid and organic liquid, between the solid and water, and between the water and organic liquid combine to produce the contact angle. The water-organic liquid-solid system proceeds toward a state of minimum free energy. If system free energy is reduced by minimizing the organic liquid-solid surface area, the organic liquid will minimize contact with the surface. Contact angle and interfacial tension are related by Young's equation (Equation 1):

$$\gamma_{OW}\cos\vartheta_W = \gamma_{OS} - \gamma_{WS} \tag{1}$$

where γ_{OW} = interfacial tension between organic liquid and water
γ_{OS} = interfacial tension between organic liquid and the solid
γ_{WS} = interfacial tension between water and the solid
θ_W = contact angle, measured in water.

The left hand side of the equation, $\gamma_{OW}\cos\vartheta_W$, is the adhesion tension.

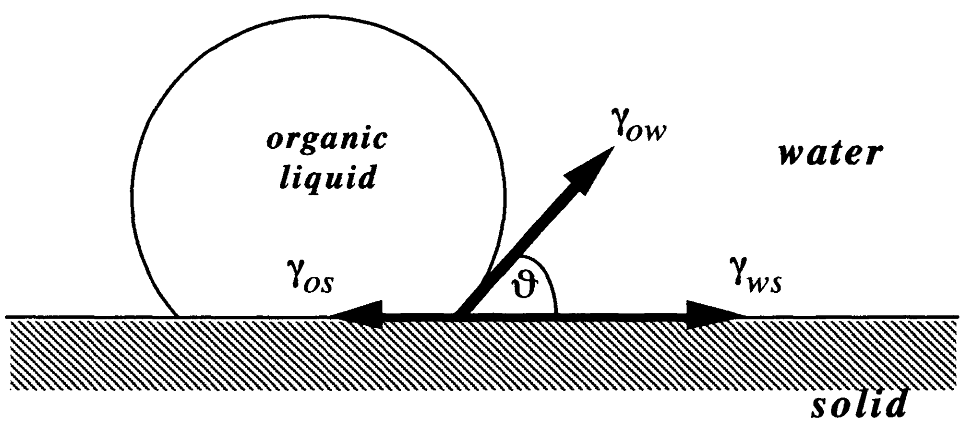


Figure 3 Schematic illustration of Young's equation: equilibrium of interfacial forces at an organic liquid-water-solid interface.

Young's equation can be looked at mathematically to determine the expected results when one interfacial tension is changed due to chemical or physical changes in the system.

$$\cos \theta_w = \frac{\gamma_{so} - \gamma_{sw}}{\gamma_{ow}} \tag{2}$$

Mathematically, with all other values remaining constant and for a non-wetting organic liquid ($0° < \theta < 90°$),

1. Increasing γ_{ow} decreases $\cos \theta$ so increases θ
2. Increasing γ_{sw} decreases $\cos \theta$ so increases θ
3. Increasing γ_{so} increases $\cos \theta$ so decreases θ

Realistically, however, changes which affect one interfacial tension will often affect another. Interfacial tension between two phases can be estimated by the magnitude of the difference between the pure phase surface tensions using Antonov's rule (:

$$\gamma_{AB} = |\gamma_A - \gamma_B| \tag{3}$$

Only the difference in surface energies is considered, so an increase in γ_A could result in either an increase or decrease in γ_{AB} depending on whether γ_A is greater or less than γ_B. Because the three phase system has three interfaces, solid-water, organic liquid-water, and organic liquid-solid, there are three equations relating surface tensions to interfacial tension.

$$\gamma_{ow} = |\gamma_o - \gamma_w| \tag{4a}$$

$$\gamma_{sw} = |\gamma_s - \gamma_w| \tag{4b}$$

$$\gamma_{so} = |\gamma_s - \gamma_o| \tag{4c}$$

For analysis of changes in any one surface tension it is helpful to know that for high energy solids such as silicates and metal oxides, the surface tension of the solid (>200 dynes/cm, Parks, 1968) is much greater than the surface tension of water (72.6 dynes/cm, Osipow 1962) and the surface tension of water is typically higher than the surface tensions of organic liquids (15 - 50 dynes/cm, Osipow 1962). More simply, $\gamma_S >> \gamma_W > \gamma_O$. For example, if the surface tension of water were increased, both the water-organic liquid interfacial tension and the water-solid interfacial tension would change. The solid-water interfacial tension would decrease (Equation 4b) and the organic liquid-water interfacial tension would increase (Equation 4a).

Effect of Wettability on Organic Liquid Removal in Sandy Aquifers

Groundwater systems contaminated with DNAPL are three phase systems containing solid, water and organic liquid. In most sandy aquifer systems, the water is the phase which wets the solid, and the organic liquid is the non-wetting phase (Schwille, 1967). The DNAPL typically occurs as globules or blobs and are difficult to displace (Sitar et al., 1987). This is because there is a pressure jump across curved interfaces. The Laplace equation,

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2}\right) \tag{5}$$

describes the pressure jump across a curved surface. For a spherical interfacial surface, $R_1 = R_2 = r$ and the Laplace equation reduces to

$$\Delta P = \frac{2\gamma}{r}. \tag{6}$$

The curvature is partially due to the contact angle of the organic liquid on the solid. In a capillary tube of radius R, the Laplace equation of the pressure drop across the curved surface becomes,

$$\Delta P = \frac{2\gamma\cos\theta}{R}. \tag{7}$$

For a liquid where θ is less than 90°, a non-wetting fluid, the pressure is less in the wetting fluid than in the non-wetting fluid and the wetting fluid rises in the capillary tube until the force from the weight of the column of liquid balances the pressure differential. Conversely, for a liquid where θ is greater than 90°, the wetting fluid is depressed in the capillary tube (See Figure 4).

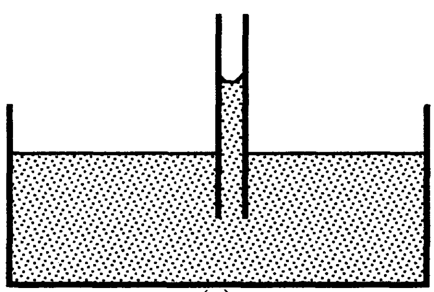


Figure 4 (a)
Capillary rise for a wetting fluid

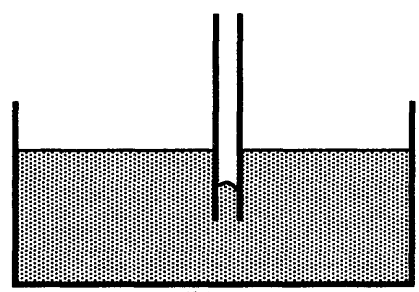


Figure 4 (b)
Capillary depression for a non-wetting fluid

In the sandy aquifer system, the water behaves as a wetting fluid would in a capillary tube and easily passes through narrow capillary sized pores. The organic liquid behaves as a non-wetting fluid would in a capillary tube. The organic liquid resists flow through narrow capillary sized pores because the pressure in the organic liquid is higher than the pressure in the surrounding water. The pressure differential between the inside of the organic liquid globule and the outside water as the organic liquid approaches the narrow pore is the capillary pressure. The capillary pressure differential causes the organic liquid to resist flow through the narrow pore. The force keeping the liquid from passing through the narrow pores is the due to the capillary pressure and is called the capillary force.

Variations in Wettability Due to Groundwater Characteristics

The characteristics of groundwater can influence the behavior of organic liquids in a sandy aquifer. Both the chemical composition of the water and the pH of the water may influence the surface tension of the water which will change the water-solid and water-organic liquid interfacial tensions. These, in turn, affect the adhesion tension of the organic liquid and therefore the minimum residual saturation and the groundwater velocity required to remove the organic liquid. The interactions between aquifer characteristics and organic liquid saturation will be discussed in the Porous Medium Properties section of this work.

Effect of Ionic Strength and pH on Water Surface Tension

The chemical composition of the groundwater will affect its surface tension. If a salt is added to water, the water's surface tension will rise (Osipow, 1962). If a salt is added to water containing a high energy solid such as quartz or corundum (which have a surface tension much higher than the surface tension of water), the solid-water interfacial tension will decrease because the difference between surface tensions will decrease (Equation 4b). When salt is added to water containing an organic liquid (which has a lower surface tension than water), the organic liquid-water interfacial tension will increase because the difference between surface tensions will increase (Equation 4a). Therefore, by Young's equation (Equation 1) the addition of a salt to the water should have the net result of decreasing the contact angle.

The pH of the water may or may not affect the water surface tension (Young and Harkins, 1928, Stumm and Morgan, 1970).

Interfacial tension has been shown to depend on surface aging or equilibration time (Defay and Hommelen, 1958). The magnitude of that effect for each component in the three phase system is unknown so the effect of equilibration time on contact angle is unknown.

Effect of pH and Ionic Strength on Solid Surface Tension

Aquifers are solid surface dominant systems, so the solid composition will influence the behavior of organic liquids in the aquifer. The composition and charge of the mineral surfaces can have a significant affect on the wettability of the sandy aquifer. Surface composition and charge can be affected by the properties of the water in the aquifer. The charge and therefore surface tension of the solid surface is dependent on both the pH and ionic strength of the groundwater (Parks, 1983). There are many chemical and physical processes which occur in the aquifer system that may have an effect on the contact angle of organic liquids. These processes will be discussed in this section.

Many reactions occur at the surface of an oxide mineral. For example, unfully coordinated Si and O groups whose coordination numbers are unmatched, made during formation of a SiO_2 surface form SiOH, SiH^+ and Si^- groups at the surface when water comes in contact with the surface (hydroxylation). These are usually called SOH groups (the S refers to solid). The type of the majority of surface groups depends on the pH of the water in which the solid is immersed. At pH's below a certain pH, called the point of zero charge (PZC), the surface is net protonated (has many H^+ ions attached). This causes the surface to be positively charged. At pH's above the PZC, the surface has many OH^- ions attached and becomes a negatively charged surface. At the PZC, the surface is net electrically neutral. The bulk pH of the water may change when a charged surface is immersed because the solid is an OH^- acceptor at $pH_w > pH_{pzc}$ and the solid is an H^+ acceptor at $pH_w < pH_{pzc}$.

The pH affects adsorption because H^+ is a potential determining ion for oxide surfaces and proton activity affects the solution phase speciation of solutes. The Triple Layer Model (Davis et al., 1978) includes three planes of adsorption: the surface (0-plane), a plane for ion pairs (β-plane), and all non-specifically adsorbed ions present to satisfy the conservation of charge, located in the diffuse layer. At a pH designated pH_{PZC}, the surface has a net zero charge in the absence of 0-plane bound species other than a proton or hydroxide. Ions which are covalently bound at the 0-plane can affect surface charge and are therefore potential determining. Ions which are located at the β-plane sorb in response to the surface charge and potential generated by potential determining ions (e.g., proton, hydroxide, and other solutes forming inner sphere, 0-plane, complexes). Thus, at a pH such that the surface charge is net zero, the driving force for the sorption of charged species (which would be located at the β-plane, outer sphere complexes) should also vanish.

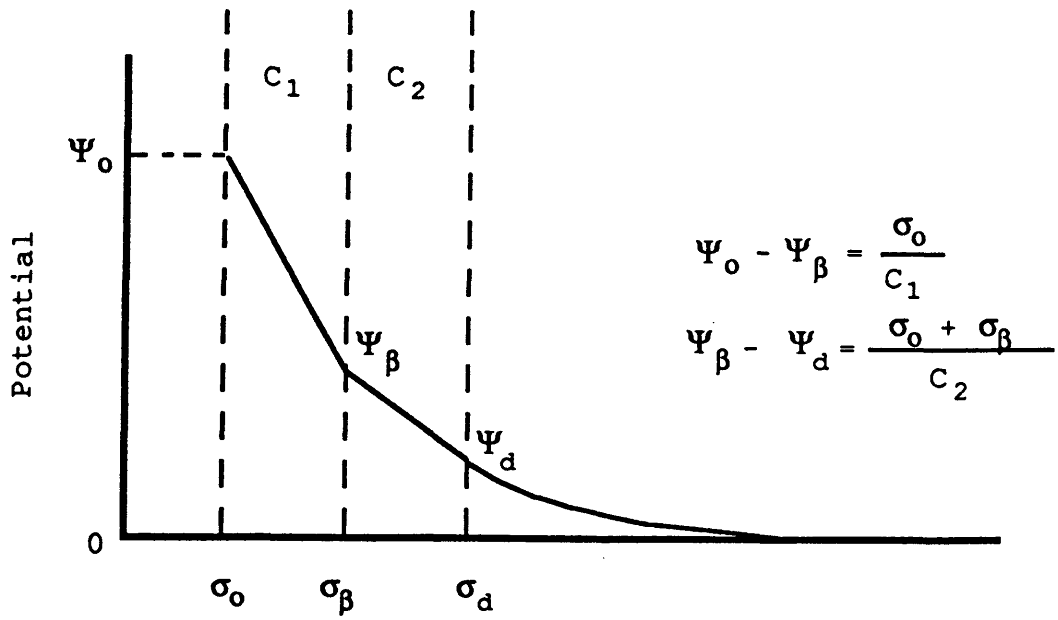


Figure 5 Schematic diagram of the Triple Layer Model (Davis et al., 1978) as modified by Papelis et al., 1988.

The possible solid surface effects of adding a salt or varying pH of the water on the solid surface tension can best be seen by looking at the Gibbs equation (Equation 9) at constant temperature and pressure. Note that γ can be an interfacial or surface tension.

$$dG_{s,tot} = \gamma dA + Ad\gamma + \Sigma\mu_i dn_{si} + \Sigma n_{si} d\mu_i + \sigma d\Psi \tag{8}$$

This is the free energy change which accompanies a change in interfacial tension, surface area, chemical composition, or electrical potential. At equilibrium, $\Delta G = 0$. Assuming surface area is constant, the Gibbs adsorption equation becomes,

$$d\gamma = -(\Sigma\frac{n_{si}}{A}d\mu_i + \Sigma\frac{\mu_i}{A}dn_{si} + \frac{\sigma}{A}d\Psi) \tag{9}$$

Equation 9 shows that the positive adsorption (i.e. positive change in n_{si}) of anything at an interface must result in a decrease in interfacial tension. This indicates physical adsorption of positive or negative ions at the solid-water interface must decrease γ_{sw}, causing a decreased contact angle (Equation 2). Equation 9 also shows that an increase in the electrical potential difference between the solid and a liquid will decrease the solid-liquid interfacial tension. This indicates that an increased surface charge may cause decreased γ_{so} and γ_{sw} (Equations 4a and 4b). The decrease in γ_{so} may be greater than the decrease in γ_{sw} because the organic liquids have much lower dielectric constants than water (CCl_4, ε = 2.23, TCE, ε = 3.4; Water, ε = 80) which would cause the potential difference across the interface to be greater between the solid and organic than between the solid and water. In other words, the water will orient itself to minimize the potential gradient where the organic liquids cannot do so. The result of a decrease in γ_{so} is an increase in θ_w (Equation 2) and the result of a decrease in γ_{sw} is a decrease in θ_w. If the magnitude of the decrease in γ_{so} is greater than the decrease in γ_{sw}, the contact angle would be expected to increase with increasing surface charge. To characterize this relationship between surface charge and surface tension/contact angle, experiments were conducted to determine contact angle at varying pH and ionic strength levels.

It is unknown at which layer the organic liquid "contacts" the solid. The organic liquid may actually touch the surface of a smooth solid in which case the surface charge will determine the potential gradient at the interface. However, even on a perfectly smooth surface there may be a thin layer of physically adsorbed ions between the solid and organic liquid in which case the charge at the beta plane or the charge at the outside of the diffuse layer would determine the potential gradient at the interface. Surface roughness would increase the probability of the organic liquid not actually touching the surface because the organic liquid would not wet the small indentations in the surface and therefore would not completely cover the actual surface. In other words, the organic liquid may or may not experience the charge from the surface or the electrical potential near the surface. This would affect any variation in organic liquid-solid interfacial tension due to the potential gradient.

Another complication in the organic liquid-solid interfacial location is the ionic strength of the water. Increasing salt concentration "reduces the charge and potential observed electrokinetically. This screening effect suggests positive ions are attracted to negative surfaces and negative ions to positive surfaces to minimize electrical potential energy and preserve electrical neutrality" (from Parks, 1983). Coagulation of solids increases at high ionic strength because the diffuse double layer is smaller so particles can get closer and coagulate. This might have implications for an organic liquid dropped on the surface. If the ionic strength is high, the surface charge is neutralized with a very short diffuse layer of counter ions, and the organic liquid drop may experience no polarity that would arise from a charged surface. The ions neutralize the charge, causing the organic liquid dropped on the surface to be unaffected by the surface charge. Under this condition, little pH dependence on the organic liquid-solid interfacial tension would be expected.

Previous work, as described above, has shown that bulk water pH can affect the contact angle of an organic liquid in contact with a solid because of the change it may cause in surface charge and adsorption of ions. If the surface is charged it will attract polar compounds such as water. This attraction will decrease the interfacial tension between the water and the solid (Parks, 1990) and increase the area of contact between water and solid. This means an increase in charge should cause a decrease in the contact angle. A neutral surface will have no additional attraction for water so the water-solid interfacial tension should be a maximum and the contact angle should be a maximum at the PZC. The PZC is about pH = 2 - 4 for quartz (SiO_2) and 8.6 for corundum (Al_2O_3). Therefore, in a pH range of 5 to 10, contact angles on quartz should show no dependence on pH, while contact angles on corundum should reach a maximum at pH 8 and be lower at both lower and higher pH. Note that this is the opposite of the effect predicted by the Gibbs equation above unless the decrease in water-solid interfacial tension is greater than the solid-organic liquid interfacial tension. The experimental portion of this work will investigate the actual effect of varying the surface charge through pH variation.

Previous experimental work has shown ionic strength to affect the quartz-water interfacial tension, where salt addition caused a decrease in the interfacial tension of quartz by as much as 15% at high pH (See Figure 6, from Parks, 1990). No study was found that reported similar behavior for corundum or other minerals. Variations in contact angle on quartz and corundum at various pH's and ionic strengths were investigated in this study.

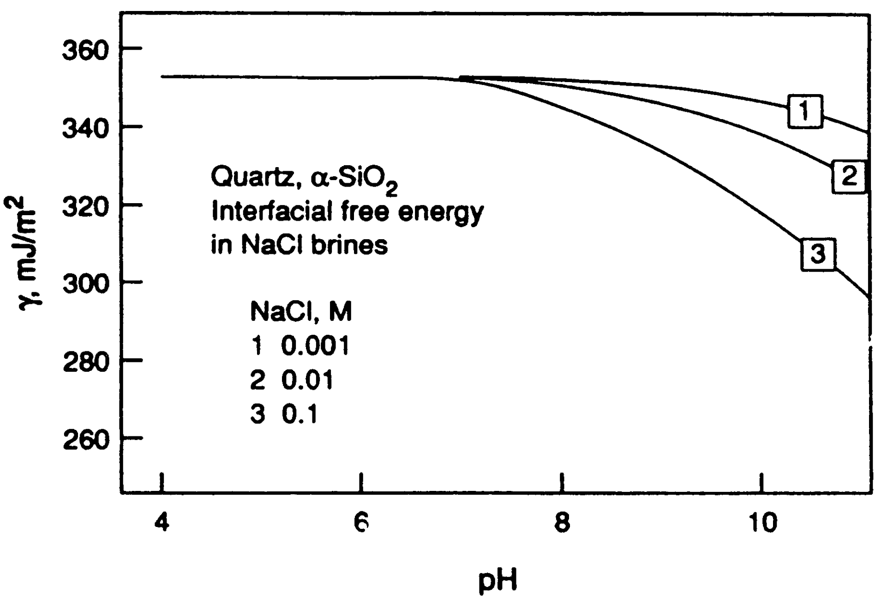


Figure 6 Surface tension of quartz vs. pH for varying pH (From Parks, 1990)

<u>Porous Medium Properties</u>

Much previous work has been done on the behavior of soluble organic liquids and petroleum hydrocarbons in the subsurface, primarily by the petroleum industry to increase production and to remediate accidental spills. Unfortunately, much of this information is not applicable to DNAPLs because petroleum hydrocarbons are "light" so less likely to penetrate the saturated zone (Schwille, 1967), while DNAPLs are dense enough to penetrate and become trapped in the saturated zone.

globules. The water (the wetting phase) in the saturated zone exists as a single continuous phase, but at residual saturation, DNAPL (the nonwetting phase) is actually a discontinuous phase (Mercer and Cohen, 1990; USEPA, 1991). Previous experimental work has been done to visualize the behavior of DNAPL in the subsurface (Schwille, 1981, 1984, 1988) and residual saturations of 10 - 30% were reported, but no quantitative relationships were developed relating chemical properties of the liquid or physical properties of the soil to the organic liquid saturation.

Displacement Model

A theoretical model of the relative effects of viscous, buoyant and capillary forces on residual saturation, and experimental work to calibrate the model was developed by Dawson (1992). The study used the Capillary Number (a dimensionless group giving the ratio of viscous to capillary forces, Equation 10) and Bond Number (a dimensionless group giving the ratio of buoyant to capillary forces, Equation 11) to relate the physical and chemical properties of a subsurface system to its residual saturation. In the current study, where only horizontal flow was considered, the Bond Number was eliminated from the model.

$$\text{Capillary Number: } N_{ca} = \frac{v_w u_w}{\gamma_{ow} \cos\theta_w} \quad (10)$$

where
v_w = velocity of displacing water
u_w = water viscosity
γ_{ow} = interfacial tension between the organic liquid and water
θ_w = contact angle, measured in water

$$\text{Bond Number: } N_{Bo} = \frac{\Delta\rho g\sqrt{k/\phi}}{g_{ow}\cos\theta_w} \tag{11}$$

Where $\Delta\rho$ = density difference
g = gravitational constant
k = permeability
ϕ = porosity
γ_{ow} = interfacial tension between the organic liquid and water
θ_w = contact angle, measured in water

Dawson primarily used vertical displacement, where water was pumped up through the porous media, so the effect of buoyant forces would be magnified; however, groundwater pumping usually produces horizontal flow. At low water flow rates, horizontal displacement is expected to produce lower residual saturations than upward displacement because gravity is not hindering the displacement of DNAPL. In contrast, the minimum residual saturation (organic liquid saturation achieved at high flow rates) is expected to be equivalent to that obtained in upward displacement (Figure 7) since the minimum residual saturation is governed by the adhesion tension of the organic liquid and the soil pore geometry. However, the hydraulic gradient required to achieve the minimum residual saturation in horizontal displacement is lower than is required in vertical displacement.

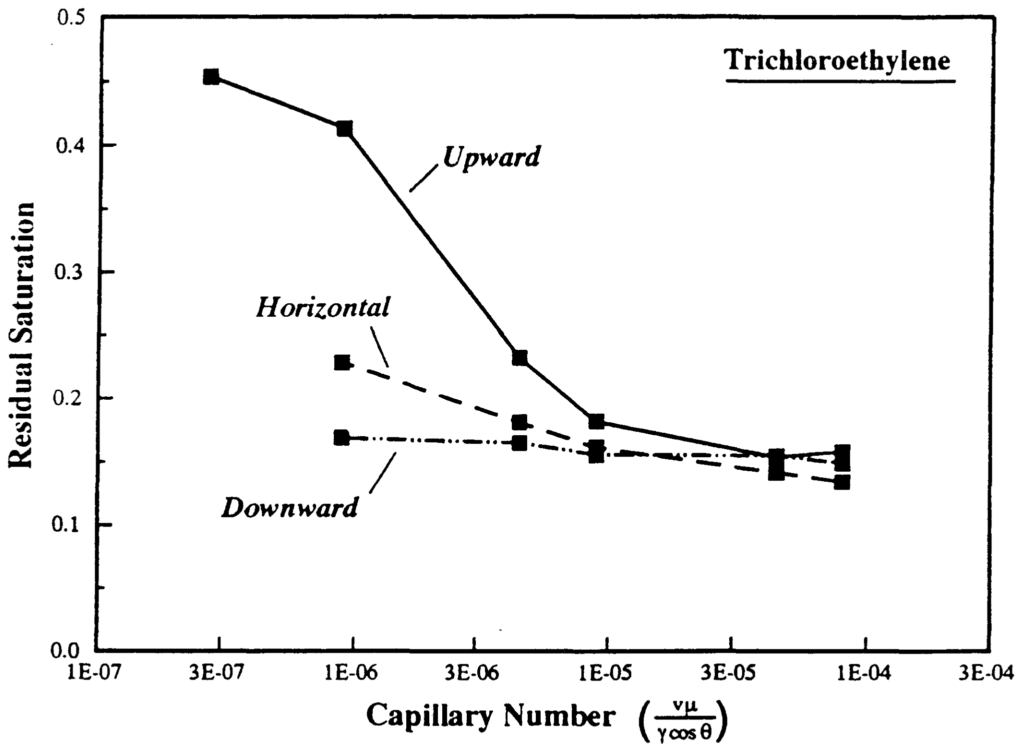
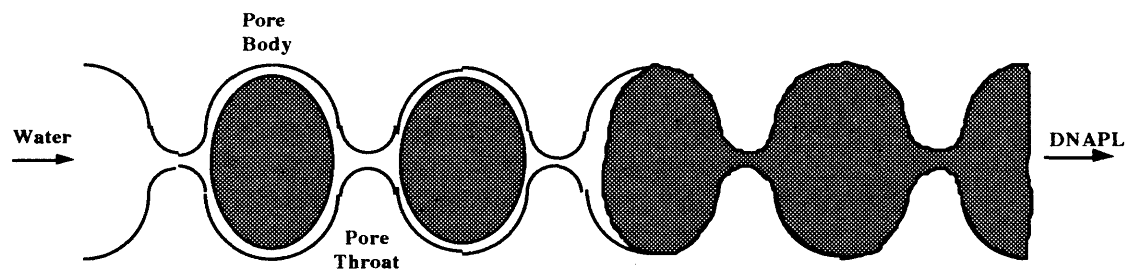


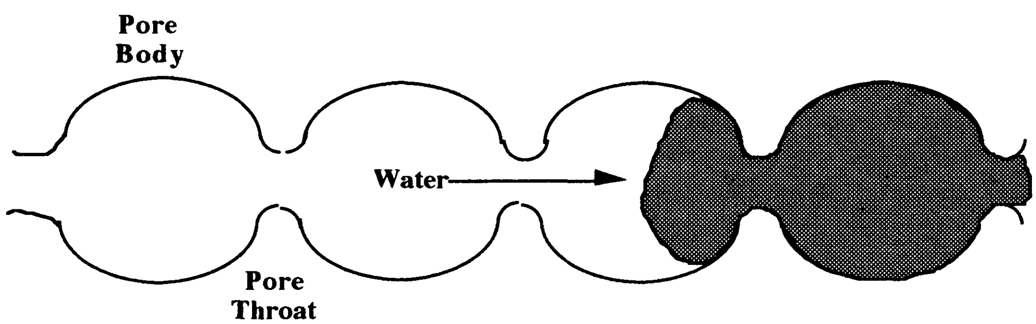
Figure 7 Residual saturation of trichloroethylene as a function of Capillary Number and displacement direction. (From Dawson, 1992)

Soil Geometry

Pore geometry and the contact angle of the organic liquid together play an important role in determining residual saturation. Even minimal soil heterogeneity can have a dramatic influence on trapping (Wilson et al., 1990). Blobs of organic liquid are trapped in the soil by two mechanisms: snap-off and by-passing (Wilson et al., 1990). Snap-off occurs when the soil has a high aspect ratio (pore body size much greater than pore throat size). Water flowing through the pores preferentially wets the soil. If the contact angle of the organic liquid (measured in water) is low, the curvature of the organic liquid front is very large allowing water to reach the outlet throat before all the DNAPL is pushed through, leaving a blob of organic liquid in the pore around which water will flow (Figure 8a). Conversely, if the aspect ratio is lower and the pore body size is closer to the pore throat size, the curvature of the organic liquid front in the pore body will fit through the pore throat and no snap-off will occur (Figure 8b).



(a)



(b)

Figure 8 (a) Entrapment of DNAPL via snap-off. (b) No snap-off. (After Wilson et al, 1990)

By-passing occurs because displacing water will take the path of least resistance. If water faces two possible paths, a narrow one (a) and a wider one (b), both filled with organic liquid, the water will enter the narrower path (a) first due to capillarity. If path (a) remains narrower, the water will continue through this narrow pore, by-passing path (b), leaving the DNAPL trapped in path (b). If, however, path (a) widens so it is wider than path (b), water will then enter the other pore space thereby displacing the DNAPL from both pathways (Figure 9).

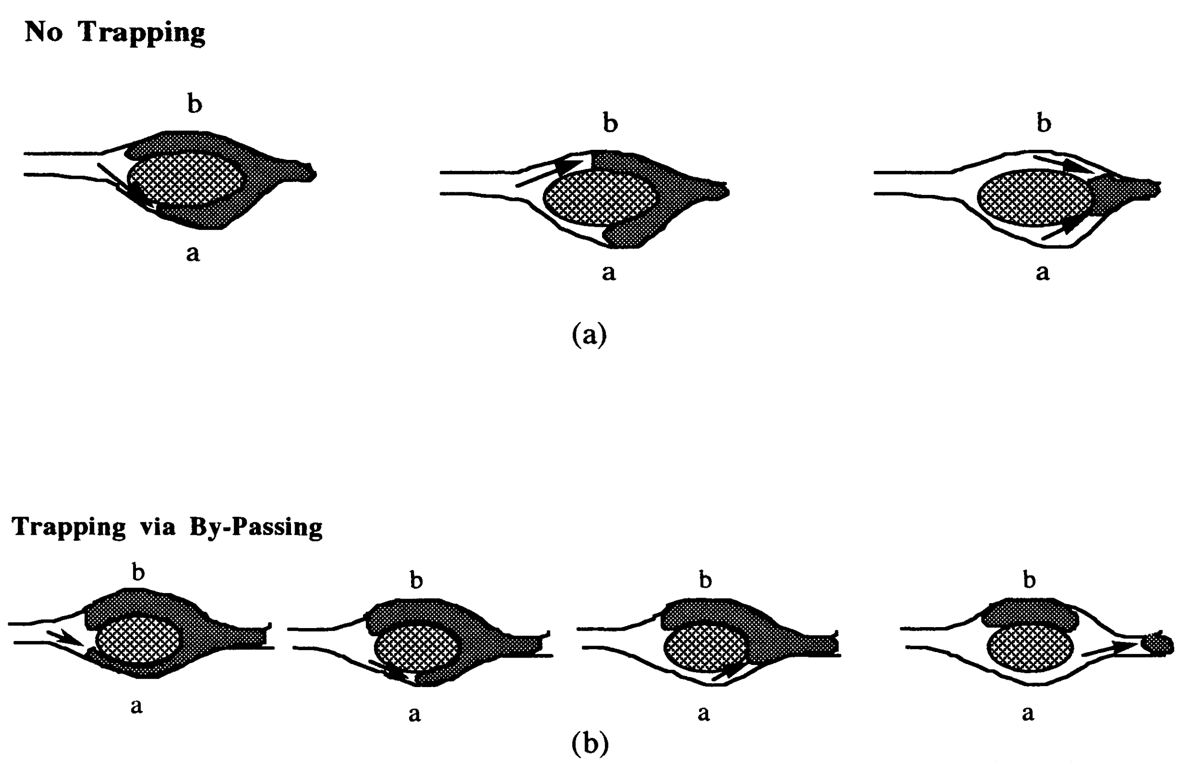


Figure 9 (a) No entrapment of DNAPL (b) Entrapment of DNAPL in pore spaces via by-passing. (After Wilson et al., 1990)

Literature on both LNAPL and DNAPL state that the only way to significantly reduce residual saturation is to reduce adhesion tension. Several methods of accomplishing this have been examined: surfactants, steam flooding (Hunt et al., 1988), CO_2 flooding (Sale and Piontek, 1988), alcohol flooding (Taber, 1981), and alkalinity adjustment.

EXPERIMENTAL PROCEDURE AND EQUIPMENT

To determine the effect of groundwater pH and ionic strength on the wettability of a sandy aquifer by an organic liquid and thus the residual saturation of the organic liquid, experiments were conducted to determine the effect of pH and ionic strength on the contact angle of organic liquids on typical aquifer solids. Two liquids, tricloroethylene and carbon tetrachloride, chosen because of their predominance in contaminated aquifers, and two solids, quartz and corundum (representing oxide minerals), were studied. Chemical and physical properties of the organic liquids are shown in Table 1.

Table 1
Properties of Organic Liquids Studied

Chemical	**Density** (g/cm^3)	**Interfacial Tension**[a] (dynes/cm)	**Contact Angle**[b]	**Viscosity** (cp)
Trichloroethylene	1.464	34.8	40°	0.566
CCl_4	1.594	49	33°	0.979

Sources: Density and viscosity data from Riddick et al., 1986. Interfacial tension and contact angle data from Dawson, 1992.
a Interfacial tensions measured between organic liquid and water.
b Contact angle measured in water on glass.

Three types of contact angle experiments were run. The first was to determine the effect of varying pH on contact angle. These were performed at constant ionic strength ($I = 1 \times 10^{-3}M$). The second was to determine the effect of ionic strength on contact angle.

These were performed without purposeful variation in pH, however pH was not regulated. The third was to determine the effect of equilibration time on contact angle. These experiments were performed at constant ionic strength ($I = 1 \times 10^{-3}$M) and without purposeful variation in pH, however pH was found to vary slightly with equilibration time.

Two types of interfacial tension experiments were also run. The first was to determine the effect of water pH on the interfacial tension between water and the organic liquid. The second was to determine the effect of water ionic strength on the interfacial tension between water and the organic liquid.

Contact Angle Experimental Setup and Procedure

Contact angle measurement may be done using various methods. In this study the flat plate method was used because it was the most practical method for measuring contact angles of the organic liquids studied. The more commonly used tilting plate method was not practical in this work because the drops have very low contact angles and would rapidly flow off very slightly unlevel surfaces and would not stay on a plate tilted any significant amount. The methods used in this study are described below.

Contact angles were observed by use of a contact angle goniometer. The goniometer is a horizontal microscope through which a liquid drop may be observed. The microscope lens has a built in protractor which allows for direct measurement of the contact angle. The specimen is placed on a platform which is adjustable in all directions to facilitate leveling the solid on which the contact angle is measured. A quartz cell, a 1" x 2" x 2" clear rectangular cup, was used to hold the mineral and liquids during contact angle measurements. The quartz cell was used because it allowed optically undistorted measurements of contact angle.

Cleaning of Glassware and Mineral Crystals

Initially, the quartz cell and syringe used to dispense organic liquid were washed in Chromerge acid at the beginning of each day and the mineral crystals were cleaned by washing in detergent, rinsing thoroughly in deionized water, rinsing in pH = 4 acid rinse, then rinsing thoroughly in nanopure water. It was thought the acid rinse might change the characteristics of the solid surface, however, so this practice was discontinued. Subsequently the crystals were just washed well in detergent, rinsed thoroughly with nonionic water, then rinsed thoroughly with nanopure water. All measurements reported and analyzed for this report were done with this second rinsing procedure to minimize potential changes in the surface with the previous method.

pH Variation Experimental Procedure

The quartz cell was filled three-quarters full with the 0.001M $NaClO_4$ solution (approximately 30 ml). The mineral crystal and some organic liquid were added. The solution was stirred to allow the organic liquid and water to become mutually saturated. The solution was allowed to sit overnight so it would reach equilibrium and insure mutual saturation of water and the organic liquid. The next day or later, pH measurement was made using an Orion pH meter while the solution was being stirred by a magnetic stir bar. Then drops of the previously water-saturated organic liquid were dropped on the mineral surface and contact angle measurements were made with the goniometer. Both sides of three drops were measured three times, giving a total of eighteen contact angle measurements per pH.

One run consisted of determining the contact angle of one organic liquid on one crystal surface at three or more pH's. pH was varied by the addition of 0.1M NaOH or HCl solutions. This allowed for one solution to be used for all three pH values to minimize surface and solution variations that might occur if the solution were changed when pH was changed. Two sets of contact angle experiments were run for each organic liquid-mineral pair.

Ionic Strength Experimental Procedure

The quartz cell was cleaned according to the previously described procedure, then was filled with 30.0 ml of nanopure water. The mineral crystal and a magnetic stir bar were added. Organic liquid was added to saturate the water and the solution was allowed to sit overnight or longer. Contact angle measurements were made as described above. Then the ionic strength of the solution was increased by the addition of powdered $NaClO_4$. The solution was stirred for several minutes then allowed to sit overnight before subsequent contact angle measurements were made.

Equilibrium Time Experimental Procedure

It was discovered that the amount of time the solution was allowed to equilibrate greatly affected the contact angle measurements. Therefore a study to determine the relationship between contact angle and equilibration time was conducted. The materials were cleaned as previously described. $1x10^{-3}$ M $NaClO_4$ solution was added to the quartz cell. Then the corundum crystal was added to the cell and as quickly as possible the contact angle measurements of TCE on corundum were made. A specified time was allowed to pass, then contact angle measurements were made again. During one run, the pH was determined after the contact angle measurements were made at the various equilibration times and pH varied from 6.5 after the first measurement to 5.3 after 24 hours; no pH measurements were made on the other run of this experiment.

Interfacial Tension Experimental Procedure

The contact angle goniometer is equipped for interfacial tension measurements using the pendant drop technique. A syringe attached to a syringe holder is used to form a drop of organic liquid and a photograph of the drop is taken. Characteristic measurements of the drop are taken to estimate interfacial tension. In this work, where interfacial tension between the organic liquid and water is of interest, the organic liquid drop was suspended in a water solution contained in the quartz cell. The photograph of the drop was taken with a Polaroid camera attachment to the goniometer using black and white Polaroid 107C or 607C film.

pH Variation Experimental Procedure

The quartz cell and glassware were cleaned as for contact angle measurements. The syringe needle was dipped in Chromerge and thoroughly rinsed with nanopure water when a new organic liquid was used. This was to keep the organic liquid from adhering to the sides of the needle instead of forming a pendant drop. The organic liquid was aspirated into the syringe and the syringe emptied twice to be sure the liquid in the syringe didn't include free water. Fresh liquid was then aspirated into the syringe.

$1x10^{-3}$ M $NaClO_4$ solution was added to the quartz cell. The syringe was inserted in the holder on the goniometer so the tip was fully immersed in water, usually 2 cm under water, and care was taken to keep the needle tip away from the sides of the quartz cell. The needle was placed in the center of the camera's viewfinder and the camera focused. A drop of organic liquid was formed and the syringe turned so the drop contained enough liquid to form a pendant drop, but not so much that the drop would fall off the needle. A picture was made of the drop and the process was repeated with a different drop. pH was adjusted using NaOH or HCl. Two drops were photographed and measured at each pH.

Ionic Strength Experimental Procedure

The same procedure as described above was used except the initial fluid in the quartz cell was nanopure water, and varying ionic strength was accomplished by addition of $NaClO_4$.

Equipment

A summary of the equipment used in the experiments is given below.

Goniometer: For contact angle measurements. A platform used to hold the specimen is available for leveling the specimen. A syringe holder is available for interfacial tension measurements and for applying drops for contact angle measurements. A Polaroid camera attachment is available for interfacial tension measurements. Two lenses are available. One has a protractor to facilitate direct contact angle measurements. The other is clear for use in interfacial tension measurement photography.

Quartz cell: Used to hold the water and mineral crystal on which an organic liquid is dropped. The optics of the cell are good which allows undistorted measurements of contact angle.

pH meter: Orion model 720A. Measures pH to nearest .001 pH unit, but measurements in this experiment were made to the 0.1 place. Measurements are made in a stirred liquid so a magnetic stir bar was inserted in the quartz cell for experiments which required pH measurements.

Corundum and Quartz crystals: The corundum crystal was about .75" long with a machine polished face about .3" wide. Opposing sides had been polished to allow the top face to sit level, but one side appeared smoother and was consistently used in contact angle measurements. The quartz crystal was longer, about 1.5" in length. It's sides had not been polished, but one side appeared very smooth so that side was always used for contact angle measurements. The quartz crystal was long and prevented the stirring rod used for pH measurements from moving freely. The surfaces of the quartz cell and crystal can cause local variation in pH so the incomplete stirring may have contributed to pH measurement inconsistencies.

0.001M $NaClO_4$ solution: Used as the water phase in pH variation contact angle measurements. This was used instead of pure nonionic water so variations in ionic strength caused by adding acid or base to alter pH did not significantly change the ionic strength. Changing ionic strength could have confounded the pH dependent results. Powdered $NaClO_4$ was used in Nanopure water to mix this solution. One solution was mixed and used in all measurements.

0.1M NaOH solution: Used to raise the pH of the water. Solid NaOH was added to nanopure water to make this solution.

0.1M HCl solution: HCl was used to lower the pH of the water, mainly when NaOH solution raised the pH higher than the desired amount.

Carbon tetrachloride: Carbon tetrachloride was placed in a clean glass bottle and water was added. The mixture was stirred well to saturate the carbon tetrachloride with water.

Trichloroethylene: Trichloroethylene was placed in a clean glass bottle and water was added. The mixture was stirred well to saturate the trichloroethylene with water.

Polaroid 107C and 607C black and white high resolution film was used for interfacial tension photographs.

Data Analysis

Two statistical tests were used to analyze the contact angle measurement data. One was the Duncan multiple range test (Pfaffenberger, 1977). The other was the Spearman rho test (Miller, 1965).

The Duncan multiple-range test is a multiple-comparison test to simplify the comparison of many means. It is performed on the data by calculating the least significant range, Rp, using equations 12 and 13, where s_x is an estimate of the standard deviation of the means, r_p is dependent on the desired level of significance and can be looked up in a table, n is the number of samples per mean, and p is the number of means being compared.

$$s_x = \sqrt[2]{\frac{\text{Mean Square Error}}{n}} \quad (12)$$

$$R_p = s_x * r_p \quad (13)$$

The range of values of the dependent variable are compared to the least significant range. If the range exceeds the least significant range, there are significant differences in the means. Any number of adjacent means may be tested using the least significant range for the desired number of means. The analysis used in this study compared adjacent means in all combinations of adjacent means.

The Spearman's rho test is used to determine if an increase in one parameter results in the increase or decrease of another parameter. To perform this test, the data are ranked in order of largest to smallest. The test statistic is calculated using equation 14, where R(X) designates the rank of the X value.

$$\rho = 1 - 6\Sigma\frac{[R(X_i) - R(Y_i)]^2}{n(n^2 - 1)} \tag{14}$$

The test statistic, ρ, is compared to a table of ρ values and if the calculated ρ is greater than the table value for the desired level of significance, there is a trend for increasing X's to be associated with increasing Y's.

MODELING

Two models were used to help visualize the physical and chemical processes expected to influence residual saturation of an organic liquid in a sandy aquifer. The first, an organic liquid displacement model developed by Dawson (1992), was used to determine the relative influence of aquifer characteristics on organic liquid saturation. Porosity, permeability, pore geometry, and the wettability of the organic liquid were the characteristics varied in this model. The second model used was the HYDRAQL (Papelis et al., 1988) model. HYDRAQL was used to conceptualize the variation in wettability due to the surface changes which occur with pH or ionic strength variation.

Displacement Model

A model developed by Dawson (1992) to describe the behavior of DNAPL in the subsurface was used in this study to predict the variation in organic liquid saturation due to variations in the chemical and physical properties of a subsurface system. The model was developed for vertical displacement, so adjustments were made to allow for horizontal flow. The model equations used in this study are shown in Table 2.

This model was available as an EXCEL spreadsheet. Organic liquid saturations for a range of displacement velocities were calculated by the model. Calculating the residual saturation at each groundwater velocity is an iterative process, so an organic liquid saturation was assumed, the spreadsheet calculated the expected saturation, and the process was repeated until the input saturation equaled the calculated saturation to three decimal places.

Table 2
DNAPL Displacement Model and Associated Equations
(From Helen E Dawson, 1992; adjusted for horizontal flow)

Description	Equation
Macroscopic Mobilization Model	$Nca(\frac{1}{k_{rw}}) = .\frac{mP^*_{c\,eq}}{\Delta L/(k/\Phi)^{.5}}$
Capillary Number	$N_{ca} = \frac{v_w \mu_w}{\gamma_{ow} \cos\theta_w}$
Residual Saturation	$P^*_{c\,eq} = \frac{P_{ceq}(k/\Phi)^{.5}}{\gamma_{ow}\cos\theta_w}$ $S_{or}(P^*_{c\,eq}) = S_{w,drn}(P^*_{c\,eq}) - S_{w\,inb}(P^*_{c\,eq})$ $S^*_{or}(P^*_{c\,eq}) = \frac{S_{or}(P^*_{c\,eq})}{S_{or}(0)}$
Relative permeability	$k_{rw} = (S_e)^n$
Globule length	$\Delta L = c(\frac{\gamma_{ow}\cos\theta_w}{q_w \mu_w / kk_{rw}})^{.5}$

(Terms defined in Nomenclature section)

<u>Adhesion Tension</u>

Adhesion tension, defined as $\gamma\cos\theta_w$, varies from chemical to chemical and when interfacial tension or contact angle is altered by surfactant addition, pH variation, ionic strength variation, or changing soil composition (see Background section). Increased adhesion tension occurs if the contact angle (measured in water) is decreased or interfacial tension between the DNAPL and water is increased. Increased adhesion tension is expected to result in lower minimum residual saturation because less of the organic liquid penetrates the smaller pore spaces where the DNAPL is most difficult to remove.

A graph of residual saturation vs. capillary number from the model shows chemicals with a wide variety of contact angles follow the same decreasing displacement curve (See Figure 10). This, along with similar graphs produced by varying porosity and permeability, shows that the dimensionless capillary number should be useful in developing universal curves to predict organic liquid saturation of any chemical in a porous medium.

Figure 10 suggests that the Capillary number vs. Normalized residual saturation relationship is similar for chemicals with different adhesion tension, but this does not mean that there is no difference in actual residual saturation. First, the figure uses normalized saturation. Normalized residual saturation is defined as the ratio of the actual saturation to the minimum residual saturation achievable for a specific chemical in a specific porous medium. Therefore the graph does not indicate the actual residual saturation, it just indicates at which capillary number the minimum residual saturation is achieved. Second, the capillary number depends on both the velocity and the adhesion tension. To separate the influences of velocity and adhesion tension, Darcy velocity vs. normalized residual saturation (See Figure 11) was plotted. Figure 11 shows a significant difference in the velocity required to reach minimum residual saturation for chemicals of varied adhesion tension. Figure 11 also shows that decreasing adhesion tension (i.e., increasing wettability of organic liquid) decreases the velocity required to reach minimum residual saturation. An increase of 2 orders of magnitude in adhesion tension causes an increase of 2 orders of magnitude in required velocity. The relationship does not appear linear.

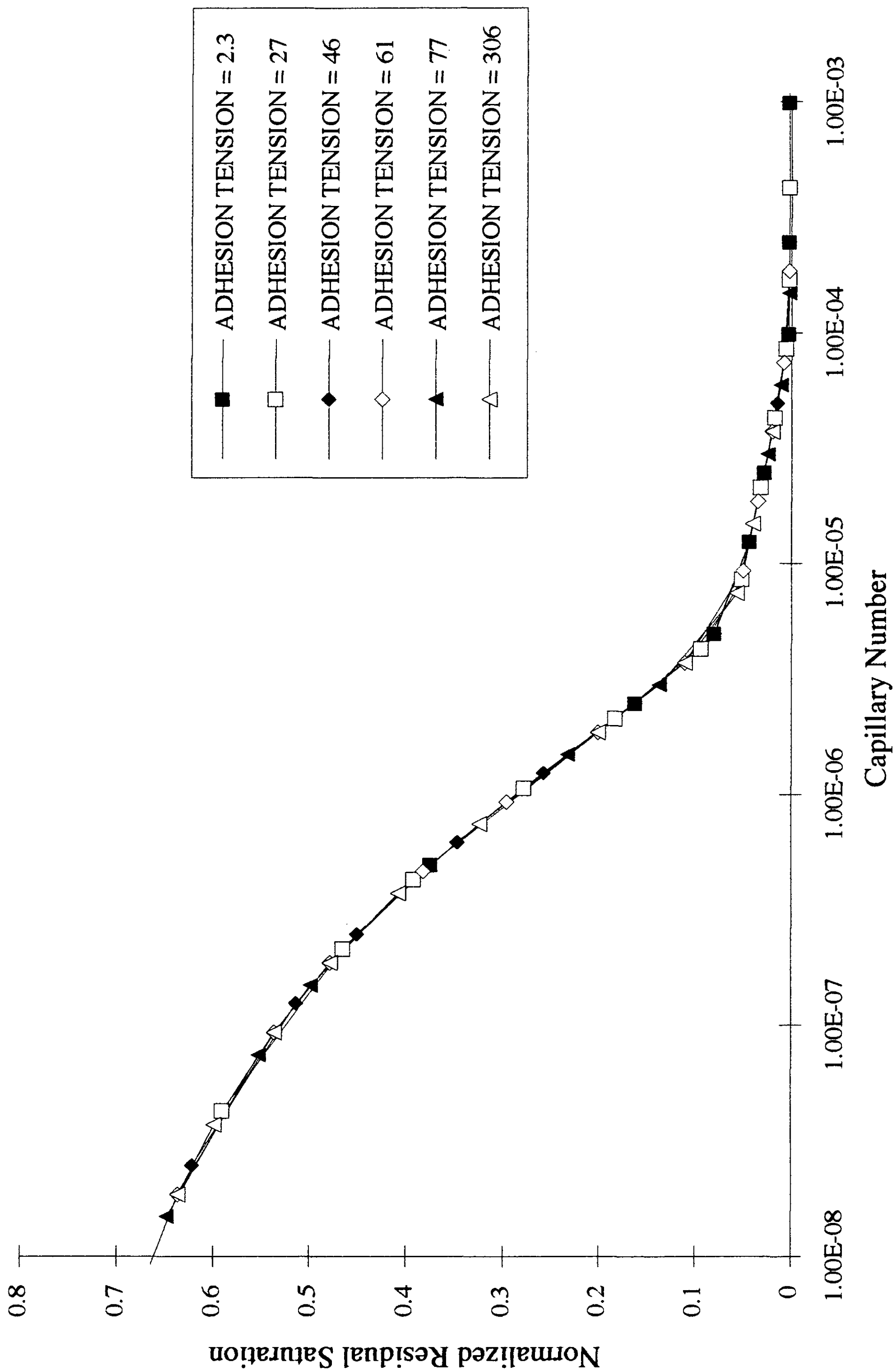


Figure 10 Residual saturation vs. Capillary Number for varying adhesion tension.

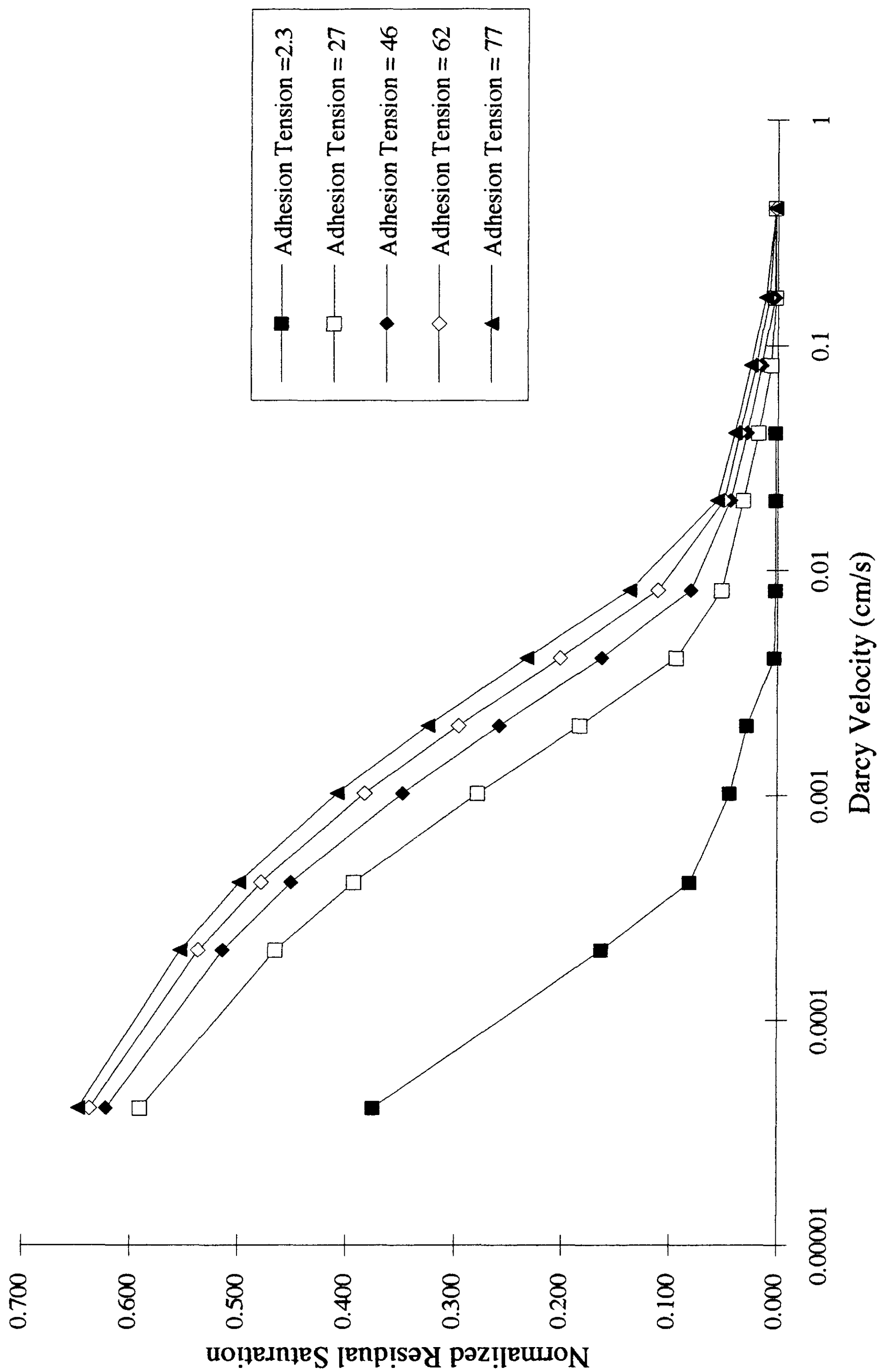


Figure 11 Residual saturation vs. Darcy velocity for varying adhesion tension.

The model showed that a change in adhesion tension can cause significant change in the maximum effective velocity for contaminant removal, so a study of the effects of groundwater conditions on contact angle and interfacial tension is potentially significant. The range of contact angles measured in this work were used in the DNAPL displacement model (Figure 12). Some variation in the organic liquid saturation curves within the range of contact angles measured is shown.

Porosity

The model predicts that changing the porosity of the porous medium does not change the residual saturation vs. capillary number relationship (See Figure 13). Varying porosity in the model causes residual saturation to change but also causes capillary number to change. Like adhesion tension changes, however, changes in porosity will change the velocity at which the minimum residual saturation is reached (See Figure 14). Decreasing porosity will cause a decreased velocity required to reach minimum residual saturation. This is an expected result since a constant Darcy velocity will produce an increased linear velocity, and therefore a higher displacement force, in a lower porosity medium.

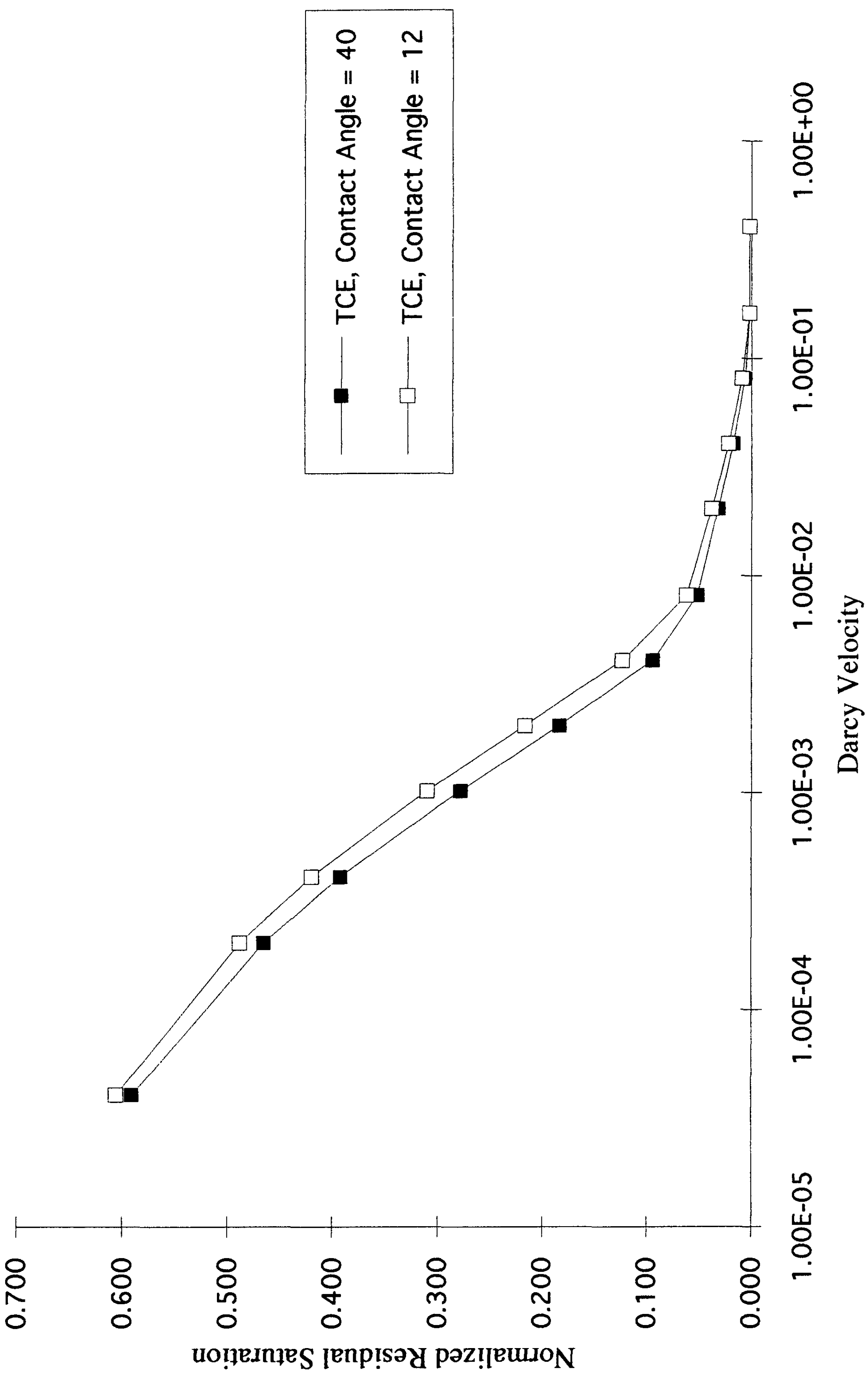


Figure 12 Variation in residual saturation due to experimental TCE contact angle variation.

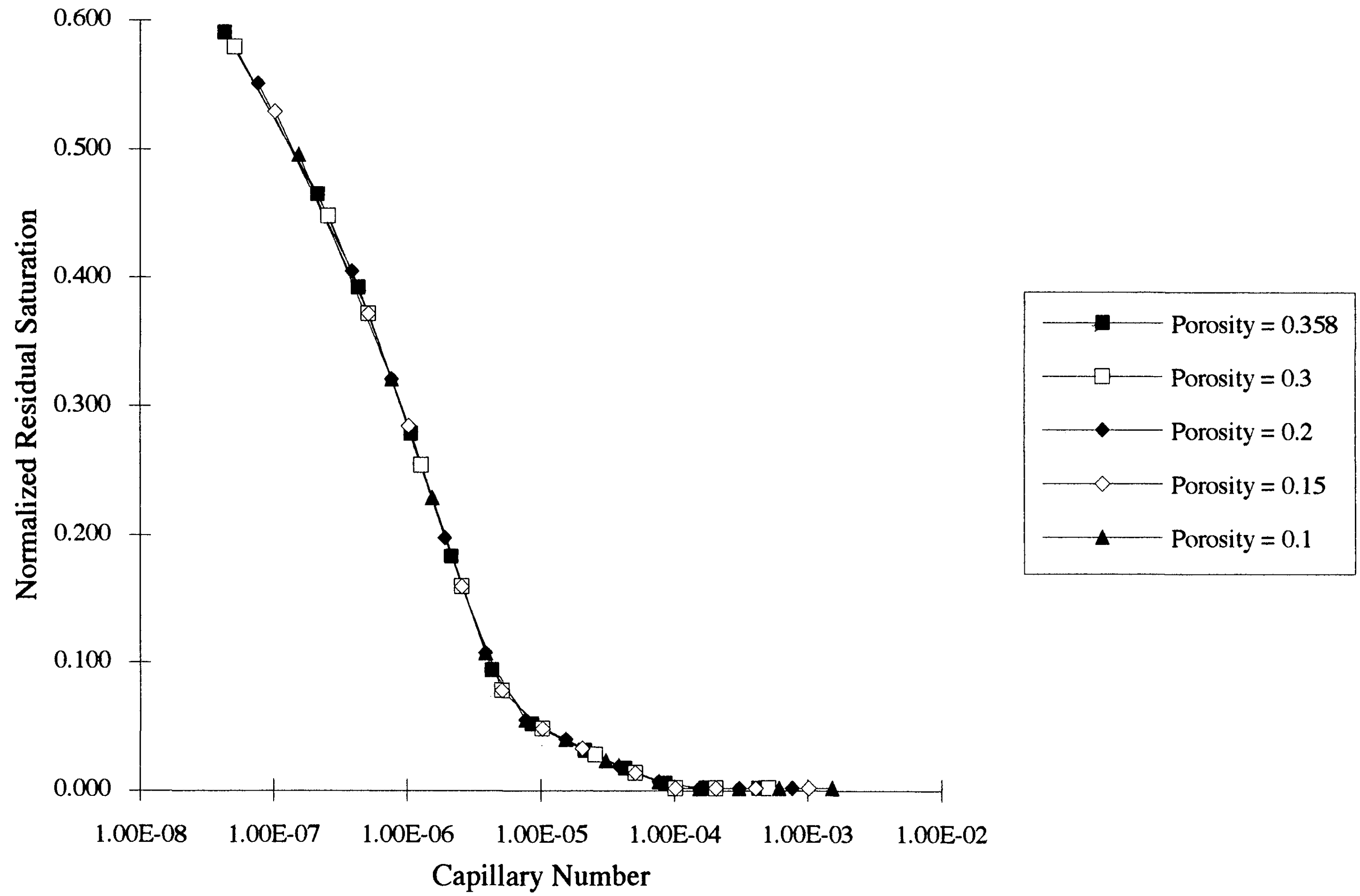


Figure 13 Residual saturation vs. Capillary Number for varied porosity.

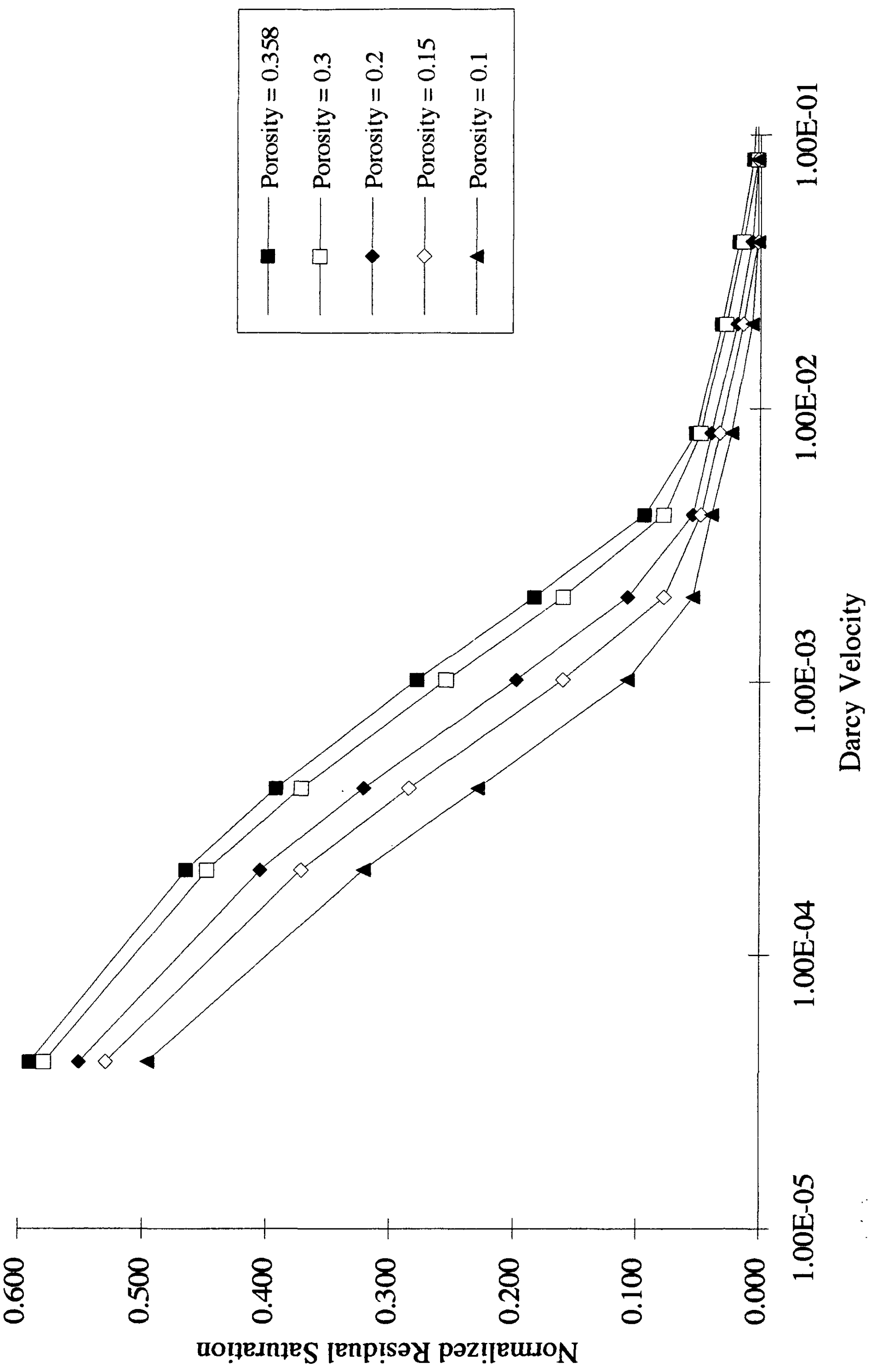


Figure 14 Residual saturation vs. Darcy velocity for varied porosity.

Permeability

The model showed no change in residual saturation or capillary number when permeability was varied in the model. A look at the equations governing the model shows that permeability cancels out of the capillary pressure equation, and permeability is not part of the capillary number, so changing permeability does not change either the abscissa or ordinate of a residual saturation vs capillary number plot. However, differences in permeability may influence the average groundwater velocity, which does appear in the Capillary number. Unlike adhesion tension changes and porosity changes, though, the velocity required to achieve minimum residual saturation does not appear to depend on permeability. This is a reasonable result when the methods of trapping are considered. Neither by-passing nor snap-off result directly due to permeability, they occur because of the pore body to pore size ratio. Pore body to pore size ratio is considered in the c value in the globule length calculation so shouldn't also be included in the permeability.

Pore Geometry

Pore geometry has long been seen as a determining factor in determining residual saturation. This model included a constant, c, that represents the filament length to filament radius ratio. Consider a filament of constant average width (e.g.. when the pore neck decreases the pore body increases to keep the average filament width constant). As the pore body to pore throat ratio increases, the stable length of a filament would decrease due to snap-off in the pores. Therefore if the stable filament length decreases, c decreases and ΔL decreases. Decreased ΔL causes decreased $P^*_{c\ eq}$ which causes increased residual saturation. This was predicted in the model as shown in Figures 15 and 16. An increase in c caused a decrease in residual saturation at a given capillary number or Darcy velocity.

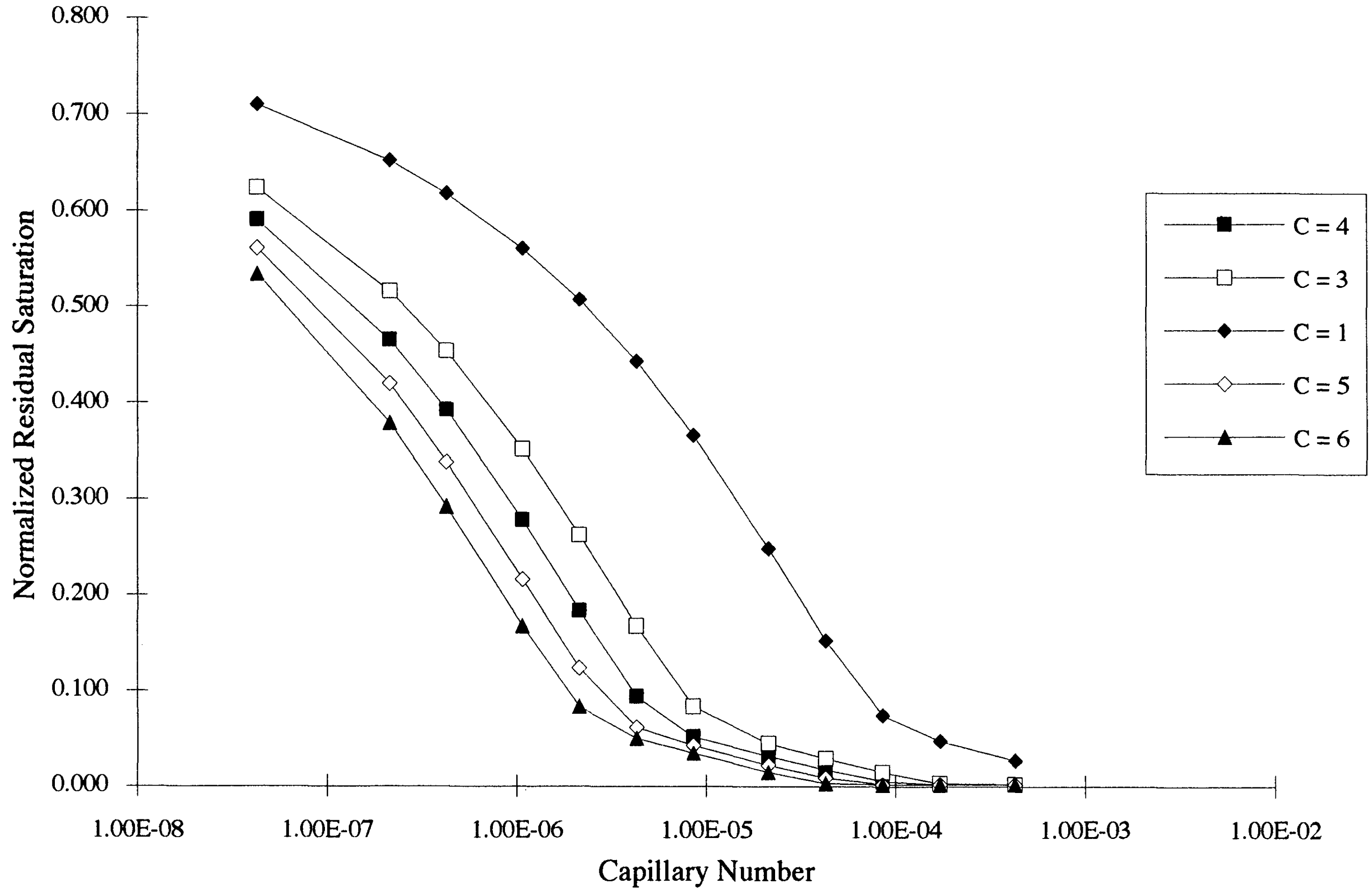


Figure 15 Residual saturation vs. Capillary Number for varied pore geometry constant.

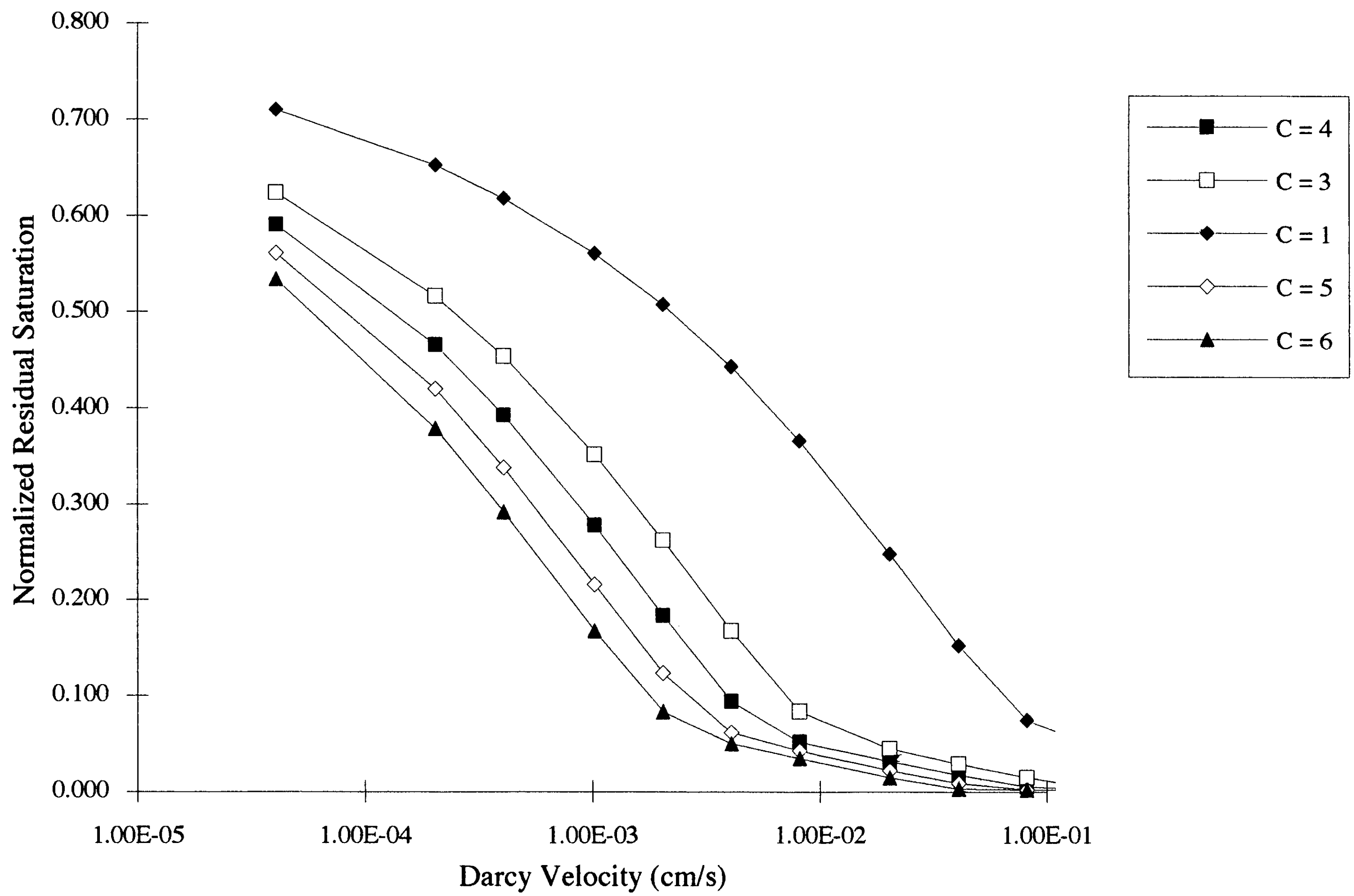


Figure 16 Residual saturation vs. Darcy velocity for varied pore geometry constant.

HYDRAQL Model

HYDRAQL (Papelis et al., 1988) is in the MINEQL (Westall et al., 1976) family of programs. It combines a computational algorithm for aqueous speciation with a series of interfacial configurations for ion adsorption at the particle/water interface. The version of the Triple Layer Model (Davis et al., 1978) used in HYDRAQL allows the assignment of adsorbing species to both the surface (as coordination complexes) and beta plane as ion pair complexes. An additional modification from the original Triple Layer Model configuration is the selection of the Standard State for all species, solution and surface, to be infinite dilution relative to the aqueous phase and zero surface charge.

As discussed in the Background section of this work, the Gibbs equation indicates that surface charge is directly related to surface tension. Because the surface tensions determine contact angle, surface charge should affect contact angle. As surface charge decreases, contact angle may decrease or increase depending on the relative effect of electrical potential on the solid-water and solid-organic liquid interfacial tensions. The HYDRAQL model was used to conceptualize the effect of varying pH and ionic strength on the mineral surface charge. The HYDRAQL model was run using equilibrium constants summarized by Davis et al., 1978.

The model was run to simulate conditions found during the corundum pH variation experiments. The ionic strength used in the model was adjusted at high pH to correlate with the addition of NaOH. The magnitude of surface charge was plotted versus pH as shown in Figure 17.

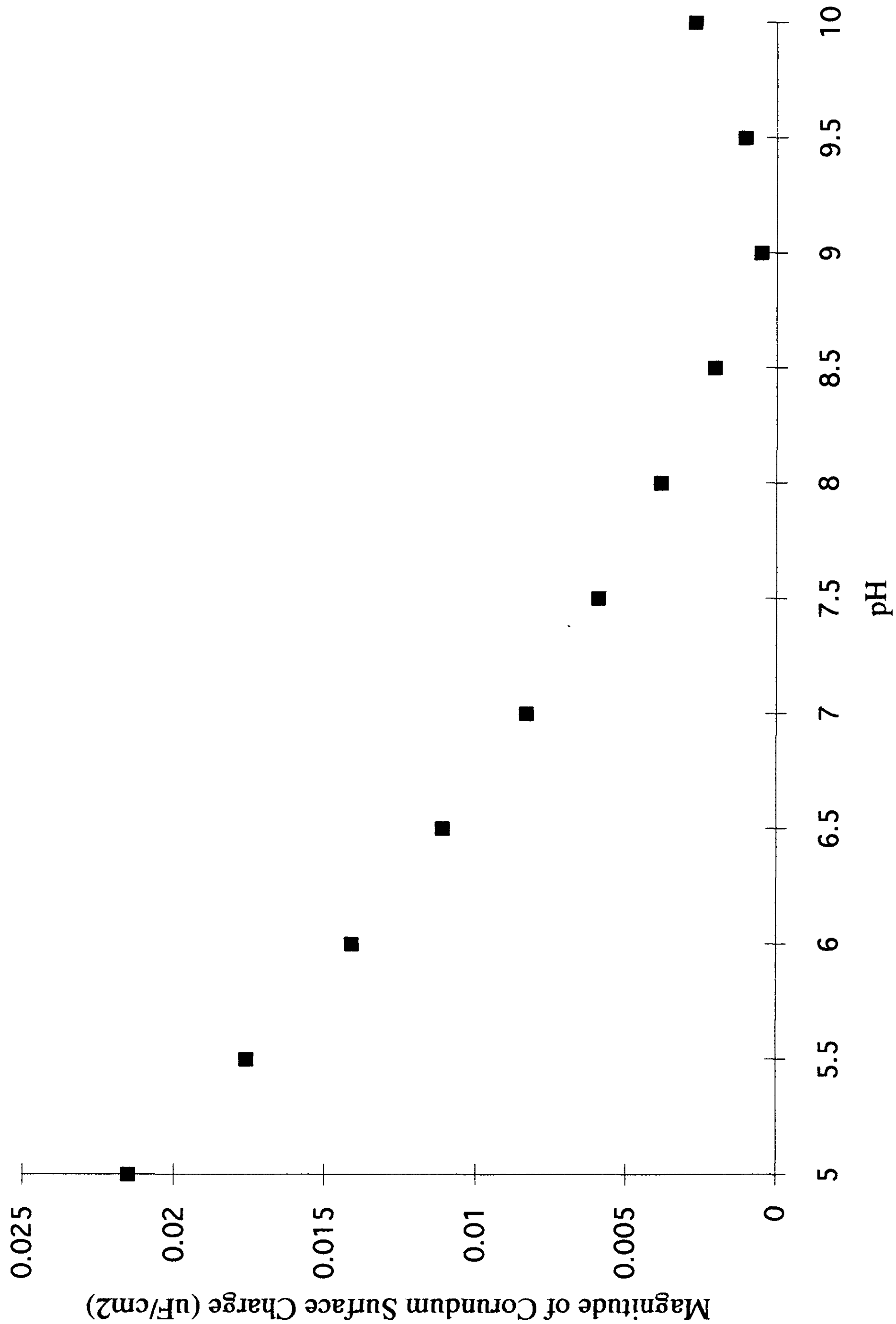


Figure 17 Magnitude of surface charge on corundum vs pH for experimental ionic strength.

This shows the expected result that surface charge will be zero at the zero point of charge and increase at pH's on either side of the PZC. This will be compared to the experimental results of the pH variation experiments on corundum.

The model was also run to conceptualize the effect of ionic strength on surface charge and therefore the effect of ionic strength on contact angle, although the ionic strength-contact angle relationship involves more than just surface charge. Surface charge vs. pH was plotted at several ionic strengths (Figure 18). Because the plane at which the organic liquid meets the solid is unknown, the net charge at the beta plane of adsorption vs. pH was also plotted (Figure 19). Both plots show that increasing ionic strength increases the magnitude of the solid surface charge at points away from the PZC. As discussed earlier, the surface charge will not change at the PZC no matter how ionic strength is varied. The increasing solid surface charge at the higher ionic strengths indicates that contact angle may increase with increasing ionic strength. It must be considered, however, that varying ionic strength causes more changes than just the surface or beta plane charge. The surface tension of water also changes and the plane of adsorption on which the organic liquid drop sits may also change.

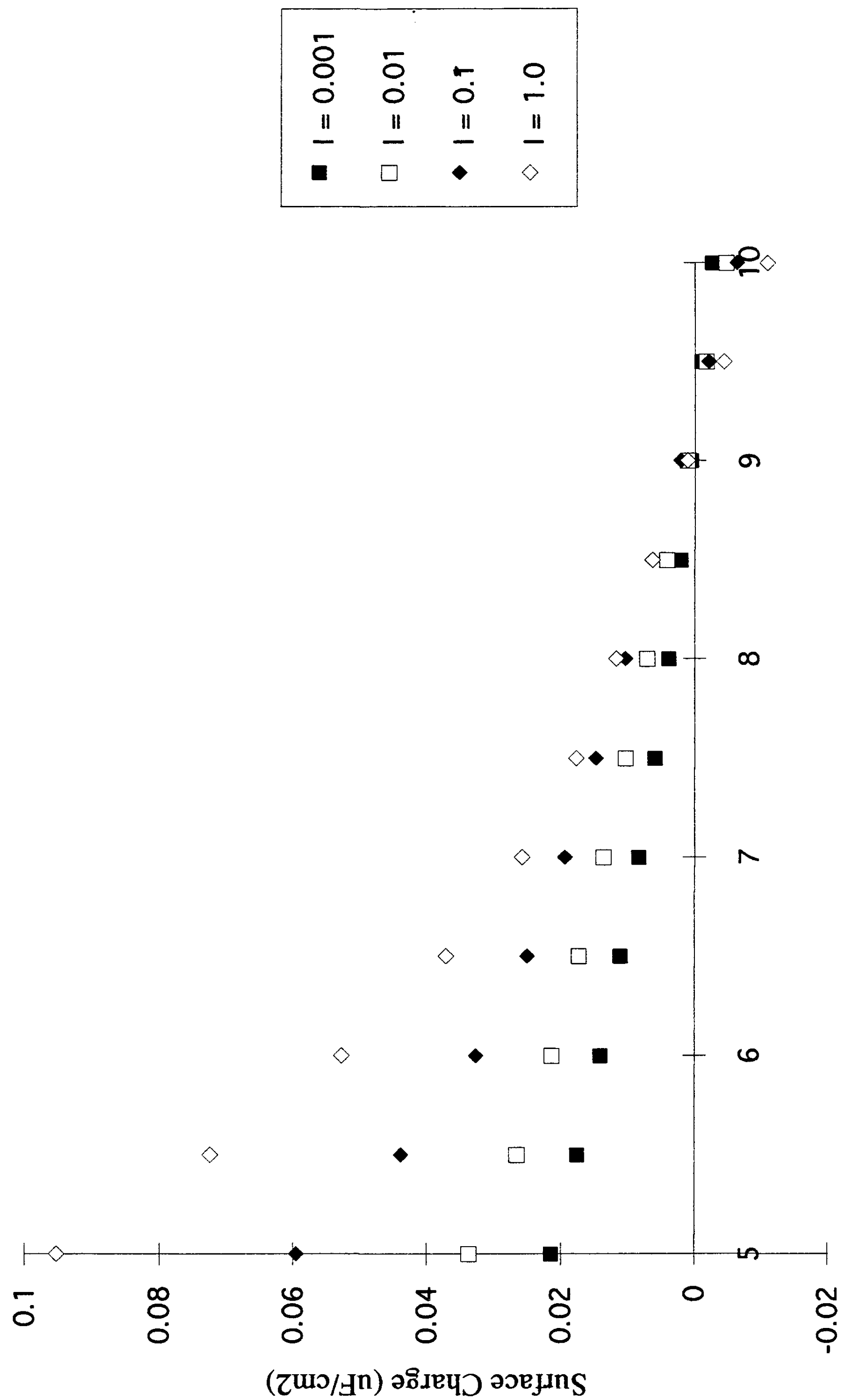


Figure 18 Surface charge vs. pH from HYDRAQL.

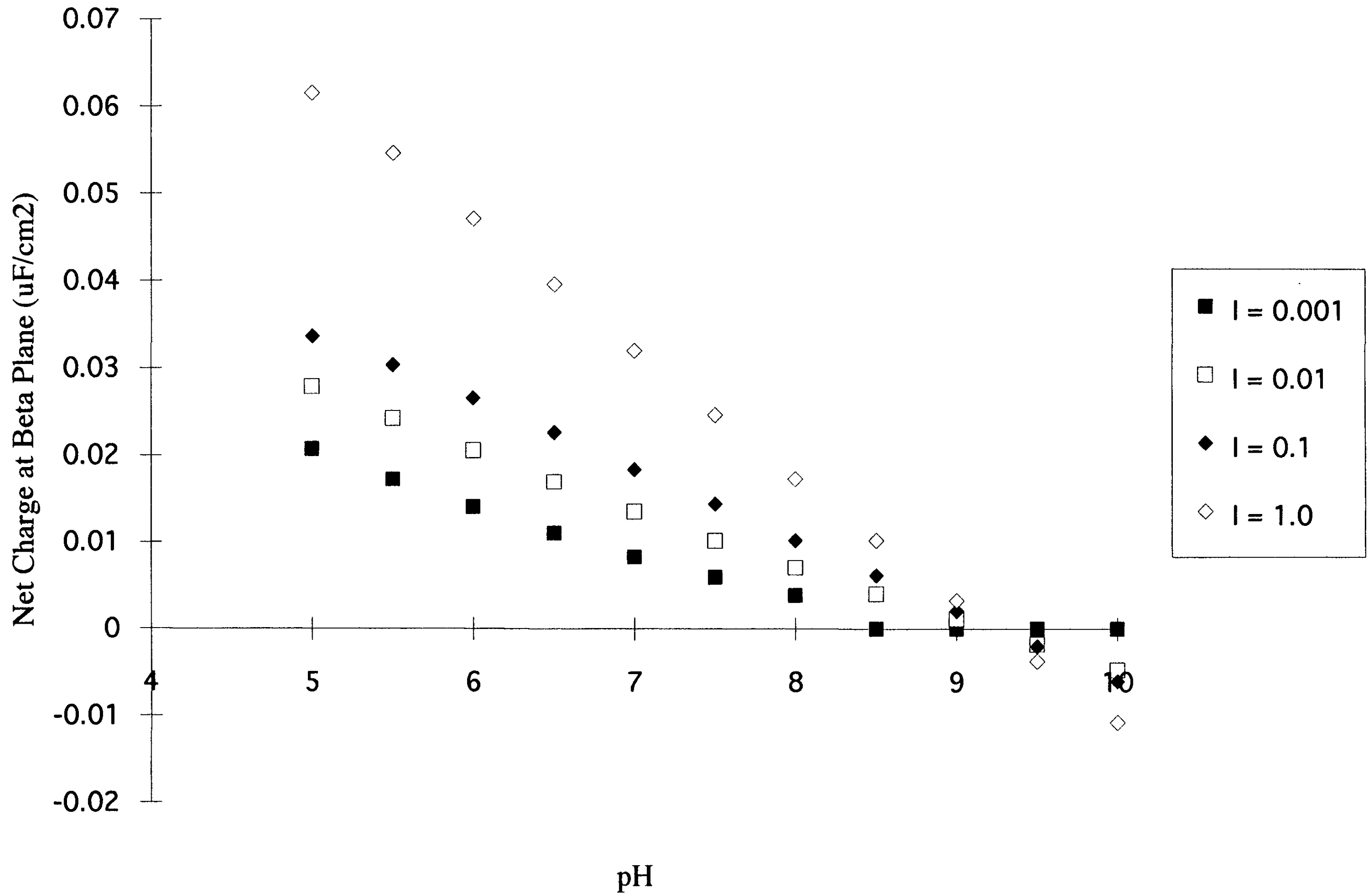


Figure 19 ***Net charge at beta plane vs. pH from HYDRAQL.***

RESULTS AND DISCUSSION

The laboratory experiments were conducted to show variation in contact angle with pH and ionic strength. The solid, water, organic system is complex and the role of surface chemistry on interfacial tension and contact angle is not well understood. However, based on the analysis presented above, a number of responses were expected. With water pH variation, the contact angle of the organic liquid was expected to change near the PZC of the solid mineral because the surface charge is varying. An increase or decrease in contact angle was expected depending on the relative effect of electrical potential on the solid-water and solid-organic liquid interfacial tensions. Addition of a salt was expected to decrease the contact angle because the water surface tension is increased by addition of a salt and because the adsorption of ions at the surface decreases the solid surface tension. The addition of a salt may also cause an increase in the surface charge, however, which would be expected to increase contact angle. The surface tensions of the solid and liquids were expected to decrease with increasing equilibration time, but no previous correlation has been shown for the variation of contact angle over time. The actual results will be presented and discussed in this section.

Analysis of Contact Angle Variation with pH

Contact angle was expected to vary near the PZC of the mineral. No contact angle variation with pH was expected for either chemical on quartz because the PZC of quartz is out of the pH range studied in this work. For corundum, however, the PZC is 8.6 so contact angle would be expected to change within the experimental pH range. As expected, the experiments on quartz showed no significant variation in contact angle with pH variation for TCE or CCl_4. The contact angle of CCl_4 on corundum showed a decrease in contact angle near the PZC, but no significant contact angle variation with pH was shown for TCE on corundum. These results are discussed below. A Duncan multiple range test for comparison of several means was performed on the data for each chemical-mineral pair studied. The test indicates which means, if any, are statistically different.

Contact angles of TCE on quartz and corundum ranged from 16.5° to 24°. The contact angle of carbon tetrachloride on the two minerals ranged from 16° to 26° (Table 3). These values, while showing a wide range, are significantly lower than previously reported values for contact angles of these liquids on glass and all four mineral-organic liquid combinations show contact angles more similar to each other than to the previously reported values of contact angles on glass. Possible reasons for this are that the charge on the mineral surfaces is not expected on glass, the long equilibration time allowed in this study, or the background electrolyte that was used in this study.

Table 3
Average and Range of Contact angles of TCE and CCl_4 on Corundum and Quartz in 1 x 10^{-3} M $NaClO_4$

Contact Angles	**Corundum**	**Quartz**
Trichloroethylene (TCE)	20° (Ranged from 18° to 22°)	19° (Ranged from 17° to 24°)
Carbon Tetrachloride	21° (Ranged from 16° to 26°)	21° (Ranged from 19° to 23°)

TCE on Corundum and Quartz

The contact angles measured for TCE on corundum and quartz as a function of pH are shown in Figures 20 and 21 respectively. The figures show the results for both experimental runs #1 (open squares) and run #2 (closed squares). The horizontal error bars indicate plus or minus one standard deviation. For TCE on corundum, the Duncan multiple range test showed that three of the contact angle means were significantly higher than the rest of the means, but not significantly different from each other. These three means were calculated from the contact angles measured at pH's 9.9, 5.6 and 8.2, which cover the entire range of pH studied and both experimental runs. The remaining means showed no variation in contact angle for a pH range of 5.2 to 9.1.

The contact angles measured for TCE on quartz as a function of pH are shown in Figure 21. The Duncan multiple range test showed that one of the contact angle means, that at pH = 5.5, was significantly higher than the rest of the means. The remaining means showed no variation in contact angle for a pH range of 5.1 to 9.7.

Due to the large amount of variation within the individual measurements and no consistent trend in contact angle with pH, the results of this experiment were inconclusive. Because the Duncan multiple range test showed some significant differences, pH may in fact have a slight effect on contact angle, but other factors not considered overshadowed the pH effect.

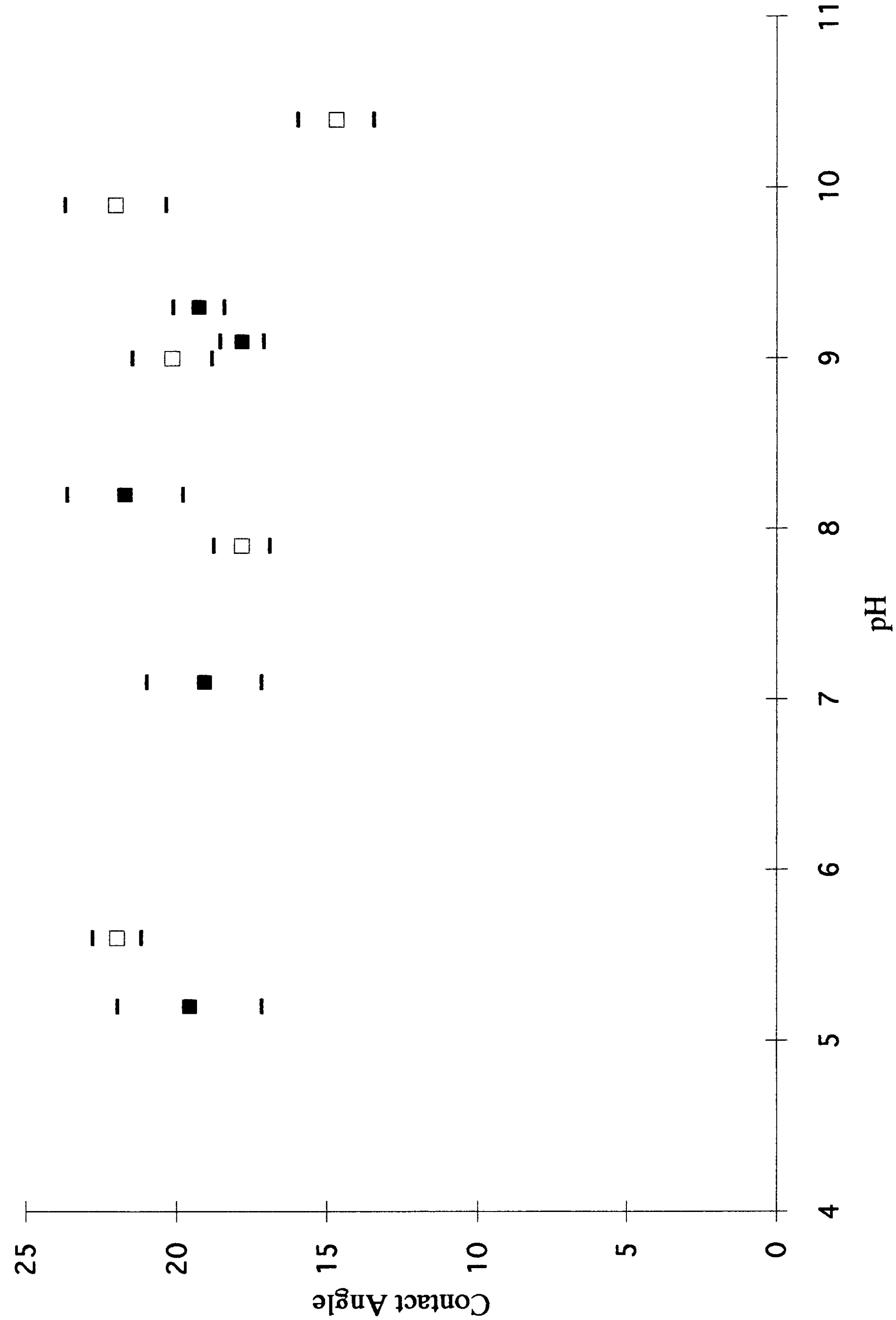


Figure 20 Contact angle vs. pH for TCE on corundum.

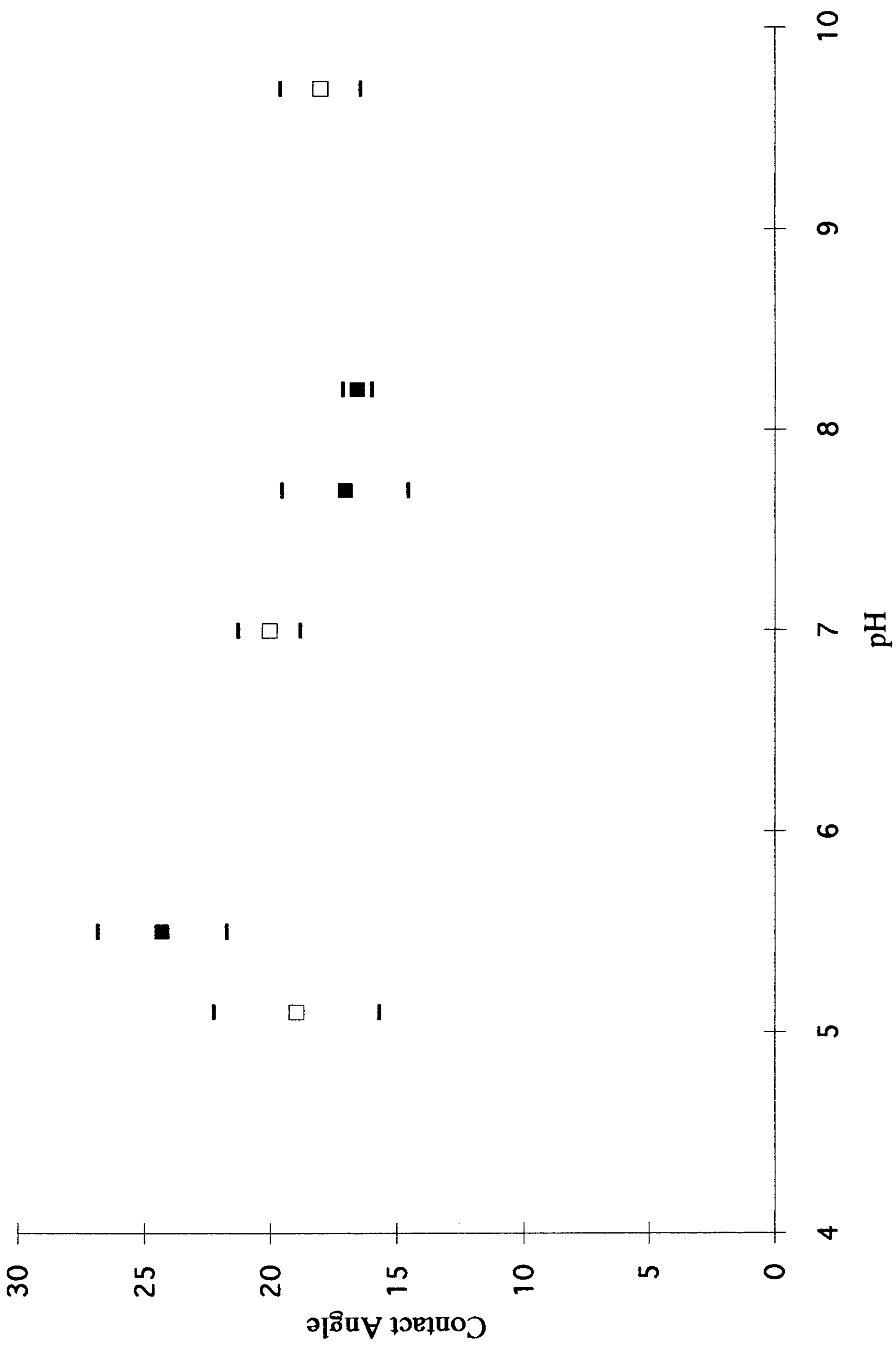


Figure 21 Contact angle vs. pH for TCE on quartz.

Carbon Tetrachloride on Corundum and Quartz

The contact angles measured for carbon tetrachloride on corundum and quartz as a function of pH are shown in Figures 22 and 23. For carbon tetrachloride on corundum, the Duncan multiple range test showed that three of the contact angle means, those at pH's 5.7, 5.8, and 9.0, were significantly different than the rest of the means. The placement of these statistically different contact angles fits the anticipated variation in contact angle near the PZC. Notice the smallest contact angles were observed near the PZC of corundum. Larger contact angles were observed at pH's away from the PZC. Surface charge would be expected to level out within two pH units of the PZC, but a corresponding leveling out of the contact angle was not observed because of the limited pH range studied.

The contact angles measured for carbon tetrachloride on quartz as a function of pH are shown in Figure 23. The Duncan multiple range test showed that one of the contact angle means, that at pH = 9.0, was significantly different than the rest of the means. The remaining means showed no significant variation in contact angle for a pH range of 5.6 to 9.4. A Spearman Rho test was run on the carbon tetrachloride on quartz data set to detect the trend. No trend for contact angle to increase or decrease with increasing pH was found.

The contact angle of carbon tetrachloride on corundum appears to be directly related to surface charge. The trend was not observed for TCE on corundum, however, and one would expect the two organic liquids to behave similarly on the same surface. Possible explanations for this are experimental error or the lack of symmetry in the TCE molecule.

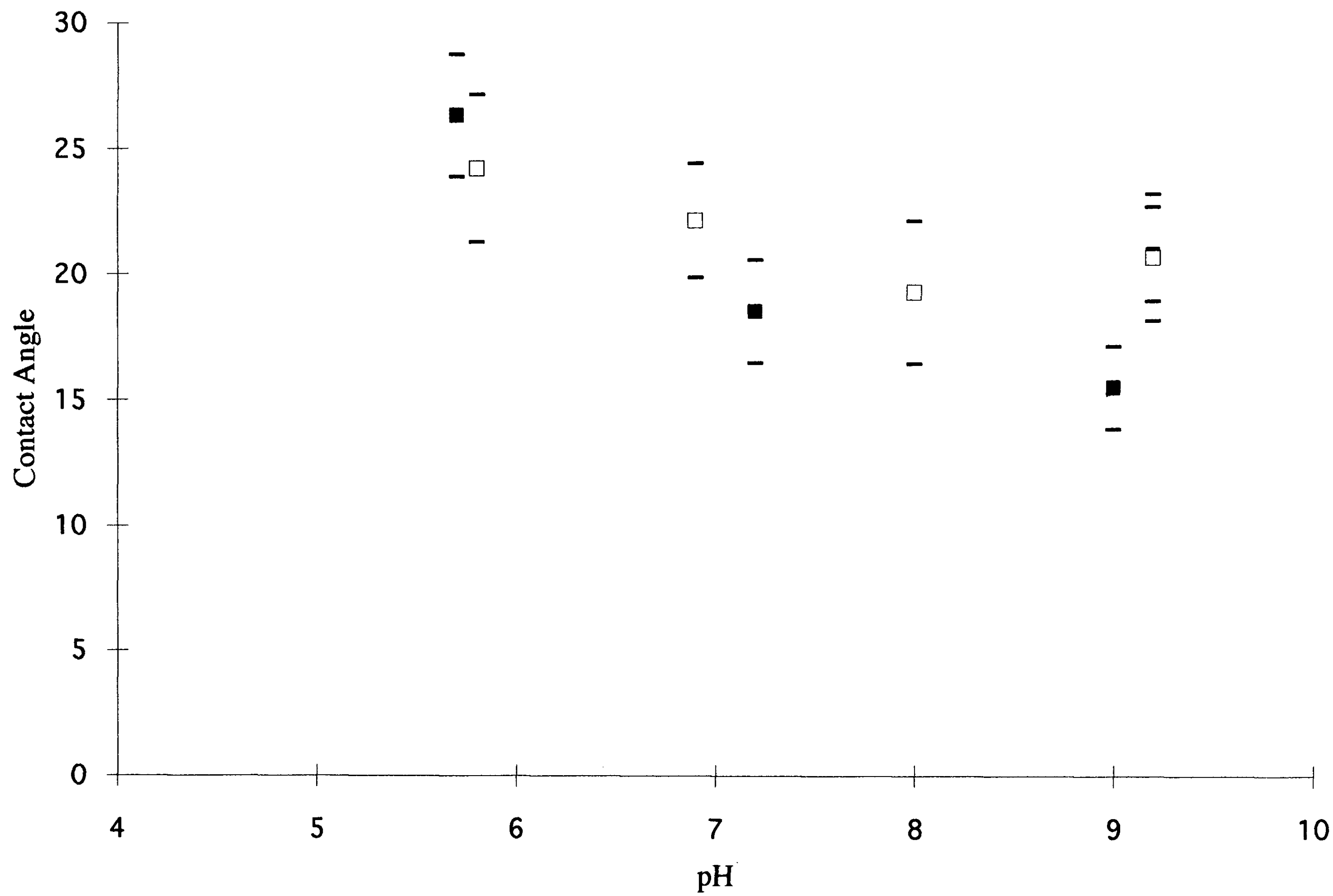


Figure 22 Contact angle vs. pH for carbon tetrachloride on corundum.

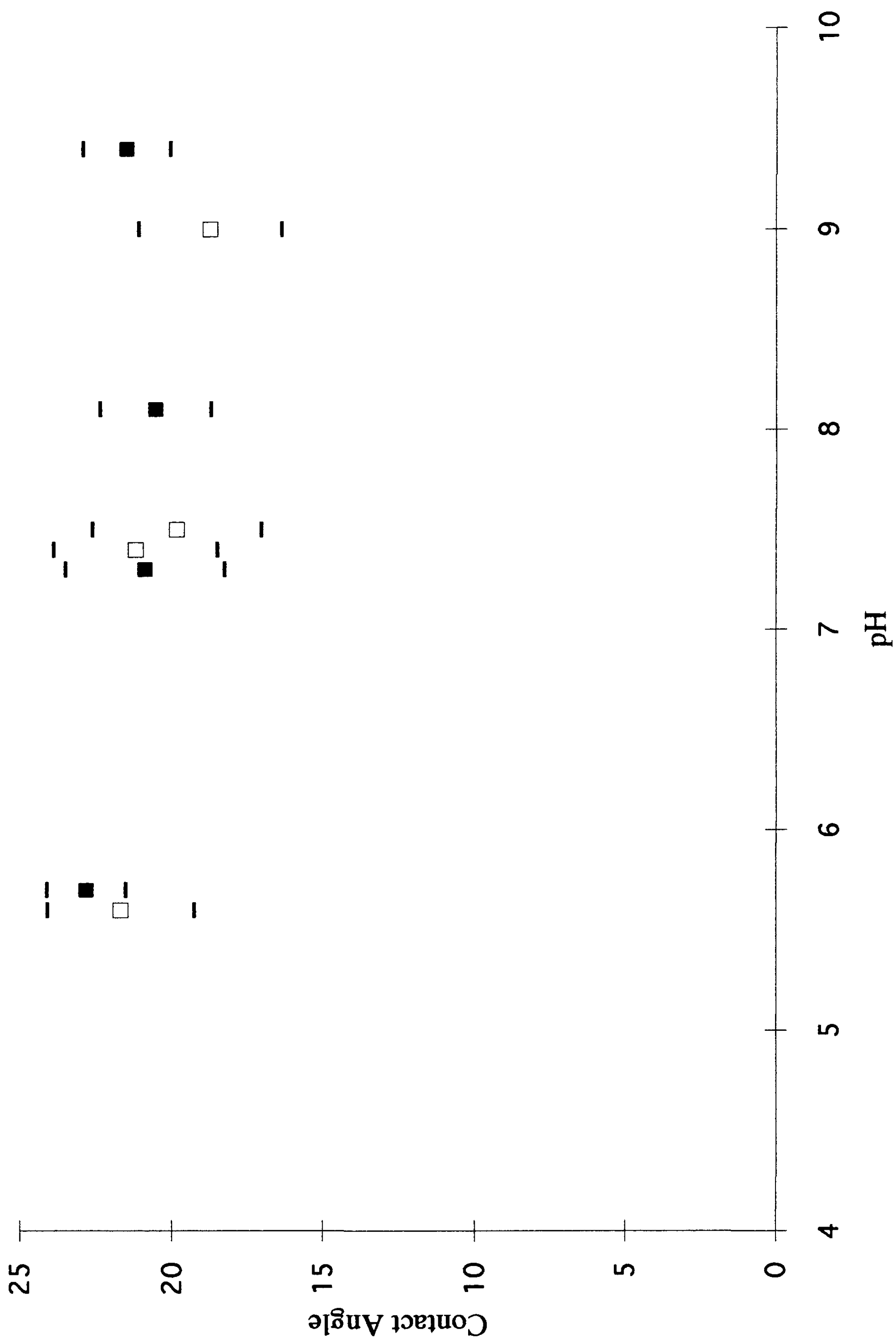


Figure 23 Contact angle vs. pH for carbon tetrachloride on quartz.

Potential sources of experimental error in contact angle experiments were temperature variations, contamination of the syringe or organic liquid, and solid surface irregularities. Further experimentation with TCE and CCl_4 contact angles on corundum where pH is varied by a very small increment near the PZC of corundum might be helpful in determining the cause of the different behavior of these two chemicals on the same surface.

Analysis of Contact Angle Variation with Ionic Strength

The contact angles measured for TCE on corundum as a function of ionic strength are shown in Figure 24. The figure shows the results for both experimental run #1 (open squares) and run #2 (closed squares). The horizontal error bars indicate plus or minus one standard deviation. The pH was not controlled for the ionic strength experiments, but the pH range seen in one run was 5.3 to 6.2. The values of contact angle at an ionic strength of 1.0 M were attained in a separate experiment, but are included here for the sake of completeness. The original tests didn't cover an adequate range of ionic strength, though most groundwater has ionic strength approximately 1×10^{-3} to 1×10^{-2} and was covered in the original range of ionic strengths studied. The Duncan multiple range test showed that the contact angle decreases significantly with increasing ionic strength within the entire range of ionic strength studied.

The ionic strength clearly has an effect on contact angle and causes variation in contact angle from 11° to 27°, with increasing ionic strength causing decreasing contact angle. This effect is much stronger than pH variations had in the previous experiments.

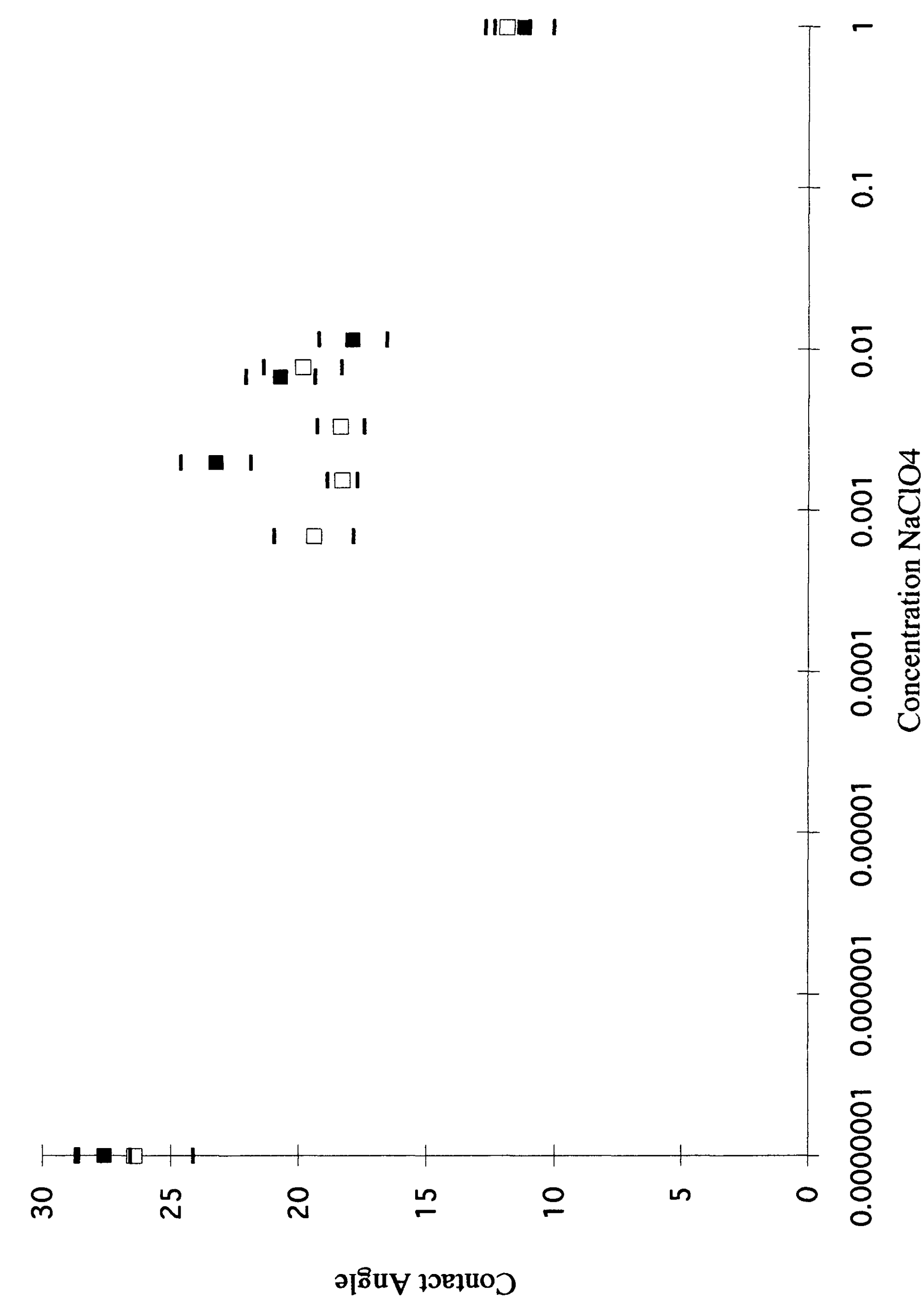


Figure 24 Contact angle dependence on ionic strength (CCl_4 on corundum).

Analysis of Contact Angle Variation with Equilibration Time

It was discovered during the experimental process that equilibration time had a significant effect on the contact angle of TCE on corundum. Originally, experiments were run with very little equilibration time allowed. The solution was saturated with the organic liquid then contact measurements were taken. To determine if equilibration time could confound the results of the ionic strength and pH experiments, a kinetic study was done to determine the effect of equilibration time on contact angle. The results are shown in Figure 25. The Duncan multiple range test showed significant changes in contact angle with time up to approximately 200 minutes. After 200 minutes there was no significant change in contact angle with increasing time. The dependence of contact angle on equilibration time is expected as the mineral and quartz cell surfaces and the water must reach local equilibrium. A decline in pH (pH = 6.5 to 5.5) was also observed with increasing equilibration time indicating equilibration was not complete during the lower equilibration times because part of the equilibration process involves the surfaces exchanging ions with the water.

Due to the significance of equilibration time to contact angle measurements, all pH and ionic strength experiments were conducted with at least 3 - 4 hours equilibration time (and only when the solution was stirred), and most were done with a minimum 12 hour equilibration time (no stirring).

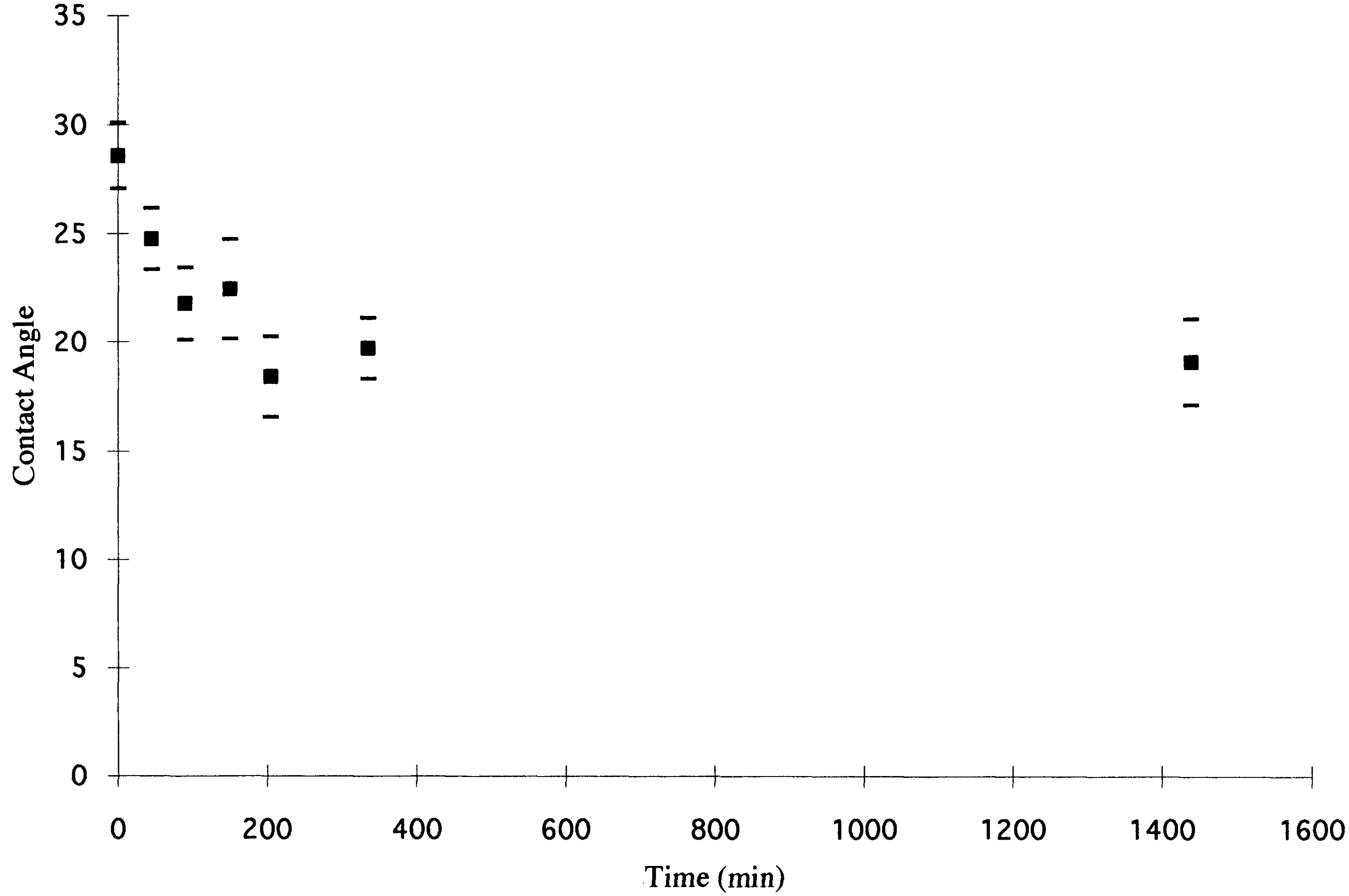


Figure 25 Contact angle dependence on equilibration time (TCE on corundum).

Analysis of Interfacial Tension Measurements

The interfacial tension measurement data has an extremely high variance due to the highly sensitive nature of the experimental procedure. The primary problem was that any focusing required changed the photographic size-actual drop size ratio. Many drops didn't fit into the cameras field of view so the syringe needle didn't appear in each picture for size comparison. Consequently, this data was not adequate for meaningful analysis.

Water-organic liquid interfacial tension information is necessary for the complete analysis of adhesion variation with varying groundwater pH and ionic strength and therefore further research in this area is indicated. Interfacial tension experiments should be done in a constant temperature environment. If the pendant drop method is used high resolution film is necessary for accurate measurements. Also, several pictures at each pH or ionic strength should be taken, and the pendant drops should be aged (allowed to hang in the water) for some time to get a true equilibrium interfacial tension.

SUMMARY AND CONCLUSIONS

This study was performed to determine the effect of aquifer conditions on the residual saturation of DNAPLs in sandy aquifers. Work with the DNAPL Displacement model showed that the groundwater velocity required to reach the minimum residual saturation depends on the adhesion tension of the organic liquid and the porosity and pore geometry of the porous medium. Factors which may affect the adhesion tension were then studied conceptually with the assistance of the HYDRAQL adsorption model and were also studied experimentally.

The experimental work attempted to determine the effect of groundwater pH and ionic strength on adhesion tension. The assumption that contact angle will increase with increasing surface charge, which increases as solution pH departs from the PZC of the solid, was shown to be correct for carbon tetrachloride on corundum, but the TCE on corundum data did not confirm this. Possible causes of the variation between the two organic liquids on the same solid surface were experimental error, differences in symmetry of the liquids, or the relatively large pH increments used in the study. Contact angle on quartz was not expected to vary with pH because the surface charge would not vary within the experimental pH range and the experimental results showed this to be true. Contact angle was expected to vary with varying ionic strength and the experimentation showed this to be true. Contact angle decreased significantly with increasing ionic strength.

The study has also shown that contact angles of organic liquids on corundum and quartz depend on the equilibration time of the water, organic liquid and solid. The results showed that the contact angle did not reach equilibrium until approximately 12 hours after the organic liquid saturated water was placed in contact with the mineral. Equilibration time should be considered in future contact angle studies of all kinds.

The study has provided reasonable estimates of contact angle of TCE and carbon tetrachloride on two common aquifer minerals at ionic strengths and pH's normally found in groundwater. These contact angles are significantly lower than those previously reported in the literature as measured on glass, possibly because of the long equilibration time used or because a background electrolyte was used. Therefore, because DNAPL's in the subsurface have a long time to equilibrate and groundwater contains electrolytes, lower contact angles should be used in modeling DNAPL's in the saturated zone. The range of contact angles measured in this work were used in the DNAPL Displacement model. Some variation in the organic liquid saturation curves within the range of contact angles measured was shown.

BIBLIOGRAPHY

Anderson, W.G.; "Wettability Literature Survey, Part 6: The effects of Wettability on Waterflooding"; Journal of Petroleum Technology, December, 1987.

Davis, J.A., James, R.O. and Leckie, J.O.; "Surface Ionization and Complexation at the Oxide/Water Interface 1. Computation of Electrical Double Layer Properties in Simple Electrolytes"; Journal of Colloid and Interface Science, Vol. 63, No. 3, March, 1978.

Dawson, H.E.; "Entrapment and Mobilization of Residual Halogenated Organic Liquids in Saturated Aquifer Material"; PhD Dissertation, Stanford Univ., 1992.

Defay, R. and Hommelen, J.R.; Journal of Colloid Science, Vol.13, p. 553, 1958.

Huang, C.P. and Stumm, W.; "Specific Adsorption of Cations on Hydrous α-Al_2O_3"; Journal of Colloid and Interface Science, Vol. 43; No.2; May 1973.

Hunt, J.R., Sitar, N., and Udell, K.S.; "Nonaqueous Phase Liquid Transport and Cleanup 1. Analysis of Mechanisms"; Water Resources Research, Vol. 24; No. 8; August, 1988.

Lake, L.W.; Enhanced Oil Recovery; Prentice Hall, Englewood Cliffs, NJ, 1989.

Mercer, J.W. and Cohen, R.M.; "A Review of Immiscible Fluids in the Subsurface: Properties, Models, Characterization and Remediation"; Journal of Contaminant Hydrology, 1990.

Osipow, L.I.; Surface Chemistry Theory and Industrial Applications, Reinhold Publishing Corporation, NY, 1962.

Papelis, C. Hayes, K.F. and Leckie, J.O.; HYDRAQL: A Program for the Computation of Chemical Equilibrium Composition of Aqueous Batch Systems Including Surface Complexation Modeling of Ion Adsorption at the Oxide/Solution Interface; Technical Report Number 306, Department of Civil Engineering, Stanford University, Stanford, CA 94305, 1988.

Parks, G.A. "Surface and Interfacial Free Energies of Quartz"; Journal of Geophysical Research, 1983.

Parks, G.A.; "Surface Energy and Adsorption at Mineral-Water Interfaces: An Introduction"; In Mineral-Water Interface Geochemistry; Reviews in Mineralogy, Volume 23, M.F Hochella, Jr. and A.F. White (Editors), Minerological Society of America, Washington D.C., 1990.

Powers, S.E., Loureiro, C.O., Abriola, L.M., Weber Jr., W.J.; "Theoretical Study of the Non-equilibrium Dissolution of NAPL in Subsurface Systems"; Water Resources Research, 1989.

Riddick, J.A., Bunger, W.B. and Sakano,, T.K.; Techniques of Chemistry, Vol.II. Organic Solvents. Physical Properties and Methods of Purification, 4th ed., Wiley, NY, 1986.

Sale, T.C. and Piontek, K.; "In Situ Removal of Waste Wood-treating Oils From Subsurface Materials"; USEPA, Forum on Remediation of Wood-preserving Sites, San Francisco, CA, October, 1988.

Schwille, F ; "Petroleum Contamination of the Subsoil - A Hydrological Problem: Joint Problems of the Oil and Water Industries": Elsevier, Amsterdam, 1967.

Schwille, F.; Groundwater Pollution in Porous Media by Fluids Immiscible with Water; "Quality of Groundwater"; Elsevier, Amsterdam; 1981.

Schwille, F.; Migration of Organic Fluids Immiscible with Water in the Unsaturated Zone; "Pollutants in Porous Media: The Unsaturated Zone Between Soil Surface and Groundwater"; 1984.

Schwille, F.; Dense Chlorinated Solvents in Porous and Fractured Media; Lewis Publishers, Chelsea, MI, 1988.

Sitar, N., Hunt, J.R. and Udell, K.S.; "Movement of Nonaqueous Liquids in Groundwater; "Proceedings of Geotechnical Practice for Waste Disposal '87/GT Div. ASCE/Ann Arbor, MI, June 15 - 17, 1987.

Stegemeier, G.L.; "Mechanisms of Entrapment and Mobilization of Oil in Porous Media"; in Improved Oil Recovery by Surfactant and Polymer Flooding, D.O. Shaw and R.S. Schechter (editors), Academic Press, NY, 1977.

Stumm, W. and Morgan, J.J.; Aquatic Chemistry, An Introduction Emphasizing Chemical Equilibria In Natural Waters; Wiley Interscience; 1970.

Taber, J.J.; "Research on Enhanced Oil Recovery, Past, Present, and Future"; In D.O. Shah (editor), Surface Phenomena in Enhanced Oil Recovery; Plenum, 1981.

USEPA; "Dense Nonaqueous Phase Liquids, A Workshop Summary"; EPA/600/R-92/30; 1991.

Westall, J.C., Zachary, J.L. and Morel, F.M.M.; MINEQL: A Computer Program for the Calculation of the Chemical Equilibrium Composition of Aqueous Systems; Ralph M. Parsons Laboratory Technical Note Number 18, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1976.

Wilson, J.L., Conrad, S.H., Mason, W.R., Peplinski, W., and Hagan, E.; "Laboratory Investigation of Residual Liquid Organics from Spills, Leaks, and the Disposal of Hazardous Wastes in Groundwater"; 1990.

Young, T.F. and Harkins, W.D.; "Interfacial Tension for Solid-Liquid and Liquid-Liquid Interfaces"; in International Critical Tables, Vol.IV, E.W. Washburn (editor), McGraw-Hill, NY, 1928.

General References

Adamson, A.W.; Physical Chemistry of Surfaces, Wiley Interscience, 1982.

Hiemenz, P.C.; Principles of Colloid and Surface Chemistry; Marcel Dekker, Inc., 1986.

Miller, I and Freund, J.E.; Probability and Statistics for Engineers; Prentice-Hall, Inc, Englewood Cliffs, New Jersey, 1965.

Pfaffenberger, R.C. and Patterson, J.H.; Statistical Methods for Business and Economics; Richard D. Irwin, Inc. Homewood, Illinois 60430, 1977.

APPENDIX A

The Duncan multiple range test (Pfaffenberger, 1977) was used to analyze the contact angle measurement data. A sample calculation is shown below.

CCl4 on Quartz (18 Samples per Mean)	
Mean Contact Angle	pH
22.833	5.7
21.694	5.6
21.556	9.4
21.222	7.4
20.583	8.1
20.361	7.3
19.861	7.5
18.778	9

Degrees of Freedom = (# Treatments)*(n-1) = 8 * 17 = 136

(MSE/n)^0.5 = 0.520677977

Least Significant Range for 136 Degrees of Freedom	
# of Means	Rp
2	1.457898335
3	1.536000032
4	1.58286105
5	1.624515288
6	1.650549187
7	1.676583085
8	1.692203425

Ref: Miller, 1965; Table X(a)

# of Means	Range	Rp	Significant?
8	4.055	1.692	yes
7	2.972	1.676	yes
7	2.916		yes
6	2.472	1.65	yes
6	1.833		yes
6	2.778		yes
5	2.25	1.625	yes
5	1.333		no
5	1.695		yes
5	2.444		yes
4	1.611	1.582	yes
4	1.111		no
4	1.195		no
4	1.361		no
4	1.805		yes
3	1.277	1.536	no
3	0.472		no
3	0.973		no
3	0.861		no
3	0.722		no
3	1.583		yes
2	1.139	1.458	no
2	0.138		no
2	0.334		no
2	0.639		no
2	0.222		no
2	0.5		no
2	1.083		no