

**THE EFFECTS OF WETTING  
ON TRANSPORT OF ORGANICS IN GROUNDWATER**

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## ABSTRACT

We investigated the effects of altered surface chemistries on fluid saturations, flow characteristics, and sorption properties in model porous media. Two distinct lines of inquiry were pursued. The first was to evaluate effects of surface chemistry on wettability and pressure/saturation relationships of chemically modified silica. The second line of inquiry was to modify the surface chemistry of a natural zeolite and determine the effects of such modification on sorption of organic chemicals from solution.

We found that we could create silica surfaces of different wettabilities which were stable for hundreds of hours in aqueous systems. We used these modified silicas to determine pressure/saturation relationships for water/oil systems and related the observations to measurements of wettability. We showed that we could use quaternary ammonium cations to predictably alter the sorptive properties of natural zeolites.

Our model experiments showed that basic information on surface characteristics can be used to predict changes successfully in fluid dynamics and sorption properties of porous media.

Keywords: fluid flow, hydrogeology, model studies, oil-water interfaces, organic compounds, pollutants, soil chemistry, soil physics, water quality

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## INTRODUCTION

### OVERALL SCOPE OF PROJECT

Groundwater contamination by organic liquids and by organic substances dissolved in water is a problem of national scope. While much has been learned about the transport of contaminants in the aqueous phase, much less is known about physical and chemical processes controlling contaminant fate in systems in which a free organic liquid phase is present. This project addresses changes in surface chemistry which can occur in multi-phase systems containing water, free organic liquid, and air, and the resultant effects on the physics and chemistry of contaminant migration.

The specific objectives of this research are:

- to determine the ability of chemical treatments, and of components present in contaminant solutions, to alter the wettability of solid surfaces.
- to determine quantitative and qualitative changes in fluid flow dynamics in porous media having altered wettabilities.
- to quantify the sorption of dissolved organic solutes from aqueous and organic liquid solutions onto surfaces having altered wettabilities.
- to determine the relative importance of changes in surface wettability to the general problem of organic contaminant sorption and transport.

To achieve these objectives, two distinct lines of inquiry were pursued. The first was to evaluate effects of surface chemistry on wettability and pressure/saturation relationships in model materials, primarily chemically modified silica glass surfaces. The second line of inquiry was to modify the surface chemistry of a natural zeolite and determine the effects of such modification on sorption of organic chemicals from aqueous solution. Such mineral modification mimics to some extent the effect of sorption of polar materials from organic liquids such as crude



oils on soil and aquifer solids.

This report summarizes the results of these two lines of inquiry. It is the product of three and one-half years of research by the principal investigators and four graduate students. Greater detail on methods, results, and interpretations can be found in Huddleston (1990), Wei (1991), Neel (1992), and in an independent study to be completed in the fall of 1992 (P. Burck 1992, personal communication).

## **WETTABILITY MODIFICATION OF MODEL MATERIALS**

### **Wetting properties of silane-treated glass exposed to water, air and oil**

Organosilanes have been used to alter the surface energy of silica and glass since the 1940s. Traditionally, silane treatment has found applications in industrial and chemical engineering. In earth science laboratory studies, organosilanes have been used to treat glass beads, silica sand, and sandstone cores. The studies include the effect of wettability on petroleum recovery (Newcombe et al. 1955; Bethel and Calhoun 1953) and, more recently, the behavior of hydrocarbons in contaminated aquifers (Wei 1991). The application of silanes to the difficult problem of wettability control (Takach et al. 1988, 1989; Menawat et al. 1984) seems to offer special advantages:

- The covalent bond between the organosilane molecule and the glass has often been assumed stable.
- Variation of the amount of organosilane and time of treatment have been proposed as means of achieving different degrees of wettability.
- Different functional organic groups of different silanes can impart different wetting properties.

However, laboratory experiments of hydrocarbon recovery involving water and oil can last up to several hundred hours. Few studies of silane-treated porous media have considered wetting stability, even though changes in wettability during the course of an experiment can be crucial

to the outcome. Although expertise exists in silanization for preparation of chromatographic materials (Berendsen and de Galan 1978), much of the information is proprietary. There is a need for systematic study of the effects and stability of silane treatments.

The principal objectives of this portion of the study were to 1) quantify the wetting properties of several organosilanes, 2) measure the stability of the altered surfaces after storage in air, water, and oil, and 3) investigate how instability can be detected. Organosilane-treated surfaces were characterized by water-air advancing and receding contact angles measured on freshly treated slides to define the wettability of the treated surfaces. Stability of the treated surfaces in various fluids was monitored by measuring the water-air contact angle of treated slides stored in air, water, and oil for up to about 1,000 hours. Water-Soltrol contact angles were also measured.

#### **Effect of wetting on capillarity and non-aqueous phase liquid saturations in homogeneous porous media**

There is growing awareness among environmental scientists about the role of wettability on the fate and transport of non-aqueous phase liquid (NAPL) contaminants beneath hazardous waste sites (Demond and Roberts 1991; Mercer and Cohen 1990; Wilson 1988). The usual assumption for an aquifer contaminated with NAPL is that the system is water-wet; water preferentially adheres to the aquifer grain surfaces in the presence of NAPL. However, wettability alteration of aquifer materials may be possible by adsorption of polar organic compounds in hydrocarbon contaminants. Evidence in the petroleum industry indicates that polar organic compounds in crude oil can adsorb onto mineral grain surfaces of reservoir rocks, rendering the rock surface hydrophobic (Morrow 1990; Anderson 1986). The change in wetting can be drastic enough to render the system oil-wet with oil preferentially adhering to the rock surface in the presence of water.

Wettability alteration affects capillarity by changing the curvature of the water-NAPL

contact angle. Effect of wettability on capillarity and NAPL trapping needs to be better understood and quantified to guide site characterization and remedial design.

Our objective here is to illustrate, through laboratory experiments, how a change in wetting of the porous medium surface affects capillary pressures and residual liquid saturations. This portion of the study focuses on the 1) influence of uniform wettability in homogeneous porous media, and 2) relation between strongly wetted conditions and capillary behavior. Intermediate and mixed wettability, heterogenous porous media, and mechanisms of wettability alteration were not investigated.

Two-phase liquid displacement experiments in glass bead pack columns were conducted to quantify how wettability alteration influences capillary pressure-saturation relationships and residual saturations ( $S_o$  and  $S_w$ ). Analogous experiments in an etched glass micromodel were also conducted to visualize the mechanisms of NAPL trapping for interpreting the column results.

In the experiments, glass represented the aquifer material. Wettability of the glass was altered by treatment with silane, an organic molecule that covalently bonds onto the glass surface. Glass treated with silane represented aquifer material rendered hydrophobic by adsorption of polar organic compounds onto the grain surface (Anderson 1986). Untreated glass represented the usually assumed condition that wettability alteration does not occur by adsorption of organics onto the aquifer grains.

In all experiments, the porous medium (glass bead pack and micromodel) was initially water-saturated. Initially, oil displaces water to irreducible water saturation (IWS). Water then displaces oil to residual oil saturation (ROS). In some experiments, water is again displaced by oil to IWS. This displacement sequence simulates migration of NAPL into an aquifer, followed by partial removal of the NAPL by ambient groundwater flow. The repeated displacement of water by oil simulates a repeated contamination event.

The treated and untreated cases were compared and contrasted with respect to:

- capillary pressure-saturation relationships,
- amount of residual oil and water saturations,
- wettability indexes, and
- mechanisms of liquid trapping and displacement.

## **SURFACE MODIFICATION OF NATURAL ZEOLITE**

In recent years, increasing attention focused on the nature of hydrophobically altered clays and their applications. Although such materials are known to have been in existence for many years, recent nationwide concern about hazardous waste disposal practices and releases has stimulated increased research in this area. While the existence of naturally occurring hydrophobic soils is well-documented, (DeBano and Letey 1969; DeBano 1981; Hendrickx et al. 1988; van Dam et al. 1990), most recent research has focused on characterization of laboratory-modified clay minerals (Bouchard et al. 1988; Boyd et al. 1988a, 1988b, 1988c; Cadena 1988, 1989; Cadena and Jeffers 1987; Jaynes and Boyd 1990; Jaynes et al. 1989; Mortland et al. 1986; Smith et al. 1990; Wolfe et al. 1985, 1986). This portion of the research was an effort to expand on the recent body of literature regarding the characterization of surface-modified minerals.

The need for research in this area was summarized nicely by Wilson (1988). Wilson discusses the potential environmental problems associated with hydrophobic soils, including golf course management, agricultural management, flooding and erosion control over burned chaparral lands, petroleum recovery, and hazardous waste recovery following uncontrolled releases at disposal sites. In addition to increasing our understanding of properties of hydrophobic soils, such materials can have potential engineering applications. These applications, discussed in detail by Alther et al. (1990), include uses of hydrophobic clay materials for waste stabilization, water treatment, spill control, tank liners, and landfill liners.

The primary goal of this portion of the project was to determine the sorptive properties of a hydrophobically altered zeolite with regard to different organic solutes. This goal directly related to applications in hazardous waste remediation. When the hydrophobic nature of soil and aquifer materials is altered, via either natural or anthropogenic mechanisms, the sorptive properties for organic contaminants can be significantly altered. Therefore, it is necessary to evaluate the effect of different hydrophobic mineral treatments, in an attempt to determine the factors influencing these changes in sorptive properties. To meet this goal, a variety of surface-modifying agents was evaluated to determine their effect on altering surface sorptive properties.

In addition, many hazardous waste releases involve large volumes of organic liquids. These organic solvents may impact the extent of dissolved organic solute sorption. To evaluate this effect, sorption studies were conducted not only from aqueous solutions, but also from a polar and a nonpolar organic liquid. The sorption of a variety of organic solutes was evaluated, primarily to evaluate the effect of different functional groups on the extent of sorption.

In summary, this portion of the research project was developed based on the hypothesis that organic solute sorption to mineral surfaces behaves differently depending upon several different factors. These factors are: the degree and stability of mineral surface hydrophobicity, the nature of the chemical causing mineral surface hydrophobicity (degree of carbon loading on the mineral surface, alkyl vs. phenyl functional groups), solute polarity/functional nature (alkyl vs. phenyl groups), and solvent composition and polarity.

Several objectives were defined to test this hypothesis. These were 1) to create a variety of hydrophobic mineral surfaces and quantify the degree of hydrophobicity, 2) to determine the surface stability of this modified mineral, and 3) to quantify organic solute sorption to the hydrophobic surfaces from aqueous and nonaqueous solvents.

While most previous studies on surface modification have employed clay minerals, a natural zeolite was chosen as the mineral sorbent for this project because the natural high cation

exchange capacity (CEC) of zeolites makes them amenable to surface modification using organic cations. This type of mineral can exist naturally with a relatively large particle size, which facilitates column leaching studies. Pure clay minerals are often so fine textured that column experiments are not practical. The material used for this study provided an easily characterizable analogue for natural clay-containing, ion-exchanging soil. Although column studies ultimately were not conducted as part of this project, these results and this zeolite can be used as a foundation for future work, including column experiments.

## METHODS

### WETTABILITY MODIFICATION OF MODEL MATERIALS

#### Wetting properties of silane-treated glass exposed to water, air and oil

##### Silanes

Five silanes, trimethylchlorosilane (TMS), *tert*-butyldimethylchlorosilane (tBDM), *tert*-butyldiphenylchlorosilane (tBDP), octadecyltrichlorosilane (OtS) and GlassClad 18 (GC18), were chosen for investigation of wettability alteration. All were obtained from Huls America Petrarch (Bristol, PA). GlassClad 18 is a C<sub>18</sub> alkoxy silane of proprietary composition.

##### Slide Preparation

Sodalime glass slides (No. 2947, Corning Glass Works, Corning, New York) were used as the substrate in nearly all experiments. Polished quartz and fused silica slides (Heraeus Amersil, Buford, GA) were also tested. Reagent-grade chemicals and solvents were from Aldrich Chemicals (Milwaukee, WI). Soltrol 130 (a refined oil of C<sub>10</sub> to C<sub>13</sub> aliphatic hydrocarbons) was obtained from Phillips 66 (Bartlesville, OK). Soltrol 130 is often used in experiments on hydrocarbon recovery. Water was double-distilled and deionized.

Batches of 24 slides were cleaned following the procedures of Menawat et al. (1984) and then inserted in a slotted Teflon block and put into a 400-mL glass Mason jar. The slides were sonicated for 20. min in 2-butanone, rinsed with water, and then sonicated again in 70% nitric acid followed by a water rinse. Prior to silanation, slides were dried at 110° +/- 5°C for 24 hours and then cooled in a desiccator.

##### Silane Treatment

For the chlorosilane treatments, the appropriate silane was diluted with 200-250 mL of redistilled toluene. Based on calculations of complete monolayer coverage, excess silane was added to encourage reaction with all active sites on the slides (Wei 1991). The solution was poured into the Mason jar containing the cleaned glass slides. The head space in the jar was

purged with N<sub>2</sub> gas before completely covering the jar with a teflon lid. The solution was heated to 70°, to 80°C on a hot plate and stirred with a Teflon-coated magnetic stir bar for 24 to 48 hours in the case of the lighter chlorosilanes (TMS, tBDM, and tBDP), and for one week for OtS, as recommended by Berendsen and de Galan (1978). One day prior to the end of reaction, 10.0 mL of pyridine was added to neutralize the HCl by-product and help drive the reaction to completion. Following the silane treatment, the slides were rinsed with redistilled toluene, methanol, 50:50 methanol:water, and methanol again. The treated slides were cured in the oven at 110° +/- 5°C for 4 to 6 hours. In the experiments with TMS the addition of pyridine and the methanol rinses were omitted.

For the GC18 treatment, 250 mL of a 1% (v/v) aqueous solution was used. The solution was poured into the Mason jar containing the slides and sonicated for 1.5 to 2 min. The slides were then rinsed with water and cured in the drying oven for 3 to 5 min at 110° +/- 5°C. This procedure was repeated five to ten times to maximize surface coverage (Wei 1991).

#### Storage of Silanized Slides in Water, Air, and Oil

Freshly treated slides were stored in air, water with 1.0 g/L sodium azide as a bactericide, or Soltrol 130. TMS-treated slides, and some GC18 and OtS treated slides, were stored in water without sodium azide. Slides in air or water were kept in covered plastic containers, while those in Soltrol 130 were stored in capped Mason jars.

When a slide was used for contact angle measurements, it was removed from the container with Teflon tweezers, and rinsed. Slides stored in water were rinsed with deionized water only; slides stored in Soltrol 130 were first rinsed with acetone and then with water. They were then oven dried at 60° to 80°C for 15 min, and cooled to room temperature. Slides stored in air were taken directly from their container. After contact angle measurements, the slides stored in water and air were returned to their containers, while slides stored in Soltrol were rinsed with acetone and then deionized water, and dried at 60° to 80°C before returned to their



containers. At the end of the experiments, random samples of the slides were inspected for bacteria using phase-contrast microscopy.

#### Contact Angle Determination

Water-air contact angles were measured following the procedures specified in ASTM C813-75 (American Society for Testing Materials 1986). A 2-mL microburet was used to expand and contract the water drop for measuring advancing,  $\theta_A$ , and receding,  $\theta_R$ , angles. The contact angle was measured directly with a microscope (Carl Zeiss Stereoscope 47 50 52-9901) fitted with a goniometer eyepiece (Tiyoda No. 4443, Tokyo). Water-Soltrol 130 contact angles were measured in a similar way except the slide and buret tip were immersed in a glass container filled with Soltrol 130. Contact angles were recorded immediately after the drop contacted the slide. Measurements at three or four positions on each slide were made and averaged. The room temperature ranged between 22.0° and 25.0°C.

#### Wetting by water/alcohol mixtures

Contact angle measurements were also made using methanol:water mixtures of 7%:93%, 25%:75%, 50%:50%, and ethanol: water at 50%:50%. Surface tensions of the solutions were determined with a Fisher 20 tensiometer (Fisher Scientific, Pittsburgh, PA). Contact angles on treated slides were measured using a sessile drop technique. The drop, having a volume of about 0.02 mL, was placed on the slide and the height and width of the drop determine (Spitze and Richards 1947).

#### **Effect of wetting on capillarity and non-aqueous phase liquid saturations in homogeneous porous media**

##### Description of the immiscible liquids and glass beads

Soltrol 130 was used as the oil phase. The aqueous liquid was deionized and de-aired water containing 1000 mg/L sodium azide ( $\text{NaN}_3$ ) to eliminate bacterial growth.

Sodalime glass beads (Cataphote Inc.) with a particle diameter of 250-297  $\mu\text{m}$  (average

diameter of 274  $\mu\text{m}$ ), typical of a medium sand, were used. The glass beads were spherical to sub-spherical in shape. Particle density, measured with pycnometers (Lambe 1951), was 2.471  $\text{g}/\text{cm}^3$ .

#### Silane treatment of glass beads

GlassClad 18 was used to treat glass beads. The beads were cleaned in 2-butanone and then in 70% nitric acid, thoroughly rinsed with distilled water, dried in an oven at 110°C for at least 24 hours, and cooled. The beads were then treated with a 1% by volume aqueous solution of GC18 and then cured in the oven at 110 °C for half an hour. The treatment was repeated 10 times to maximize silane coverage (Wei 1991).

#### Conventional columns

The conventional column apparatus used for the cleaned, untreated beads is shown in Figure 1. The glass columns were 5-cm diameter and 5-6 cm long. The short length of the columns helps maintain uniform pressures and saturations along the column length.

Each column was sealed at both ends with Teflon endcaps fitted with O-rings. Liquids entered and left the column via a single hole in each endcap. The nylon filter on the bottom endcap allowed water but not Soltrol to pass through. The polypropylene mesh at the top endcap was permeable to both liquids.

The beads were wet-packed into each column under about 1 cm of water. The volume of the unpacked column, mass of beads used, and particle density of the beads were used to calculate the bulk density, pore volume, and porosity of the packed beads (Wilson et al. 1990). Each column was saturated completely by flushing at least 20 pore volumes of de-aired water through the column over a period of 2 to 3 days until the mass of the column stabilized.

#### Dual-Filter Columns

The dual-filter column was developed to measure capillary pressure-saturation relationships in the treated beads (Figure 1). The conventional columns could not measure

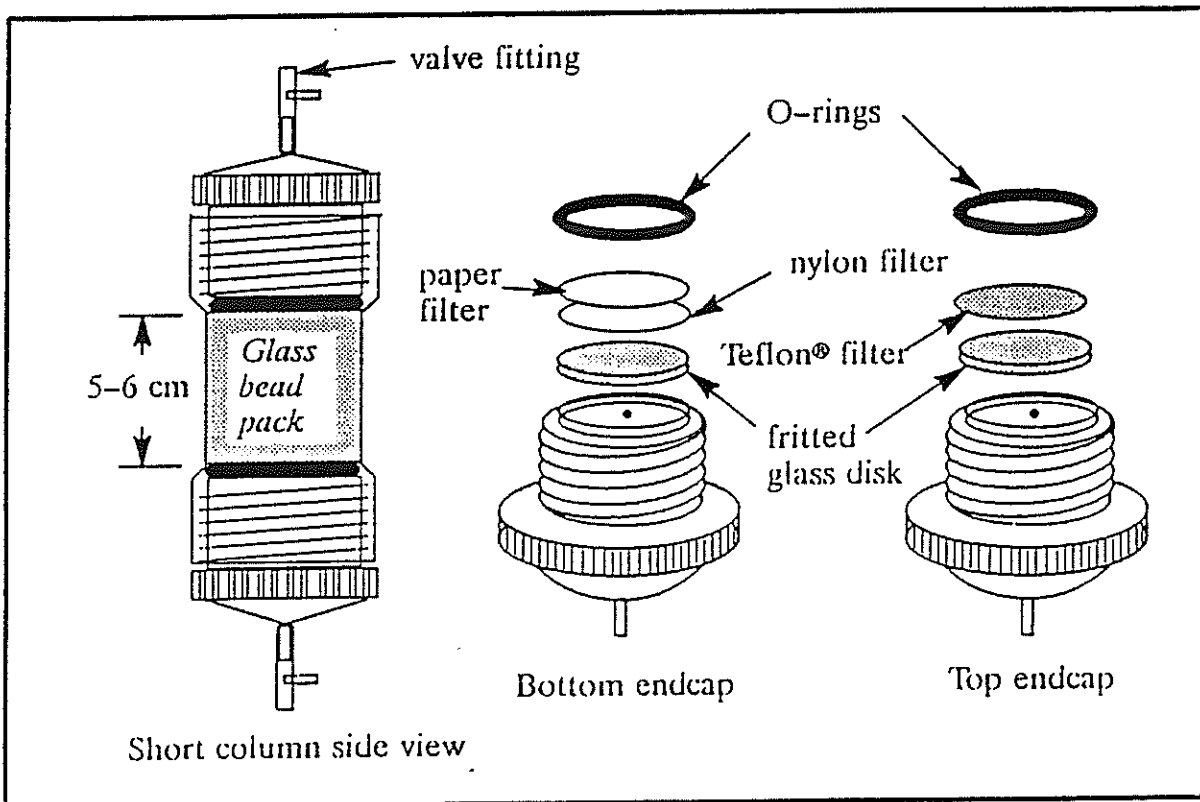
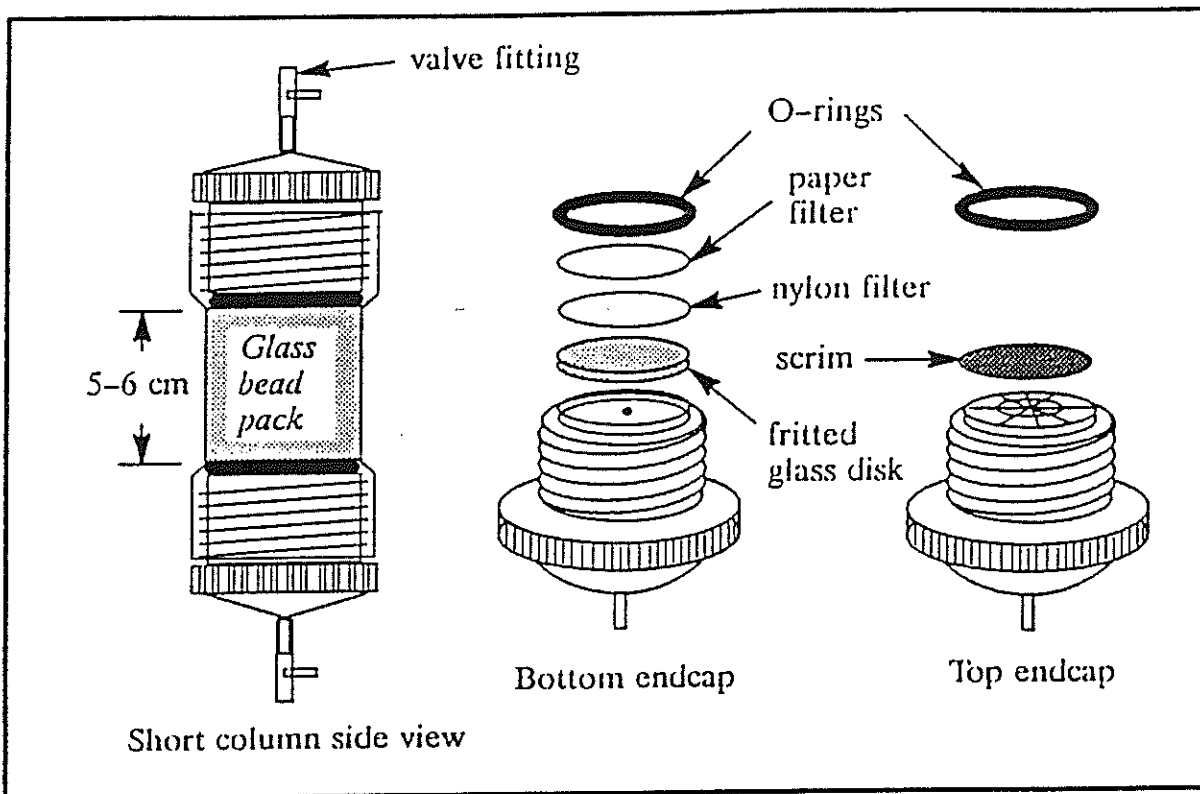


Figure 1. Apparatus for conventional and dual-filter columns.

negative capillary pressures (pressure in the water > pressure in the oil) because water broke prematurely through the mesh at the top endcap as zero capillary pressure was reached. In the dual filter column, a Teflon filter at the top endcap allowed Soltrol but not water to pass through so that negative capillary pressures could develop in the treated beads.

The treated beads were wet-packed in ethanol (treated beads packed in water would float). Once the correct number of beads was packed into the column, the ethanol was flushed out by at least 20-pore volumes of water. The surface tension of the effluent flushed out of the column was measured and flushing was completed when the measured surface tension was greater than 72 dynes/cm for two consecutive days. After flushing, the top endcap was screwed gently onto the column.

#### Experimental procedures for glass bead packed columns

The initial weight of the water-saturated column was recorded to the nearest 0.01 g before each experiment. In every experiment, the column was oriented vertically (Figure 2). The bottom of the column was connected to a water-filled buret. The top of the column was connected to a buret filled with Soltrol.

Each experiment began with Soltrol, the lighter liquid, displacing water from the top of the column by lowering the water-filled buret and raising the Soltrol-filled buret. Displacement continued until equilibrium was reached when the liquid levels in the burets stabilized. Equilibrium generally occurred within 8 to 10 hours.

The capillary pressure at equilibrium, measured as cm of head of water, was calculated by measuring the liquid levels in the burets above and below the center of the column:

$$h_c = (\gamma_o ( h_o - h_{col} ) + ( h_{col} - h_w ) )$$

where  $h_c$  is the capillary pressure head in height of water,  $\gamma_o$  is the specific gravity of Soltrol 130, and  $h_o$ ,  $h_w$ , and  $h_{col}$  are the heights of the Soltrol and water in the burets and the height of the

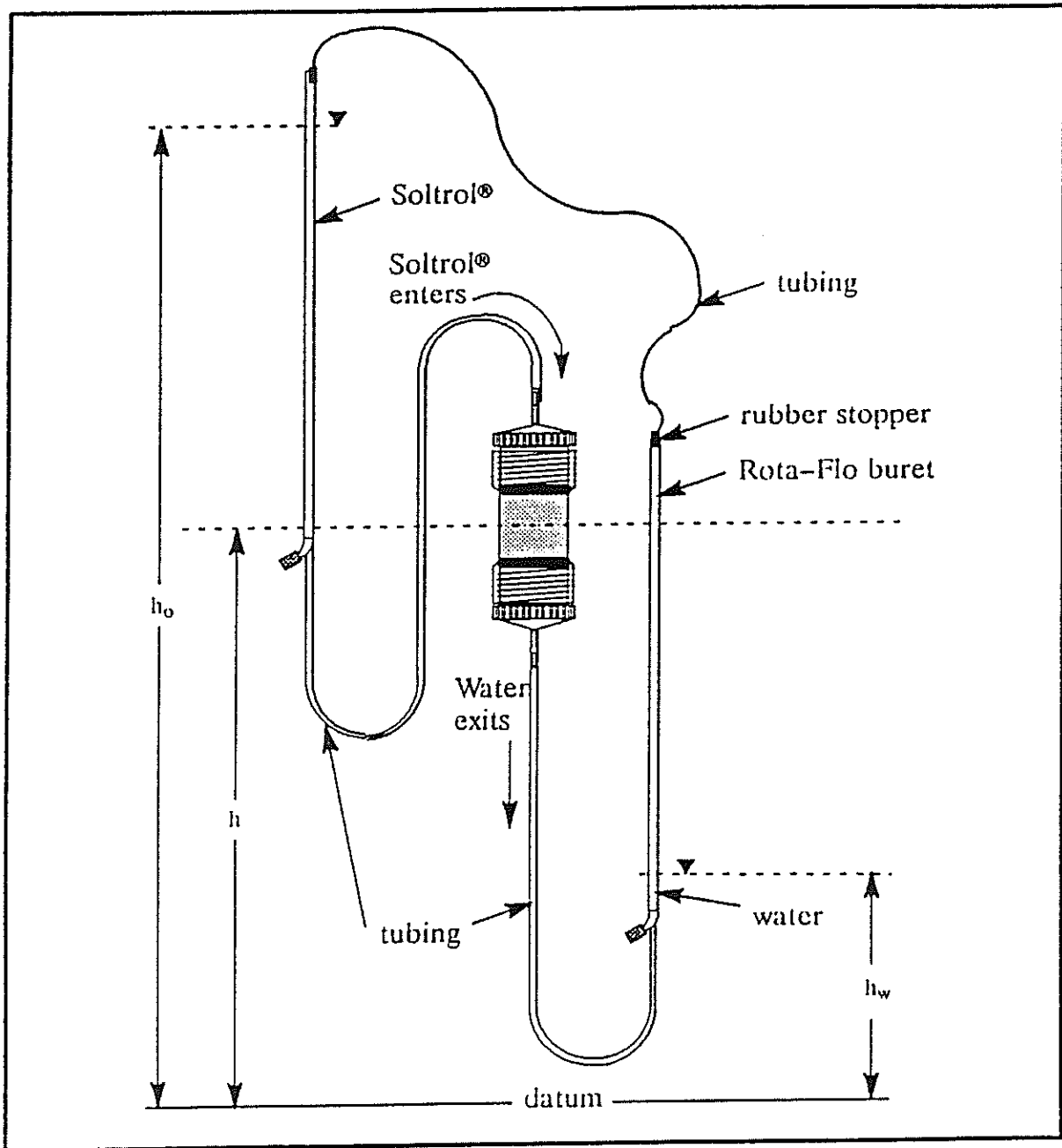


Figure 2. Column experimental set-up for measurement of capillary pressure-saturation relationships. The set-up shows water displacement by Soltrol.

$h_o > h_w$  and negative capillary head is when  $h_o < h_w$ . Displacement occurred incrementally in this fashion throughout the experiment. Liquid saturations after each incremental displacement were determined gravimetrically by weighing the column, to the nearest 0.01 g, at the end of each incremental displacement.

Primary displacement of water by Soltrol occurred until IWS was reached. Water then displaced Soltrol incrementally to ROS from the bottom of the column (primary displacement of Soltrol by water). Residual saturations (IWS and ROS) occurred when liquid saturations did not change appreciably with continued changes in capillary pressure. In some experiments, secondary displacement of water by Soltrol was done to bring the saturation in the column from ROS to IWS again.

## **SURFACE MODIFICATION OF NATURAL ZEOLITE**

### **Sorbent selection**

The clinoptilolite-dominated zeolite used was supplied by the Zeotech division of Leonard Minerals (Albuquerque, New Mexico), from their mine near Tilden, Texas. The material was sieved to a gradation of grain sizes ranging from 0.2-2.0 mm. The sample was not a pure zeolite, but contained a significant percentage of smectite clay minerals. This combination of zeolites and clay minerals was an ideal mix for this study, providing a high CEC and suitable particle diameter. Quaternary ammonium cations could exchange on sites between clay lamellae and on external zeolite surface sites, thus creating an outer hydrophobic surface, with only the internal zeolitic channels remaining hydrophilic.

### **Surface-modifying agent selection**

Several quaternary ammonium cations were evaluated for use as surface-altering agents. These were: tetramethylammonium (TMA), phenyltrimethylammonium (PTMA), hexadecyltrimethylammonium (HDTMA), and methyl-4-phenylpyridinium (MPP). The first three cations were selected because they have been used by other researchers and have proven effective

in altering clay hydrophobicity (Boyd et al. 1988b, 1988c; Cadena 1988, 1989; Cadena and Jeffers 1987; Jaynes et al. 1989; Mortland et al. 1986; and Smith et al. 1990). The last cation, MPP, was chosen specifically because pyridinium compounds have not been studied extensively in the field of mineral surface alteration, and because this particular compound emphasized the phenyl functional group.

Both preliminary analyses of this project and research by others (Boyd et al. 1988c; Mortland et al. 1986) indicated that TMA and PTMA gave lower organic carbon contents than the larger organic cations. In addition, TMA and PTMA may not fully cover the mineral surface, resulting in a mixed hydrophobic-hydrophilic surface that is generally not as effective at removing nonpolar organic contaminants from solution as larger organic cations. As a result, HDTMA and MPP cations were chosen as surface-modifying agents. These two cations have 19 and 12 carbons, respectively, so their effect on soil organic carbon content is significant. In addition, they emphasize the differences between the alkyl functional group and the phenyl functional group on surface alteration. HDTMA was supplied in liquid form as the chloride salt from Aldrich Chemical Co., (Milwaukee, Wisconsin). MPP is no longer commercially available, so it was synthesized in our lab. Details of the synthesis are provided in Huddleston (1990).

### **Organic solute and solvent selection**

The organic solutions chosen for study were: phenol (Ph), ethylbenzene (Eben), tetrachloroethylene (PCE), and 1,1,1-trichloroethane (TCA). These solutes have been used in relatively few studies of sorption to organo-clays, and thus are a new addition to the increasing literature database. In addition, each of these chemicals is listed on the U.S. Environmental Protection Agency's priority pollutant list, and is commonly found at industrial and hazardous waste sites (Keith and Telliard 1979). Eben and Ph emphasize the phenyl functional group, with Ph a polar molecule (dipole moment,  $\mu = 1.70$  debyes), and Eben an essentially nonpolar molecule ( $\mu = 0.35$  debyes). PCE and TCA emphasize the alkyl structure, with TCA having

a small dipole moment of 1.57 debyes and PCE a completely nonpolar molecule ( $\mu = 0$ ; dipole moments from Wesson 1948).

Because most environmental investigations and cleanups involve fate and transport analyses of organics in water, water was an obvious solvent. To simulate a typical natural water, aqueous solutions were made of distilled water with calcium chloride added to make a 0.005 M solution.

However, some organic releases may involve large volumes of free organic liquid containing other dissolved organic solutes. In these instances, sorption of the organic solutes may behave quite differently from when the solutes are dissolved in water. Therefore, adsorption of these solutes from organic solvents was also determined. To evaluate the effects of contrasting properties, both polar and nonpolar organic solvents were desirable. Methanol was chosen as the polar solvent, and benzene as the nonpolar solvent. All the organic solutes were obtained from Aldrich Chemical Co.; benzene and methanol were obtained from Fisher Scientific (Pittsburgh, Pennsylvania). HPLC-grade methanol and thiophene-free benzene were used, while solutes were the highest purity available (99%-99.9%). All compounds were used as received from the supplier.

### **Characterization of porous medium**

Prior to conducting sorption experiments, the zeolite sorbent was characterized. The zeolite was characterized using x-ray diffraction (XRD), CEC analyses, and scanning electron microscopy (SEM). Although the material had been sieved to a sand-sized fraction, preliminary experiments showed that some of the zeolite aggregates would break down with mechanical agitation into clay-sized particles. As a result, a sample was submitted to the New Mexico Bureau of Mines for XRD analysis of both the bulk mineral fraction and of the  $<2\mu\text{m}$  fraction.

Because the literature indicated that the organic cations would only be exchanged on the external zeolite surfaces, it was important to characterize not only the total zeolite CEC, but also



to determine the external CEC. Total CEC was determined by the method of Rhoades (1982), and internal and external CEC were determined by the method of Ming and Dixon (1987b). Detailed descriptions of these analytical methods and the procedures used are presented in Huddleston (1990).

To characterize the zeolite surface morphology, the sample was submitted to the New Mexico Institute of Mining and Technology Materials and Metallurgy Department for SEM photography.

### **Quantification of surface modification**

A procedure was developed to modify the zeolite surface using the large organic cations HDTMA and MPP. Several different zeolite:solution ratios and solution concentrations were investigated, along with the time necessary for complete exchange. The best method for surface modification was determined on the basis of simplicity and effectiveness in altering the surface.

The method ultimately chosen to create the modified surface was to add an amount of organic cation equal to the external CEC, equilibrate 24 hours, then rinse and dry the treated zeolite. Once the modified surface was created, it was necessary to quantify the extent of surface modification so that comparisons could be made between differently treated surfaces. Two different methods were used for this purpose: sorption isotherms of each organic cation were developed, and the organic carbon content of the resultant treated zeolite was measured.

Sorption isotherms were generated using a  $^{14}\text{C}$ -radiolabelled organic cation. Methyl-labelled HDTMA and MPP cations were supplied by American Radiolabelled Chemicals, Inc., (Saint Louis, Missouri). A radioactive spike of the appropriate cation was added to each of several solutions of different concentrations. The solutions were added to the zeolite and equilibrated for 24 hours. A 1-mL aliquot of equilibrated and centrifuged solution was withdrawn from each sample and added to a 20-mL glass scintillation vial. Ten mL of Ecolite scintillation cocktail (ICN Biochemicals, Inc., Irvine, California) was added to each sample. All samples

were stored at 5°C overnight before analysis in a Tri-Carb 46OCD liquid scintillation system (Packard Instrument Co., Inc., Downer's Grove, Illinois). MPP samples were corrected for quenching using a quench curve generated from MPP standards.

Organic carbon content was measured using a carbon oxidation method conducted in a sealed ampule, after which CO<sub>2</sub> generated was quantified. The organic carbon analyzer (O.I. Corp., College Station, Texas) consisted of Model 524 P.S. purging and sealing unit, Model 524 D ampule analyzing unit, and Model 3300 IR gas analyzer.

### **Quantification of modified surface stability**

Once the modified surface was successfully created and quantified, it was necessary to confirm the modified surface would remain stable in the solutions in which studies would be conducted. Because the studies in this project were all batch studies of 72 hours or less in duration, the stability over 72 hours, under conditions identical to those of the studies to be conducted, was assessed. Long-term stability studies were not conducted.

Surface stability was assessed in a variety of aqueous and organic solutions, and in a range of pH buffers (Huddleston 1990). Calcium chloride solution was chosen because all the aqueous isotherms were to be conducted in 0.005 M CaCl<sub>2</sub> solution. Cesium solutions were chosen because clays and zeolites have a high specificity for cesium sorption. Organic cation desorption in cesium solutions was considered to be worst-case condition for replacement by inorganic cations. Buffers were used to evaluate surface stability over a range of pHs. In addition, these pH buffers contained high concentrations of sodium or potassium ions which may potentially exchange for the organic cations. Distilled water was evaluated because it was the solution used for rinsing the zeolites immediately after they had been treated. Methanol and benzene were chosen because they were the two organic solvents evaluated in the sorption isotherm experiments. Soltrol was chosen as an additional organic mixture since it was used in our wettability studies. Organic cations were chosen to evaluate the strength of other large

organic cations in displacing the modified-surface cations. A cation concentration of 0.15 M was equal to the external zeolite CEC at the zeolite mass and liquid volume used for these studies. All salt solutions were added at one concentration below the CEC equivalent concentration, and at one concentration above the CEC equivalent concentration. Specific concentrations, however, were arbitrarily selected.

These studies were conducted by treating a large mass of zeolite with  $^{14}\text{C}$ -labelled organic cation. After exchange, the supernatant  $^{14}\text{C}$  concentration was measured, the zeolite was rinsed and dried, and  $^{14}\text{C}$  concentration in the rinsate was measured. Based on the initial amount of  $^{14}\text{C}$ -labelled cation added to the zeolite, the treated zeolite activity was calculated. Five grams of the radioactively labelled MPP- or HDTMA-zeolite was mixed with 10 mL of each test solution. These mixes were sampled after 4, 8, 24, 48, and 72 hours to analyze the organic cation desorption over a span of a typical batch study. Supernatant solutions were analyzed using liquid scintillation in the same manner as was done for the cation sorption isotherms.

### **Quantification of Organic Solute Sorption to Modified Zeolites**

Batch sorption studies were conducted to quantify the extent of organic solute sorption to each of the modified zeolites from the different solvents. For comparison, and to evaluate the effectiveness of internal zeolitic channel sorption studies to the natural (untreated) zeolite were also conducted. Prior to obtaining results of the sorption studies, an assessment of equilibrium time was performed. For this assessment, an intermediate concentration of each solute in each solvent was chosen and mixed with each zeolite. The solution concentrations were measured at 4-, 8-, 24-, 48-, and 72-hour intervals, to determine the equilibration time. Once the equilibrium time was established, the full suite of solution concentrations was prepared, and the complete isotherm was run.

Two different techniques were used to generate the sorption isotherms. The method used was dependent on the solute's volatility, as estimated from its Henry's Constant ( $K_H$ ). Phenol,

which has a very low Henry's Constant, was studied differently from the method used for Eben, PCE, and TCA, which have very high Henry's Constants. All studies, however, were conducted in duplicate, with tube blanks carried throughout and treated exactly as any other samples, to determine loss due to volatilization or tube sorption.

Phenol sorption isotherms were generated using  $^{14}\text{C}$  universally-labelled Ph (American Radiolabelled Chemicals, Inc.). Several Ph solutions ranging from 100-50,000 mg/L in each solvent were prepared, and spiked with the radiolabelled phenol. The solution was added to each different zeolite in a ratio of 2:1, respectively, with 5.0 mL solution pipetted into 50 mL, screw-cap (Oak Ridge-type) teflon centrifuge tubes containing 2.50 g zeolite. The mixture was equilibrated, centrifuged, and 1.0 mL supernatant removed and placed into 20 mL glass scintillation vials. Ecolite scintillation cocktail was added to each vial in a ratio of 10 mL cocktail:1 mL sample. Samples and standards were then analyzed via liquid scintillation. Since quenching was not observed, no correction for quenching was made. Since Ph recovery in blank samples (containing no zeolite) was never less than 97%, no correction for blanks was made.

The remaining three solutes required special care due to their volatility. For these isotherms, solutions were prepared in 125 mL Wheaton (Millville, New Jersey) crimp-top bottles at different concentrations, ranging from approximately 10 mg/L to 100 mg/L. Bottles were capped with teflon-lined butyl rubber septa. Solution was withdrawn using a 100 mL gas-tight syringe. From this syringe, solution was added to 10 mL Wheaton crimp-top vials containing 2.50 g zeolite. These vials had already been sealed with teflon-lined silicone septa, so the solution was added by piercing the septa and injecting solution until the vial was filled. To permit maximum filling of the vials with solution, a vent needle was pierced through the septum to allow gas in the vial to escape. Even with the vent needle, however, vials could not be completely filled with solution. The headspace volume remaining in each vial, however, was negligible relative to the total vial volume, and was consistent among vials.

Following solution addition, samples were equilibrated, centrifuged, and 2.0 mL supernatant was withdrawn by piercing the septum again with the gas-tight syringe and placed in 2.0 mL gas chromatograph (GC) autosampler analysis vials. Blank vials, containing no zeolite, were prepared, equilibrated, and sampled identically to the zeolite-containing samples. All solutions were analyzed with a Hewlett Packard (Palo Alto, California) Model 5890 GC equipped with a flame-ionization detector and Model 3396A integrator. Concentrations in the blank samples after equilibration were considered to be the initial solution concentration for isotherm calculations.

Details of the chromatographic analyses are presented in Huddleston (1990). Data were analyzed as peak areas and compared to known standards at 200 mg/L concentration in methanol as supplied by Supelco, Inc. (Bellefonte, Pennsylvania).

## RESULTS AND DISCUSSION

### WETTABILITY MODIFICATION OF MODEL MATERIALS

#### Wetting properties of silane-treated glass exposed to water, air and oil

Water/air wetting properties of freshly treated surfaces are shown in Table 1. Contact angles from cleaned, untreated slides are included for comparison. - Values were averaged from replicate batch experiments (Wei 1991). Standard deviations for contact angles ranged up to 8.6°. The initial advancing angles show that when water advances against air, TMS-, tBDM-, tBDP-, and GC18-treated slides are fairly close to neutral (90°) wettability. The initial advancing water-air contact angles for tBDM- and tBDP-treated slides were close to the angles at high silane concentrations reported by Menawat et al. (1984). The advancing water-air contact angle for OtS-treated slides was significantly higher (151.9° vs. 105°) than the value measured by Spitze and Richards (1947) and higher than any previously reported values for air/water/solid, with any treatment. The high advancing angle may reflect a variable multimolecular layer on the glass resulting from the trifunctional character of OtS. The receding angles were 15°-20° lower than advancing angles except for OtS, which showed very large hysteresis (73°). The receding angles for tBDM- and tBDP-treated slides match those observed by Menawat et al. (1984) for slides treated at low silane concentrations. In contrast to our results for tBDM and tBDP, Menawat et al. (1984) observed contact angle hysteresis only at low silane concentrations.

**Table 1. Water-air contact angles, contact angle hysteresis, and critical surface tensions for freshly treated slides.**

<u>Silane</u>	<u>Advancing Angle (°)</u>	<u>Receding Angle (°)</u>	<u>Contact Angle Hysteresis (°)</u>	<u>Critical Surface Tension (dynes/cm)</u>
TMS	81.1 (4.3) <sup>a</sup>	nm <sup>b</sup>	-	nm
tBDM	75.3 (3.7)	57.4 (5.5)	17.9 (1.8)	23
tBDP	69.0 (5.1)	54.0 (2.2)	15.0 (2.4)	26
GC18	98.9 (7.9)	79.1 (8.6)	19.7 (4.5)	26
OtS	151.9 (3.5)	79.7 (8.1)	72.6 (6.9)	15-30
Untreated Glass	6.7 (0.7)	4.5 (1.6)	2.2 (0.9)	-

<sup>a</sup> Values in parentheses are standard deviations of three to four replicate measurements.

<sup>b</sup> Not measured.

The smoothness of the solid surface virtually precludes surface roughness of the glass substrate as an explanation of the observed contact angle hysteresis (Table 1). Using a Wilhelmy plate apparatus, Takach et al. (1988, 1989) reported negligible wettability hysteresis for freshly treated slides. The unusually large hysteresis for OtS-treated slides compared to the untreated slides suggests that the functional character of the silane can also impart heterogenous wetting properties to the glass surface. Also, it has been shown that the advancing contact angle is relatively insensitive to the extent of coverage once it has exceeded a certain fraction of the surface (Dettre and Johnson 1965). Thus, incomplete coverage could still result in a near maximum advancing angle even though the receding angle is low.

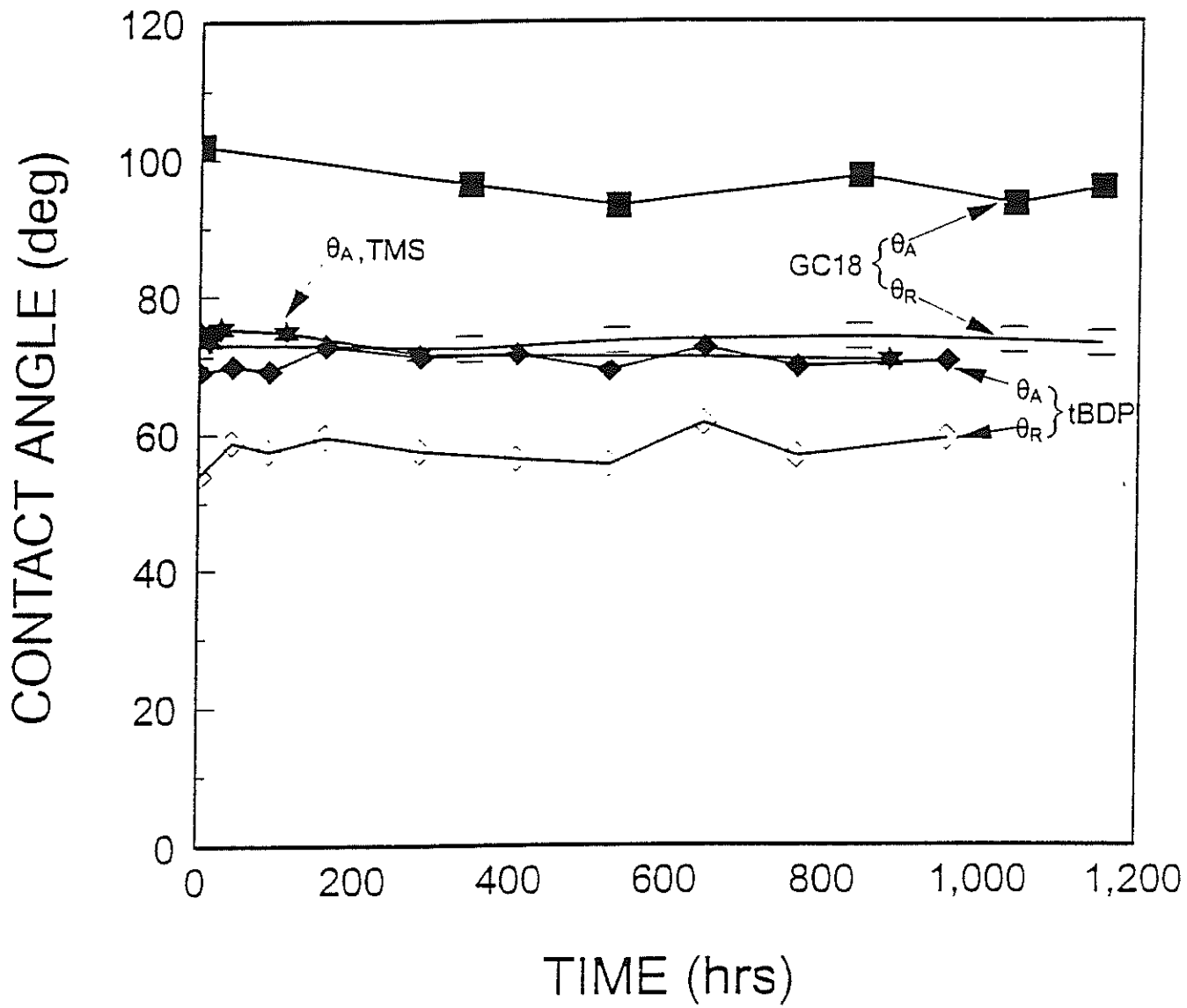


Figure 3. Advancing and receding water-air contract angles for silanized glass slides stored for different lengths of time in air.



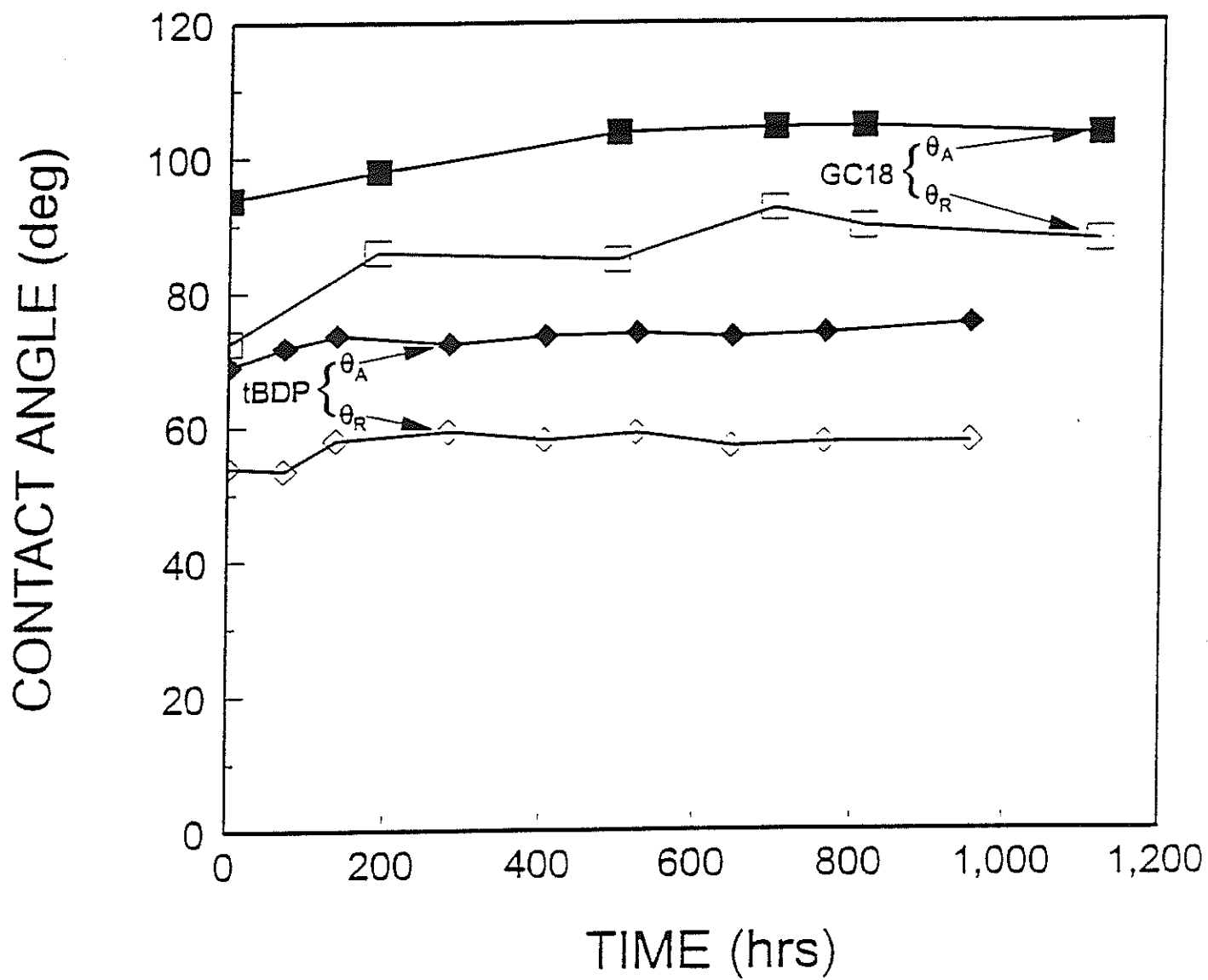


Figure 4. Advancing and receding water-air contact angles for silanized glass slides stored for different lengths of time in Soltrol 130.

## Storage in air and oil

Stability of the treated slides stored in air and Soltrol is shown in Figures 3 and 4, respectively. For clarity, only results for TMS-, tBDP-, and GC18-slides are shown; tBDM- and OtS-treated slides showed essentially the same trends. Similar stability characteristics were also found for storage in ethanol. The figures show that treated slides remained stable for up to 1,000 hours when stored in air and Soltrol 130. The advancing and receding angles, and hence, contact angle hysteresis, remained essentially constant throughout the observation period for all treatments.

## Storage in water

Contact angles decreased over time for all treated slides stored in water (Figure 5). TMS-treated slides showed the greatest overall decrease in advancing angle ( $33^\circ$  over 1000 hours) while GC18-treated slides showed the least ( $10^\circ$  over 940 hours); the advancing angle decreased  $15^\circ$  over 950 hours for tBDP-treated slides. The advancing angle for GC18-treated slides did not begin to decrease until after 400 hours, while for TMS- and tBDP-treated slides the decrease was immediate (Figure 5). The receding angle for tBDP- and GC18-treated slides decreased at a greater rate than the advancing angle. The receding angle decreased  $21^\circ$  over 940 hours for GC18-treated slides and  $25^\circ$  over 950 hours for tBDP-treated slides. The receding angle also started to decrease earlier than the advancing angle (Figure 5). As a consequence of this receding angle behavior, there was gradual increase in contact angle hysteresis over the time period of observation. Takach et al. (1988, 1989) also observed an increase in hysteresis as silane-treated slides aged in brine. As the treated surface breaks down, the silane coverage on the glass surface decreases with the receding angle being more affected than the advancing angle by the resulting increase in chemical heterogeneity of the surface.

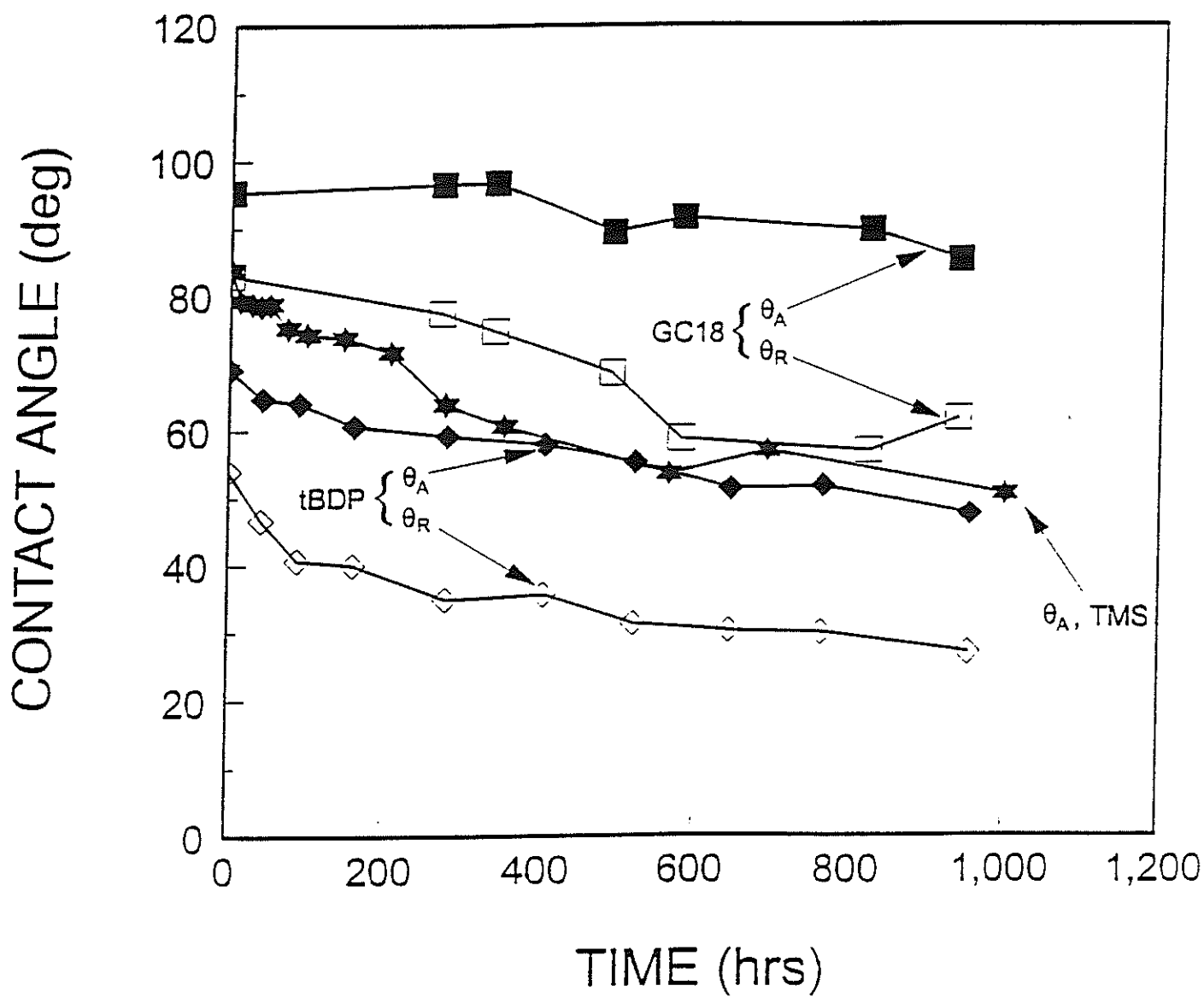


Figure 5. Advancing and receding water-air contact angles for silanized glass slides stored for different lengths of time in water.

## Mechanism of Decrease in Hydrophobicity

Deterioration appears inevitable for silane-treated surfaces immersed for prolonged periods in water. Takach et al. (1988) greatly improved the stability of slides stored in water by utilizing vapor-phase silanization, although the surface still eventually broke down.

Menawat et al. (1984) presented two explanations for why contact angle decreased with time for treated slides stored in water: desorption of weakly adsorbed silane molecules, and hydrolysis. Desorption appears unlikely in this case because it occurred only in water, and not in air or Soltrol. Unreacted silanes adsorbed onto the glass surface should also be easily dissolved in Soltrol. Significant decreases in contact angles with time for treated slides stored in Soltrol were never observed, however. On the other hand, hydrolysis can occur in the presence of moisture as suggested by Menawat et al. (1984). This reaction would affect treated slides stored in water and, to some extent, moist air. If hydrolysis is the cause, deterioration should be minimized if all the silanol sites on the glass surface are reacted with silane. In this case water could not easily penetrate to the base of the silane to attack the Si-O-Si covalent bond. This implies that achieving different degrees of wettability by varying the amount of silane in the reaction may not be feasible for experiments in which longer-term stability is desired.

### Solid substrate

In one experiment, TMS was used to treat quartz and fused-silica slides in addition to glass slides. Results of this experiment are plotted in Figure 6. The sodalime, quartz, and silica slides were silanized in the same batch experiment and stored in water. Decrease in the advancing angle for all three types of solid substrate were similar, but with quartz and silica showing a slight minimum in advancing angle at about 300 hours.

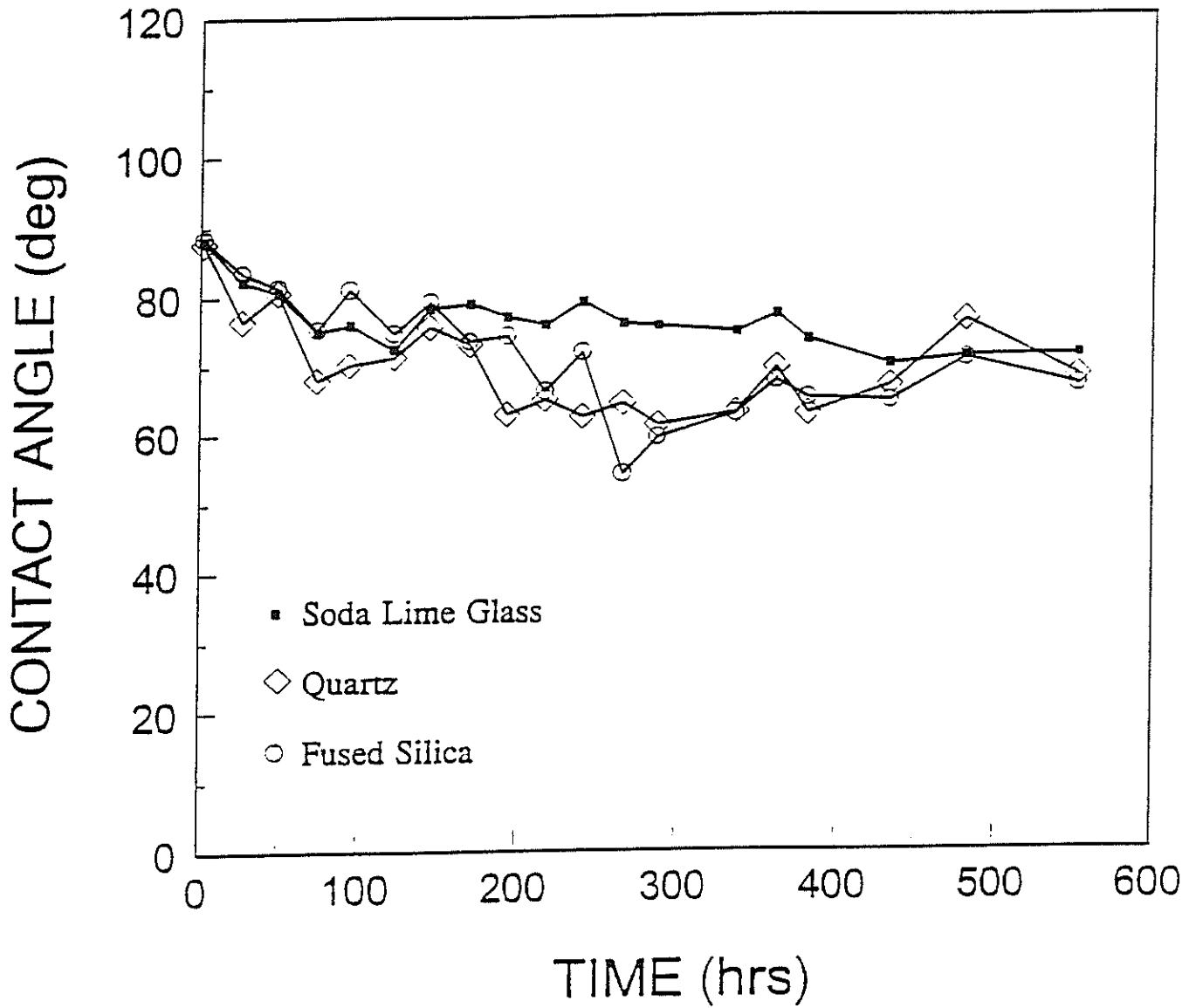


Figure 6. Advancing water-air contact angles for different TMS-treated substrates stored for different lengths of time in water.

## Bacterial Action

GC18- and OtS-treated slides were also stored in water without sodium azide. At the end of the storage period (approximately 1000 hr) microscopic examination revealed the presence of bacteria on the slides. Bacteria on GC18-treated slides were readily removed by washing and therefore judged to be only weakly (reversibly) attached to the solid surface. For OtS-treated slides, bacteria were more strongly (irreversibly) attached. Contact angle deterioration for these slides was essentially the same as for those stored in water with sodium azide. Thus, bacterial action was ruled out as a major cause of the observed deterioration.

## Organic liquid coating

In the experiments with tBDM and tBDP, some treated slides were coated with Soltrol 130 and then stored in water containing 1.0 g/L sodium azide. Comparison of results for the tBDP-treated with and without an organic film on them prior to storage is shown in Figure 7. The coating prolonged stability of the treated slides in water, although deterioration was still evident from the decrease in the receding angle and increase in contact angle hysteresis. The overall decrease in the advancing angle was minor ( $5^\circ$  over 950 hours) and significantly less than that observed for tBDP-treated slides with no coating ( $15^\circ$  over 950 hours). The overall decrease in the receding angle was just slightly less than for the uncoated tBDP-treated slides stored in water ( $23^\circ$  difference for the Soltrol 130 coated slides and  $25^\circ$  difference for the slides with no coating). However, the receding angle for the Soltrol 130-coated slides began to decrease at a much later time, after about 400 hours. Comparable behavior was observed for tBDM-treated slides (Wei 1991).

## Contact angle, $\theta$ , and interfacial tension, $\sigma$

The relationship between interfacial tension and wetting properties was tested using water:alcohol mixtures. Extrapolation to zero contact angle of linear plots of  $\cos \theta$  vs.  $\sigma$  are used to estimate critical surface tensions for spreading (Fox and Zisman 1950; Zisman 1964).

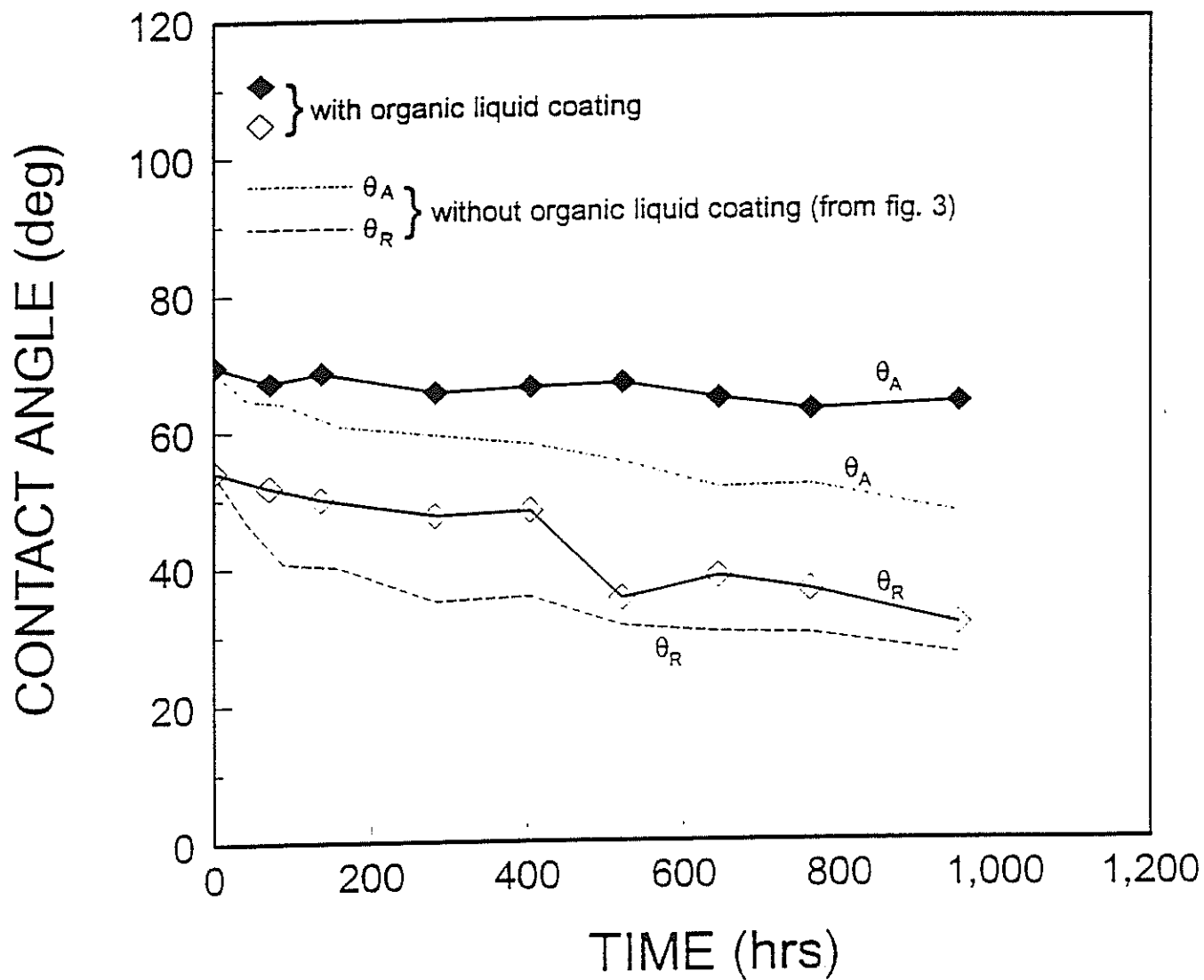


Figure 7. Advancing water-air contact angles for tBDP-treated glass slides coated with Soltrol 130 and stored for different lengths of time in water.

Non-spreading liquids have surface tensions above the critical surface tension of the solid and therefore exhibit a finite contact angle. Plots for tDBP-and GC18-treated slides are shown in Figure 8 for freshly treated slides and for treated slides after storage for about 1,000 hours in water with 1.0 g/L sodium azide. The plots are non-linear but show similar trends. Extrapolation of low contact angle results for freshly treated slides suggests critical surface tension estimates of 23 to 26 dynes/cm (Table 1). These values compare with the values of 28 dynes/cm for polyvinyl fluoride (Fox and Zisman 1950). The critical surface tension of 26 dynes/cm for GC18-treated slides is lower than the 31 dynes/cm reported in Petrarch Systems Silanes & Silicones (1987). This difference may be due to our repeated treatments. The contact angle was seen to increase to a constant value after successive treatment. Figure 8 also shows that surface deterioration is less apparent for lower surface tension. The critical surface tension appears to be insensitive to aging.

#### Comparison of air/water and oil/water contact angles

Contact angles measurements on freshly silanated glass slides were also made using the liquid pair of Soltrol-130 and water (Table 2). As with the air/water measurements, contact angles were measured through the aqueous phase. With Soltrol as the second phase rather than air, the surfaces were always more hydrophobic and there was larger hysteresis. The results permit comparison between air/water and oil/water contact angles for a given substrate.



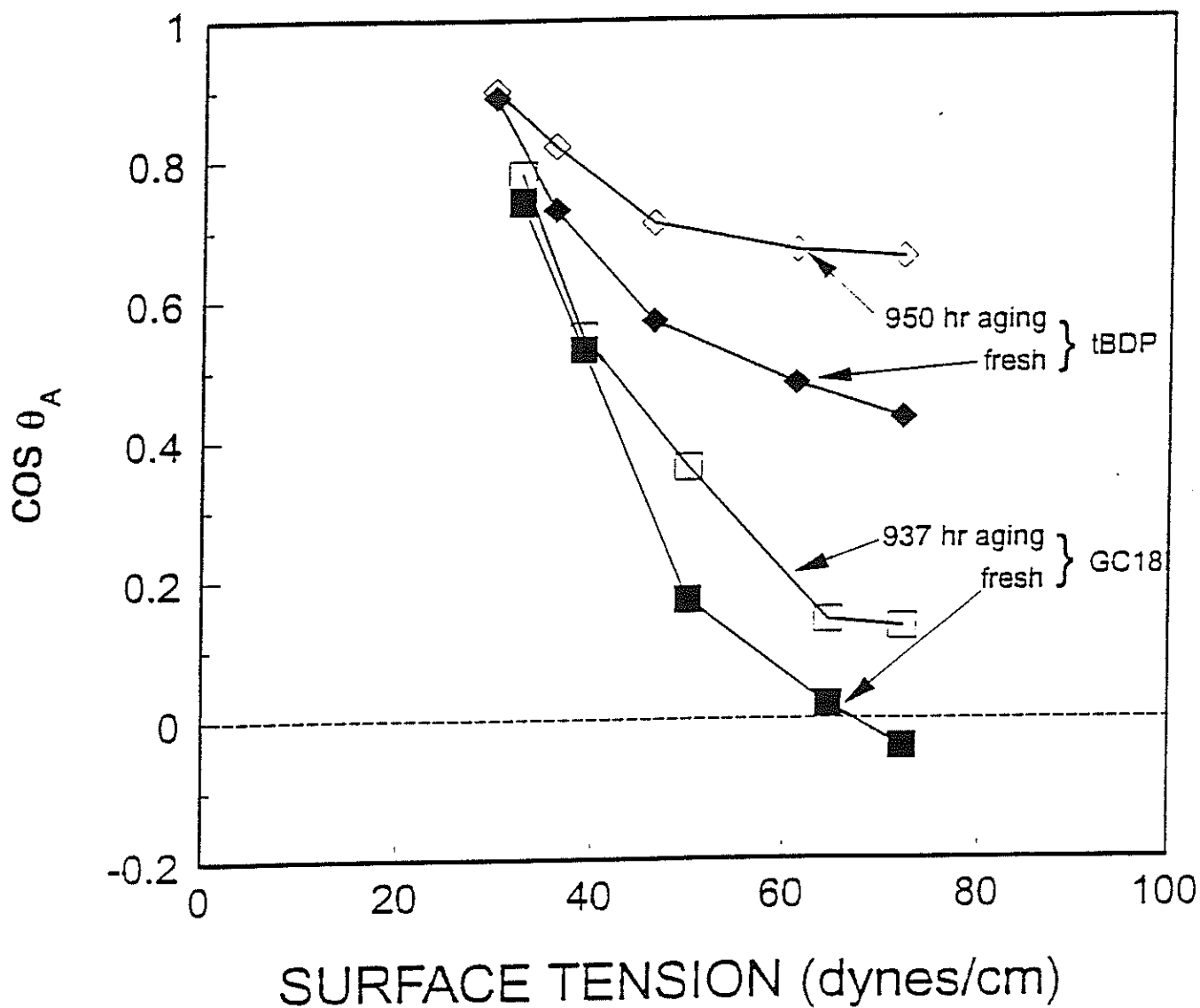


Figure 8.  $\text{Cos } \theta_A$  vs. interfacial tension for fresh and aged silanized surfaces stored in water (test liquids were water/methanol and water/ethanol mixtures).

**Table 2. Water-Soltrol 130 contact angles and contact angle hysteresis for freshly treated slides.**

<u>Silane</u>	<u>Advancing Angle(°)</u>	<u>Receding Angle(°)</u>	<u>Contact Angle Hysteresis(°)</u>
TMS	114.3 (7.2) <sup>a</sup>	nm <sup>b</sup>	-
tBDM	108.0 (2.7)	81.8 (7.8)	26.1 (7.0)
tBDP	98.1 (3.3)	81.3 (4.0)	16.8 (2.9)
GC18	151.4 (6.8)	119.8 (5.0)	31.6 (3.3)
OtS	nm	nm	-
Untreated Glass	43.5 (3.0)	19.9 (2.5)	23.6 (3.3)

<sup>a</sup>Values in parentheses are standard deviations of three to four replicate measurements.

<sup>b</sup>Not measured.

Plots of  $\cos \theta_{A(wa)}$  vs.  $\cos \theta_{A(wo)}$ , with standard deviations indicated by error bars, are presented in Figure 9. Corresponding plots for receding angles are presented in Figure 10. Both sets of data are remarkably linear with the receding angles having somewhat higher slope. Results of this form indicate that the silane treatments provide a series of surfaces that show consistent relationships in wetting properties when tested with different pairs of fluids.

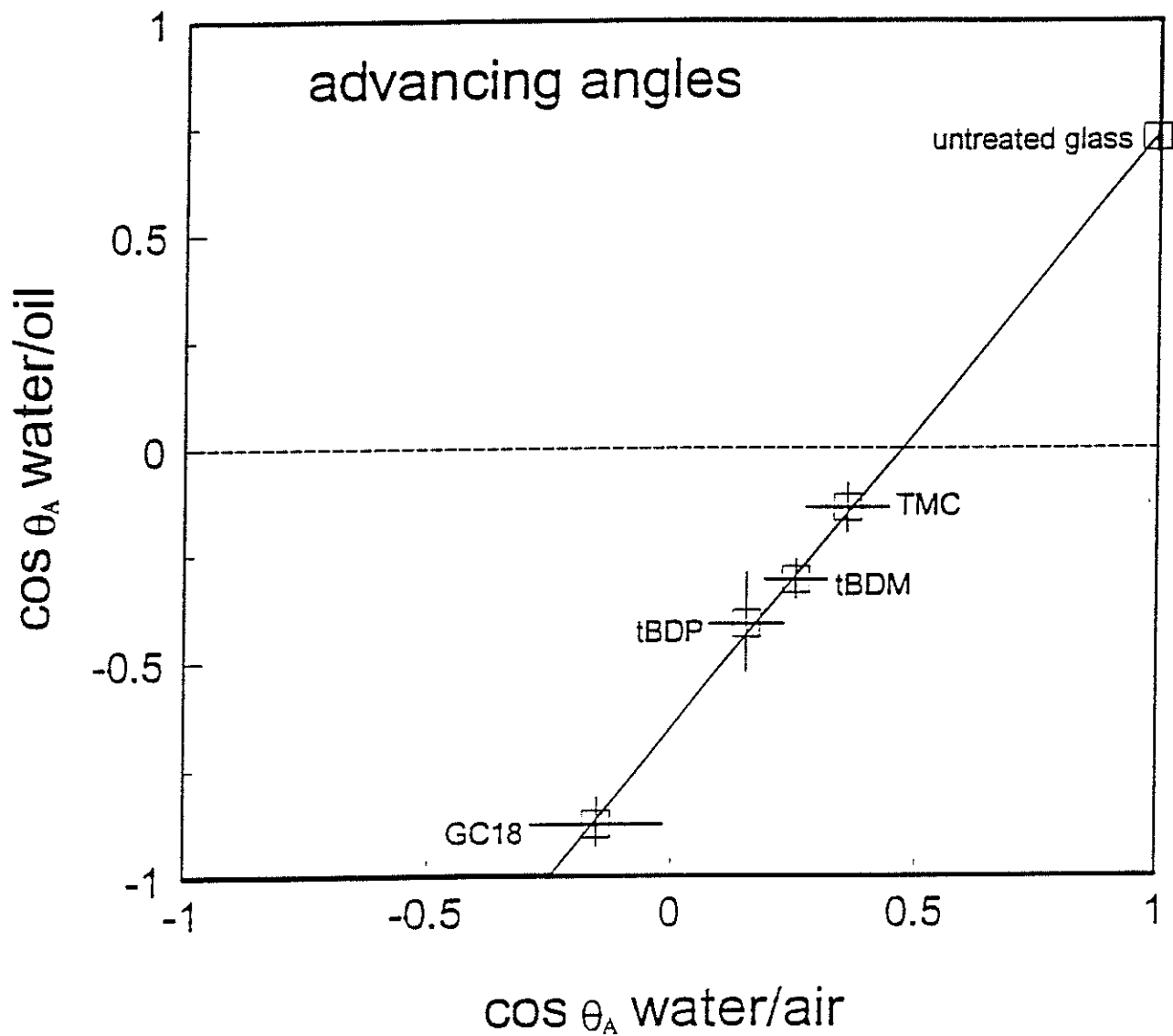


Figure 9. Cosine of advancing water/oil contact angle vs. cosine of advancing water/air contact angles for untreated and silanized surfaces (angles are measured through the water phase).

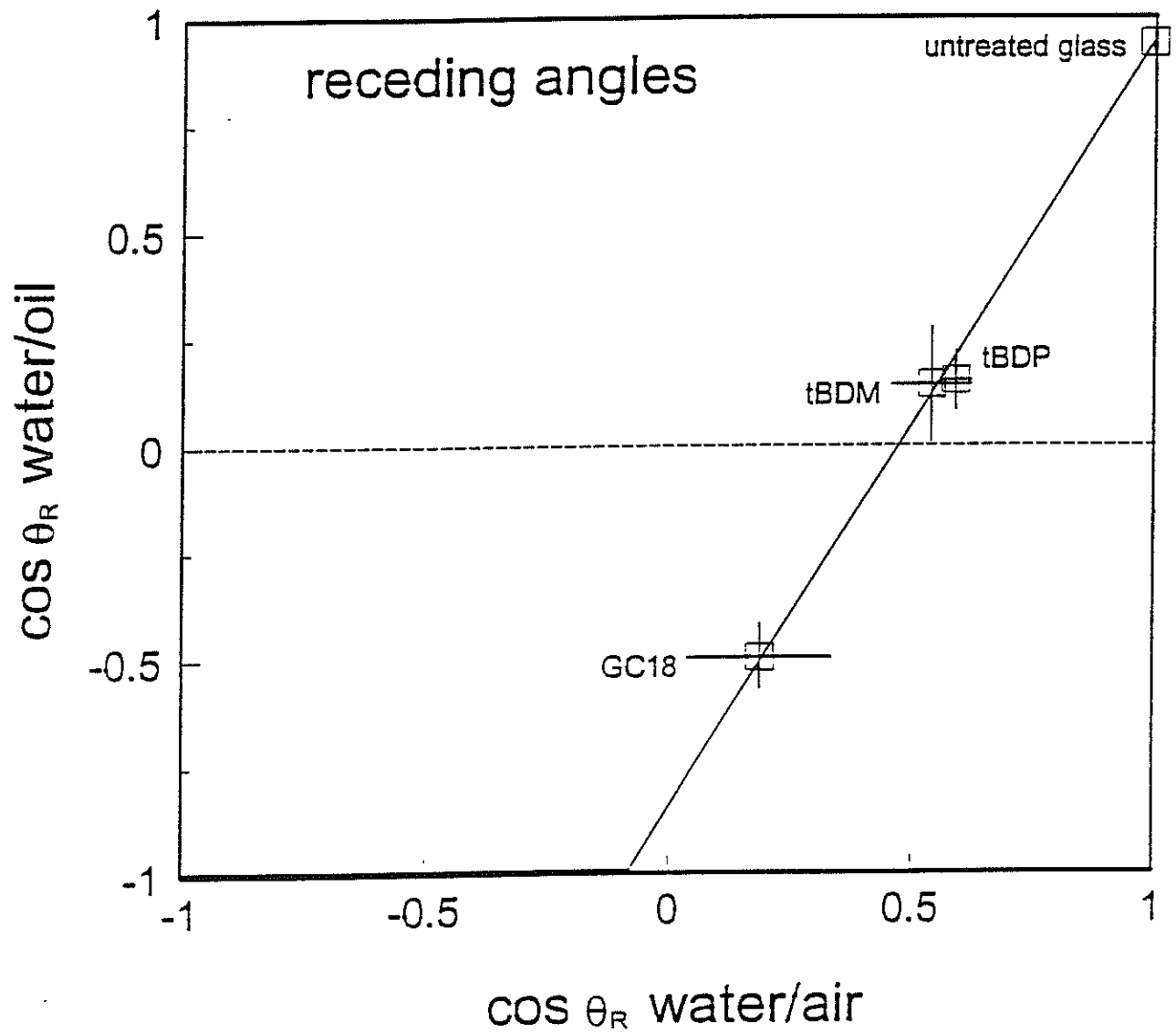


Figure 10. Cosine of receding water/oil contact angle vs. cosine of receding water/air contact angles for untreated and silanized surfaces (angles are measured through the water phase).

## Effect of wetting on capillarity and non-aqueous phase liquid saturations in homogeneous porous media

### Results of the bead pack columns

Typical capillary pressure-saturation relationships for untreated and GC18-treated beads are presented in Figures 11 and 12. Other figures relevant to the following discussion are presented in Wei (1991) and are not repeated here.

The values of porosity (Table 3) indicated a random bead packing arrangement. The small variability of the bulk density and porosity values suggest the packing was consistent among columns.

**Table 3. Summary of Column Experiments with Untreated Beads**

Glass Bead Pack	Bulk Density (g/cc)	Porosity	IWS (% Water)	ROS (% Soltrol)
untreated <sup>a</sup>	1.582	0.357	7.4	17.2
untreated <sup>a</sup>	1.585	0.356	6.1	16.8
untreated <sup>b</sup>	1.555	0.370	10.5	12.9
<b>Average</b>	<b>1.574+/-0.017</b>	<b>0.361+/-0.008</b>	<b>8.0+/-1.6</b>	<b>15.6+/-1.7</b>

a = conventional column; b = dual-filter column

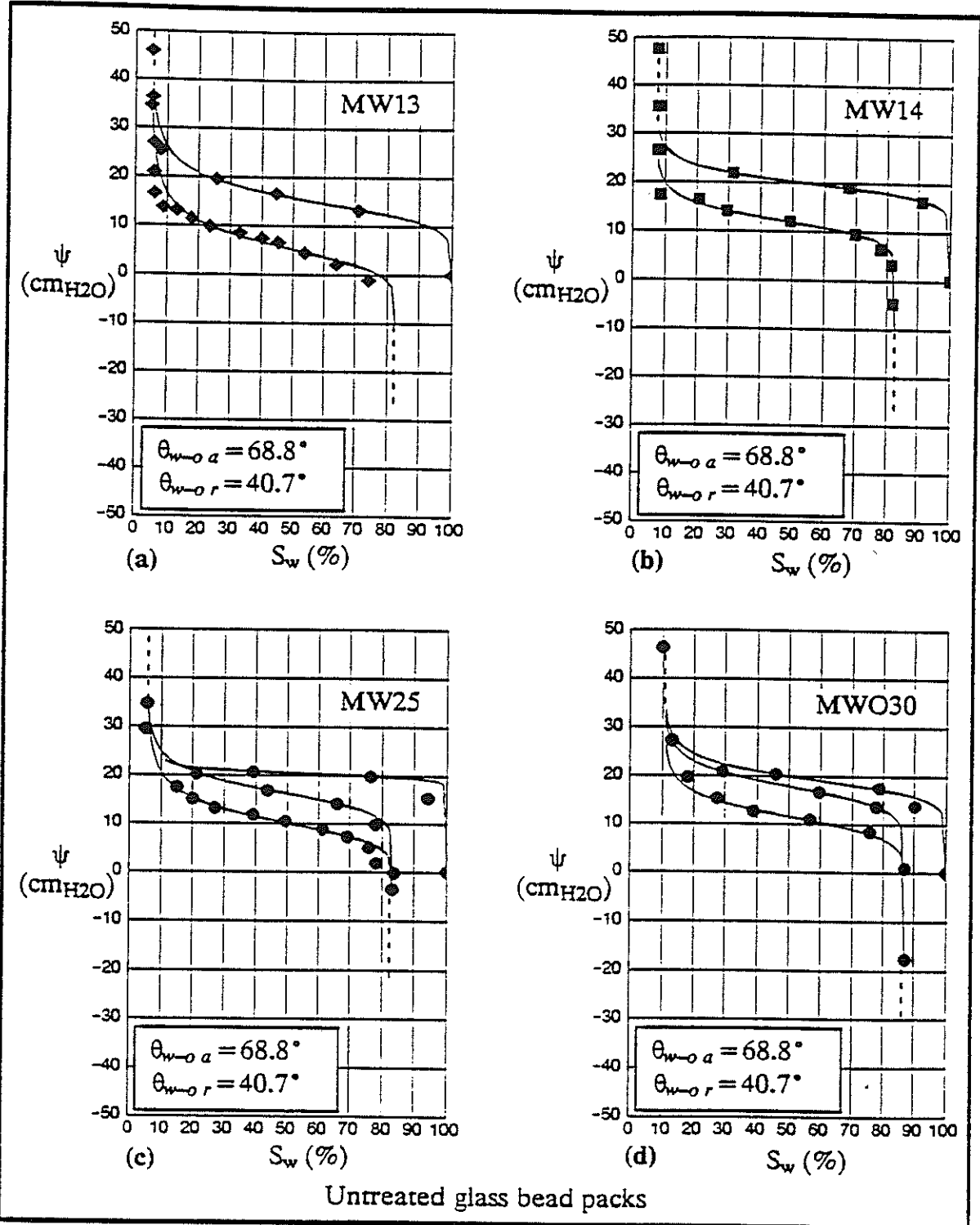


Figure 11. Water saturation-capillary pressure data for untreated beads.

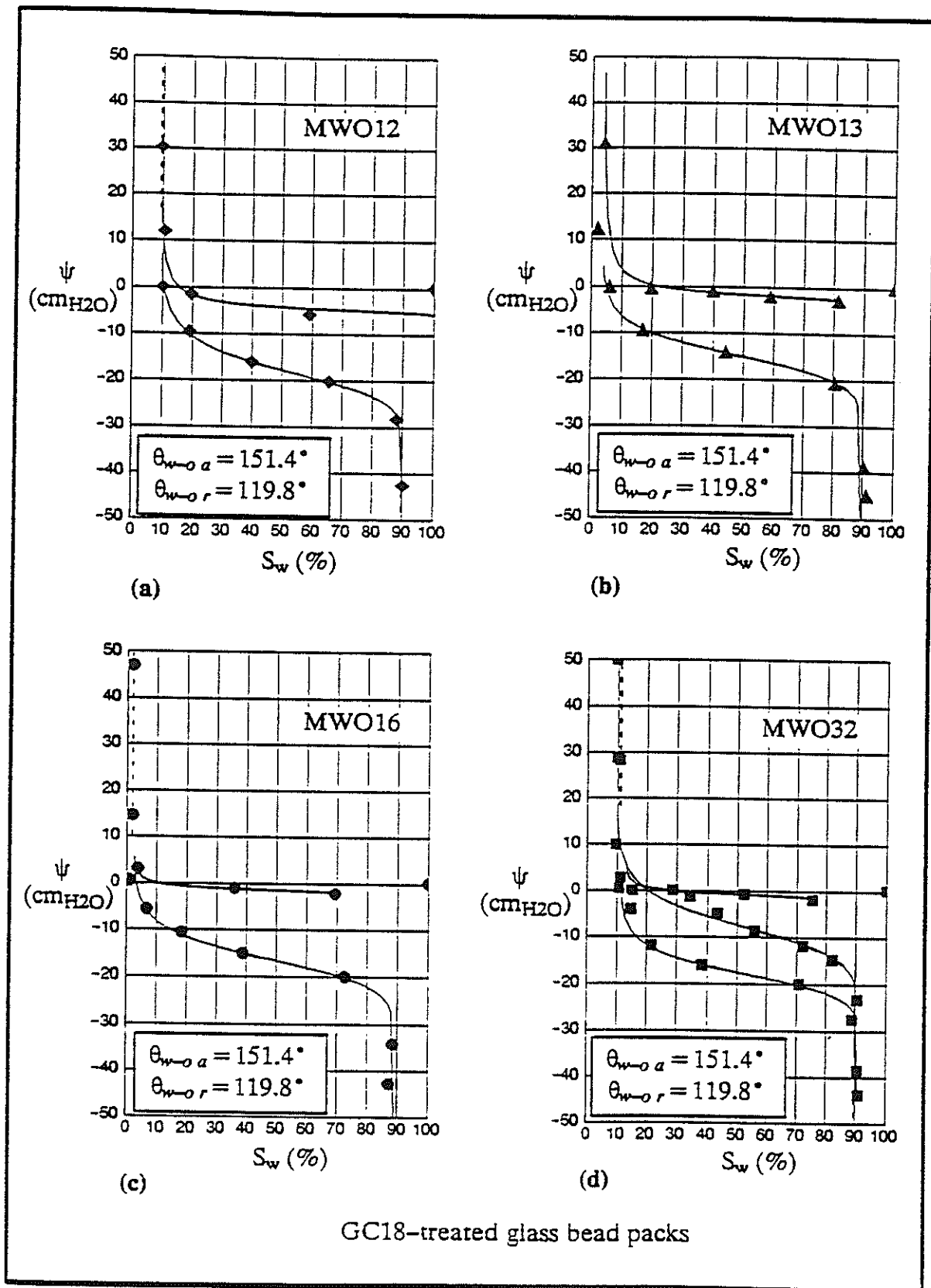


Figure 12. Water saturation-capillary pressure data for GC-18 treated beads.

**Table 4. Summary of Dual-Filter Column Experiments with GC18-Treated Beads**

Glass Bead Pack	Bulk Density (g/cc)	Porosity	IWS (% Water)	ROS (% Soltrol)
GC18-treated <sup>a</sup>	1.636	0.338	9.3	9.9
GC18-treated <sup>a</sup>	1.604	0.351	3.7	10.4
GC18-treated <sup>a</sup>	1.628	0.341	2.3	10.9
GC18-treated <sup>a</sup>	1.614	0.347	11.3	9.1
<b>Average</b>	1.621 +/- 0.014	0.344 +/- 0.006	6.6 +/- 4.3	10.1 +/- 0.7

a = dual-filter column



## Untreated Beads

Primary displacement of water by Soltrol was not spontaneous; an entry pressure of about 12 cm of water was required for Soltrol to begin displacing water. Irreducible water saturation was reached above 30 cm of water. Conversely, primary displacement of Soltrol by water was spontaneous; water began imbibing into the beads to displace Soltrol at about 22 cm. Residual oil saturation was reached just above 0 cm. Secondary displacement of water by Soltrol, as with primary displacement of water by Soltrol, was not spontaneous. Capillary behavior of the untreated beads shows that the system was water-wet.

The value of IWS (8.0% +/- 1.6% water; Table 3) is consistent with values measured by others in spherical bead packs using other pairs of immiscible fluids (Morrow et al 1988; Laroussi and De Backer 1979; Morrow 1970; Topp and Miller 1966; Brooks and Corey 1964; Haines 1930). The mean value of ROS for untreated beads (15.6% +/- 1.7% Soltrol; Table 4) is similar to the value of residual non-wetting phase saturation reported by Morrow et al. (1988), Topp and Miller (1966), and Haines (1930). The value of ROS for the one dual-filter column is slightly lower than the ROS for the conventional columns. This slight discrepancy in the ROS may be attributed to larger errors in estimating the effective volume of the column ( $V_{ce}$ ) for the dual-filter column (Wei 1991).

## GC18-Treated Beads

Capillary behavior was reversed from the untreated beads. Primary displacement of water by Soltrol was spontaneous; no entry pressure was required for Soltrol to displace water. The slight negative capillary pressure during primary displacement suggests that Soltrol has a slight tendency to imbibe into the treated beads to displace water. Irreducible water saturation was reached at below 10 cm, much lower than for the untreated beads. Unlike in the untreated beads, primary displacement of Soltrol by water was not spontaneous and did not begin until the capillary pressure reached about -5 cm compared to 22 cm in the untreated beads. Residual oil saturation was reached below -25 cm. Secondary displacement of water by Soltrol, as with primary displacement of water by Soltrol, was spontaneous; displacement began at -20 cm .

In general, capillary pressures during each displacement sequence were lower than in the corresponding displacement sequence in the untreated beads. Lower capillary pressures reflected a decrease in the curvature of the water/oil interface. Negative capillary pressures measured for GC18-treated beads imply that the curvature of the interface was reversed. The spontaneity of the displacement processes was reversed from the untreated case and indicate that the treated beads were oil-wet.

Analogous capillary pressure-saturation data for oil-wet spherical bead packs could not be found in the literature. Capillary pressure-saturation data from Haines' (1930) experiment were used to test if scaling by cosine of the contact angle could explain the results in the GC18-treated beads (Wei 1991).

Primary displacement of Soltrol by water for GC18-treated beads corresponds with secondary displacement of water by air for Haines' experiment; both processes represent displacement of the wetting liquid by the non-wetting liquid from residual non-wetting liquid saturation. Secondary displacement of water by Soltrol for GC18-treated beads corresponds with primary displacement of air by water for Haines' experiment. Primary displacement of water by

Soltrol for GC18-treated beads had no equivalent for untreated beads that were initially completely water-saturated.

Capillary pressures from secondary displacement for the untreated beads in Haines' experiment were scaled using the cosine of the advancing water-Soltrol contact angle ( $151.4^\circ$ ) to simulate the primary displacement of Soltrol by water in GC18-treated beads (Figure 13). Likewise, scaled pressures from primary displacement of the non-wetting phase by the wetting phase for Haines' experiment were scaled by the cosine of the receding water-Soltrol contact angle ( $119.8^\circ$ ) simulating secondary displacement of water by Soltrol (Figure 13).

The simulated curves and actual data are plotted as saturation of the wetting phase,  $S_w$  (Figure 13). Results show that primary displacement of Soltrol by water in the GC18-treated beads could be reproduced accurately, lending credibility to the capillary pressures measured in GC18-treated beads. Secondary displacement could not be as closely reproduced; predicted pressures were generally higher than measured capillary pressures. This discrepancy suggests that, for this simple system, scaling by  $\cos \theta$  may be valid only for predicting pressures from one strongly wetted condition to the other (close to  $0^\circ$  and  $180^\circ$ ) and not for intermediate wettability conditions (Demond and Roberts 1991).

The value of IWS in GC18-treated beads, averaged from four trials, was  $6.6\% \pm 4.3\%$  (Table 4). Although this value was similar to the IWS value for untreated beads, the variation was greater. Morrow (1970) found experimentally that the irreducible wetting-phase saturation was insensitive for contact angles between  $0^\circ$  and  $108^\circ$  and is about 7%. The values of IWS here are consistent with his conclusions (Table 4). The receding contact angle of Soltrol displacing water in GC18-treated glass was  $119.8^\circ \pm 5.0^\circ$ , just beyond the range covered by Morrow (1970). The mean ROS of  $10.1\% \pm 0.7\%$  for GC18-treated beads is lower than the mean ROS in untreated beads (Table 4). ROS in treated and untreated beads may be more directly comparable if experiments were all conducted with the dual-filter column.

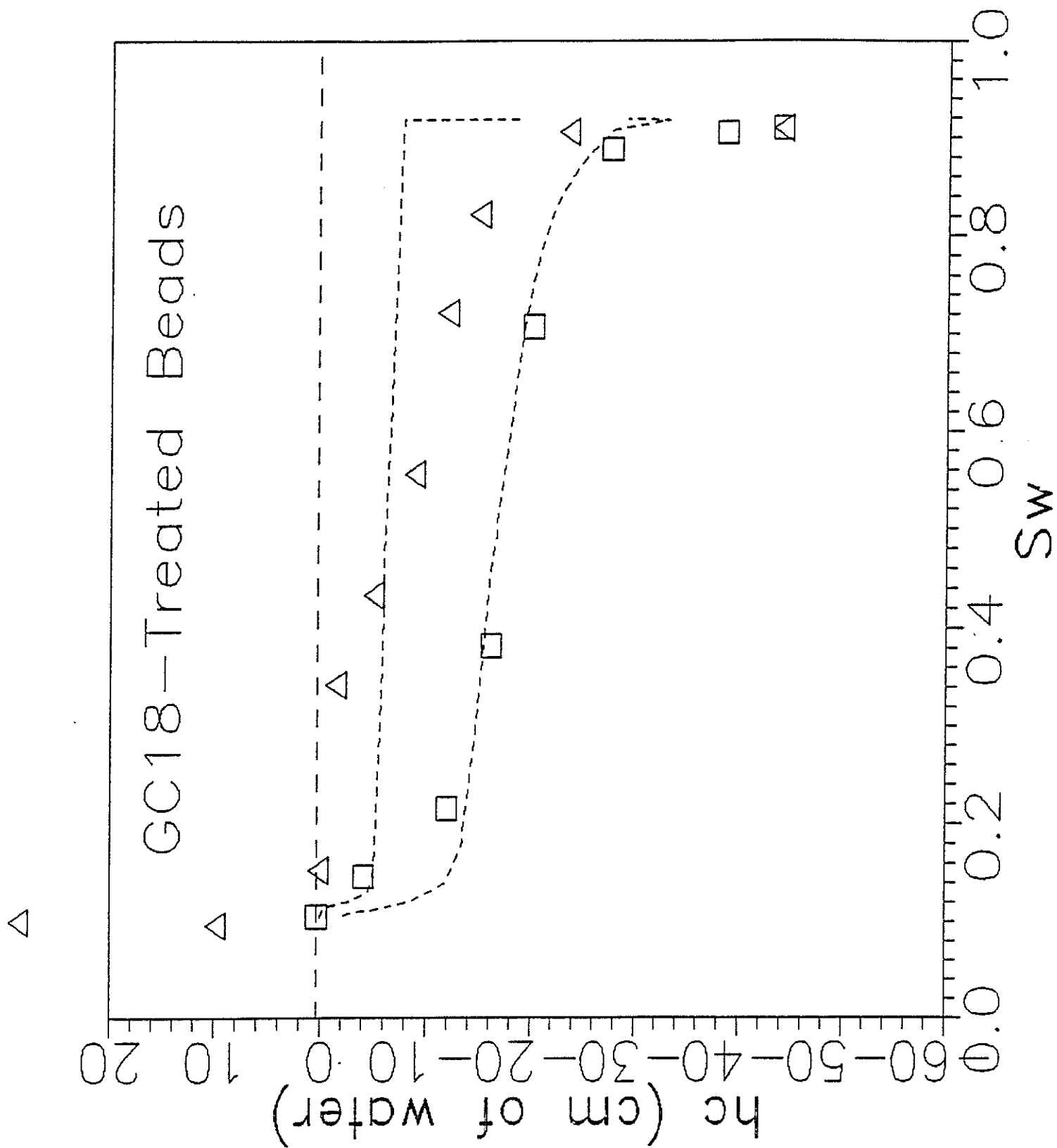


Figure 13. Scaling Haixes' capillary pressure-saturation data by the cosine of the contact angle (dashed line) to predict capillary pressures for the GC-18-treated bead pack (symbols).

## Implications for NAPL Contamination

Column experiment results indicate that wettability alteration could have implications in NAPL distribution beneath hazardous waste sites and subsequent design for NAPL remediation. In an aquifer rendered hydrophobic by adsorption of polar organic compounds, free NAPL product could more easily move into the aquifer because the entry pressure for NAPL would be lower. The location of residual NAPL in the pores would differ, however. NAPL may be preferentially trapped in finer grained lenses under oil-wet conditions as opposed to in coarser grained lenses under the normally assumed water-wet conditions.

## **SURFACE MODIFICATION OF NATURAL ZEOLITE**

### **XRD and SEM results**

Sample mineralogical data provided by Leonard Minerals indicated that the zeolite sample mineralogy was approximately 60% clinoptilolite, 20% montmorillonite, 15% amorphous material, and the remainder carbonates and other materials. The Bureau of Mines XRD analysis of the bulk sample confirmed this analysis, although the amorphous materials were not well identified on the XRD output. Dr. Doug Ming, currently of NASA, has extensively studied the Tilden deposit and other zeolites, and has found that acid pretreatments such as the one we used to remove carbonates will often mask the presence of amorphous materials (personal communication, 1989). Analysis of the  $<2\mu\text{m}$  fraction, however, indicated this particle range was primarily smectite minerals ( $\sim 80\%$ ), with the remainder clinoptilolite. Ming (personal communication, 1989) conducted XRD analyses on a range of sizes of the Tilden clinoptilolite, and confirms that the smaller particle sizes are predominantly smectite minerals, while the larger particle sizes contain higher percentages of clinoptilolite.

Scanning electron microscope photography failed to reveal crystalline zeolitic surfaces. The material appears to be mineral aggregates of zeolite cemented with smectite minerals and amorphous materials.

It was noticed during the course of the research that zeolite aggregates often mechanically broke down into smaller particles upon agitation. Apparently, some of the clay minerals are poorly cemented to the aggregates, and can be dislodged when the material is shaken for a prolonged period of time (> 24 hours). In addition, treatment with HDTMA cations resulted in a finer particle size than initially added... It is theorized that the HDTMA cations enter into the interlamellar spaces of the smectites, and upon sorption force the layers apart. A corresponding widening of layer spacing has been documented by other researchers doing XRD analysis of treated clay minerals (Cowan and White 1962). As the cations can force apart clay layers of a single mineral, these cations may also force apart adjacent clay plates, inducing a dispersing effect, and thus resulting in a smaller particle size. This dispersing effect appears to be primarily mechanical in nature; that is, the mineral chemistry is not changed except that the surface is saturated with organic rather than inorganic cations, so the resulting smaller particle size does not change the sample characteristics. The exchange of the organic cation may, however, result in an increased available surface area for sorption.

### **CEC results**

Results of the bulk sample CEC indicated a total CEC of approximately 60 me/100 g, an internal CEC (zeolitic internal channels) of approximately 30 me/100 g, and an external CEC (smectite CEC and external zeolite surface CEC) of approximately 30 me/100 g. These values are significantly lower than the CECs reported by others for different subsamples of the Tilden zeolite. The Leonard Minerals data indicated a total CEC of approximately 160 me/100 g. Data from Ming (personal communication 1989) indicated a CEC of 90-120 me/100 g, and data from Haggerty (personal communication 1990) indicated a total CEC of approximately 40 me/100 g.

These differences may be explained in part by differences in CEC measurement methodology. Methods used for this research followed those of Rhoades (1982). This method is essentially a sodium saturation of exchange sites, followed by sodium replacement by

magnesium. The method used by Leonard Minerals was an ammonium acetate exchange, whereby exchange sites were saturated with sodium, followed by replacement with ammonium. This method may often result in an overestimation of CEC, especially in zeolitic minerals, where ammonium may extract nonexchangeable sodium from the zeolite structure (Polemio and Rhoades 1977). Conversely, an exchange of magnesium for sodium, as is done in the Rhoades method, may result in an underestimation of CEC, since sodium is preferred greatly by clinoptilolite over magnesium (Ming and Mumpton 1989), and therefore Mg exchange for Na may be incomplete. In addition, sodium saturation of exchange sites may be incomplete, since some common exchangeable cations, particularly potassium and calcium, are preferred greatly over sodium (Ming and Dixon 1987a). The method used by Ming was a potassium/cesium exchange, whereby exchange sites were saturated with potassium, then replaced with cesium. This method should be very accurate, since both potassium and cesium are preferred strongly by clinoptilolite (Ming and Dixon 1987a).

Although these differences in CEC measurement methodology may contribute to small errors in sample CECs, it is not likely that more than a factor of four (40-160 me/100g) is due to simple method variations. More likely is that the mineralogy of the deposit varies spatially, and the sample location will affect its mineralogical and thus CEC properties. This is further supported by the fact that in this study, two different methods were used to determine CEC, one for the total CEC and one for the internal and external CEC. Both these methods gave comparable results.

### **Organic cation sorption isotherms**

Sorption isotherms for HDTMA and MPP exchange to the zeolite are presented as Figures 14 and 15, respectively. These isotherms are classical Type H isotherms, indicating the sorbent has a strong preference for the sorbate up to a certain point, after which point the sorption

capacity is essentially satisfied and sorption decreases significantly or ceases (Giles et al. 1974). In these cases the point at which sorption begins to decrease is very near the sorbent's external CEC. At concentrations beyond the external CEC, the figures clearly show that HDTMA is much more strongly sorbed than MPP, but that sorption continues to as much as 2.5 times the external CEC for MPP and up to 7.5-times the external CEC for HDTMA. Duplicate agreement was poor at very high cation concentrations.

The poor duplicate agreement may be due in part to the type of bonding that occurs at concentrations greater than the sample CEC. At organic cation concentrations above the CEC, hydrophobic tails of the large cations in solution may sorb to the hydrophobic ends of cations already bound to the mineral surface. Some researchers have referred to this type of bonding as "hydrophobic bonding" (Hamaker and Thompson 1972; Mortland 1986), whereby the hydrophobic tails of organic molecules associate with each other as a result of both weak van der Waals forces between organic chains and an entropy driven effect, as discussed in section II. However, in the case of organic cations, perhaps a more accurate term describing the type of bonding that occurs is "amphipathic adsorption" (Black 1989). An amphipathic molecule is one having both a polar and nonpolar functional group. In the case of these large organic cations, the polar group is the charged quaternary ammonium end, and the nonpolar group is the long organic chain. Amphipathic adsorption occurs when the long hydrophobic tail is oriented away from the water and toward the mineral surface, with the polar group oriented toward the water.

Thus, two completely different sorption mechanisms operate, depending on whether the organic cation concentration is above or below the sorbent's CEC. At cation concentrations below the external CEC, sorption is via cation-exchange. The large cation simply replaces the smaller inorganic cations saturating surface exchange sites, oriented with the positive end toward the mineral surface, to satisfy the surface charge imbalance. This type of sorption results in an



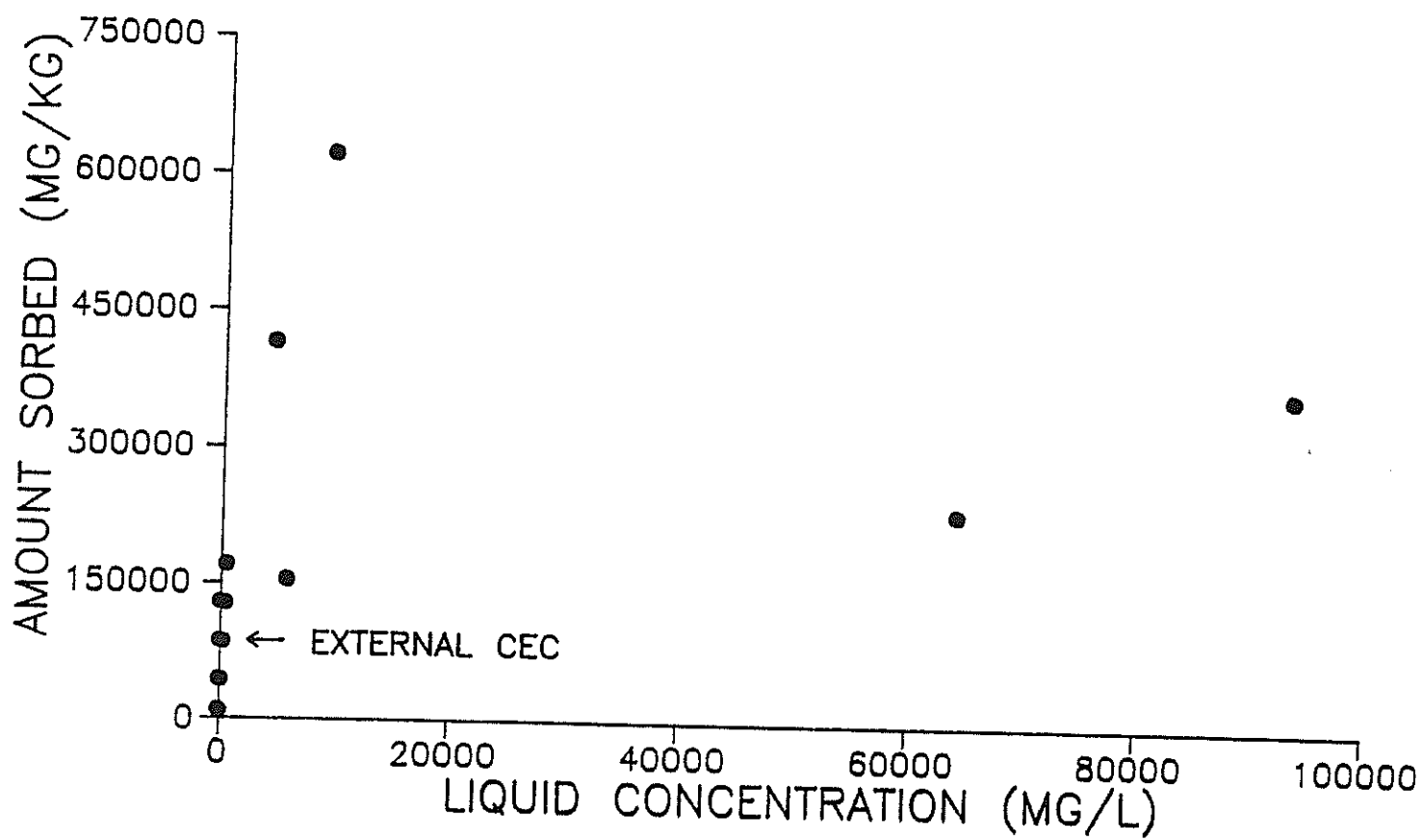


Figure 14. HDTMA Sorption to Zeolite

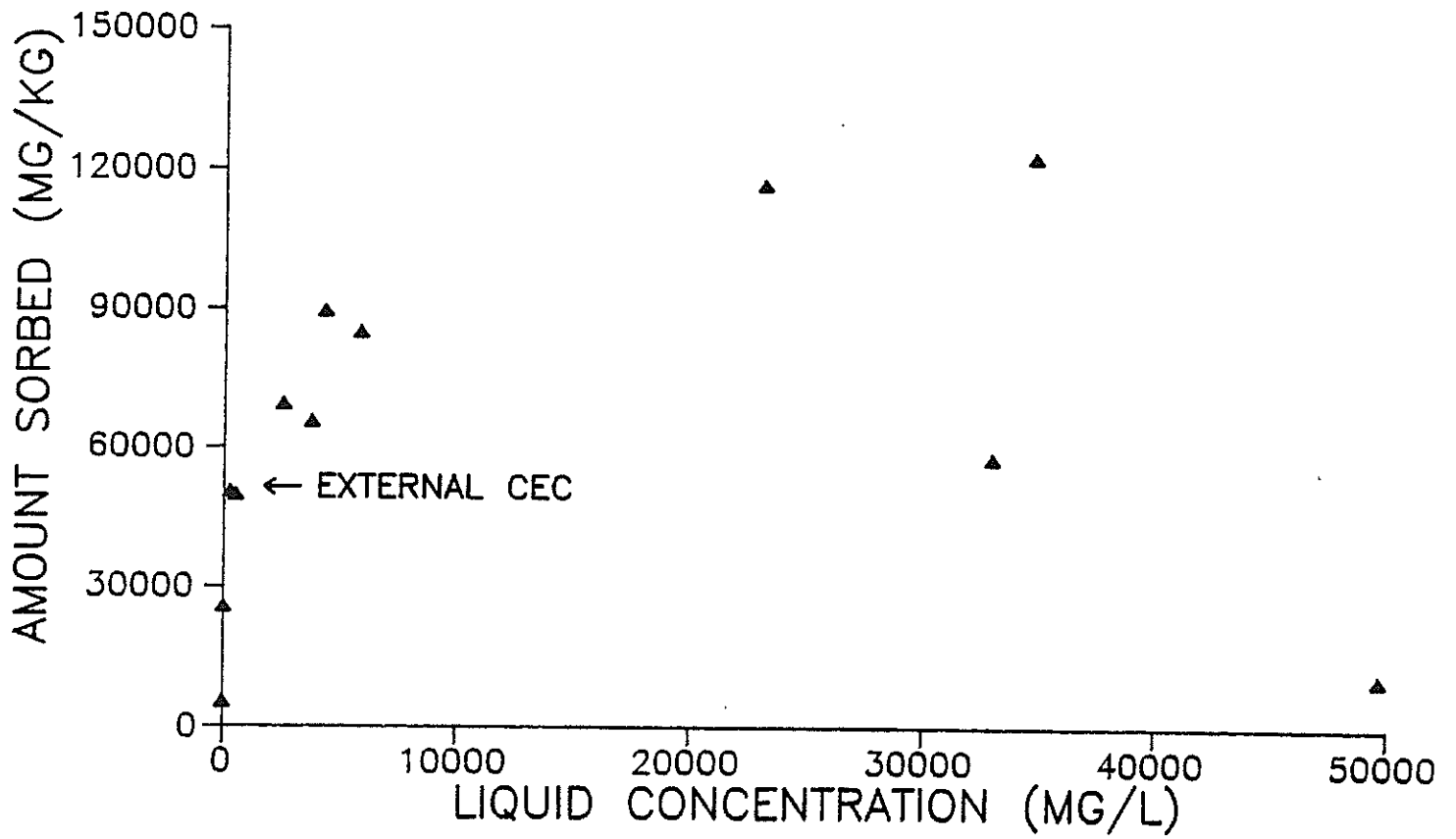


Figure 15. MPP Sorption to Zeolite

ionically balanced mineral surface that has long organic chains extending out into the solution, and thus imparting hydrophobic properties to the surface.

Once the external CEC is met, molecules can no longer orient themselves with the positive end toward the mineral surface, because there is no counterbalancing negative charge to maintain the charge balance. However, amphipathic adsorption does take place, presumably entropy driven by the disintegration of the rigid water structure surrounding the hydrophobic tails. In this case, the molecule orientation is reversed. The hydrophobic tails orient themselves toward the mineral surface, which is saturated with other hydrophobic tails, and the positive quaternary ammonium cation is oriented toward the solution. If the surface-saturating hydrophobic tails create an essentially continuous organic medium, the amphipathic sorption may more nearly behave as partitioning. However, because this type of partitioning is not necessarily exothermic, and may be only weakly favorable thermodynamically (Chiou et al. 1979), it may not necessarily occur consistently and reproducibly. In addition, steric hinderances of these large organic cations, which, once sorbed, block other potential amphipathic adsorption sites, may contribute to the poorly reproducible nature of high concentration sorption. In any case, these sorption isotherms show that the organic cations are quantitatively sorbed at concentrations up to the CEC, and that sorption can occur at concentrations well above the sorbent CEC.

### **Organic carbon content**

The second method used to quantify the extent of surface modification was via organic carbon content on the modified zeolite. The results showed that HDTMA zeolite had an organic carbon content of 6.33% (by weight), and MPP zeolite had an organic carbon content of 3.80%. Comparing these results to the theoretical zeolite organic carbon content at 100% organic cation exchange efficiency showed 99% and 91.8% exchange efficiency of HDTMA and MPP ions, respectively. The values disagree slightly with the values determined from the sorption isotherms primarily because of the different methods employed for each of the carbon loading

determinations ( $^{14}\text{C}$  vs. carbon oxidation). Nonetheless, the organic carbon analysis confirmed that the organic carbon increased significantly over the untreated zeolite, which had a measured organic carbon content of 0.16%.

### **Quantification of modified surface stability**

Equilibrium desorption of the surface-altering organic cation was reached in almost every case after four hours, the shortest time increment evaluated. Figure 16 is representative of the pattern shown by the HDTMA and MPP zeolites in essentially all the solutions evaluated. The figure shows equilibrium was reached within four hours, slightly more MPP desorption than HDTMA desorption, and excellent duplicate agreement (duplicate points at each time are plotted).

The results indicated that the HDTMA zeolite was stable over a range of pHs, in all the inorganic salt solutions, in benzene, and in soltrol, with over 99% of the original HDTMA loading retained on the zeolite after equilibrium (Huddleston, 1990). In methanol, however, almost 9% of the HDTMA was removed. The reasons for this are unclear; however, this experiment was repeated with nearly identical results, so it is unlikely that experimental error was to blame. This result is consistent with results found by Jordan (1963). As Jordan proposed, this amount of desorption may represent only weakly amphipathically bonded HDTMA rather than an actual desorption of surface-exchanged ions.

In the organic salt solutions, TMA caused only a small amount of HDTMA desorption, and only very high concentrations of PTMA caused a significant amount of HDTMA desorption. MPP was not very effective at competing with HDTMA for surface sorption sites once the HDTMA ion was sorbed.

Comparison of MPP desorption in the same solutions showed that in general, approximately one-half to one percent more MPP cations than HDTMA ions were removed at equilibrium (Huddleston, 1990). This indicates that MPP was not quite as strongly bound to the

FIGURE 4-4. ORGANIC CATION DESORPTION.  
pH 3.02 SOLUTION

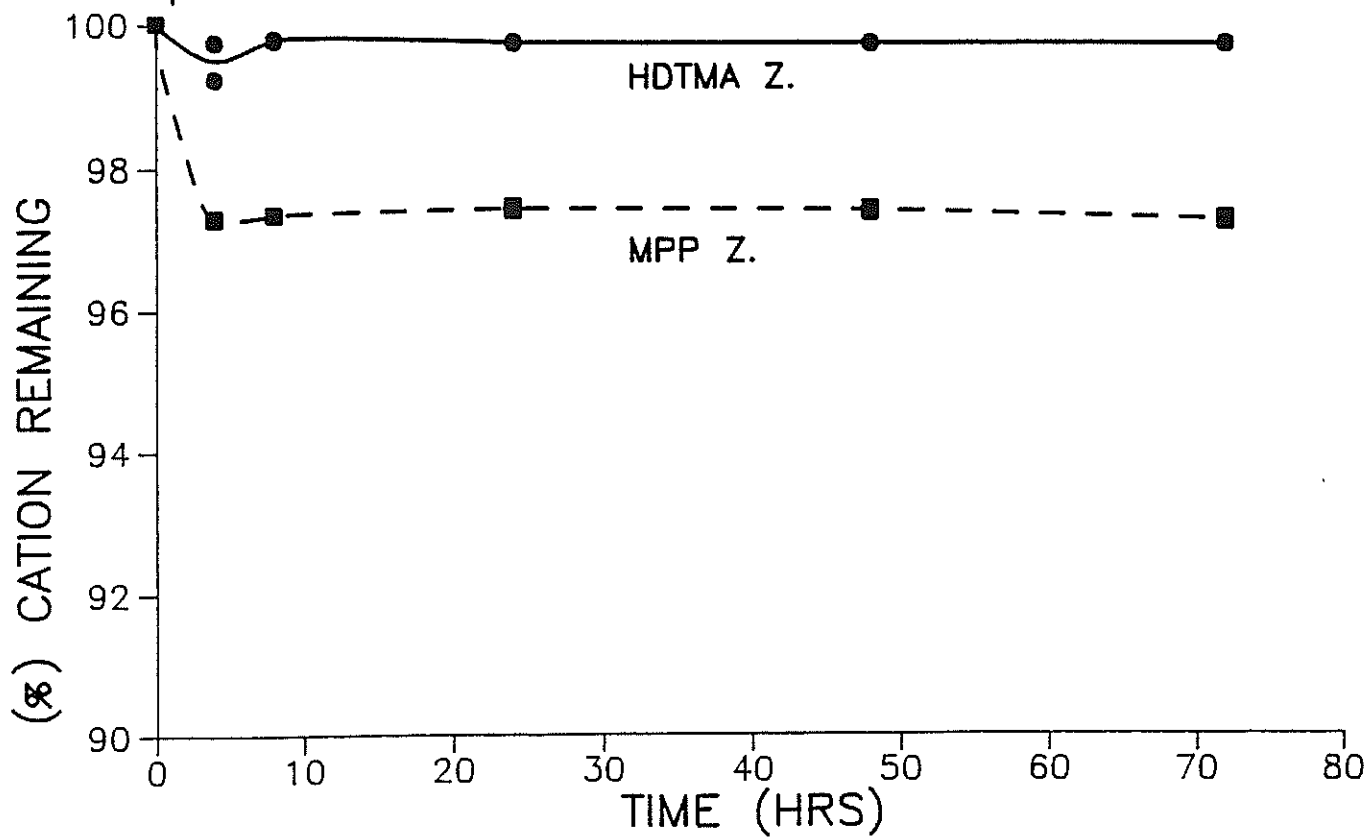


Figure 16. Organic Cation Desorption

zeolite surface as HDTMA was. There are some minor differences in the desorption behavior of the two surface-altering agents. For instance, essentially no MPP was removed in methanol. However, MPP was removed by almost 10% in the most concentrated cesium chloride solution. At the zeolite mass and solution volume used, a concentration of 0.15 moles/L of charge was equivalent to the external CEC. Therefore, an amount of cesium in large excess of the CEC was required to affect a 10% desorption of MPP. Similar trends were seen with the other organic cations. While MPP replacement by PTMA was essentially the same as that for HDTMA, high concentrations of TMA were somewhat more effective at replacing MPP than HDTMA. In addition, HDTMA was effective at replacing almost 25% of the sorbed MPP ions.

In summary, the data showed that equilibrium desorption of sorbed organic cations was reached within a few hours. HDTMA was slightly more strongly sorbed than MPP ions; however, generally an extreme excess of cations over the external CEC was required to affect as much as a 10% removal of the originally sorbed organic cation. Other large organic cations, however, were slightly more effective than inorganic cations at replacing the sorbed organic cations, especially at the high concentrations. The relatively high desorption of HDTMA in methanol cannot be fully explained at this time.

### **Quantification of organic solute sorption of modified zeolites**

Organic solute sorption isotherms for each zeolite-solvent combination are presented in Huddleston (1990) and are not repeated here. A representative isotherm for PCE sorption on untreated, HDTMA-treated, and MPP-treated zeolite is shown in Figure 17. An assessment of basic isotherm shapes and characteristics reveals several general trends. Phenol isotherms were nonlinear, and covered a much larger concentration range than Eben, PCE, or TCA. The latter three solutes all showed very linear sorption isotherms. While Ph was slightly sorbed from benzene and methanol, the other solutes are not sorbed at all from the organic solvents.

These differences in sorption isotherm shapes can be explained largely in terms of different properties between Ph and the other solutes. Specifically, the hydroxyl group of Ph imparts several properties absent in the other compounds. The hydroxyl group not only contributes to the strong dipole moment of Ph, but also allows the molecule to enter into hydrogen-bonding type of interactions. While TCA has a dipole moment approaching that of Ph (1.57 vs. 1.70 debyes, respectively), TCA has little propensity for hydrogen bonding interactions. Eben and PCE are both essentially nonpolar, so they will not enter into hydrogen bonding associations or ion-dipole type interactions. Because of the Ph hydroxyl group and the accompanying hydrogen bonding, Ph is much more soluble in aqueous solutions than the other molecules, and therefore the range of solution concentrations evaluated for Ph spanned two and a half orders of magnitude more than all the other solutes. Because of these differences in properties, solubility, concentration range evaluated, and isotherm shape, phenol behavior differed both qualitatively and quantitatively from the other three solutes. A detailed discussion of the reasons for these differences is provided in Huddleston (1990).

#### Estimates of $K_{oc}$ from solute properties

Many researchers have noticed an empirical correlation between solute properties and the organic-carbon-based partition coefficient ( $K_{oc}$ ) among structurally similar compounds. Specifically, correlations between aqueous solubility ( $S_{aq}$ ) and octanol-water partition coefficient ( $K_{ow}$ ) or between  $K_{ow}$  and  $K_{oc}$  typically give estimates within an order of magnitude of measured  $K_{oc}$ s. Because the overall relationship between observed and literature  $K_{oc}$ s for the compounds evaluated in this study was within this range, it may be possible to estimate the  $K_{oc}$ s for these compounds from other properties. Karickhoff et al. (1979), Karickhoff (1981), Hasset et al. (1980), Briggs (1981), and Chiou et al. (1983), derived empirical and semi-empirical relationships for a range of aromatic compounds. Chiou et al. (1979) derived a relationship between  $K_{oc}$ , and  $S_{aq}$  among a number of halogenated compounds, including chlorinated

FIGURE 4-2. HDTMA SORPTION TO ZEOLITE  
CEC IS SATISFIED AT 85,465 MG/KG

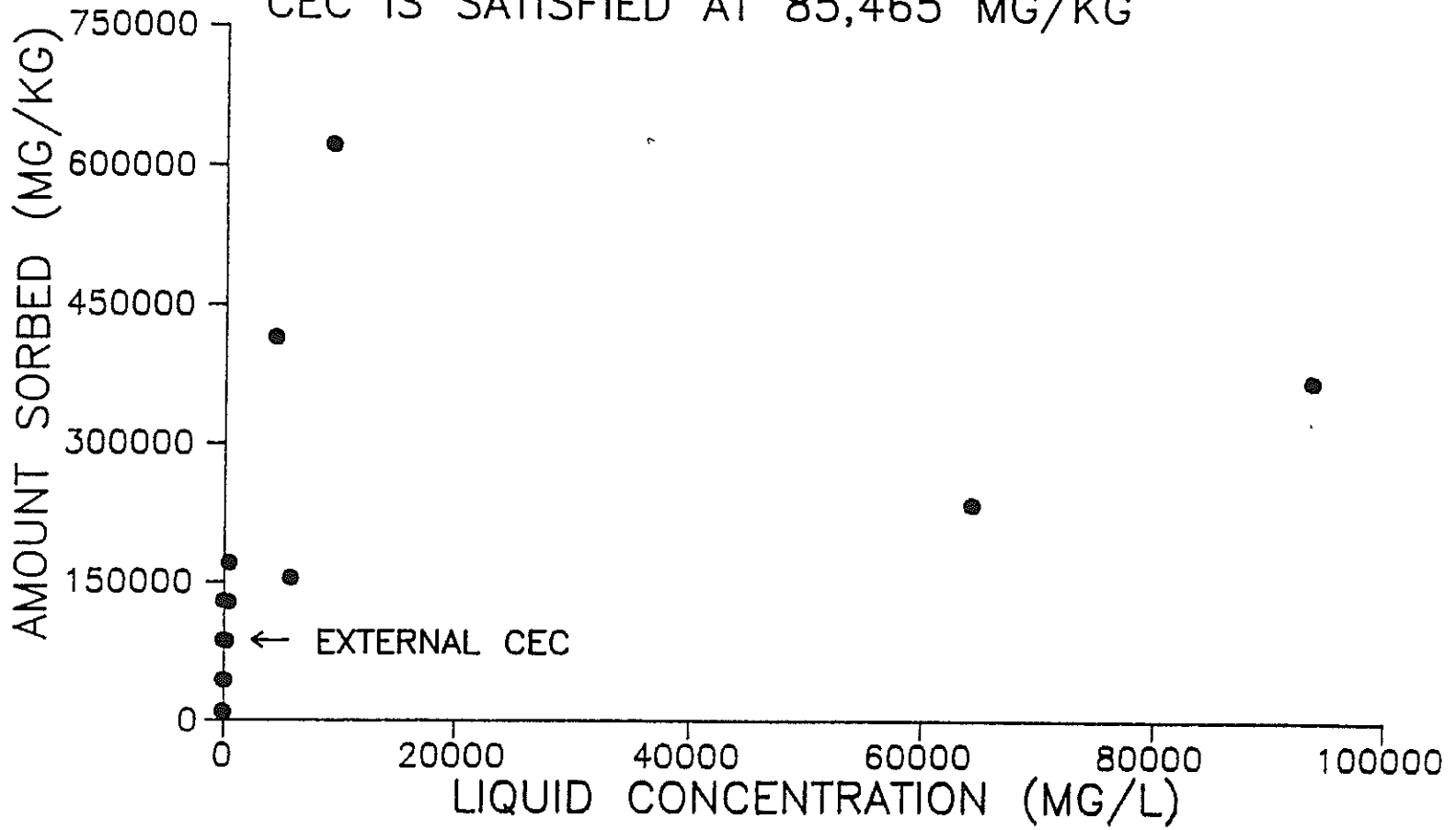


Figure 17. PCE Sorption from Aqueous Solution



benzenes, TCE, TCA, tetrachlorethane, and brominated propanes. Equations derived by these researchers were compared to the measured results from this study.

Because only three compounds were evaluated in this study, and they are not structurally similar, (they were chosen because they were structurally different), no attempt was made to derive a  $K_{oc}$ - $K_{ow}$  or  $K_{oc}$ - $S_{aq}$  relationship from the database generated in this study. In fact, correlations between groups of structurally different compounds may not be valid, as different sorption mechanisms may dominate for groups of different structural classes (Mingelgrin and Gerstl 1983).

In general, correlations between  $K_{oc}$ , and  $K_{ow}$  give better results than correlations of  $K_{oc}$  with  $S_{aq}$ , the latter which often give results only within no better than an order of magnitude (Karickhoff 1981). Often, correlations based on aqueous solubility give better overall results when a "crystal energy" term is added (Karickhoff 1981). However, a crystal energy term is usually only necessary for large, high melting-point solids, and this term is usually assumed to be zero for organics that are liquid at 25°C (Gschwend and Wu 1985; Karickhoff 1981).

Surprisingly, the best overall agreement between estimated and observed  $K_{oc}$ s for compounds analyzed in this study was given by the correlation between  $\log K_{oc}$  and  $\log S_{aq}$  developed by Karickhoff et al. (1979) for 10 different aromatic compounds. The correlation between  $\log K_{oc}$  and  $\log K_{ow}$  presented in the same paper was also reasonable. The correlations from Chiou et al. (1979), which would be expected to be best for the chlorinated compounds TCA and PCE gave reasonable results, but did not predict the measured values as accurately as the Karickhoff et al. (1979) equations.

Comparisons of predicted data from these equations shows that although agreement is not perfect, it is always within an order of magnitude, and often agreement is within about half an order of magnitude. As expected, predictions from the Chiou et al. (1979) equation are better for PCE and TCA than for Eben. However, these predictions are still not as accurate as those

from the Karickhoff equations, especially with respect to sorption to HDTMA-zeolite. In general, however, these estimates show that predictive equations may provide a reasonable first estimate for sorption parameters when no other data are available.

## SUMMARY

### WETTABILITY MODIFICATION OF MODEL MATERIALS

#### Wetting properties of silane-treated glass exposed to water, air and oil

Organosilanes were used to alter the wettability of glass slides. GC18- and OtS-treated slides had the highest contact angles while tBDM- and tBDP-treated slides had the lowest contact angles. Contact angle hysteresis was always observed.

Water-Soltrol 130 contact angles were higher than water-air contact angles. Thus, treated surfaces were more hydrophobic in the presence of Soltrol 130 than in air (Figures 9 and 10). The hydrophobicity of all treated slides deteriorated when stored in water but remained stable for storage in air and oil. Comparable deterioration after storage in water was observed when quartz and silica slides were used as substrates. Generally, the receding angle decreased earlier and at a greater rate than the advancing angle and was the more sensitive indicator of deterioration. Although bacteria were identified on the slides stored in water without bactericide, their effect on wettability was probably negligible because treated slides also deteriorated in water containing bactericide. Presence of an organic liquid coating on the treated surface prolonged stability of the treated slides in water but did not prevent eventual decrease in hydrophobicity. Hydrolysis is a plausible explanation of observed decrease in hydrophobicity. Of the silanes investigated in this study, tBDP and GC18 are considered the most suitable, with respect to stability, for rendering glass, silica, or quartz porous media hydrophobic. Such surfaces can be used as models for studying the effect of wettability alteration on petroleum recovery and aquifer remediation.

#### Effect of wetting on capillarity and non-aqueous phase liquid saturations in homogeneous porous media

The influence of wettability alteration of aquifer materials on trapping of NAPL beneath hazardous waste sites was investigated using water-oil displacement experiments in glass bead

packs and an etched glass micromodel. Wettability of the glass was rendered hydrophobic by treatment with GC18 silane.

Wettability alteration affects capillary pressures and displacement processes in homogeneous porous media. In GC18-treated bead packs, displacement of water by Soltrol is spontaneous but displacement of Soltrol by water is not. This is opposite from what is observed in untreated bead packs.

Residual oil saturation appears lower in the treated beads than untreated beads. The roles of water and oil, as the wetting and non-wetting liquids, are reversed in the treated beads. Preference of residual Soltrol as the wetting liquid for the smaller pore spaces in the treated case could explain the lower ROS in GC18-treated beads.

Use of cosine of the contact angle to predict capillary pressures seems valid for predicting pressures from one extreme wetting condition to the other for this simple system. The use of cosine of the contact angle to predict pressures for intermediate wetting conditions may not work based on the results here. Additional experiments for intermediate-wet conditions are required to investigate if scaling by  $\cos \theta$  is valid for a range of wettability conditions.

Wettability indexes calculated from the ratio of the area under the displacement curves indicate that, overall, the GC18-treated beads are oil-wet and the untreated beads are water-wet. This is consistent with capillary behavior and micromodel results (Wei 1991).

Further studies for intermediate wetting, mixed wetting, and wetting in heterogeneous porous media are recommended.

Although wettability alteration has potentially serious implications in NAPL contamination, the occurrence and mechanisms of wettability alteration at hazardous waste sites need to be verified.

## SURFACE MODIFICATION OF NATURAL ZEOLITE

Zeolites were treated with different large organic cations to create a hydrophobic surface medium that would enhance the sorption of dissolved organic compounds. Two different organic cations, HDTMA and MPP, were used to alter the surface hydrophobicity. The HDTMA ion emphasized the alkyl group, while the MPP ion emphasized the aromatic structure. The organic cations were sorbed up to the external CEC, but did not enter into the zeolite channels. Treating the surfaces significantly increased the zeolite organic carbon content from 0.16% to 6.3% with HDTMA and 3.8% with MPP.

Once sorbed, the organic cations were not significantly desorbed in a variety of pH buffers, inorganic salt solutions, and organic solvents. In general, HDTMA was more strongly bound to the surface than MPP. A large excess of other organic cations was effective in desorbing as much as 30% of the originally bound cations.

Sorption of phenol followed Freundlich-type isotherms, with most the phenol sorbed to the HDTMA-zeolite, and least sorbed to the natural zeolite. Phenol sorption was strongest from aqueous solutions at the concentrations evaluated. Isotherms for the other organic solutes were highly linear, again with strongest sorption to HDTMA-zeolite.  $K_{om}$  values for sorption of all species to HDTMA-zeolite were higher than the  $K_{om}$  values for the other two zeolites, and were about a factor of 2-5 times higher than reported literature  $K_{om}$  values.  $K_{om}$  values for MPP and natural zeolite were within a factor of approximately 2 of those reported in the literature. The measured  $\log K_{om}$  values for all compounds to HDTMA-zeolite agreed well with literature values for  $\log K_{ow}$  for these compounds. Empirical equations developed by others gave reasonable estimates of  $\log K_{oc}$  values for these compounds to the treated zeolites.

Interpretation of the results led to several conclusions. In summary, these were:

- Large organic cations will quantitatively exchange for inorganic cations on available mineral surface sites.

- The exchange of such large organic cations onto the mineral surface results in a significant increase in organic carbon content.
- Once sorbed, these organic cations are essentially irreversibly bound.
- Such hydrophobically treated materials are much more effective sorbents for neutral organic compounds than identical untreated materials.
- The extent of organic compound sorption to these modified surface is controlled primarily by the amount of surface organic carbon.
- The sorption mechanism is dominated by a partitioning into the surface hydrophobic medium, especially with HDTMA as the surface-altering agent.
- The nature of the surface-altering agent functional groups is not as important as the overall hydrophobicity imparted to the mineral in influencing the extent of nonionic organic compound sorption.
- HDTMA appears to create a continuous hydrophobic medium on the mineral surface that more effectively sorbs organic compounds than MPP treated surfaces or natural soil organic matter.
- Organic solute properties are important in determining the nature and extent of sorption. Specifically, the phenol hydroxyl group can hydrogen-bond with water, resulting in different sorption behavior than low-solubility, nonpolar organic compounds. In general, compound polarity affects the nature and extent of sorption.
- Zeolites do not display molecular selectivity for any or the compounds evaluated.
- When no other data are available, reasonable estimates of  $\log K_{oc}$ s may be obtained from empirically derived correlations between  $\log K_{oc}$  and aqueous solubility or  $K_{ow}$ .

## CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

The objectives proposed at the beginning of this research project were, for the most part, achieved. We determined the ability of a variety of chemical treatments to alter the wettability of solid surfaces. We quantified the effects of this altered wettability on fluid dynamics in model porous media. We quantified the sorption of dissolved organic solutes from aqueous solution and from organic solutions onto surfaces having altered surface chemistries.

We did not fully explore the relative importance of changes in surface wettability to the general problem of organic contaminant sorption and transport. There is much more work which could be done in this area. Outstanding problems include quantifying the wettability alteration of natural porous media in contact with nonaqueous contaminants such as crude oils, characterizing systems of mixed or intermediate wettabilities, characterizing three-phase (water-oil-air) systems, and investigating the effects of chemically altered surfaces on flow and sorption in heterogeneous systems.

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