Organic dye effects on DNAPL entry pressure in water saturated porous media

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ABSTRACT

One of three diazo dyes with the same fundamental structure have been used in most studies of DNAPL behavior in porous media to stain the NAPL: Sudan III, Sudan IV, or Oil-Red-O. The dyes are generally implicitly assumed to not influence DNAPL behavior. That assumption was tested using simple entry pressure experiments. Sudan IV significantly changes surface chemistry in the tetrachloroethene (PCE)-water-glass system. Sudan IV makes PCE more mobile by lowering adhesion tension in the system. A statistically significant reduction in PCE entry pressure was observed at a dye concentration of 0.0411 g/L, a concentration approximately two orders of magnitude lower than those typically used in experimental studies. Dye type, concentration, and surface chemistry are therefore important experimental parameters in studies of multiphase flow in porous media. PCE entry pressure was also strongly influenced by intrinsic permeability, providing experimental support for the Bond number formulation of *Pennell et al.* [1996].

INTRODUCTION

Subsurface contamination by non-aqueous phase liquids (NAPLs) remains one of the biggest challenges facing the environmental remediation community, particularly NAPLs denser than water (DNAPLs) such as chlorinated solvents. The physical behavior of multiple fluid phases is extremely complex arising from the interaction and interdependence of the interfacial chemistry governing the system with the pore- and larger-scale heterogeneity in the porous medium. Visualization studies have provided a wealth of information to help us understand these complexities. Most visualization studies using DNAPLs conducted in the past twenty years involved the use of one of three diazo dyes [*Tuck,* 1999]. Virtually no systematic work has been done to examine the influence of those dyes on multiphase flow. Our objective was to investigate the effects of a frequently used organic dye, SUDAN IV, on the entry pressure of a common DNAPL, tetrachloroethene (PCE), into a water saturated porous medium.

Dyes are essential to all visualization experiments in which pure solvents are used as the NAPL. They are used to stain one of the fluid phases (usually the organic phase) to observe its paths through the medium [*Schwille,* 1988; *Kueper et al.,* 1989; *Kueper and Frind,* 1991; *Poulsen and Keuper*, 1992; *Powers et al.*, 1992; *McBride et al.*, 1992; *Kueper et al.*, 1993; *Mayer and Miller*, 1993; *Schroth et al.*, 1995; *Brewster et al.*, 1995; *Pennell et al.*, 1996; *Kennedy and Lennox*, 1997; *Fortin et al.*, 1997; *Stephens et al.*, 1998]. The dyes and NAPLs used along with the dye concentration and type of study are listed in Table 1. A general, unstated assumption most authors make is that the dye has no effect on the multiphase flow phenomena under study.

By their nature, dye chromophores are likely to cause surface active behavior. Dye type and concentration are therefore important experimental conditions that should be accurately reported. All the studies mentioned above use one of three dyes with the same fundamental structure as illustrated in Figure 1. Sudan III is the fundamental molecule, having no additional substitutions. The other two dyes contain different numbers of methyl groups substituted in positions *a*, *b*, *c*, and *d* shown in Figure 1. Sudan IV has two

methyl groups, in positions *a* and *d*. Oil-red-O has four methyl groups, one in each of the lettered positions. These dyes are available under several trade names [*Lide and Milne*, 1995]; for example Sudan III is also known as D & C Red 17, which is how Stephens et al. [1998] reported it. These dyes belong to an oil soluble azo, class of *dyes [Catino and Farris*, 1978].

 Little consideration has been given to whether dyes influence experimental behavior. Powers et al. [1992] documented an interfacial tension reduction caused by Oil-Red-O in trichloroethene (TCE) and styrene. But they did not further evaluate the dye influence on the dissolution process under study. *Mayer and Miller* [1993] studied NAPL blob dimensions at residual saturation under varying viscous and gravity force conditions. They measured interfacial tensions with dye present, and incorporated the results into their capillary and Bond number formulations. They specifically demonstrated that the Oil-Red-O concentration they used resulted in statistically significant reductions in PCE-air surface tension and PCE-water interfacial tension. *Pennell et al.* [1996], in their study of surfactant mobilization of PCE, gave a qualitative assessment. They used a low dye concentration (1 x 10^{-4} M), and merely stated (p.1330) that at this concentration the dye "… had no discernable effect on the amount or rate of PCE mobilization during surfactant flushing." In general, the surface activity of these dyes will be modest compared with a surfactant. Hence their qualitative result is very reasonable. *Kennedy and Lennox* [1997], in their study of NAPL dissolution, mentioned the potential of surface active substances to slow the dissolution process. While they acknowledged the surface active nature of dyes, they did not quantitatively evaluate the dye effect. *Pirkle, et.al.* [1996; 1997] indicated that entry pressures may be considerably different for PCE/Sudan IV dye solutions than for undyed PCE. This is important since the majority of multiphase visualization studies involving DNAPLs have used Suden IV or a minor variation of the parent molecule (see Figure 1 and Table 1).

The surface activity of dyes based on Sudan III arises from the hydroxy group which is part of a primary ingredient of the dyes (2-naphthol) and from the azo bonds (i.e., the N=N bonds). Aromatic groups are also known to partition to solid surfaces where they

can alter the contact angle between fluids in simultaneous contact with the solid [*Tuck and Rulison*, 1998]. *Ringwald and Pemberton* [2000] determined that aromatic compounds generally adsorb to silica surfaces via weak π-system hydrogen-bonding with silanol groups. They found more specific and stronger hydrogen-bonding between silanol groups and lone pair electrons on N atoms included in the aromatic ring structure. *Tuck et al.* [1998] and *Tuck and Rulison* [1998] have demonstrated the surface activity of Sudan IV in the PCE-water-glass system, examining its effect on both interfacial tension and on contact angles against glass. The objective of this work was to examine and quantify the magnitude of influence this dye has on the mobility of PCE in the Sudan IV-PCE-water-glass system.

THEORY

Capillary forces play a major role in governing multiphase flow in porous media. They control the position of fluid interfaces in pore throats and also establish the stability limits of the fluids within a given pore throat, i.e., the maximum capillary pressure the pore throat can support. We use the terms oil and NAPL interchangeably in the following discussion.

One method to quantify capillary influence is to assume fluid-fluid interfaces may be approximated by spherical sections bound in cylindrical pores. *Hobson* [1954] makes this assumption implicitly in his derivation of the following equation for the buoyant stability of an isolated vertically continuous column or ganglion of oil within a saturated, water-wet porous medium:

$$h_c = \frac{2\gamma_{o/w}}{\Delta\rho_{o/w}\, g} \left(\frac{1}{r_l} - \frac{1}{r_u} \right) \qquad\qquad (1)$$

where h_c is the critical vertical length or height of the ganglion where it will no longer be buoyantly stable (cm), $\gamma_{o/w}$ is the interfacial tension between oil (o) and water (w) (dynes/cm), $\Delta\rho_{o/w} = \rho_o - \rho_w$ is the density difference between the fluids (g/cm^3), g is the acceleration of gravity (cm/s^2), r_l is the radius of curvature of a lower interface (assumed to be the radius of the lower pore throat in which the interface is trapped (cm), and r_u is the radius of a higher or upper ganglion interface (cm). The buoyancy force will be downward if we assign down as the positive direction and $\Delta\rho_{o/w}$ is positive, i.e., if the oil is denser than water (as in the case of DNAPLs). Hobson's equation can be simplified if the radius of the upper interface is much greater than that of the lower interface, i.e., if $r_u \gg r_l$. Under these conditions, Hobson's equation becomes

$$h_c = \frac{2\gamma}{\Delta\rho g r} \qquad\qquad\qquad (2)$$

where r is the radius of the lower bounding interface (cm) and the subscripts for density and interfacial tension are understood.

Hobson's derivation assumes a perfectly water-wet medium in which the contact angle between the oil-water interface and the solid surface is zero. Hobson's equation can be modified for a nonzero contact angle, θ, as follows:

$$h_c = \frac{2\gamma\cos\theta}{r_t\,\Delta\rho g} \qquad\qquad\qquad (3)$$

where r_t is an "effective" pore throat radius controlling the buoyant stability (cm). The product of the interfacial tension and cosine of the contact angle appears frequently in surface chemistry, and hence has been defined as adhesion tension [*Adamson* 1990]. The Hobson equation can thus be further simplified to

$$h_c = \frac{2\gamma_\theta}{r_t \Delta\rho g} \qquad\qquad [4]$$

where γ_θ is the adhesion tension [dynes/cm) and the density difference is understood to be between the oil and water phases as defined above. The pore throat radius is an "effective" radius because cylindrical geometry is assumed for the pore throats in equation [1]. It will also be an average value when working with real porous media since the details of all pore throats are unknown.

Hobson's equation can be used to quantify the entry pressure at which a NAPL will enter a water-saturated porous medium. The smaller the "effective" pore throat radius, the larger the entry pressure should be so long as the oil-water interfacial tension and the contact angle between the water-oil interface and the silica glass beads remain constant [*Berg*, 1975; *Hunt et.al.*, 1988].

Hobson's equation was derived under conditions in which an oil ganglion is completely surrounded by water. Under conditions where the oil phase is not surrounded, i.e., not buoyed by water, using the density difference to determine capillary pressure is not appropriate. Instead, the density of the oil phase alone, ρ_o, must be used to determine the capillary pressure. Such situations occur in the field when NAPL is released into the subsurface and it encounters the water table. Under these conditions, the Hobson equation may thus be expressed as:

$$h_c = \frac{2\gamma_\theta}{r_t \rho_o g} \qquad\qquad (5)$$

Hobson's equation was derived from a balance of gravity and surface forces. In fluid dynamics, force ratios are frequently addressed through the formulation of dimensionless groups often given specific names. The Bond number, N_{Bo}, is used to express the relative

magnitude of gravity versus surface forces. The general formula for the Bond number is [*Boucher and Alvers*, 1960, *Perry and Chilton*, 1973, *Weast*, 1989].

$$N_{Bo} = \frac{\Delta\rho g L^2}{\sigma} \qquad (6)$$

where L is some characteristic length and σ the surface or interfacial tension. This formulation is generally used when considering atomization or the motion of bubbles or droplets of one fluid suspended in a second immiscible fluid, in which case L is the bubble or droplet diameter [*Weast*, 1989]. *Morrow and Songkran* [1981] took L to be the median grain size when considering the behavior of two fluid flow in a porous medium. *Mayer and Miller* [1993] take L to be an average pore-throat radius. *Pennell et al.* [1996] incorporate intrinsic permeability into the Bond number as follows:

$$N_{Bo} = \frac{\Delta\rho g k k_{rw}}{\gamma_{ow} \cos\theta} \qquad (7)$$

where k is the intrinsic permeability and k_{rw} is the relative permeability to water. The relative permeability to water in a medium is unity prior to NAPL entry. In this case, *Pennell et al.'s* Bond number reduces to

$$N_{Bo} = \frac{\Delta\rho g k}{\gamma_{ow} \cos\theta} \qquad (8)$$

One implication of equations (7) and (8) is that the gravitational stability limit given by Hobson's equation, h_c, should be a function of intrinsic permeability since it was derived from a balance of gravity and capillary forces.

EXPERIMENTAL METHODS

The experimental system consisted of tetrachloroethene (PCE, Mallinckrodt, Inc.) as the "oil", water, and glass beads as the porous media. The composition of the "oil" phase was varied by dissolving different concentrations of Sudan IV, an oil-soluble diazo dye [*Catino and Ferris*, 1978] also known as oil red, oil red IV, solvent red 24, among other trade names [*Lide and Milne*, 1995]. The dye was purchased from Kodak (Sigma Lot #123H3685). The dye content was 81%. The remaining 19% of the dye powder is inorganic salts from the manufacturing process [*Aldrich Chemical Company*, personal communication]. Dye concentrations should be corrected for dye content; the uncorrected and corrected dye concentrations used in this work are presented in Table 2. The aqueous phase consisted of deionized, deaerated water.

Interfacial tension between the Sudan IV-PCE solutions and water was determined as a function of time with a dynamic drop-volume technique using a Krüss Drop Volume Tensiometer (model DVT10) [*Tuck and Rulison*, 1998]. Contact angles between the Sudan IV-PCE solutions, water, and a glass slide were determined as a function of time using a Krüss model G10 Goniometer. Angles were measured through the PCE phase, and the supplement taken to express the contact angle through the aqueous phase [*Tuck and Rulison*, 1998].

The experimental apparatus is illustrated in Figure 2. It consisted of a 2.54 cm ID glass column. Porous media were retained on a stainless steel mesh screen. A 0.64 cm ID standpipe was used to minimize the PCE volume required to attain any given DNAPL height, h. All porous media consisted of glass beads (Potter Industries Inc). They were dry sieved, and the fraction between US standard sieve numbers 140 and 170 was retained. This fraction was washed with ethanol by soaking overnight, rinsed several times with deionized water, and then wet sieved with deionized water through the 170 mesh screen. Over 50% of the dry classified beads, which were supposedly US 140-170 in size, were found to pass the US 170 mesh sieve upon wet-sieving. The washed and re-sieved

beads were air-dried, homogenized and stored in a dessicator. The resulting grain-size range was 0.105 mm to 0.088 mm which is a very fine sand size [*Folk*, 1980].

The porous media were prepared by pouring a known mass of air-dried beads into the experimental apparatus (see Figure 2) and tapping to cause initial settling. The tops of the porous media were left unconstrained to prevent attenuation and loss of Sudan IV dye on any boundary material above the porous medium such as a hydrophobic pressure plate. A vacuum of 21 inches of Hg was applied for a half-hour, after which the media were saturated under vacuum from below with deionized water. The water was allowed to rise 2 cm above the media surface in order to prevent any disturbance during addition of water to the standpipe for hydraulic conductivity determinations. Several pore volumes of water were flushed downward through the media to cause settling. The porous media columns varied in length from approximately 7.6 to 11.4 cm in final length after settling prior to measuring hydraulic conductivity. Water was added to the top of the standpipe, and hydraulic conductivity was determined using the falling head method [*Heath and Trainer*, 1968]. Intrinsic permeability of the porous media was calculated using the viscous properties of water adjusted for the experiment temperature, which ranged between 21° and 25° C.

The right side high vacuum valve of the apparatus (see Figure 2) was shut off and excess water was drained downward through the left side high vacuum valve and the three way stopcock after the hydraulic conductivity measurements were completed. This prevented any disturbance to the media while switching to the entry pressure determination mode of the apparatus since all flow continued downward. The burette simultaneously was adjusted so that an equal head was established between the burette reservoir water level and the top of the porous medium. A two mm excess of water was left above the media surface to assure the media remained saturated.

The water levels between the porous media column and the burette/reservoir were allowed to equilibrate for fifteen minutes. Finally, a column of PCE was carefully built up in the standpipe until the PCE entry pressure occurred. The PCE entry pressure was indicated by

a distinct decrease in the burette readings that indicated water was being expelled from the media by PCE entering it.

The critical height of PCE (h) was considered to be the height of PCE in the column at the last equilibrium level, as indicated by the water in the burette, before a decrease of approximately 0.005 ml in the burette reading with the next PCE addition. A decrease in the water reservoir burette reading indicated that water had been forced out of the porous medium by PCE entry into the medium. For most of the experiments in the undyed PCE series five minutes was considered sufficient for equilibrium to have been established between additions of PCE. As h_c was approached PCE was added at a rate of 0.1 - 0.2 ml per addition. This was equivalent to a change of 0.45 - 0.95 cm in the PCE height (h) in the standpipe. A potential excess of PCE beyond the entry pressure resulting in an error of 1.7% - 3.7% was minimized by choosing the average between the last stable level of PCE and the level determined as unstable as the entry pressure (h_c).

A Schellbach burette was utilized for the water reservoir in this research because it is more sensitive than a standard burette and permits accurate readings to 0.01 ml. It is sensitive enough that indications of flow into or out of the medium on the order of 0.001 ml are detectable if not measurable. If one assumes orthorhombic packing [*Graton and Fraser*, 1935] of the US 140-170 sized spherical glass beads ($105\mu m > d_b > 88\mu m$) a .01 ml change in the burette represents a fluid volume change equivalent to emptying or filling approximately 33,000 pores within the media. A sense of movement in the range of 0.001 ml would relate to a volume equivalent of only 3300 pores. These detection limits represent NAPL saturation detection limits ranging from $7x10^{-4}$ to $1x10^{-3}$ assuming an average porosity of 0.36.

The experiments were divided into seven treatments with each characterized by the concentration of Sudan IV dye in PCE. First was a series of experiments on entry pressures for undyed PCE. The remaining six series are experiments involving a series of SUDAN IV dye/PCE solutions (see Table 2).

RESULTS AND DISCUSSION

Surface Chemistry

Addition of Sudan IV dye to PCE alters the interfacial tension between PCE and water
[*Tuck et al.*, 1998; *Tuck and Rulison*, 1998]. It also modifies the wetting relationship
between the fluid phases and glass by changing the contact angle [*Tuck et al.*, 1998; *Tuck
and Rulison*, 1998]. The rate of change and extent to which interfacial tension reduction
and wetting changes take place depend upon the concentration and activity of the dye.
Interfacial tension decreases as dye concentration increases. Contact angles through the
aqueous phase increase with increasing dye concentration, i.e., water wets the glass less
strongly. Log-linear equations were fit to express interfacial tension and contact angles
through the aqueous phase as a function of time. Adhesion tension was calculated from
those equations. Adhesion tension in the PCE-water-glass system is shown as a function
of time in Figure 3 for the different dye concentrations.

The surface chemical kinetics is relatively slow [*Tuck and Rulison*, 1998]. This
complicates the behavior of dyed PCE solutions in porous media [*Tuck et al.*, 1998; *Tuck*,
in press]. An arbitrary interface age of 2500 seconds has been selected to simplify
consideration of the surface chemical effects of the dye. Adhesion tension values are
given in Table 3 for the dye concentrations used here at an interface age of 2500 seconds.
The ratio of adhesion tension for the dyed PCE solutions to that for undyed PCE are also
given. PCE entry pressure should decrease in direct proportion to this ratio according to
equation (4).

The results in Figure 3 are specific to this system, i.e., Sudan IV-PCE-water-glass. Based
on the similarity of structure, however, surface activity should also be expected for
systems in which the other two dyes illustrated in Figure 1 are used, i.e., Sudan III and
Oil-Red-O. The magnitude of total interfacial tension and contact angle changes and the
surface chemical kinetics are expected to decrease in the order Sudan III > Sudan IV >
Oil-red-O based on their structure and methyl group content. *Miller and Mayer* [1993]
measured the dyed-PCE-water interfacial tension of 40.0 dynes/cm using the ring method

at an Oil-Red-O concentration of 1.00 g/L. The ASTM procedure they followed [*ASTM*, 1982] calls for measuring the tension at an interface age of 30 ± 1 seconds. Using this time and interpolating for a Sudan IV dye concentration of 1.00 g/L yielded an estimated PCE-water interfacial tension of between 38.3 and 39.8 dynes/cm. This is consistent with the predicted pattern.

PCE Entry Pressure

Intrinsic Permeability.

All porous media experimental results are presented in Figure 4 where PCE entry pressures, h_c, expressed as cm of PCE, are plotted versus porous medium intrinsic permeability. Results for undyed PCE clearly indicate that pore entry pressure does indeed depend upon intrinsic permeability as suggested by *Pennell et al.* [1996] and implied in equations (7) and (8) for the Bond number. The regression coefficient (slope of the regression line) is statistically significantly different from zero only for undyed PCE. The small number of experiments for the other treatments (i.e. dye concentrations) along with the relatively narrow range of intrinsic permeability for the other media are the likely reasons for the lack of statistically significant dependence on intrinsic permeability for the dye treatments. Time-dependence of the surface chemistry further complicates the behavior [*Tuck et al.*, 1998; *Tuck*, in press].

The dependence on intrinsic permeability illustrated in Figure 4 is surprisingly large. The range of PCE entry pressure (h_c) for the undyed experiments (approximately 9.9 cm of PCE) is more than 36% of the mean entry pressure (26.9 cm of PCE). These results provide stronger, more direct support for *Pennell et al.'s* [1996] incorporation of intrinsic permeability into a Bond number formulation for porous media than their own experimental results because intrinsic permeability effects are not confounded with surface chemical effects. The influence of the porous medium intrinsic permeability should be taken into account when assessing the influence of the dye on the PCE entry pressure, h_c.

Dye Concentration Effects.

The intrinsic permeability of all media for the experiments with higher dye concentrations ($C \geq 0.04 \text{ g}/\text{L}$) ranged between $1.3\text{x}10^{-8}$ and $1.7\text{x}10^{-8}$ cm^2. Experiments in which the intrinsic permeability fell outside this range for the undyed and the C4-experiment series (C = 0.00411 g/L) were set aside in order to minimize the influence of intrinsic permeability on the dye concentration effects. The resulting mean values of the entry pressure, $\overline{h}_c$, are presented in Table 3 and plotted against the dye concentration in Figure 5. The mean PCE entry pressure results were fit to an exponential equation: $h_c = 25.76 * 10^{-0.5357*C}$ where C is the corrected mass concentration (g/L) of Sudan IV dye in the PCE. The r^2 value for the fit is 0.983. These results clearly indicate the decrease in entry pressure as dye concentration increases.

Comparison of the results for undyed PCE with those for PCE dyed with 0.00411 g/L of Sudan IV in Figure 4 indicate that the dye has no significant influence on the entry pressure at this low concentration. This mass concentration translates to a molar concentration of $1.16\text{x}10^{-5}$ M (see Table 2). This concentration is approximately an order of magnitude lower than the Oil-Red-O concentration reported by *Pennell et al.* [1996]. Noticeable reductions in the PCE entry pressure begin to appear at the next higher dye concentration. The mean PCE entry pressure, $\overline{h}_c$, for the C3 solutions (C = 0.0411 g/L) was statistically significantly different from that for undyed PCE. The t-test probability that the means are equal is $2\text{x}10^{-7}$.

The ratios of mean entry pressure to that for undyed PCE are also given in Table 3. The entry pressure ratios should correspond roughly to the adhesion tension ratios. Small to moderate discrepancies should be expected because of the complexity introduced by the time-dependent nature of the surface chemistry [*Tuck et al.*, 1998; *Tuck*, in press]. The mean entry pressure values for the three lowest dye concentrations appear to correspond reasonably well with the adhesion tension ratios. The $\overline{h}_c$ value for the C1.0 solution, however, is much lower than expected based on behavior predicted by the Hobson equation alone.

Qualitative observations of the C1.0 experiments (C = 1.03 g/L) indicated significantly different behavior compared with the other experiments. The experimental set-up was gravitationally unstable; higher density PCE was above the water-saturated porous media. The risk was that simple exchange of PCE for water might occur at the PCE-porous medium interface. Such an exchange could be difficult to detect in our set-up. The trade-off of eliminating a capillary barrier, which would prevent fluid exchange, was that we need not worry about adsorption loss of dye on it. Water remained sufficiently strongly wetting on the glass bead surfaces that simple exchange with PCE did not occur when the dye concentration was ≤ 0.04 g/L. There were indications, however, from the C3 and C2 experimental series (C = 0.0411 and C = 0.411 g/L, respectively) that the dye was beginning to qualitatively change the fluid behavior. Qualitative observations of the experimental results for the C1.0 series (C = 1.03 g/L) left no doubt that fluid exchange at the free-PCE-porous-medium boundary occurred in those experiments. Hence, no porous media experiments were run using the two highest dye concentrations (C1.4 and C3.2).

Entry of undyed PCE into the glass bead media was clear-cut. Entry was detected by a distinct upward change in the burette water level (lower burette reading, see Figure 2). Entry pressure was taken to be the average between the last stable PCE height and the height after which PCE entry definitely occurred. Behavior of the lowest concentration solution, C4 = 0.00411 g/L, followed the same behavior as undyed PCE. This is another indication that the dye had no effect on PCE entry pressure at this lowest concentration.

Perturbations in burette readings began as the entry pressure was reached when dye concentration exceeded that of the C4 solutions, i.e., C ≥ 0.04 g/L. The perturbations took the form of oscillating burette readings. The perturbations were very slight and would have been imperceptible without the use of a Schelbach burette sensitive to ±0.001 mL. These fluctuations are assumed to be indications of fluid exchange occurring at the porous medium-free PCE boundary. More distinct burette-reading changes and/or visual indications of entry appeared shortly after perturbations occurred. PCE appeared in the dead space below the porous medium after sitting overnight when an experiment was stopped after the occurrence of these perturbations. Hence entry pressure was taken as the

pressure when these perturbations appeared in experiments using the C3, C2, and C1.0 PCE solutions.

Qualitative Observations

Several qualitative observations were noted regarding dye effects with increasing concentration. PCE ran as thin stringers down the glass standpipe during its introduction at zero and the lowest dye concentration (C4 = 0.00411g/l), displaying no tendency to coat the glass walls. As dye concentration increased, the solutions displayed an increasing tendency to wet the glass or spread over a water-film remaining on the glass following the permeability measurements. A thin film of dyed PCE completely coated the inner wall of the tube at the highest dye concentration.

Whereas undyed PCE and the C4 PCE-solution would leave the mouth of the glass tube and spread out over the surface of the bead media relatively rapidly, the dye solutions displayed a tendency to remain in the mouth of the standpipe due to capillary forces. At the highest concentration used in the porous media experiments (C1.0 = 1.03 g/L), the dyed PCE would not leave the mouth of the standpipe until several centimeters of solution had built up within the tube.

It was apparent by an oscillatory motion or fluctuation of the water level of the burette that some kind of disequilibrium, never present with undyed PCE, was occurring in the system. As noted above, these fluctuating water-reservoir burette readings began to appear with the C3 solutions (C = 0.0411g/l). This contrasted with the stable "plateau" of values for undyed PCE experiments prior to entry, after which, the burette values would steadily decrease indicating water being expelled from the media into the burette [*Pirkle et al.*, 1997].

For higher concentrations of the dye there was never, except for temporary oscillations attendant upon the addition of more PCE, an indication of water being expelled from the media into the burette. Rather, there was an indication of a miniscule amount of water leaving the burette through the media. Tiny cylindrically shaped fibers of water would

leave the media surface, coalesce, and form irregularly shaped water bubbles as they rose upward in the column of dyed PCE solution. The bubbles never rose above approximately 4 cm apparently dissolving into the dye solution.

Unlike with undyed PCE, the dye solutions of concentration higher than C4 would not penetrate the stainless steel support screen following complete penetration of the media. Eventually the solution found its way around the screen and wet the teflon support prior to dropping off into the dead volume of the apparatus.

Glass-bead media grains would be permanently dyed red where there had been contact with the dye solution following experiments with the higher concentrations of dye (C3 and higher). This indicates that dye was adsorbing onto the glass surfaces from the dyed PCE solutions. This adsorption process is the cause for the contact angle change and hence the change in the wetting relationships.

Another striking change in behavior relative to low dye concentrations (< 0.04 g/L) was the fact that at no time, until final breakout from the media, did the water reservoir burette indicate water leaving the media due to PCE entry. Instead, lower burette levels indicated that minute amounts of water were leaving the water-reservoir burette into the media. This was again due to the gravitationally unstable configuration. In addition, when the reservoir burette readings were plotted against elapsed time from the start of the experiment, shorter duration plateaus were evident before changes began to occur [*Pirkle et al.*, 1996]. The time delay before water levels began changing may reflect the time-dependent nature of the interfacial chemistry [*Tuck et al.*, 2000; *Tuck*, in press] (see Figure 3). All of the qualitative observations mentioned above are manifestations of the surface activity of the dye in the Sudan IV-PCE-water-glass system.

CONCLUSION

Sudan IV dye exhibits significant surface activity in the PCE-water-glass system. Interfacial tension decreases and contact angles measured through the aqueous phase increase as the dye concentration increases. Both of these effects reduce the adhesion tension. The similarity in dye structure of the other two frequently used dyes, Sudan III and Oil-Red-O, suggest that they will also be surface active in similar fluid-porous media systems. Dye type and concentration and the resulting surface chemical effects are therefore important considerations in experimental studies of multiphase flow in porous media.

Sudan IV dye significantly reduces the entry pressure of tetrachloroethene into water-saturated glass-bead porous media. The results in Figures 4 and 5 clearly support this conclusion. The reduction in entry pressure follows the expected reduction due to reduced adhesion tension as indicated by *Hobson's* [1954] equation (eq. 4). There is an apparent breakdown of Hobson's equation suggested by increasing discrepancy between the adhesion tension ratio and the entry pressure ratio (see Table 3) at the highest dye concentration used in the porous media experiments (1.03 g/L). This discrepancy, however, is most likely an artifact of the gravitational instability in our experimental set-up rather than a real failure of the theory.

Entry pressure of undyed PCE is a statistically significant function of the porous medium permeability. These results provide strong experimental support for the Bond number formulation proposed by *Pennell et al.* [1996] in which intrinsic permeability, k, is taken as the representative squared length in the general Bond number equation (eq. 6).

The time-dependence of the surface chemistry complicates these (and likely other) experimental results [*Tuck et al.*, 1998; *Tuck et al.*, 2000; *Tuck* in press]. An example evident in the current results is the shorter time before penetration of the media that occurred as the dye concentration increased. This complication deserves more careful

study. We have also only examined one dye-NAPL combination. Other systems should be examined experimentally.

REFERENCES

Adamson, A. W., *Physical Chemistry of Surfaces*, 5th ed., John Wiley, New York, 1990.

ASTM, Standard test method for interfacial tension of oil against water by the ring method, ASTM D971-91, in *1982 Annual Book of ASTM Standards*, pp. 103-105, American Society for Testing and Materials, Philadelphia, 1982.

Berg, R. R., Capillary Pressure in Stratigraphic Traps, *Am. Assoc. of Petroleum Geology*, 59, 939-956, 1975.

Boucher, D. F. and G. E. Alves, Dimensionless numbers, *Chem. Eng. Prog.* 55, 55-64, 1959.

Brewster, M. L., A. P. Annan, J. P. Greenhouse, B. H. Kueper, G. R. Olhoeft, J. D. Redman, and K. A. Sander, Observed migration of a controlled DNAPL Release by Geophysical Methods, *Ground Water* 33(6): 977-987, 1995.

Catino, S. and R. E. Farris, Azo dyes, in *Kirk-Othmer Encyclopedia of Chemical Technolog,* vol. 3 Eds. H. F. Mark, D. F. Othmer, C. G. Overberger and G. T. Seaborg, pp. 387-433, John Wiley & Sons, New York, 1978.

Folk, R. L, *Petrology of Sedimentary Rocks,* Hemphill Publishing Company, Austin, Texas, 1980.

Fortin, J., W. A. Jury, and M. A. Anderson, Enhanced removal of trapped non-aqueous phase liquids from saturated soil using surfactant solutions, *J. Contam. Hydrol.,* 24(3-4), 247-267, 1997.

Graton, L. C. and H. J. Fraser, Systematic Packing of Spheres with Particular Relation to Porosity and Permeability, *J. Geology*, 43, 785-909, 1935.

Heath, R.C. and F. W. Trainer, *Introduction to Ground-Water Hydrology*, John Wiley, New York, 1968.

Hobson, G. D., *Some Fundamentals of Petroleum Geology*, Oxford University Press, New York, 1954.

Hunt, J. R., N. Sitar, and K. S. Udell, Non Aqueous Phase Liquid Transport and Cleanup: 1. Analysis of Mechanisms, *Water Resour. Res.*, 24, 1247-1258, 1988.

Kennedy, C. A. and W. C. Lennox, A pore-scale investigation of mass transport from dissolving DNAPL droplets, *J. Contam. Hydrol.,* 24, 221-246, 1997.

Kueper, B. H., W. Abbott, and G. Farquhar, Experimental observations of multiphase flow in heterogeneous porous media, *J. Contam. Hydrol.,* 5, 83-95, 1989.

Kueper, B. H. and E. O. Frind, Two-Phase flow in heterogeneous porous media 2. Model application, *Water Resour. Res.*, 27(6), 1059-1070, 1991.

Kueper, B. H., D. Redman, R. C. Starr, S. Reitsma, and M. Mah, A field experiment to study the behavior of tetrachloroethylene below the water table: Spatial distribution of residual and pooled DNAPL, *Ground Water*, 31(5): 756-766, 1993.

Lide, D. R. and G. W. A. Milne, Eds., *Names, Synonyms and Structures of Organic Compounds,* CRC Press, Boca Raton, FL, 1995.

Mayer, A. S. and C. T. Miller, An experimental investigation of pore-scale distributions of nonaqueous phase liquids at residual saturation, *Transport Porous Media*. 10, 57-80, 1993.

McBride, J. F., C. S. Simmons, and J. W. Cary. Interfacial spreading effects on one-dimensional organic liquid imbibition in water-wetter porous media, *J. Contam. Hydrol.,* 11, 1-25, 1992.

Morrow, J. C. and B. Songkran, Effects of viscous and bouyancy forces on mon-wetting phase trapping in porous media, in D. O. Shah, ed. *Surface Phenomena in Enhanced Oil Recovery*, pp. 387-411, Plenum Press, New York, 1981.

Perry, R. H. and C. H. Chilton, *Chemical Engineers' Handbook*, 5th ed. McGraw-Hill Book Company, New York, 1973.

Pennell, K. D., G. A. Pope, and L. M. Abriola, Influence of viscous and buoyancy forces on the mobilization of residual tetrachloroethylene during surfactant flushing, *Env. Sci. Tech.,* 30(4), 1328-1335, 1996.

Pirkle W. A., G. M. Iversen, and D. M. Tuck, DNAPL Entry Pressure Into Water Saturated Porous Media, *Rep. SCUREF TO185*, Univ. of South Carolina Aiken, 1996.

Pirkle, W. A., G. M. Iversen, and D. M. Tuck, The Effect of An Organic Dye on DNAPL Entry Pressure Into Water Saturated Porous Media, *Rep. SCUREF TO185 Phase II*, Univ. of South Carolina Aiken, 1997.

Poulsen, M. M. and B. H. Keuper, A field experiment to study the behavior of tetrachloroethylene in unsaturated porous media, *Env. Sci. Tech.,* 26, 889-895, 1992.

Powers, S. E., L. M. Abriola, and W. J. Weber, Jr., An experimental investigation of nonaqueous phase liquid dissolution in saturated subsurface systems: steady state mass transfer rates, *Water Resour. Res.*, 28(10), 2691-2705, 1992.

Ringwold, S. C. and J. E. Pemberton, Adsorption interactions of aromatics and heteroaromatics with hydrated and dehydrated silica surfaces by Raman and FTIR spectroscopies, *Env. Sci. Tech.,* 34, 259-265, 2000.

Schroth, M. H., J. D. Istok, S. J. Ahearn, and J. S. Selker, Geometry and position of light nonaqueous-phase liquid lenses in water-wetted porous media, *J. Contam. Hydrol.,* 19, 269-287, 1995.

Schwille, Friedrich, *Dense Chlorinated Solvents in Porous and Fractured Media: Model Experiments*, Translated from German and edited by J. F. Pankow, Lewis Publishers, Inc., Chelsea, MI, 1988.

Stephens, D. B., J. A. Kelsey, M. A. Prieksat, M. G. Piepho, C. Shan, and M. D. Ankeny, DNAPL migration through a fractured perching layer, *Ground Water* 36(4), 605-610, 1998.

Tuck, D. M., Discussion of "DNAPL migration through a fractured perching layer" by D. B. Stephens, J. A. Kelsey, M. A. Prieksat, M. G. Piepho, C. Shan, and M. D. Ankeny, *Ground Water*, 37(4), 485-486, 1999.

Tuck, D. M., Primary drainage of NAPL governed by time-dependent interfacial properties, in press.

Tuck, D. M., and C. Rulison, Interfacial effects of a hydrophobic dye in the tetrachloroethylene-water-glass system (U), *Re p. WSRC-TR-97-0038*, Westinghouse Savannah River Co., Aiken, SC. 1998.

Tuck, D. M., G. M. Iversen, W. A. Pirkle and C. Rulison. 1998. "Time-dependent interfacial property effects on DNAPL flow and distribution." in G. B. Wickramanayake and R. E. Hinchee, ed. *Nonaqueous-Phase Liquids: Remediation of Chlorinated and Recalcitrant Compounds*, pp. 73-78, Battelle Press, Columbus, OH.

Tuck, D. M., G. M. Iversen, and W. A. Pirkle, DNAPL penetration of saturated porous media under conditions of time-dependent surface chemistry. *Savannah River Site Environmental Remediation Systems in Unconsolidated Upper Coastal Plain Sediments - Stratigraphic and Structural Considerations: Carolina Geological Society 2000 Field Trip Guidebook*, pp. K1-K16, Carolina Geological Society, Aiken, SC, 2000.

Weast, R. C., ed., *CRC Handbook of Chemistry and Physics*, 70th ed,. CRC Press, Boca Raton, FL, 1989.

Reference	Dye	NAPL(s)	Concentration	Type of Experiments
Schroth et al. (1995)	Sudan III	Soltrol®, Duoprime®	0.01% by mass (0.081 to 0.086 g/L)	Lab-multiphase flow
Stephens et al. (1998)	Sudan III	1,1,1-TCA	N.A.	Lab-multiphase flow
Schwille (1988)	oil red (Sudan IV)	PCE, TCE, DCM	1 to 2 g/L	Lab-multiphase flow
Kueper et al. (1989)	? [1]	PCE	N.A.	Lab-multiphase flow
Keuper & Frind (1991)	Sudan IV	PCE	1 g/L	Lab-multiphase flow
Poulsen & Keuper (1992)	Sudan IV	PCE	1 g/L	Field-multiphase flow-distribution following release
McBride et al. (1992)	Sudan IV	Soltrol®, Soltrol® + Lubrizol® [2], mineral oil, TCE	0.02% by mass (0.16 to 0.29 g/L)	Lab-multiphase flow, spreading
Brewster et al. (1995)	Sudan IV	PCE	1.16 g/L	Field-multiphase flow-distribution following release
Fortin et al. (1997)	Sudan IV	o-xylene, DCB	1 g/L	Lab-multiphase flow-surfactant enhanced remediation-mobilization & dissolution
Kennedy & Lennox (1997)	Sudan IV	PCE, TCE	"sparing amount" [3]	Lab- multiphase flow-NAPL dissolution
Powers et al. (1992)	Oil-Red-O	TCE, styrene	0.5 g/L	Lab- multiphase flow-NAPL dissolution
Mayer & Miller (1993)	Oil-Red-O	PCE, TCE, DCB, 1,1-DCE, DBM	1.00 g/L	Lab-multiphase flow-blob formation
Pennell et al. (1996)	Oil-Red-O	PCE	1×10^{-4} M	Lab-multiphase flow-surfactant enhanced remediation-mobilization

Notes: NAPL abbreviations: PCE=tetrachloroethene, TCE=trichloroethene, 1,1,1-TCA=1,1,1-trichloroethane, DCB=1,2-dichlorobenzene, DCM=dichloromethane,DCE=1,1 dichloroethene, DBM=dibromomethane

(1) Probably Sudan IV based on use in subsequent studies.

(2)   Lubrizol® is a surfactant. NAPL solution was Soltrol® + 0.5% Lubrizol®.

(3) In their discussion, Kennedy & Lennox talk about Schwille (1988) as using "sparing amounts of dye." Hence their dye concentrations may be comparable.

Table 1. Experimental studies in the literature where the Sudan III family of dyes was used.

Solution Symbol	Uncorrected Mass Concentration of Sudan IV in PCE (g/L)	Corrected Mass Concentration of Sudan IV in PCE (g/L)	Corrected Sudan IV Concentration (M)
C0	0.00000	0.00000	0.000
C4	0.00508	0.00411	1.16×10^{-5}
C3	0.0508	0.0411	1.16×10^{-4}
C2	0.508	0.411	1.16×10^{-3}
C1.0	1.27	1.03	2.89×10^{-3}
C1.4	1.69	1.37	3.85×10^{-3}
C3.2	4.00	3.24	9.12×10^{-3}

Table 2. Sudan IV dye concentrations in the PCE solutions.

Solution Symbol	Corrected Mass Dye Concentration (g/L)	Adhesion Tension, γ_θ (dynes/cm)	Mean PCE Entry Pressure (cm of PCE)	95% Confidence Interval Error Bar (cm of PCE)	Adhesion Tension Ratio	Entry Pressure Ratio
C0	0.00000	44.2	27.3	2.2	1.000	1.000
C4	0.00411	38.8	26.9	5.7	0.878	0.985
C3	0.0411	32.1	21.7	2.1	0.726	0.795
C2	0.411	26.6	15.9	1.6	0.602	0.582
C1.0	1.03	19.9	7.2	3.8	0.450	0.264
C1.4	1.37	15.9	--	--	0.360	--

Table 3. Adhesion tension and mean PCE entry pressure into glass bead media. Adhesion tension is estimated for an interfacial age of 2500 seconds. The mean entry pressures for the C0 and C4 systems exclude results for media with intrinsic permeability outside the range 1.3×10^{-8} cm^2 < k < 1.7×10^{-8} cm^2. The ratios are calculated with respect to the results for the undyed PCE (C0) system.
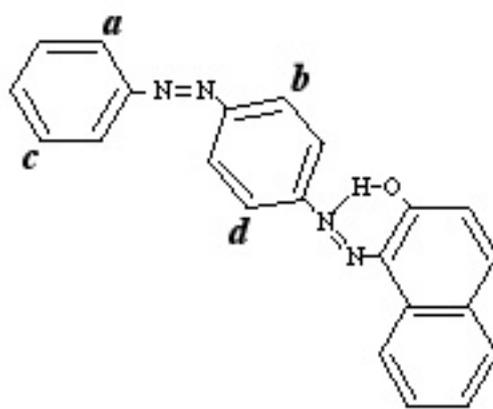
Figure Legends

Figure 1. Sudan III, Sudan IV, and Oil-Red-O dye structures. Sudan III is the fundamental molecule. The other two dyes contain different numbers of methyl groups substituted in positions *a*, *b*, *c*, and *d*. Sudan IV has methyl groups in positions *a* and *d*. Oil-Red-O has methyl groups in all four positions.

Figure 2. Experimental set-up.

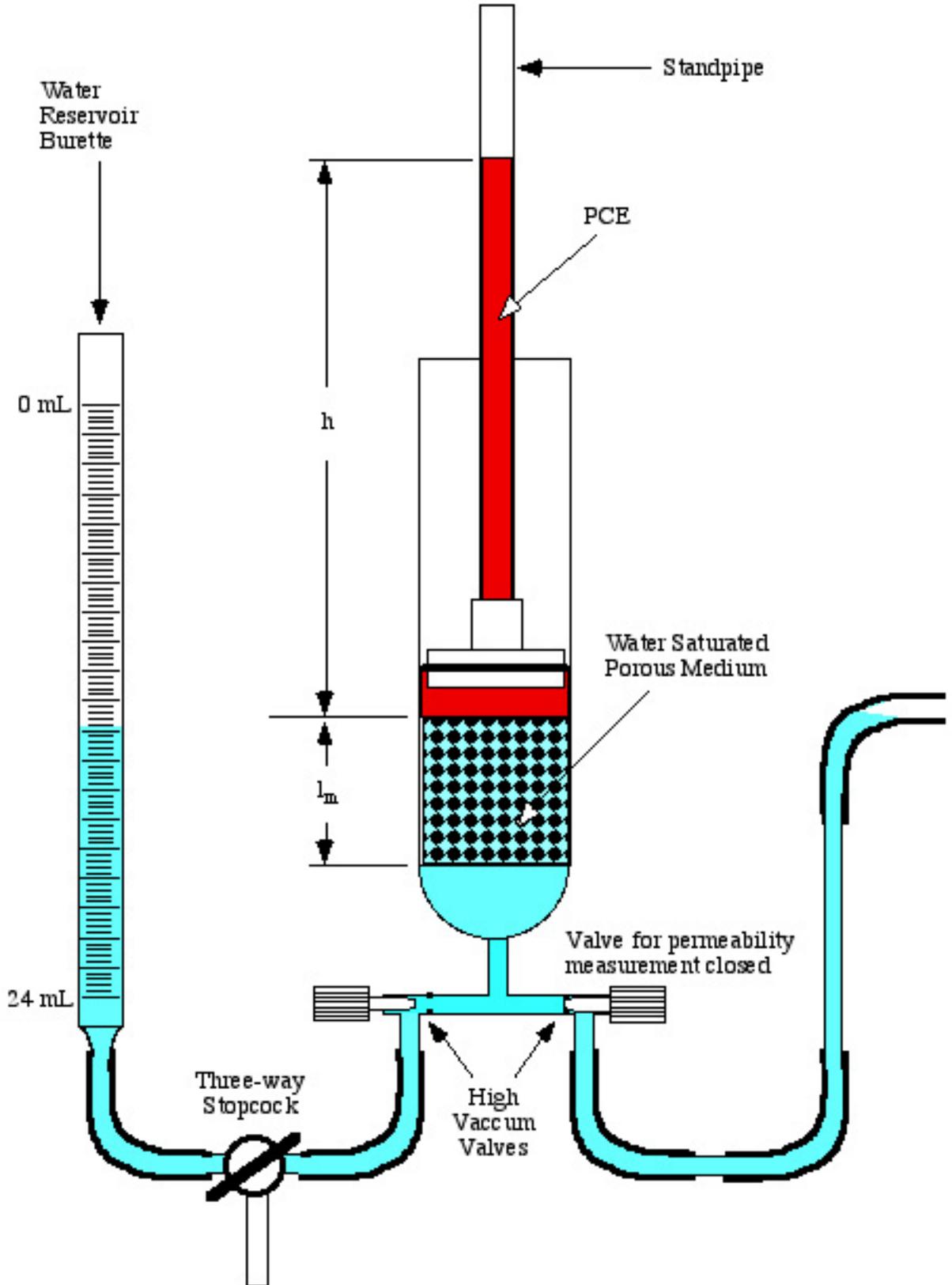Figure 3. Adhesion tension in the Sudan IV-PCE-water-glass system.

Figure 4. PCE entry pressure as a function of intrinsic permeability and Sudan IV dye content.

Figure 5. Mean PCE entry head as a function of dye concentration.

Sudan III, Sudan IV, and Oil-Red-O dye Structures.

Sudan III is the fundamental molecule. The other two dyes contain
different numbers of methyl groups substituted in positions *a*, *b*, *c*,
and *d*. Sudan IV has methyl groups in positions *a* and *d*. Oil-Red-O
has methyl groups in all four positions.

Water
Reservoir
Burette

Standpipe

PCE

0 mL

h

Water Saturated
Porous Medium

l_m

24 mL

Valve for permeability
measurement closed

Three-way
Stopcock

High
Vaccum
Valves

System Description

□ C0=0.00000 g/L

● C4=0.00411 g/L

▲ C3=0.0411 g/L

■ C2=0.411 g/L

○ C1.0=1.03 g/L

▲ C1.4=1.37 g/L

■ C3.2=3.24 g/L
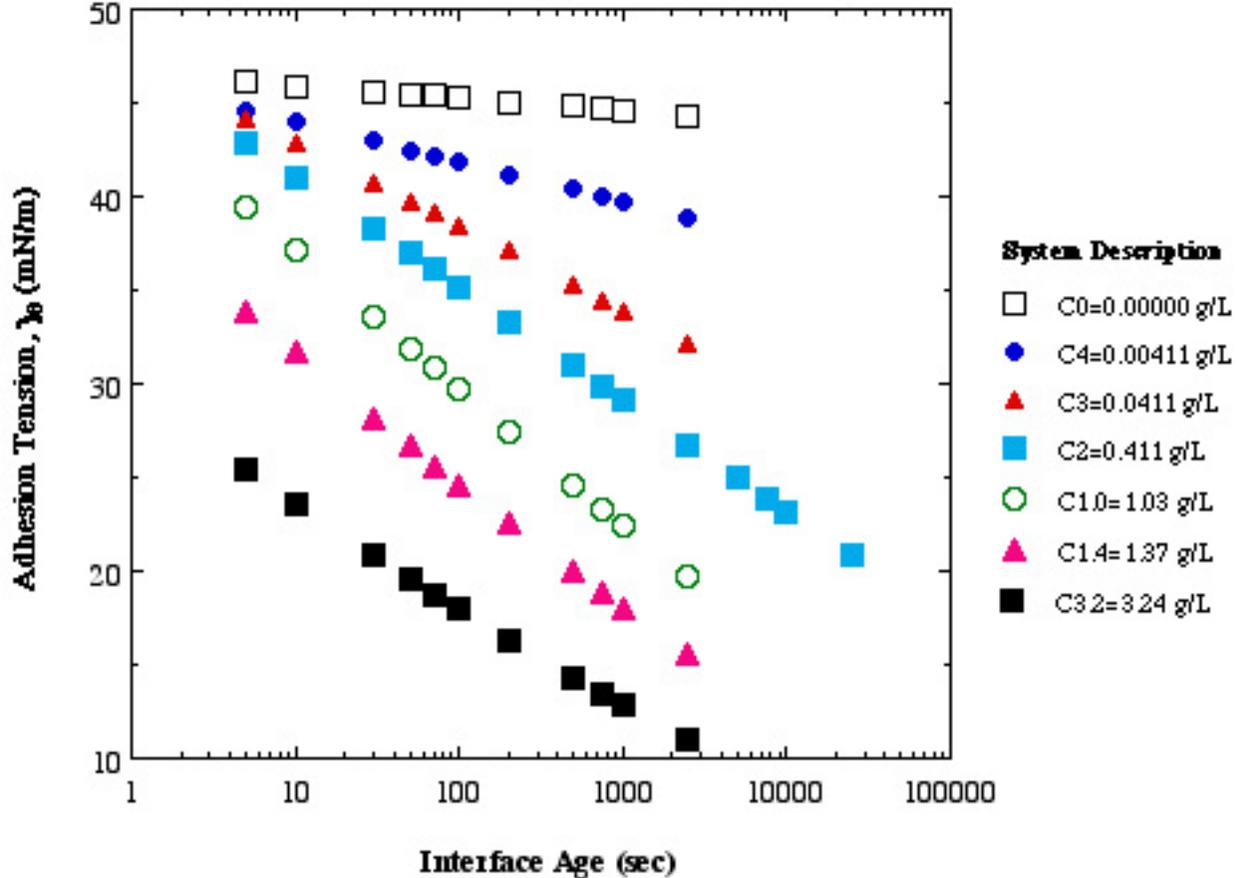
filename: "USCA paper #1 Fig. 3"

revised 8/30/01, revised 9/18/01
by Dr. David M. Tuck

Chart: PCE Height at Entry, h_e (cm) vs. Intrinsic Permeability (cm^2)

Legend:

- C = 0.00000 g/L
  $h_e(C=0) = 35.7 - 5.66\text{e}+8*k$ $R^2 = 0.738$
- C = 0.00411 g/L
  $h_e(C4) = 34.9 - 5.07\text{e}+8*k$ $R^2 = 0.084$
- C = 0.0411 g/L
  $h_e(C3) = 12.6 + 6.40\text{e}+8*k$ $R^2 = 0.157$
- C = 0.411 g/L
  $h_e(C2) = 10.6 + 3.78\text{e}+8*k$ $R^2 = 0.088$
- C = 1.03 g/L
  $h_e(C1.0) = 14.1 - 4.76\text{e}+8*k$ $R^2 = 0.330$

graph filename: "USEA paper1 Fig. x"

generated 7/16/01, revised 9/4/01
by Dr. David M. Tuck

Corrected Dye Concentration (g/L)

Mean PCE Entry Head (cm of PCE)

Lcrit = 25.76 * 10^(-0.5357*C')   R^2 = 0.983

Fig. 5"