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Azo Dyes and their Interfacial Activity: Implications for Multiphase Flow Experiments

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INTRODUCTION

Interfacial effects play an important role in governing multiphase fluid behavior in porous media (Neustadter 1984; Tuck et al. 1988). For instance, several dimensionless numbers have been developed to express important force ratios applicable to multiphase flow in porous media (Morrow and Songkran 1981; Chatzis and Morrow 1984; Wardlaw 1988; Pennell et al. 1996; Dawson and Roberts 1997). These force ratios emphasize the importance of interfacial properties. Our objectives are to provide chemical information regarding the dyes commonly used in multiphase flow visualization studies and to show the surface chemistry effects of the most commonly used dye, Sudan IV, in the tetrachloroethylene (PCE)-water-glass system.

Two dimensionless numbers used to define the major force ratios for multiphase flow in porous media are the capillary number, N_{ca}, and the Bond number, N_B. The capillary

number expresses the ratio of the viscous drag force of a flowing, continuous phase to the capillary force acting on a discontinuous phase. The viscous force acts to mobilize the discontinuous phase while the capillary force resists mobilization. For residual non-aqueous phase liquids (NAPLs) in water saturated porous media, the capillary number is given as

$$N_{ca} = \frac{\mu_w \upsilon_w}{\gamma_{nw}}$$ (1)

where μ_w is dynamic viscosity of water (g/cm-sec), υ_w, is average water pore velocity (cm/sec), and γ_{nw} is NAPL-water interfacial tension (mN/m (dynes/cm), g/sec^2). The Bond number expresses the ratio of gravity to capillary forces. It is expressed as (Morrow and Songkran 1981)

$$N_B = \frac{(\rho_n - \rho_w)gR^2}{\gamma_{nw}}$$ (2)

where ρ_n and ρ_w are the NAPL and water densities (g/cm^3), g is the acceleration of gravity (cm/sec^2), and R is a characteristic length (cm), generally taken to be the mean grain diameter (cm). In analogy with the capillary number, the gravity forces act to mobilize the discontinuous phase (assuming a density difference exists) while the capillary forces resist mobilization.

Both viscous drag forces and gravity forces effect residual NAPL ganglia in porous media during enhanced recovery processes using surfactants or cosolvents, and thus should be considered when evaluating NAPL mobilization potential. Addition of the two force ratios cannot be done directly, however, because of the difference in their magnitudes (Morrow and Songkran 1981; Morrow et al. 1988). Pennell et al. (1996) suggested the difference in magnitude between Bond and capillary numbers is due to different characteristic length scales over which they are defined. They derived an expression for a "total trapping number" (NT), which is, effectively, a sum of the capillary and Bond numbers, where both are based on the same length scale, the porous medium intrinsic permeability. Total trapping number is the ratio of the summed mobilizing forces (viscous and buoyancy) to the resistive force (capillary). Dawson and Roberts (1997) derived similar equations. The importance of fluid force ratios make knowledge of the fluid-fluid interfacial tension essential when conducting or interpreting experiments on multiphase fluid flow in porous media (Tuck, Discussion of "DNAPL migration through a fractured perching layer" by Daniel B. Stephens, James A. Kelsey, Mark A. Prieksat, Mel G. Piepho, Chao Shan, and Mark D. Ankeny, accepted for publication in Ground Water).

Another important consideration in multiphase fluid flow in porous media is the wetting relationship between the fluids and solid. Wetting is generally measured via the contact angle, defined as the angle between the fluid-fluid interface and the mineral/grain solid surface. Contact angle represents a mechanical balance between interfacial tensions at each of the three interfaces. It is defined by the Young equation as follows (Young 1805; Dullien 1992):

$$\cos\theta = \frac{(\gamma_{ns} - \gamma_{ws})}{\gamma_{nw}} \tag{3}$$

where γ_{ns} is the NAPL-solid interfacial tension (mN/m (dynes/cm), i.e., g/sec^2) and γ_{ws} is the water-solid interfacial tension (mN/m). This relationship controls the distribution of the fluid phases in a porous medium (Dullien 1992).

Application of force ratio concepts implicitly assumes a uniformly-wet porous medium, i.e., the porous medium is composed of a single solid phase. Water is generally assumed to be the wetting phase. This is the most common assumption made regarding multiphase flow in porous media involving water and NAPL. Fine-grained sediments are therefore assumed to act as capillary barriers to NAPL migration (Cohen and Mercer 1993). Thus NAPL exists as residual blobs or ganglia or as "pools" perched on fine-grained materials acting as vertical barriers. Components in either fluid phase that adsorb onto the solid surface can alter the wetting relationship by changing the solid-fluid interfacial tensions, γ_{ns} and γ_{ws}. Water-soluble surfactants are commonly used in solutions to change wetting properties. For example, Jaffé and co-workers (Hohmann 1987; Jaffé et al. 1989; Jaffé et al. 1991; Tuck 1992; Tuck 1994) examined the influence of a nonylphenyl phosphate ester which was found to reverse the wetting relationship between PCE and water on a glass surface. Other researchers have also documented changing wetting relationships with surfactant adsorption onto the solid surface (Gau and Zografi 1990; Varadaraj et al. 1991). Thus surface active components in the aqueous phase can significantly alter the expected subsurface NAPL distribution. The same will be true of surface active components in a NAPL or dense, non-aqeous phase liquid (DNAPL). In fact, several researchers have found that NAPL wetting tends to increase with contact time against the solid (Cohen and Mercer 1993). This must occur due to sorption of NAPL components at the solid-solution interfaces.

Strongly hydrophobic compounds generally partition strongly to solid surfaces from aqueous solution, but are usually assumed to remain dissolved in NAPL. Strongly hydrophobic organic dyes have been used in many experimental studies of multiphase flow to facilitate visual observation of fluid-phase distributions (Schwille 1988; Kueper et al. 1989; Kueper and Frind 1991; Kueper et al. 1993; Poulsen and Keuper 1992; Powers et al. 1992; Brewster et al. 1995; Pennell et al. 1996; Fortin et al. 1997; Stephens et al. 1998). Sudan IV is the most commonly used dye for non-aqueous phase liquids (NAPLs) in laboratory experiments (Kueper et al. 1989; Kueper and Frind 1991; Brewster et al. 1995; Fortin et al. 1997), and has been used in at least two field experiments (Poulsen and Keuper 1992; Kueper et al. 1993). Typical dye concentrations used in these experiments ranged between 1.0 and 1.7 g/L. Of the visualization studies listed above, only Pennell et al. (1996) mention evaluating the effect of dye on multiphase flow behavior. They reported that an Oil-Red-O dye concentration of 0.0001 M (approximately 0.04 g/L) had "no observable effect" on PCE mobility in the quartz sand media they used. Powers et al. (1992), however, reported that Oil-Red-O lowered interfacial tension between trichloroethylene (TCE) and water and between styrene and water at a concentration of 0.5 g/L. This interfacial activity can be understood in terms of the dye structure.

We present some background information on the chemistry and structure of several common azo dyes which have been used in multiphase flow visualization studies. This information will provide insight into why they should be expected to be interfacially active. We accomplish our second objective by presenting data illustrating the effects of Sudan IV on interfacial properties of the tetrachloroethylene (PCE)-water-glass system.

AZO DYES AND DYE STRUCTURES

Azo dyes are characterized by the azo group(s) (nitrogen-nitrogen double bond, -N=N-) which form part of their structure. The first synthesis of an azo dye occurred in 1859, and commercial production of azo dyes commenced within a few years (Catino and Farris 1978). Their versatility has made them the dominant category of commercially produced dyes, accounting for more than half the dyes available on the market and an even larger market share in terms of mass produced and sold (Catino and Farris 1978).

All multiphase flow visualization studies that we have encountered in the environmental literature (Schwille 1988; Kueper et al. 1989; Kueper and Frind 1991; Kueper et al. 1993; Poulsen and Keuper 1992; Powers et al. 1992; Brewster et al. 1995; Pennell et al. 1996; Fortin et al. 1997; Stephens et al. 1998) have used one of three azo dyes, Sudan III, Sudan IV, or Oil Red O. Table 1 contains a list of various trade names for these dyes along with a few other related dye compounds. It also contains the IUPAC nomenclature, Chemical Abstracts Service (CAS) numbers, and Color Index numbers. Lide and Milne (1995) present many additional trade name variations for Sudan III and Sudan IV. All of these dyes are minor variations of Sudan III; they simply contain different numbers of methyl groups on the benzene rings (see Table 2).

The potential for surface activity of these azo dyes arises from their asymmetrical structure and the fact that the azo groups and the phenol group are all polar and all on one "side" of the molecules (see Table 2). These criteria are necessary for partitioning at the water-NAPL interface. These dyes are also likely to partition to solid surfaces because of their aromatic nature (Girifalco and Good 1957). The dyes might be expected to become more strongly hydrophobic and potentially less surface active as additional methyl groups are substituted on the benzene rings. Hence we might surmise that surface activity of the dyes would increase in the following order: Oil Red O, Sudan IV, Sudan III.

SURFACE CHEMISTRY OF SUDAN IV

Solutions

Sudan IV dye was acquired from Sigma. The lot from which it came had a dye content of approximately 81%. The remaining 19% is inorganic salts, most likely either NaCl or KCl (Aldrich Chemical Company, Inc. 1998). The PCE used to prepare all solutions was "Tetrachloroethylene 99%". It was used as received from Mallinckrodt Inc. (Paris, KY). Dyed PCE solutions were prepared by dissolving 0.508 g of dye, as received, into 100 mL of PCE. Serial dilutions of this stock solution were prepared. Characteristics of the solutions are presented in Table 3. All PCE solutions were allowed to equilibrate with

water for several days prior to measuring the interfacial properties. The density of all PCE-saturated aqueous phases was 0.9962 g/cm^3 with a standard deviation of 0.0025 g/mL (n = 13).

Interfacial Tension

Interfacial activity of Sudan IV was studied in the tetrachloroethylene (PCE)-water-glass system with all fluid phases mutually saturated. Dyed-PCE-water interfacial tensions were measured as a function of Sudan IV dye concentration. Dynamic interfacial tension values were measured using a Krüss Drop Volume Tensiometer (model DVT10, Krüss USA, Charlotte, NC) by pumping PCE as the discontinuous (drop-forming) phase into PCE-saturated water. Varying the PCE pump rate varies the average time to form a drop. Average interface age of a drop was calculated by multiplying the drop formation time by 3/7 (Joos and Rillaerts 1981). Interfacial tension is computed from drop volume using the following equation (Tate 1864):

$$\gamma_{nw} = \frac{V_D \Delta \rho g}{\pi d} \tag{4}$$

where γ_{nw} is the NAPL-water interfacial tension (mN/m), V_D is the volume of the drop (cm^3), $\Delta \rho$ is the density difference between the two fluids (g/cm^3), g is gravitational acceleration (cm/sec^2), and d is the diameter of the tip from which the drop is suspended (cm). Further experimental details are presented elsewhere (Tuck and Rulison 1998).

Contact Angle: Wetting Relationships against Glass

Wetting relationships between Sudan IV-dyed PCE and PCE-saturated water on a glass surface were examined by measuring contact angle as a function of dye concentration. Contact angles were measured using a Krüss Goniometer (model G10). For each concentration, a drop of dyed PCE was placed on a glass slide which had been submerged in water pre-equilibrated with undyed PCE. The drop was allowed to equilibrate on the glass surface for approximately five minutes. The contact angle was then measured through the PCE phase (Tuck and Rulison 1998), the supplement giving the angle through the aqueous phase.

RESULTS

Interfacial Tension

Mean interfacial tension results between Sudan IV-dyed PCE and water are illustrated for the different dye concentrations as a function of average interface age (inversely proportional to PCE flow rate) in Figure 1. In all cases, interfacial tension decreases as average interface age increases.

The undyed PCE-water interfacial tension leveled off at approximately 50.4 mN/m (dynes/cm). The lowest dye concentration solution, 0.00508 g/L, also appeared to level off, but at a lower interfacial tension of approximately 40.3 mN/m (dynes/cm). Interfacial tension for all remaining solutions of higher dye concentration still appeared to be decreasing with increasing interface age. At the lower dye concentrations (< 0.5 g/L) the dye appeared to increase the interfacial tension at the higher flow rates (lower interface ages). At the highest dye concentration, 5.08 g/L, all interfacial tension results were significantly less than the results for the undyed-PCE-water system. Figure 2 is a plot of the lowest measured interfacial tension as a function of the dye concentration. The results indicate that Sudan IV reduces the PCE-water interfacial tension even at the lowest dye concentration tested.

PCE-Water Wetting Relationship on Glass - Contact Angle Measurements

Contact angle results for the Sudan IV dyed PCE with respect to water are shown in Figure 3 as a function of dye concentration. Contact angle, through the aqueous phase, for undyed PCE was $58° \pm 3°$. At the lower three dye concentrations, the dye appeared to increase the hydrophobic/non-polar nature of the PCE phase. Contact angles measured through the aqueous phase decreased, indicating that the aqueous phase was relatively more wetting on the glass surface than was the case for undyed PCE. At the highest concentration, however, the wetting relationship was rendered neutral; contact angle, measured through the aqueous phase, increased to $93° \pm 3°$. Two additional solutions were prepared to examine the contact angle behavior at concentrations between 5.08 and 0.508 g/L. Dilutions of the 5.08 g/L solution were prepared to yield dye concentrations of approximately 1.27 g/L and 1.69 g/L. Contact angles for these solutions also indicated significant changes in the wetting relationship. The contact angles, measured through the aqueous phase, were $70° \pm 3°$ for the 1.27 g/L and $75° \pm 3°$ for the 1.69 g/L solutions. The wetting relationship clearly changes as the dye concentration increases.

DISCUSSION

Interfacial Tension

The dynamic interfacial tension results obtained by the drop volume method illustrate three points. First, the small decrease in interfacial tension with decreasing flow rate suggests that there were slight impurities in the "pure" PCE that we used. While a high grade of PCE was used, it did contain 0.5% ethanol as a stabilizing agent. This emphasizes the sensitivity of surface chemistry to "minor" constituents within the system. The second thing indicated by the dynamic interfacial tension results is that Sudan IV dye is interfacially active. Interfacial tension between the PCE phase and water was reduced even at the lowest dye concentration. Third, the interfacial activity exhibits a strong time dependence, i.e., the interfacial tension reduction depends on the age of the interface as well as on the dye concentration.

Standard methods for measuring surface and interfacial tension (ASTM 1998; ASTM 1994a; ASTM 1994b) recommend relatively little time for equilibration of the interface. Two procedures recommending use of the du Nouy ring method suggest equilibration times of "at least 5 minutes after the interface is formed" (ASTM 1994a) and approximately one minute (ASTM 1994c). The third method is a drop-weight method in which they recommend that the "total time to expose the drop is between 45 and 60 s" (ASTM 1998). These recommended equilibration times are likely to yield relatively high interfacial tension values. This can be seen by examining the data of Figure 1 for interfacial ages older than approximately 60 seconds. These standard interfacial tension measurement procedures are thus likely to lead to underestimating the mobility of Sudan IV-dyed PCE in saturated porous media.

Wetting Relationships

NAPL wetting has been shown to increase with time of exposure to the solid surface for complex NAPLs characteristic of natural or refined oil (Treiber et al. 1972; Cohen and Mercer 1993), presumably due to adsorption and/or deposition of organic matter onto the solid surface. As a result, Anderson (1986) has suggested that equilibrium contact angle measurements involving NAPLs containing surface active agents may require aging for hundreds to thousands of hours. It is therefore possible that, given longer equilibration time, dyed PCE could become the wetting phase, even at lower dye concentrations. This prediction is based on the previous literature results together with the fact that only a very short equilibration time (approximately 5 minutes) was used during this study. Recent experimental evidence supports this prediction (Tuck et al. 1996; Pirkle et al. 1997).

Reversal of the wettability relationship has major implications for DNAPL mobility in the saturated subsurface. First, the wettability relationship controls the fluid phase distribution in the subsurface (Dullien 1992). As the wettability relationship changes, so the fluid phase distribution will change. Second, the mechanism of DNAPL migration into fresh, uncontaminated areas will change as wettability changes. DNAPL moves pore-to-pore by piston-type displacements governed by the capillary and Bond number force ratios when it is non-wetting with respect to the aqueous phase. As DNAPL becomes the wetting phase, however, may begin to migrate via thin-film flow (Tuck et al. 1996; Pirkle et al. 1997). Surface active components in a DNAPL could therefore change both the pattern of expected subsurface DNAPL distribution and the mechanism by which the DNAPL migrates.

CONCLUSIONS

The azo dyes commonly used to stain NAPLs in multiphase flow visualization experiments are all likely to be surface actvue given their molecular structure. We have presented an example here; Sudan IV dye significantly influences interfacial properties in the PCE-water-glass system. It reduced the interfacial tension between water and the dyed PCE even at concentrations approximately three orders of magnitude lower than the commonly used dye concentration range (1 to 2 g/L). This will therefore result in a decreased

capillary force resisting PCE mobility. In addition, at concentrations greater than 1 g/L the dye appears to significantly alter the wetting relationship between the fluid phases. The wetting relationship may change significantly even at lower dye concentration. This prediction has been confirmed experimentally (Tuck et al. 1996; Pirkle et al. 1997), and is further supported by slow changes in wetting relations noted in the literature (Cohen and Mercer 1993; Anderson 1986; Villaume et al. 1983).

These results indicate the importance of testing the effects of dyes prior to using them in experimental systems. At the very least, it is very important to report what dye was used and its concentration. The interfacial effects of the dye also suggest that previous experimental results obtained using Sudan IV-dyed DNAPLs should be used with caution. Qualitative interpretrations should be made bearing in mind the increased DNAPL mobility due to the dye.

Similarity noted between behavior of the dyed-PCE-water interface and an SRS DNAPL-water interface during du Noüy ring method interfacial tension measurements (Tuck and Rulison 1998) suggests that the dye makes PCE behave in a fashion similar to what might occur in the field. From this perspective, the dye may make visualization experiments more comparable to the field by increasing the DNAPL complexity in a manner that begins to approximate the complexity of "real" field DNAPLs. The effects of this complex chemisty and surface chemistry are generally not considered by models of multiphase flow. The importance of this complexity needs to be investigated further in order to improve our understanding of DNAPL behavior in the subsurface.

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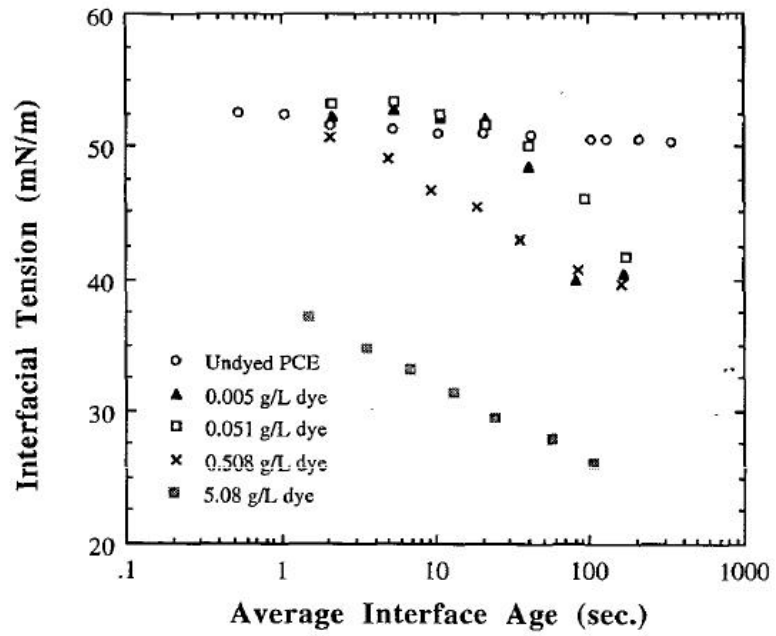
Figure 1. Interfacial tension between Sudan IV-dyed PCE and water as a function of dye concentration and average interface age.
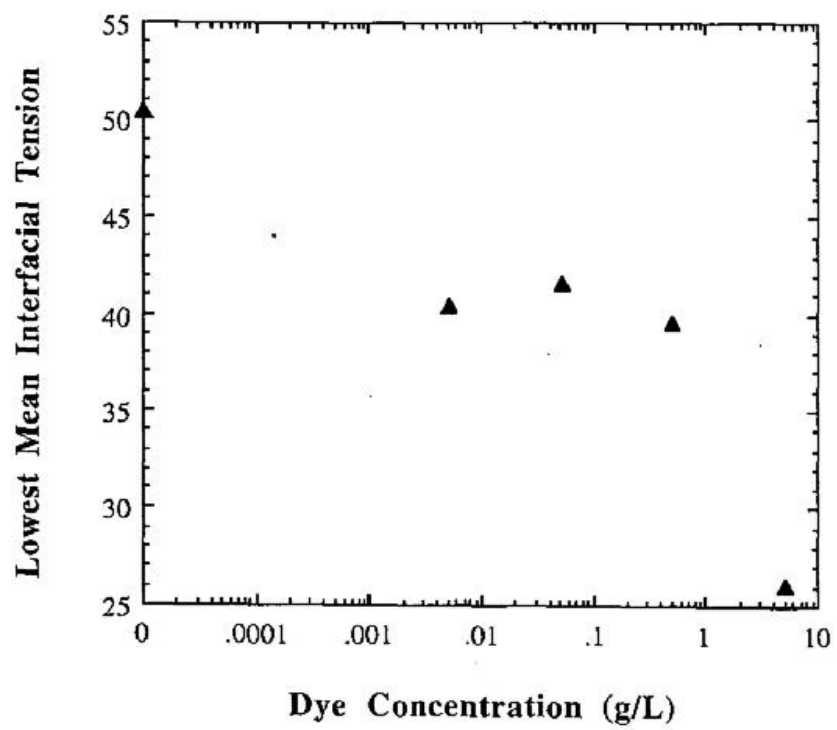
Figure 2. Lowest measured interfacial tension as a function of the Sudan IV dye concentration.
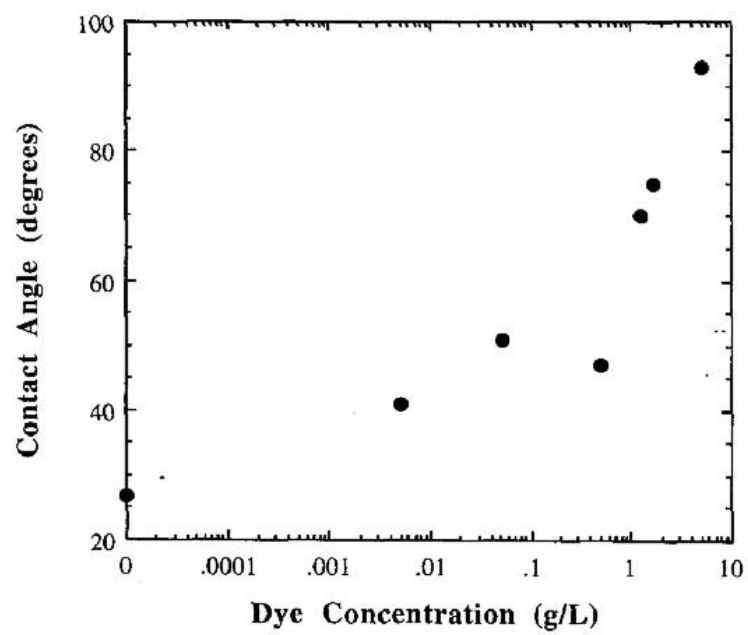
Figure 3. Contact angle between dyed-PCE, water, and glass measured through the water phase as a function of Sudan IV dye concentration in the PCE.

"Primary" Trade Name	IUPAC Name	CAS / Color Index Numbers	Trade Name Variations
Sudan III	1-[[4-(phenylazo)phenyl]azo] -2-naphthalenol	85-86-9 / 26100	D and C Red 17; Cerasin Red; Fat Ponceau G; Fat Soluble Sudan; Oil Red OB; Oil Red OB3; Scarlet B; Solvent Red 23; Sudan; Sudan G; Sudan Red B; Tony Red
Sudan IV	1-[[2-methyl-4-[(2-methylphenyl) azo]phenyl]azo]-2-naphthalenol	85-83-6 / 26105	Biebrich Scarlet R; Fat Ponceau; Fat Ponceau R; Fat Ponceau 4; Lipid Crimson; Oil Red; Oil Red IV; Sudan R; Sudan BB; Scarlet Red; Scharlach; Solvent Red 24
Sudan Red B	1-[[3-methyl-4-[(3-methylphenyl) azo]phenyl]azo]-2-naphthalenol	3176-79-2 / 26110	
Oil Red EGN	1-[[2,5-dimethyl-4- [(2-methylphenyl)azo]phenyl] azo]-2-naphthalenol	4477-79-6 / 26120	Solvent Red 26
Oil Red O	1-[[2,5-dimethyl-4- [(2,5-dimethylphenyl)azo]phenyl] azo]-2-naphthalenol	1320-06-5 / 26125	Solvent Red 27

Table 1. Azo dye nomenclature, Chemical Abstracts Services (CAS) numbers, and Color Index numbers.

Dye Name(s)	Dye Structure	References
Sudan III D & C Red 17		(Schroth et al. 1995; (Stephens et al. 1998)
Sudan IV Solvent Red		(Kueper and Frind 1991) (Poulsen and Keuper 1992) (Brewster et al. 1995) (Fortin et al. 1997)
Sudan Red B		
Oil Red EGN		
Oil Red O		(Schwille 1988) (Powers et al. 1992) (Pennell et al. 1996)

Table 2. Dyes used in flow visualization studies in the ground water literature.

Sudan IV Dye Concentration (g/L)	Active Fraction Dye Concentration (g/L)	PCE Solution Density (g/mL)
0.00000	0.00000	1.6153
0.00508	0.00411	1.6150
0.0508	0.0411	1.6158
0.508	0.411	1.6147
1.27	1.03	1.6145
1.69	1.37	NA
5.08	4.11	1.6141

Table 3. Tetrachloroethylene (PCE) solutions and Sudan IV dye concentrations. NA indicates that the density was not measured.