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UNIQUE INTERFACIAL PROPERTIES OF THE CHLORINATED SOLVENT DNAPL AT SAVANNAH RIVER NATIONAL LABORATORY

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The unsaturated zone at the Department of Energy's Savannah River Site (SRS) contains significant quantities of DNAPL. Tetrachloroethene (90-95%) (PCE) and trichloroethene (5-10%) (TCE) have been identified as the primary constituents in this DNAPL. The surfactants dibutylbutylphosphonate (DBBP) and tributylphosphate (TBP) used by the DOE facility might also be present in the DNAPL. Remediation efforts conducted at the site have reduced the DNAPL contamination level, but the efficiency was less than expected due to the unexpected presence of DNAPL in small pores (BHI, 1996). It is hypothesized that variable interfacial properties in this DNAPL/water/porous medium system could have contributed to its migration into low conductivity regions, effectively entrapping it in small pores, thereby rendering it difficult to extract. For better accessibility and recovery of the DNAPL in the SRS contaminated sand, it is essential to understand factors governing the DNAPL mobility in the subsurface. The objective of this research was to characterize the interfacial properties of the SRS DNAPL. Related work then sought to determine if these properties could have contributed to the presence of DNAPL in pore spaces that are inaccessible to remediation efforts.

MATERIALS AND METHOD

A DNAPL sample taken from the Savannah River site was used as the site DNAPL. Surrogate DNAPL mixtures were prepared with TCE (99.5%, Sigma Aldrich Co.) as the base with other constituents used at the SRS facility. Tributylphosphate (99%, Sigma Aldrich Co.) and dibutylbutylphosphonate (90%, Sigma Aldrich Co.) were added to the TCE as surfactants to represent those used in the plutonium production process.

Personnel at SRS used Raman spectroscopy to compare the signatures of the SRS DNAPL to pure PCE with a variety of different oils used historically at SRS. They found similarities in the spectrum between the SRS DNAPL and PCE containing a bearing and circulating oil at 1% concentration (Mobil DTE oil heavy medium, number 6001638). This oil was also added to TCE to create a surrogate DNAPL.

De-ionized water was used in all aqueous phase solutions preparations. An Orion pH meter model 420A was used in all titrations and pH adjustments. The pH was adjusted with 0.1N HNO_3 or 0.1N KOH solutions.

All interfacial tension (IFT) and surface tension (ST) measurements were conducted using the Du Nouy ring method. A ring tensiometer (Fisher surface tensiomat, model 21) was used to determine the surface and interfacial tension of all fluid systems according to the ASTM method at room temperature (25±1 ºC)[1].

Non-aqueous potentiometric titration was used to determine the acid content of the DNAPL following the method used by Zheng and Powers[2]. The DNAPL was diluted in methyl isobutyl ketone (98.5%, Fisher Scientific Co.). Tetrabutyl ammonium hydroxide (Fisher Scientific Co.) was used as a titrant.

RESULTS AND DISCUSSION

Measured surface and interfacial tensions are presented in Table 1. The SRS DNAPL clearly has properties that differ from pure TCE or PCE. The interfacial tension is more than an order of magnitude lower than TCE and the surface tension at the interface between air and water equilibrated with the DNAPL is 43% less than for water equilibrated with pure TCE or PCE.

Surrogate mixtures of TCE and surfactant or oil contaminants expected to be present in the DNAPL also had lower interfacial tensions than pure TCE (Table 1). The reduction in IFT (9 - 38%) was minimal, however, compared with the very low IFT of the SRS DNAPL. Thus, there are constituents in this DNAPL other than the historically used oil and surfactant that have significant impact on the IFT and ST associated with the SRS DNAPL.

Table 1. Measured interfacial tension (DNAPL/water) and surface tension (air/water) following equilibration with DNAPL

Sample	$ST^{a/w}$ (dynes/cm)	$IFT^{D/w}$ (dynes/cm)
SRS DNAPL	39.8 (±0.9)	1.2 (±0.2)
TCE	72.7*	34.9 (±0.1)
PCE	72.8*	47.5*
TCE w/ 5% oil	--	23.3 (±0.6)
TCE w/ 10% oil		21.6 (±0.5)
TCE w/ 7% TBP	--	25.3 (±0.3)
TCE w/ 7% DBBP		23.3 (±0.3)

* published values[3]

The pH of 20 mL water equilibrated with 10 mL SRS DNAPL was 3.8, clearly suggesting the presence of acidic constituents in this DNAPL. The acid content of the SRS DNAPL was measured by a non-aqueous titration technique. Results of this technique are presented in units of mg acid (as KOH) per g of DNAPL sample. The SRS DNAPL contains 4.0 mg acid/g. Zheng and Powers[Error! Bookmark not defined.] showed that the increased acid content of creosote DNAPLs is directly correlated to a reduction in interfacial tension. For example, a creosote sample with an acid content of 3.2 mg acid/g had an interfacial tension less than 10 dynes/cm. Neither of the surfactants (TBP or DBBP) or hydraulic oil constituents in our surrogate DNAPL had measurable acidic content (≤0.1 mg acid/g), thus providing further evidence that there are additional unknown constituents in the SRS DNAPL.

IMPLICATIONS

Application of the Laplace equation, which quantifies the rise of a wetting fluid in a capillary tube, is often used to predict that the entry pressure of a non-wetting fluid (our DNAPL) into a pore is directly proportional to the interfacial tension. Thus, the 40-fold factor between the IFT of the SRS DNAPL and pure PCE indicates that – under the same hydraulic head conditions – the SRS DNAPL can enter pores that are $1/40^{th}$ of the diameter of pores that PCE can enter. This difference could explain the presence of DNAPL in a clay sandy silt layer (d_{90}~0.05 mm) where pure PCE could only enter the gravelly sand layers (d_{90}~2 mm).

On-going work with funding through the DOE EMSP is focused on further analytical work to understand the constituents and sources for the constituents that contribute to the low IFT measured at the DOE SRS facility.

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