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INTERFACIAL PARTITIONING TRACER TEST MEASUREMENTS OF ORGANIC-LIQUID/WATER INTERFACIAL AREAS: APPLICATION TO SOILS AND THE INFLUENCE OF SURFACE ROUGHNESS

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Abstract

Interfacial areas between an organic immiscible liquid and water were measured for two natural soils using the aqueous-phase interfacial partitioning tracer test method. The measured values were compared to measured values for silica sands compiled from the literature. The data were compared using the maximum specific interfacial area as a system index, which is useful for cases wherein fluid saturations differ. The maximum specific interfacial areas measured for the soils were significantly larger than the values obtained for the sands. The disparity between the values was attributed to the impact of surface roughness on solid surface area and hence film-associated interfacial area. A good correlation was observed between maximum specific interfacial area and specific solid surface area measured with the N₂/BET method. The correlation may serve as a means by which to estimate maximum specific organic-liquid/water interfacial areas. Interfacial areas measured with the interfacial partitioning tracer method were compared to interfacial areas measured with high-resolution microtomography. Values measured with the former method were consistently larger than those measured with the latter, consistent with the general inability of the microtomography method to characterize roughness-associated surface area.

INTRODUCTION

Two primary methods are available to measure fluid-fluid interfacial areas for natural porous-media systems, interfacial partitioning tracer tests and microtomography employing high-resolution imaging. Interfacial partitioning tracer tests (IPTT) provide indirect measurements of interfacial area based on the retention behavior of tracers that accumulate at the interface. These tracer tests can be conducted in several ways, including the use of either aqueous-phase or gas-phase modes (1–16).

Interfacial partitioning tracer tests have been used to examine the influence of fluid saturation, porous-medium texture, and fluid-displacement regimes on the organic-liquid/water interface (e.g., ^{4,8,10,11,13,16}). These prior IPTT applications have used porous media comprised of glass beads or silica sands. The applicability and efficacy of the partitioning tracer method has not been evaluated significantly for natural soils and sediments.

The objective of this study was to evaluate the use of the IPTT method for measuring organic-liquid/water interfacial areas for natural soils. The results of these experiments were integrated with the results of several previously published studies employing silica sands to evaluate the influence of porous-medium texture and surface-area properties on measured interfacial areas. The data were compared using the maximum specific interfacial area as a system index.

MATERIALS AND METHODS

Materials

Two natural soils were used in this study. One (Vinton) was collected from Pima County, AZ, and the other (Eustis) was collected from Alachua County, FL. Selected properties of the soils are presented in Table 1. Volume-normalized specific solid surface areas were determined using two methods. For the first, the surface areas were obtained using a simple geometric-based calculation along with an assumption that the surfaces of the solids are smooth (see Table 1). The impact of surface roughness is not incorporated into this calculated value. For the second method, specific solid surface areas were measured using the N₂/BET method. These surface areas (to be referred to as NBET surface area) do incorporate the contributions of surface roughness. Tetrachloroethene was used as the model organic immiscible liquid.

Methods

The aqueous-phase interfacial partitioning tracer test was used to measure organic-liquid/water interfacial areas. Sodium dodecyl benzenesulfonate (SDBS) (~50 or ~200 mg/L) was used as the interfacial partitioning tracer and pentafluorobenzoic acid (PFBA) (~100 mg/L) was used as the non-reactive tracer. The solutions were prepared with deionized water saturated with tetrachloroethene. The columns used for the tracer tests were constructed of stainless steel, and were 7-cm long by 2.2-cm diameter. All tubing, porous frits, and connectors were constructed of stainless steel.

The columns were dry packed to obtain uniform bulk densities. The packed columns were then flushed with CO₂ to displace air, then saturated with de-aerated water using a single-piston precision-flow HPLC pump to provide constant flow to the bottom of the vertically oriented column. The results of prior studies employing microtomographic imaging have shown that water-saturated conditions are obtained with this method (e.g., 15). Non-reactive tracer tests were conducted before emplacement of the organic liquid to characterize the hydrodynamic properties of the packed columns. In addition, tracer tests were conducted in separate packed columns to measure adsorption of SDBS by the porous media. Measurable sorption was observed for both soils.

After completion of the non-reactive tracer test, a few pore-volume equivalents of the organic liquid were pumped into the bottom of the water-saturated column using a syringe pump (Sage, Model 355). Tetrachloroethene-saturated water was then pumped into the column from the top to displace mobile organic liquid and thus establish a residual saturation. The capillary number for this displacement was calculated to be $1 \cdot 10^{-6}$, which is similar to values typically used to establish a stable, discontinuous distribution (i.e., residual saturation) of non-wetting liquid (e.g., 15,17). The porous frits were replaced after the displacement process to ensure that no organic liquid was entrapped within the frits.

Non-reactive tracer tests were conducted after emplacement of the organic liquid. Comparison of the results to those obtained for the tracer tests conducted prior to emplacement indicated minimal impact of organic-liquid saturation on overall tracer transport. The non-reactive and interfacial partitioning tracer tests were conducted sequentially. Four sets of tracer tests were conducted for each soil, employing two separate packed columns for each soil. All tracer tests

were conducted at a flow rate equivalent to an average pore-water velocity of approximately 25 cm/h. Effluent concentrations of PFBA and SDBS were analyzed using UV-Vis spectrophotometry (Shimadzu, model 1601). At the completion of each set of experiments, the porous medium was subjected to solvent extraction to determine organic-liquid saturation.

Data Analysis

Retardation factors for SDBS were obtained by moment analysis of the breakthrough curves. The specific organic-liquid/water interfacial area (A_{nw} , L^{-1}), which represents interfacial area normalized by the porous-medium volume, was obtained with knowledge of the retardation factor R , interfacial partition coefficient (K_i), equilibrium sorption coefficient (K_d), and volumetric water content (θ_w):

$$R = 1 + K_d \rho_b / \theta_w + K_i A_{nw} / \theta_w \quad (1)$$

where K_i was determined by measurement of interfacial tension as a function of SDBS concentration (e.g., 3,4). The contribution of SDBS adsorption by the porous medium was subtracted from the total retardation. Fluid-fluid interfacial area is comprised of two components, area associated with capillary domains (e.g., menisci) and area associated with non-wetting fluid in contact with films of wetting fluid covering grain surfaces. Interfacial partitioning tracer tests characterize both components of interfacial area (i.e., total interfacial area).

The surface-area-to-volume ratio (SA/VOL) is a fundamental descriptor used for example to characterize the basic morphology of three-dimensional bodies. Herein, the SA/VOL represents the organic-liquid/water interfacial area normalized by the volume of the organic liquid. The SA/VOL was calculated as the quotient of A_{nw} and θ_n , where θ_n is volumetric organic-liquid content. Interfacial areas are most often presented in the literature as normalized by the volume of the porous medium. To be consistent with this standard, the SA/VOL was scaled to the volume of the porous medium by multiplying SA/VOL by porosity. This scaled SA/VOL term will be referred to as the maximum specific interfacial area (A_m). The A_m serves as an index for a given system, indicative of the theoretical maximum interfacial area associated with that system (18). Comparison of fluid-fluid interfacial areas for systems wherein fluid saturations differ is facilitated by use of such a system index. The results of prior research have shown that SA/VOL and A_m values obtained under different conditions, such as drainage versus imbibition, are similar when based on total interfacial areas (18,19).

RESULTS AND DISCUSSION

Interfacial Partitioning Tracer Test Results

Residual tetrachloroethene saturations of approximately 0.15 and 0.17 were obtained for the Vinton and Eustis soils, respectively. Breakthrough curves obtained from the tracer tests are illustrated in Figure 1. The curves for SDBS exhibited tailing, perhaps indicating an influence of mass-transfer constraints on transport. Retardation factors for SDBS, the interfacial partitioning tracer, were relatively large for both systems. Specific organic-liquid/water interfacial areas of 939 (± 447 , 95% confidence interval) cm^{-1} and 422 (± 230) cm^{-1} were obtained for Vinton and Eustis, respectively. These values are significantly larger than values reported in prior tracer-test studies employing sand and glass-bead media, which range from approximately 30 to 100 cm^{-1} for similar S_n values (3,4,8,10,11,13,16).

The measured interfacial areas have a fair degree of uncertainty, with coefficients of variation of approximately 25%. This degree of uncertainty is similar to that observed in prior IPTT studies (15,16). A comprehensive analysis of several possible sources of uncertainty for the

IPTT method was conducted in a prior study (15). One concern associated with the tracer-test method is the potential impact of the interfacial tracer on the configuration of the fluid phases, and resultant inaccuracies in measured interfacial areas. This issue was examined by using X-ray microtomography to measure interfacial areas and fluid distributions for the same column before and after emplacement of a SDBS solution. The results indicated that the surfactant tracer had minimal impact on the configuration of the fluid phases, and thus on measured interfacial areas (15). Another concern associated with the IPTT method is that some interfacial-area domains may be physically inaccessible to the tracer, or that access may be rate limited via diffusive mass transfer. For both of these cases, such constraints would result in calculated interfacial areas that are smaller than the actual value. Another factor that can cause uncertainty in tracer-test results is uncertainty in the magnitude of tracer sorption by the porous medium, which contributes significantly (~50%) to total tracer retention for both porous media used in the current study. Brusseau et al. (15) conducted a detailed analysis of the impact of tracer sorption, and found that uncertainty associated with tracer sorption contributes to the overall uncertainty associated with the IPTT method, but when accounted for, does not deleteriously impact accuracy. A similar analysis for the soils used in the current study produced similar results.

The maximum specific interfacial areas are $6257 (\pm 2978) \text{ cm}^{-1}$ and $2480 (\pm 1352) \text{ cm}^{-1}$ for the Vinton and Eustis soils, respectively. For both soils, the measured interfacial areas as well as the maximum specific interfacial areas are much larger than the volume-normalized specific solid surface areas calculated using the smooth-sphere assumption (149 and 138 cm^{-1} for Vinton and Eustis, respectively). This disparity indicates that the aqueous-phase IPTT method measures interfacial area associated with surface roughness. This is consistent with the results of prior research (e.g., 3,13–15).

The maximum interfacial areas are significantly smaller than the volume-normalized specific solid surface areas measured for Vinton (53454 cm^{-1}) and Eustis (10816 cm^{-1}) using the N_2/BET method. In contrast, maximum interfacial areas measured with the gas-phase IPTT method have been shown to be similar in magnitude to NBET solid surface areas (e.g., 6,9, 12–14). For example, Peng and Brusseau (12) reported a maximum interfacial area for the Vinton soil, measured with the gas-phase IPTT method, that was similar to the NBET solid surface area, and is approximately 10-times larger than the value reported herein obtained with the aqueous-phase IPTT method. Differences in the magnitudes of interfacial areas obtained with the two methods are a function of wetting-phase saturation, with relatively similar values observed for higher saturations, whereas the gas-phase values become increasingly larger than the aqueous-phase values as saturations decrease (6,9,14). This indicates that the aqueous-phase method provides an incomplete measure of interfacial area at lower saturations. This disparity is attributed to the nature of the fluid distributions and relative accessibility of interfaces to the tracers for the two methods (9,14).

Comparison to Literature Data

Several IPTT studies have been reported in the literature and, as noted above, these studies have typically employed glass beads or silica sands. The results of these studies have to date not been examined in a comprehensive, comparative manner. The data for all studies employing silica sands were composited (see Table 2). It should be noted that the data, except for the value from reference ⁸, were obtained under residual-saturation conditions (i.e., imbibition conditions).

The maximum specific interfacial areas calculated from analysis of the literature data are plotted as a function of inverse median grain diameter in Figure 2. Inspection of the data shows that a relatively good correlation exists between interfacial area and inverse grain diameter. Such a relationship would be expected based upon the impact of grain size on pore size and

surface area, and thus on interfacial area, as noted previously (9,11,12,16,18,20). The relative consistency of results shown in Figure 2, across a number of studies and associated investigators, supports the general robustness of the aqueous IPTT method.

The maximum specific interfacial areas obtained herein for the Vinton and Eustis soils are plotted with the literature data in Figure 2. The values for the soils are observed to be significantly larger than the values for the silica sands. The disparity between the two sets of data remains when accounting for the uncertainty associated with the measured values (including tracer sorption effects).

Evaluating the Impact of Surface Roughness

A line representing specific solid surface area calculated with the smooth-sphere assumption is presented in Figure 2 for comparison. The maximum interfacial areas obtained for the sands are significantly above the line. Also included in Figure 2 is a value obtained for a glass-bead medium that has no measurable surface roughness (19). In contrast to the sands and soils, the maximum interfacial area for the glass beads is similar to the specific solid surface area predicted using the smooth-sphere assumption. These observations support the hypothesis that the IPTT method measures some fraction of interfacial area associated with surface roughness.

The results presented above suggest that surface roughness has a significant impact on the interfacial areas characterized by the aqueous-phase IPTT method. This is consistent with results reported for the gas-phase IPTT method (9,12–14). The apparent impact of surface roughness indicates that film-associated area is a significant component of the interfacial areas measured with the IPTT method.

Given that film-associated area is a significant component of interfacial areas characterized by the IPTT method, and given the apparent impact of surface roughness on surface area, it is anticipated that a relationship may exist between IPTT-measured interfacial areas and NBET solid surface area. Such a relationship is presented in Figure 3, wherein a good correlation is observed, inclusive of the sands and the soils. It should be noted that this simple relationship is based solely on the magnitude of the surface roughness. While this first-order approach may provide a useful means by which to estimate interfacial areas, it does not take into account the nature of the surface roughness, which may vary as a function of weathering conditions and other factors.

Comparison of IPTT and Microtomography Measurements

As noted previously, fluid-fluid interfacial areas may also be measured using high-resolution microtomography. Maximum specific organic-liquid/water interfacial areas measured with the microtomography method (18) are compared in Figure 2 to the maximum interfacial areas obtained with the IPTT method. The microtomography data comprise several of the same porous media that were used for the IPTT studies.

The areas measured with the microtomography method are similar to the smooth-sphere surface areas, due to the inability of the microtomography method to measure roughness-associated area (13–15). The IPTT-measured values are consistently larger than the microtomography-based values. This observation is consistent with the results of a prior study, employing two porous media, that compared organic-liquid/water interfacial areas measured with the two methods (15), and further supports the contention that the IPTT method measures some portion of interfacial area associated with surface roughness. In contrast to the results presented in Figure 2 for the sands and soils, all of which have measurable surface roughness, interfacial areas obtained with the two methods were identical for a glass-bead medium that has no measurable surface roughness (19).

Implications

The aqueous-phase interfacial partitioning tracer test method was used to measure organic-liquid/water interfacial areas for two natural soils. The results were compared to data reported for several silica sands compiled from the literature. Analysis of the results showed that surface roughness has a significant impact on IPTT-measured interfacial area. A correlation was observed between IPTT-measured interfacial area and NBET solid surface area. The correlation may serve as a means by which to estimate maximum specific organic-liquid/water interfacial areas for natural porous media. Additional research is needed employing a wide variety of natural soils and sediments to further evaluate the results presented herein. As noted above, interfacial areas obtained with the aqueous-phase method are significantly smaller than values obtained with the gas-phase IPTT method at lower wetting-phase saturations, indicating that the aqueous-phase method provides an incomplete measure of interfacial area. Hence, use of this correlation should be restricted to conditions of higher wetting-phase saturations. Interfacial areas measured with the IPTT method were compared to values measured with high-resolution microtomography. The IPTT method was shown to produce consistently larger values. Thus, application and interpretation of data obtained with either method must be mediated by awareness of their associated method specificity.

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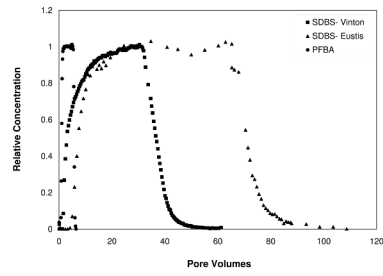


Figure 1. Breakthrough curves for PFBA (nonreactive tracer) and SDBS (interfacial tracer) transport in columns containing a residual saturation of organic liquid.

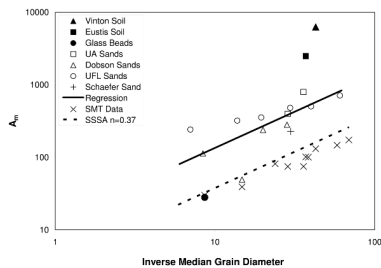


Figure 2. Relationship between maximum specific organic-liquid/water interfacial area (A_m , cm^{-1}) and inverse median grain diameter (IMGD, cm^{-1}). Data for the sands are compiled from the literature (see Table 2); regression equation for the sand data is: $A_m = 13.5 \text{IMGD}$ ($r^2 = 0.90$). The dotted line represents specific solid surface area calculated using the geometric-based smooth-sphere approach with porosity of 0.37 (Table 1). Also included for comparison are values obtained with the microtomography (SMT) method (data from 18).

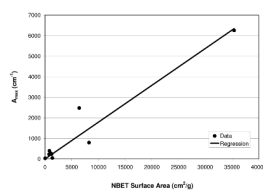


Figure 3. Relationship between maximum specific organic-liquid/water interfacial area (A_m , cm^{-1}) and specific solid surface area (NBET, cm^2/g) measured with the N_2 /BET method ($A_m = 0.18\text{NBET}$, $r^2 = 0.95$).

Table 1

Soil Properties

Medium	Median Diameter (mm)	Smooth-sphere Surface Area ¹ (cm ⁻¹)	Specific surface area ² (m ² /g)	Porosity	Bulk density (g/cm ³)
Vinton	0.234	149	3.54	0.42	1.51
Eustis	0.27	138	0.64	0.36	1.69

¹ Volume-normalized specific solid surface area (SSA) calculated using the smooth-sphere assumption: $SSSA = 6(1-n)/d$, where n is porosity and d is median grain diameter.

² Measured with the N₂/BET method by Quantachrome Instruments (Boynton Beach, FL) and Micromeritics Corporation (Norcross, GA).

Table 2

Data sets for aqueous-phase interfacial partitioning tracer tests.

Porous Medium	S_n	N^a	Data Source
Vinton Soil	0.15	4	This study
Eustis Soil	0.17	4	This study
Mixed sand	0.26	2	Brusseau et al., ^{15b}
45–50 mesh sand	0.17	8	Brusseau et al., ^{15b}
12–20 mesh sand	0.29	6	Dobson et al., ¹⁶
20–30 mesh sand	0.28	5	Dobson et al., ¹⁶
30–40 mesh sand	0.27	6	Dobson et al., ¹⁶
40–50 mesh sand	0.28	5	Dobson et al., ¹⁶
10–20 mesh sand	0.12	1	Cho and Annable, ^{11c}
20–30 mesh sand	0.14	1	Cho and Annable, ^{11c}
30–40 mesh sand	0.12	1	Cho and Annable, ^{11c}
40–60 mesh sand	0.15	1	Cho and Annable, ^{11c}
80–100 mesh sand	0.16	1	Cho and Annable, ^{11c}
40–100 mesh sand	0.19	3	Saripalli et al., ^{4c}
40–50 mesh sand	variable	5	Schaefer et al., ^{8d}

S_n = saturation of organic liquid

^a number of measurements

^b denoted as “UA sand data” in Figure 2

^c denoted as “UFL data” in Figure 2

^d this study was conducted using the surfactant mass balance method under drainage conditions; all other studies employed the advective tracer-test method with the organic liquid at residual saturation (imbibition conditions).