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Novel methods for measuring air–water interfacial area in unsaturated porous media

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HIGHLIGHTS

- Interfacial partitioning tracer tests (IPTT) are used to measure air–water interfacial area.
- Two novel alternative approaches for conducting IPTTs are presented.
- System monitoring during the tests revealed no measurable surfactant-induced drainage.
- The measured interfacial areas compared well to those obtained with the standard IPTT method.

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ABSTRACT

Interfacial partitioning tracer tests (IPTT) are used to measure air–water interfacial area for unsaturated porous media. The standard IPTT method involves conducting tests wherein an aqueous surfactant solution is introduced into a packed column under unsaturated flow conditions. Surfactant-induced drainage has been observed to occur for this method in some cases, which can complicate data analysis and impart uncertainty to the measured values. Two novel alternative approaches for conducting IPTTs are presented herein that are designed in part to prevent surfactant-induced drainage. The two methods are termed the dual-surfactant IPTT (IPTT-DS) and the residual-air IPTT (IPTT-RA). The two methods were used to measure air–water interfacial areas for two natural porous media. System monitoring during the tests revealed no measurable surfactant-induced drainage. The measured interfacial areas compared well to those obtained with the standard IPTT method conducted in such a manner that surfactant-induced drainage was prevented.

1. Introduction

The air–water interface plays a fundamental role in the distribution and transport of water and contaminants in unsaturated porous media. Understanding the influence of physicochemical properties and conditions on interfacial area is critical to accurate representations of multiphase flow and contaminant transport. Concomitantly, measuring and predicting air–water interfacial area for natural porous media has garnered great interest in the past two decades. Interfacial partitioning tracer tests (IPTT) are one of the few methods available for measuring air–water interfacial area (e.g., Karkare and Fort, 1996; Brusseau et al., 1997; Kim et al., 1997; Saripalli et al., 1997; Kim et al., 1999; Anwar et al., 2000; Schaefer et al., 2000; Costanza-Robinson and Brusseau, 2002; Peng and Brusseau, 2005; Brusseau et al., 2006; Chen and Kibbey, 2006; Brusseau et al., 2007; Costanza-Robinson et al., 2012).

The standard IPTT method involves conducting miscible-displacement tests wherein an aqueous tracer solution is introduced into a packed column under unsaturated flow conditions. The concentrations of the tracers in the column effluent are monitored to construct breakthrough curves, which are used to determine the retardation of the tracer that partitions to the interface relative to that of a non-reactive (non-partitioning) tracer. The magnitude of the retardation corresponds to the magnitude of the interfacial area. A surfactant is typically used as the partitioning tracer. One potential issue associated with the use of surfactant solutions is the well-known phenomenon of induced drainage related to the reduction in interfacial tension caused by the surfactant (e.g., Karkare and Fort, 1993; Henry and Smith, 2003). Surfactant-induced drainage can complicate data analysis and impart

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uncertainty to the measured interfacial areas. Conflicting results have been reported regarding the observation of surfactant-induced drainage for IPTT applications. Such drainage did not occur for some tests (Brusseau et al., 2007), but was observed for other tests (Chen and Kibbey, 2006; Costanza-Robinson et al., 2012). This difference in results may in part be due to variations in the specific techniques used to implement the IPTT. For example, the apparatus used by Brusseau et al. (2007) employed a vacuum chamber system that maintains strong steady flow conditions, which minimizes the impact of changes in interfacial tension caused by introduction of the surfactant solution. Conversely, the apparatuses used in other IPTT applications may have been more susceptible to the impacts of changes in interfacial tension, and thus surfactant-induced drainage was observed.

The objective of this research is to present two novel alternative approaches for conducting IPTTs that are designed in part to prevent surfactant-induced drainage. The first alternative, termed the dual-surfactant IPTT (IPTT-DS) method, is based on using a two-surfactant system. In this case, one surfactant is used as the partitioning tracer, with its attendant breakthrough curve used to determine retardation, similarly to the standard IPTT method. In addition, a second, different surfactant is added to the aqueous solution that serves as the background solution for the miscible-displacement tests. Note that the background solution is devoid of surfactant for the standard IPTT method. Hence, the addition of the second surfactant to the background solution eliminates the condition present in the standard IPTT wherein there is an abrupt change in solution chemistry (and associated change in interfacial tension). The two surfactants and their respective concentrations are selected to ensure similar interfacial-tension reductions, which minimizes the potential to develop gradients in interfacial tension (and thus minimizing drainage).

The second novel method, termed the residual-air IPTT (IPTT-RA) method, is based on developing a fluid distribution within the column such that the air exists as a trapped, disconnected phase (i.e., "residual" saturation). The potential for drainage effects to occur is ameliorated under such conditions. In addition, this tracer test can be conducted similarly to a saturated-flow experiment, which can significantly reduce the required experiment time. This approach is similar to the standard IPTT method used to measure interfacial area between organic liquids and water (e.g., Saripalli et al., 1997; Cho and Annable, 2005; Dobson et al., 2006; Brusseau et al., 2008; Brusseau et al., 2010; Narter and Brusseau, 2010), but has to date not been used to measure air–water interfacial area. Experiments are conducted with the two novel approaches to measure air–water interfacial areas for two natural porous media. The results are compared to those obtained with the standard IPTT method for which a specific technique was used to prevent surfactant-induced drainage.

2. Materials and methods

2.1. Materials

Two porous media were used in this study. Vinton soil (sandy, mixed thermic Typic Torrifluvent), collected locally in Tucson, AZ, and a 45/50 mesh quartz sand (Accusand). Vinton soil was sieved to remove the fraction larger than 2 mm. Relevant properties of the porous media are presented in Table 1.

Sodium dodecyl benzene sulfonate (SDBS, 35 mg L^{-1}) was used as the air–water interfacial partitioning tracer. Pentafluorobenzoic acid (PFBA, 100 mg L^{-1}) was used as the nonreactive tracer. Sodium chloride (0.01 M) was used as the background electrolyte solution to maintain a constant ionic strength, thus minimizing potential changes in electrostatic properties of the system. Sodium dodecyl sulfate (SDS, 65 mg L^{-1}) was used to create the background surfactant solution for the dual-surfactant tests. The interfacial partition coefficients (K_i), determined by measuring the interfacial tension functions, are $2.9 \cdot 10^{-3}$ cm and $3.1 \cdot 10^{-3}$ cm for SDBS and SDS, respectively, for the concentrations employed. Sorption of SDBS by the sand was minimal ($K_d = 0.05$ cm^3 g^{-1}) and greater for the soil ($K_d = 0.5$ cm^3 g^{-1}). SDS sorption by the soil was slightly larger than that of SDBS.

Table 1
Relevant physical properties of the porous media.

Medium	Median diameter (mm)	Uniformity coefficient, U^{a}	Bulk density, ρ_b (g/cm^3)	Porosity, n	K_{sat} (cm min^{-1})
Vinton	0.23	2.4	1.50	0.376	0.2
Sand	0.35	1.1	1.65	0.326	1.3

[a] $U = (d_{60}/d_{10})$.

The column used for the standard IPTT and IPTT-DS tests was constructed of stainless steel and was 15 cm long by 2.2 cm in diameter. The column used for the IPTT-RA tests was constructed of glass and was 15 cm long by 2.5 cm in diameter. A porous frit was placed at the ends of the column to retain the media and to promote uniform water injection. The columns were packed with air-dried media to obtain uniform bulk densities. The columns were oriented vertically for all experiments.

2.2. Methods

2.2.1. Standard IPTT method

The tracer tests for the standard IPTT technique were conducted after steady-state unsaturated flow was established at the desired water content. Tests were conducted for both primary drainage and primary imbibition conditions. For tests conducted under drainage conditions, the packed column was first completely saturated with electrolyte solution devoid of surfactant. Once saturated, the top cap of the column was removed to initiate drainage. A HPLC pump was used to provide a constant solution flow (0.5 ml min^{-1}, equivalent to a mean pore-water velocity of ~0.5 cm min^{-1}) to the exposed top of the column. Tubing connected to the bottom of the column was connected to a vacuum chamber that housed a fraction collector to which the column effluent line was connected for sample collection. The tracer solution was injected once steady flow was established. After the selected volume of tracer solution was injected, electrolyte solution was again injected to elute the tracer. The tests for imbibition conditions were conducted similarly, with the exception that the column was not saturated first.

The samples were weighed, providing a means of monitoring for potential variations in the amount of solution exiting the column, and determination of any changes in water saturation within the column. The mass of the column was also directly measured periodically as a second determination of changes in water saturation. A PFBA tracer test was performed before each SDBS injection to characterize hydrodynamic properties of the column. Each set of tracer tests was conducted in a newly prepared column. In addition, partitioning tracer tests were conducted under water-saturated conditions to measure the adsorption of SDBS by the solid matrix.

2.2.2. IPTT-DS method

The tracer tests for the dual-surfactant method were conducted similarly to those for the standard method, with two exceptions. One difference was the addition of SDS to the electrolyte solution. Preliminary tests were conducted to measure the interfacial-tension functions for both SDBS and SDS, and the associated K_i