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Surfactant-induced flow compromises determination of air-water interfacial areas by surfactant miscible-displacement

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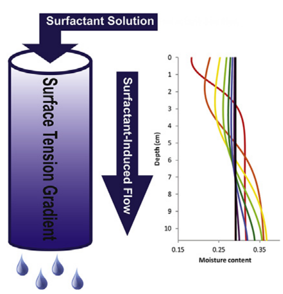
HIGHLIGHTS

- Surfactant-induced drainage compromises air-water interfacial area measurement.
- Internal redistribution of water compromises interfacial area measurement.
- Physical interpretation of absolute interfacial area estimates is challenging.

GRAPHICAL ABSTRACT



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ABSTRACT

Surfactant miscible-displacement (SMD) column experiments are used to measure air-water interfacial area (A_I) in unsaturated porous media, a property that influences solute transport and phase-partitioning. The conventional SMD experiment results in surface tension gradients that can cause water redistribution and/or net drainage of water from the system ("surfactant-induced flow"), violating theoretical foundations of the method. Nevertheless, the SMD technique is still used, and some suggest that experimental observations of surfactant-induced flow represent an artifact of improper control of boundary conditions. In this work, we used numerical modeling, for which boundary conditions can be perfectly controlled, to evaluate this suggestion. We also examined the magnitude of surfactant-induced flow and its impact on A_I measurement during multiple SMD flow scenarios. Simulations of the conventional SMD experiment showed substantial surfactant-induced flow and consequent drainage of water from the column (e.g., from 75% to 55% S_W) and increases in actual A_I of up to 43%. Neither horizontal column orientation nor alternative boundary conditions resolved surfactant-induced flow issues. Even for simulated flow scenarios that avoided surfactant-induced drainage of the column, substantial surfactant-induced internal water redistribution occurred and was sufficient to alter surfactant transport, resulting in up to 23% overestimation of A_I. Depending on the specific simulated flow scenario and data analysis assumptions used, estimated A_I varied by nearly 40% and deviated up to 36% from the system's initial A_I. We recommend methods for A_I determination that avoid generation of surface-tension gradients and urge caution when relying on absolute A_I values measured via SMD.

1. Introduction

Accurate measurement of the air-water interfacial area (A_I) is

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important because A_I influences the accumulation of surface-active solutes at the air-water interface (AWI), solute- and particle transport in unsaturated systems, and mass-transfer kinetics of solutes across the AWI. A_I is commonly measured using laboratory-scale unsaturated surfactant miscible-displacement (SMD) experiments in which the accumulation of a surfactant tracer at the AWI retards its transport relative to a non-reactive tracer. The processes considered to affect the total retardation factor, R_T (−), of the interfacial tracer are shown in Eq. (1) (Kim et al., 1997, 1999):

$$R_T = 1 + \frac{\rho_b K_D}{\theta_W} + \frac{A_I K_{IW}}{\theta_W} \quad [1]$$

where, ρ_b is porous medium bulk density (g cm^{-3}); θ_W is volumetric water content (−); K_D is the solid-phase sorption coefficient (cm^3 g^{-1}); and K_{IW} is the interfacial accumulation coefficient (cm). A_I used here and throughout refers to the area of the total air-water interface (i.e., area associated with water held via both film adsorption and capillarity), defined as the interfacial area per unit system volume (cm^2 cm^{-3} = cm^{-1}). As shown in Eq. (1), R_T is a function of A_I, thereby allowing A_I to be estimated for a system with steady flow and constant θ_W if R_T and the remaining variables in Eq. (1) are known.

The R_T necessary for use in Eq. (1) is typically determined using tracer breakthrough curves as the ratio of the average travel time of the interfacial tracer, a surfactant, to that of a non-reactive tracer:

$$R_T = \frac{t_{\text{surfactant}}}{t_{\text{non-reactive}}} = 1 + R_S + R_I \quad [2]$$

where, $t_{\text{surfactant}}$ and $t_{\text{non-reactive}}$ are the average travel times for the surfactant and non-reactive tracer pulses. The terms R_S and R_I represent the surfactant retardation due to sorption to the solid and accumulation at the AWI and correspond to the terms on the RHS of Eq. (1), subject to the assumptions of steady flow and constant θ_W. A body of work has demonstrated, however, that surfactants can affect unsaturated flow, including by inducing non-steady flow and drainage (e.g., see review (Henry and Smith, 2003)). Such disruptions to flow would influence solute transport and, thereby, measured R_T (Eq. (2)) and A_I (Eq. (1)).

The primary effect of surfactants on unsaturated flow is due to the dependence of soil-water pressure head, ψ (cm), on surface tension, σ (mN m^{-1}):

$$\psi = -\frac{2\sigma \cos\gamma}{\rho_W g r} \quad [3]$$

where ρ_W is the solution density (g cm^{-3}); g is the gravitational acceleration (m s^{-2}); γ is the contact angle, assumed zero herein (Kibbey and Chen, 2012; Tokunaga et al., 2004); and r is the radius of an equivalent cylinder (m). For example, at concentrations typically used in SMD experiments (0.05–2 mM), the surface tension of the conventionally used surfactant, sodium dodecyl benzene sulfonate (SDBS) is 43–57 mN m^{-1}, compared to the surface tension of pure water, which is ~72 mN m^{-1} (Costanza-Robinson et al., 2012; Kim et al., 1997). The impact of concentration-dependent surface tension depression manifests as a shift in the moisture content-pressure head relationship (Karagunduz et al., 2001). As shown in Fig. 1, at moisture contents less than saturation, the pressure head in a surfactant-wetted medium is higher (less negative) than in the water-wetted medium (Henry and Smith, 2003). Because pressure head gradients drive flow from regions of higher pressure toward regions of lower pressure, there is a tendency for water to flow from surfactant-containing regions (lower σ, higher ψ) toward surfactant-free regions (higher σ, lower ψ). Considerable variation in surfactant concentration can occur over short distances (i.e., the length of a solute front), resulting in pressure head gradients that can induce flow.

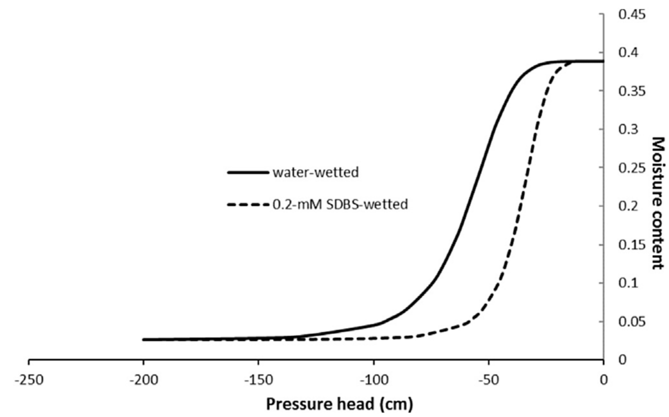

Fig. 1. Soil water characteristic curves for pure-water wetted and surfactant-wetted sand.

The potential for surfactant-induced flow to affect conventional SMD experiments, and thereby A_I measurement, is recognized (Brusseau et al., 2015; Karagunduz et al., 2015; Kibbey and Chen, 2012; Kim et al., 1997). Costanza-Robinson et al. (2012) found that as the surfactant (SDBS) pulse displaced resident water within the column, 24–51%, depending on influent SDBS concentration, of the water drained from the column. This drainage was associated with transient effluent flowrates of up to 27% above the steady-state conditions that existed prior to the surfactant introduction and 300% variation in estimated A_I, depending on how the drainage was accommodated in the data analysis. Studies utilizing surfactants for A_I determination by methods other than SMD, as well as unsaturated SMD experiments unrelated to A_I determination report similar surfactant-induced drainage (Bashir et al., 2011; Chen and Kibbey, 2006; Karagunduz et al., 2015; Smith and Gillham, 1999; Zartman and Barsch, 1990). While use of lower surfactant concentrations reduces the magnitude of surfactant-induced flow (Chen and Kibbey, 2006; Zartman and Barsch, 1990), even low concentrations (e.g., 0.05 mM) can induce substantial surfactant-induced flow and drainage (Costanza-Robinson et al., 2012). Such surfactant-induced drainage represents non-steady flow and a non-constant θ_W, violating basic assumptions of the SMD method.

Surfactant effects, typically measured as net drainage from the system, have not been observed in all experimental systems, however. Brusseau et al. (2007, 2015) only observed surfactant-induced drainage when using a hanging water column and not when using a vacuum chamber. They suggested that the strong vacuum control of the vacuum chamber prevents surfactant-induced drainage from occurring, even as others have observed surfactant-induced drainage when utilizing a vacuum chamber (Karagunduz et al., 2015). No explanation was provided regarding why a hanging water column should offer any less experimental control, nor for why a vacuum chamber should render the system immune to the uncontested physical basis for surfactant-induced drainage. Even so, it is worthwhile to examine this possibility because SMD is the principle experimental method used to measure air-water interfacial areas and is often used as the benchmark against which alternative methods are compared (e.g., Araujo et al., 2015).

In this work, we evaluated the suggestion that surfactant-induced effects can be avoided during SMD experiments by proper control of boundary conditions. We used a numerical flow and transport model that had been modified previously to include