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Influence of Air−Water Interfacial Adsorption and Gas-Phase Partitioning on the Transport of Organic Chemicals in Unsaturated Porous Media

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We investigated in laboratory column experiments, the aqueous-phase transport of four *n*-alcohols (*n*-hexanol−*n*-nonanol), three chlorinated aromatic compounds (chlorobenzene, *o*-dichlorobenzene, and *o*-chlorophenol), and two alkylbenzenes (ethylbenzene and *p*-xylene) in a water-unsaturated porous medium (sand). The influence of gas-phase partitioning and interfacial adsorption on solute retardation during steady unsaturated water flow was evaluated over a range of water contents. Air−water interfacial adsorption was a significant factor for the retardation of *n*-alcohols. For example, nearly 90% of the measured retardation of *n*-nonanol could be attributed to interfacial adsorption at a water saturation of 34%. Aromatic compounds used in this study were not significantly affected by adsorption at the air−water interface because of both low air−water interfacial area (0−50 cm^2/cm^3) generated in the unsaturated porous medium and the small interfacial−adsorption coefficients. Instead, gas-phase partitioning was the primary mechanism responsible for the measured retardation of most of the aromatic compounds evaluated in this study. Using the batch-measured interfacial adsorption coefficients for *n*-octanol and *n*-nonanol and the column-measured retardation factors, the effective air−water interfacial areas were estimated. These values agreed closely with those we reported earlier, based on displacement experiments with an anionic surfactant as an interfacial tracer.

Introduction

Because air coexists with water and the solid matrix in the vadose zone, chemical distribution between the aqueous and gaseous phases and adsorption at the air−water interface become potential sources of chemical retention in addition to the uptake by the solid phase (adsorption or partitioning). In water-unsaturated soils, the significance of air−water interfacial adsorption of organic contaminants with respect to other solute sorption sources were discussed in recent reports (*1*, *2*). In an unsaturated soil with a fine texture and at a very low water saturation, more than half of the applied mass of some volatile aromatic compounds (e.g., *p*-xylene) was found at the air−water interface (*1*). The effect of air−water interfacial adsorption on the gas-phase transport of several volatile organic chemicals has been reported using a gas chromatographic technique (*2*−*6*). Straight-chain alcohols dissolved in pure water have been found to decrease the surface tension significantly (*7*, *8*), indicating their accumulation at the air−water interface. Aromatic compounds without surfactant-like chemical structures (e.g., hydrophobic tail and charged functional group) were also observed to accumulate at the air−water interface to a certain degree depending on their hydrophobicities (*9*−*13*).

Experimental determination of the air−water interfacial areas in water-unsaturated porous media has been reported independently by Saripalli et al. (*14*), Kim et al. (*15*), Brusseau et al. (*2*), and Karkare and Fort (*16*). Two types of measurement techniques have been reported. One method is to induce water migration using a water-insoluble surfactant under static conditions (*16*), and the other method is to measure chemical adsorption at the air−water interface either from gaseous phase (*2*) or aqueous phase (*14*, *15*) under dynamic flow conditions. In this study, the retardation of *n*-octanol and *n*-nonanol was analyzed to estimate the effective air−water interfacial area of the system using the same experimental and calculation procedure we reported recently (*15*).

In the present study, we examine the effect of an air−water interface on the retardation of organic chemicals during aqueous-phase miscible displacements in a partially water-saturated column packed with a clean sand. Contribution of various solute sorption mechanisms to observed retardation was estimated and compared with experimental results. The effective air−water interfacial areas estimated from *n*-octanol and *n*-nonanol retardation were compared with those obtained by displacement experiments with an anionic surfactant as an interfacial tracer (*15*).

Theoretical Background

Aqueous transport of organic compounds in a water-unsaturated medium is subject to retardation due to sorption by the solids, partitioning into the gas phase, and accumulation at the air−water interface. The effect of partitioning of a chemical to any potential domains in a water-unsaturated porous medium on the average travel velocity of the chemical is often expressed using a partial differential equation derived on the basis of mass conservation and continuity. Assuming no convective or diffusive gaseous transport and steady water flow in a homogeneous porous medium, the one-dimensional advective−dispersive model equation is (*17*)

$$R_t \frac{\partial C_w}{\partial t} = -v_x \frac{\partial C_w}{\partial x} + D_w \frac{\partial^2 C_w}{\partial x^2} \qquad (1)$$

where R_t is the total retardation factor (dimensionless), C_w is the aqueous concentration (mol/cm^3), v_x is the pore water velocity (cm/min), D_w is the hydrodynamic dispersion coefficient (cm^2/min), x is distance (cm), and t is time (min). In applying eq 1 for unsaturated steady water flow, a homogeneous volumetric water content (θ_w) is required. This condition was satisfied in our experiments by appropriate manipulation of the inlet and outlet boundary conditions for the column experiments (see Supporting Information). The total retardation factor, R_t, contains all terms that account for the retention of a chemical in the porous medium:

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$$R_t = 1 + \beta_T \quad (2)$$

where

$$\beta_T = \beta_d + \beta_a + \beta_i \quad (3)$$

with

$$\beta_d = \frac{\rho K_d}{\theta_w} \qquad \beta_a = \frac{\theta_a H}{\theta_w} \qquad \beta_i = \frac{a_i K_i}{\theta_w} \quad (4)$$

In the above equations, ρ is the bulk density of the medium (g/cm^3); K_d is the sorption coefficient of a chemical to the solid matrix (cm^3/g); θ_a and θ_w are volumetric gas and water contents (dimensionless), respectively; H is the Henry's constant (dimensionless); K_i is the adsorption coefficient for the chemical accumulation at the air−water interface (cm); and a_i is the specific air−water interfacial area (cm^2/cm^3).

According to eqs 3 and 4, the relative contribution of each term to the overall retardation factor (R_t) can be evaluated as follows:

$$f_d = \frac{\beta_d}{\beta_T} \qquad f_a = \frac{\beta_a}{\beta_T} \qquad f_i = \frac{\beta_i}{\beta_T} \quad (5)$$

Note that f_d, f_a, and f_i represent, respectively, the fractional contributions to the measured total retardation as a result of soil sorption, gas-phase partitioning, and interfacial adsorption.

The phase distribution constants (K_d, H, and K_i) needed in eq 4 can be estimated using data from independent batch or column experiments. The soil sorption coefficient (K_d) can be estimated from a sorption isotherm measured in a series of batch experiments or from miscible displacement experiments in a saturated column ($\beta_i = 0$, $\beta_a = 0$). If the sorbed concentration of a chemical (S, mol/g) is a simple linear function of the equilibrium aqueous concentration (C_w, mol/cm^3), then

$$S = K_d C_w \quad (6)$$

In Henry's region, the gaseous concentration of an organic compound (C_g, mol/cm^3) is also proportional to the aqueous concentration of the compound:

$$C_g = HC_w \quad (7)$$

The gas-phase partitioning coefficients, or Henry's constants (H), in the dilute aqueous solutions of volatile organic compounds are available in the literature (*18*).

Unlike the Henry's constant (H) and the sorption coefficient (K_d), direct measurement of surface (or interfacial) excess of a compound at the air−water interface in unsaturated porous media is usually not feasible. However, using the Gibbs adsorption equation, an adsorption isotherm for the surface excess of a compound at the air−water interface can be determined using surface tension (or interfacial tension) data (*14*, *15*, *19*):

$$\Gamma = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial C_w}\right)_T C_w \quad (8)$$

where Γ is the surface excess of a chemical (mol/cm^2), R is the ideal gas constant (erg mol^{-1} K^{-1}), T is the absolute temperature (K), and γ is the surface tension (dyn/cm). The assumptions associated with eq 8 are that the aqueous molar concentration of the compound of interest is close to its actual activity (e.g., C_w < 10 mM), and the compound is nonionic (*19*). Since γ is a nonlinear function of C_w, the interfacial adsorption isotherm is nonlinear (*20*). When the change of γ is a linear function of C_w over a limited concentration range (as will be shown to be the case for our experiments), eq 8 simplifies to a linear model:

$$\Gamma = K_i C_w \quad (9)$$

with K_i being the concentration-independent adsorption coefficient. The thermodynamic parameters for air−water interfacial adsorption of organic compounds of environmental importance are available in the literature (*21*).

As seen in eq 4, when the interfacial adsorption coefficient (K_i) and the air−water interfacial area per unit volume of bulk matrix (a_i) are sufficiently large, the product of these terms must be taken into account for estimating the total retardation factor of an organic compound. At the same time, if the interfacial adsorption is within a detectable range (e.g., $\beta_i > 0.01$) and if the contribution of the other two terms [soil sorption (β_d) and gas-phase partitioning (β_a)] are known, it will be possible to estimate the specific air−water interfacial area (a_i) in a water-unsaturated medium.

The total retardation factor (R_t) for an organic compound can be estimated from a mass balance analysis for a step input (*22*) and temporal moment analysis for a pulse input (*23*). For a step input of a chemical solution, the total retardation factor is

$$R_t = \frac{\int [1 - C_t(t)/C_t^0]\, dt}{\int [1 - C_{nt}(t)/C_{nt}^0]\, dt} = \frac{\bar{t}_t}{\bar{t}_{nt}} \quad (10)$$

where C is the effluent concentration of a chemical (mol/L); C^0 is the influent concentration (mol/L) with subscripts t and nt denoting the adsorbing chemical and nonreactive tracer, respectively; and $\bar{t}$ is the mean travel time of a chemical for transport through the system. The total retardation factor from a breakthrough curve generated by applying a pulse input is calculated by the ratio of the normalized first temporal moment of the chemical to that of a nonreactive tracer:

$$R_t = \frac{\mu_t}{\mu_{nt}} \quad (11)$$

where μ is the pulse-corrected normalized first temporal moment of a chemical (subscript t) and a nonreactive tracer (subscript nt).

Experimental Section

Materials. Three classes of organic compounds were investigated: (a) four straight-chain alcohols (*n*-hexanol, *n*-heptanol, *n*-octanol, and *n*-nonanol); (b) three chlorinated aromatic hydrocarbons (chlorobenzene, *o*-dichlorobenzene, and *o*-chlorophenol); and (c) two alkylbenzenes (ethylbenzene and *p*-xylene). Reagent-grade (purity >99%) alcohols were supplied by Aldrich Chemical Co., while reagent-grade (purity >99%) aromatic compounds were purchased from Fisher Scientific Co. All of the chemicals were used as received. Bromide as sodium bromide (purity >99%) was supplied by Mallinckrodt Chemical Works Co. and used as a nonreactive tracer. HPLC-grade water (Fisher Scientific Co.) was used in all batch and column experiments.

Two different stock solutions were prepared for the alcohol displacement experiments. The first stock solution contained all of the alcohols and bromide at the following concentrations: *n*-hexanol, 4.9 mmol/L; *n*-heptanol, 1.1 mmol/L; *n*-octanol, 0.44 mmol/L; *n*-nonanol, 0.35 mmol/L; and bromide, 0.35 mmol/L. The second stock solution contained only 0.35 mmol/L of *n*-nonanol and the same concentration of bromide. An aqueous stock solution of the aromatic

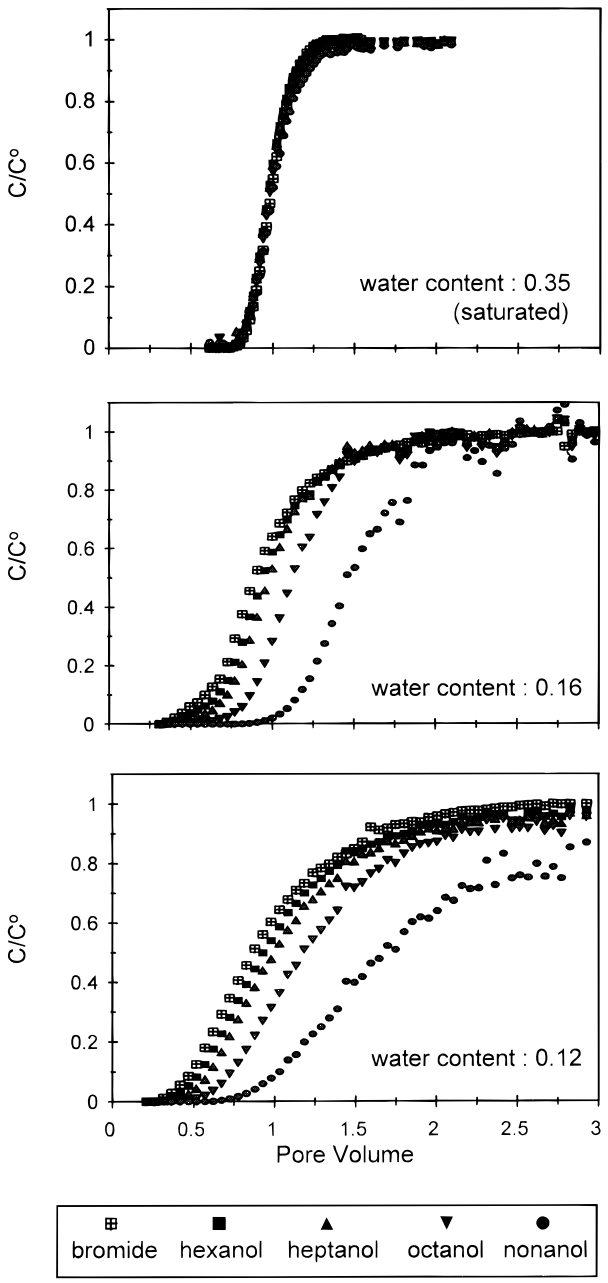

FIGURE 1. Breakthrough curves for alcohol transport at three different volumetric water contents.

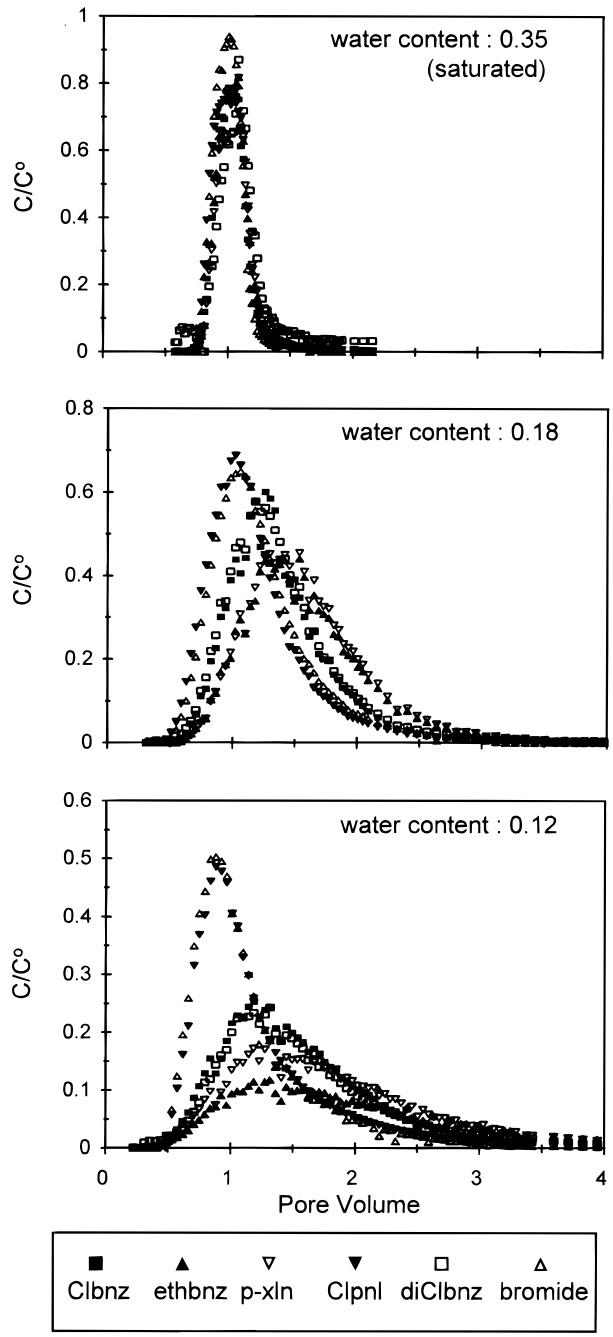

FIGURE 2. Breakthrough curves for the transport of aromatic compounds; Cl, chloro; bnz, benzene; eth, ethyl; xln, xylene; pnl, phenol.

compounds was prepared at the following concentrations: chlorobenzene, 0.73 mmol/L; ethylbenzene, 0.21 mmol/L; *p*-xylene, 0.24 mmol/L; *o*-chlorophenol, 1.5 mmol/L; *o*-dichlorobenzene, 0.22 mmol/L; and bromide, 0.35 mmol/L. These stock solutions were used as the displacing solutions for the miscible displacement experiments in both saturated and unsaturated sand columns.

The sand sample used for the column experiments was cleaned using the following procedure. A bulk sample of blast sand was first sieved to different sizes, washed with tap water several times, and then dried in an oven at 105 °C for 24 h. To remove any organic carbon residue, the sand samples were baked in a muffle furnace at 500 °C for more than 24 h. Baked sand samples were then remixed with a known size distribution: 1 mm−500 μm (diameter, based on sieve size), 20%; 500−300 μm, 40%; 300−180 μm, 30%; 180−105 μm, 10%. The source and treatment procedure of the sand sample used in this study are the same as in the previous study (*15*).

Miscible Displacement Experiments. The experimental procedures used were essentially identical to those used in an earlier study (*15*). A glass column (10.4 cm length, 5.45 cm diameter), which has the same design described by Annable et al. (*24*), was packed with the sand mixture. Small increments of the sand were added successively into the column, which was initially filled with water. This packing procedure eliminated air entrapment in the water-saturated sand column. Considerable care was taken not to generate any layer formation during the packing process. The saturated hydraulic conductivity of the packed column was 10.7 cm/h. The air-entry pressure was about 25 mbar, and the porosity was 0.35. A stainless steel capillary barrier (air-entry pressure of 250 mbar) was sealed at the bottom of the column. A glass fiber filter paper was placed at the top of the packed sand. The top of the sand column was sealed

TABLE 1. Sorption Coefficients and Contribution of Different Modes of Solute Retention to Total Retardation Factor at a Water Content of 0.12

chemical	K_d (cm³/g)	H^a (dimensionless)	K_i [b] (cm)	β_d	β_a	β_i [c]	R_t (predicted)	R_t (experiment)
			Alcohols					
n-hexanol	ND[d]	7.64×10^{-4}	9.36×10^{-5}	ND	1.5×10^{-3}	0.033	1.03	1.15
n-heptanol	ND	4.74×10^{-4}	4.39×10^{-4}	ND	9.1×10^{-4}	0.155	1.16	1.24
n-octanol	0.0021	6.48×10^{-4}	9.73×10^{-4}	0.029	1.2×10^{-3}	0.345	1.38	1.46
n-nonanol	0.0084	6.75×10^{-4}	2.45×10^{-3}	0.12	1.3×10^{-3}	0.868	1.99	2.11
			Aromatic Compounds					
chlorobenzene	0.00843	0.127	2.09×10^{-5}	0.117	0.243	0.007	1.37	1.39
o-dichlorobenzene	0.0274	0.0766		0.379	0.147		1.53	1.49
o-chlorophenol	0.00633	2.3×10^{-5}		0.088	4.4×10^{-5}		1.09	1.06
p-xylene	0.0127	0.286	6.98×10^{-5}	0.176	0.548	0.025	1.75	1.74
ethylbenzene	0.0105	0.344	7.07×10^{-5}	0.145	0.659	0.025	1.83	1.91

[a] Data from refs *18* (all alcohols), *29* (*o*-chlorphenol), and *30* (chlorobenzene, *o*-dichlorobenzene, *p*-xylene, ethylbenzene). [b] Data from refs *7* (*n*-hexanol, *n*-heptanol), *21* (ethylbenzene, chlorobenzene), and *1* (*p*-xylene). Data not available for *o*-dichlorobenzene and *o*-chlorophenol. [c] An air–water interfacial area of 42.5 cm²/cm³ estimated using eq 12 was used to predict β_i. [d] ND, not detectable at 10^{-4} cm³/g level (K_d).

with a stainless steel plate to prevent volatilization losses. A small orifice at the top plate allowed atmospheric pressure at the upper region of the column during the unsaturated flow experiments. The packed sand column was used for both saturated and unsaturated flow experiments without repacking.

Prior to unsaturated flow experiments, water-saturated displacement experiments were conducted for both the alcohol mixture solution and the aqueous solution of aromatic compounds to obtain the values for the soil sorption coefficients (K_d). Aqueous solutions were displaced through the saturated columns in an upward mode. For the unsaturated column experiments, the required degree of unsaturation was achieved by maintaining a steady flux boundary condition at the inlet and a constant negative pressure at the bottom of the column. The inlet of the solution was changed to the top of the column, and a stainless steel tubing (35–100 cm) was installed at the outlet end to maintain a constant negative pressure at the bottom of the column equal to the length of the tubing. The target level of water saturation was achieved by controlling primarily the influent flow rate of the solution for each experiment. Short stainless steel tubings (35 and 38 cm) were used only for high water saturation conditions. Volumetric water contents were measured gravimetrically after establishing steady-state water flow conditions (i.e., outlet flow rate is equal to inlet flow rate), both before and after the displacement experiments. These were compared with the estimates based on the mean residence time of bromide. A step input of aqueous solution was used for the alcohols. For the aromatic compounds, a 0.2–0.4 pore volume solution pulse was applied to the column. Detailed information for the unsaturated column experiments (apparatus, column configuration, and boundary conditions) is shown in the Supporting Information.

Effluent samples from the column were collected using a fraction collector (ISCO, Retriever 500) and analyzed using a gas chromatograph (Perkin-Elmer, AutoSystem) equipped with flame ionization detector. Nonreactive tracer (bromide) was analyzed using a high-performance liquid chromatograph with an ion exchange column (Dionex, AS4A) and a UV detector (LDC Analytical, spectroMonitor 3100) set at 205 nm. On the basis of the measured breakthrough curves, the total retardation factors (R_t) were determined using eqs 10 (alcohols) and 11 (aromatic compounds).

Surface Tension Measurements. Surface tensions of *n*-octanol and *n*-nonanol aqueous solutions were measured by the drop-weight method (*25*). A series of *n*-octanol and *n*-nonanol aqueous solutions were prepared from stock solutions. At least 10 drops of the alcohol solution from a glass tubing (radius 0.2445 cm) were collected and weighed using a chemical balance (Mettler AE260). Drop forming rate was 30 ± 2 s/drop. The loss of solution weight during drop collection was less than 0.4% of the total weight. An aliquot of each sample from the glass tubing was taken for the gas chromatography (GC) analysis to estimate the exact alcohol concentration in the solution.

Results and Discussion

Retardation of Chemicals. A consistent trend of increasing total retardation with decreasing water content was observed for the *n*-alcohols and the two classes of aromatic compounds (Figures 1 and 2). Also with decreasing water content, all solute breakthrough curves are quite skewed and show considerable tailing (Figures 1 and 2), which might be the result of rate-limiting mass transfer processes during miscible displacement (*2*, *15*). Note that according to eqs 2–4 the total retardation factor (R_t) increases with decreasing water content (θ_w) no matter which domain is the major contributor to the total retardation factor provided that the a_i term in eq 4 is either constant or increases as water content decreases.

The relative contribution of different modes of solute retention can be calculated since the values of all of the parameters in eq 4 can be estimated from independent sources. From the retardation factors measured under saturated water flow conditions, the K_d values were estimated and used to predict the contribution of soil sorption (β_d) at all other water contents. This requires the assumption that K_d is independent of θ_w, at least over the range of θ_w we investigated. Contribution of the gas-phase partitioning (β_a) can be estimated given the published values for the Henry's constants (see Table 1). The use of Henry's constants requires that the experiments are conducted at low solute concentrations (*26*). The interfacial adsorption coefficient (K_i) can be estimated based on published data (*7*, *12*, *21*) or from the air–water interfacial tensions measured in the presence of the organic compound under investigation (*14*, *15*) (see Table 1). The specific air–water interfacial area (a_i) at different water saturations was estimated using the following empirical regression equation we reported earlier (*15*), based on measured data for surfactant adsorption:

$$a_i = -64.7S_w + 64.7 \qquad (12)$$

where $S_w = \theta_w/(\theta_a + \theta_w)$ is the degree of water saturation. In Figure 3, the measured and predicted retardation factors are compared. In all cases, the predicted decrease in the total

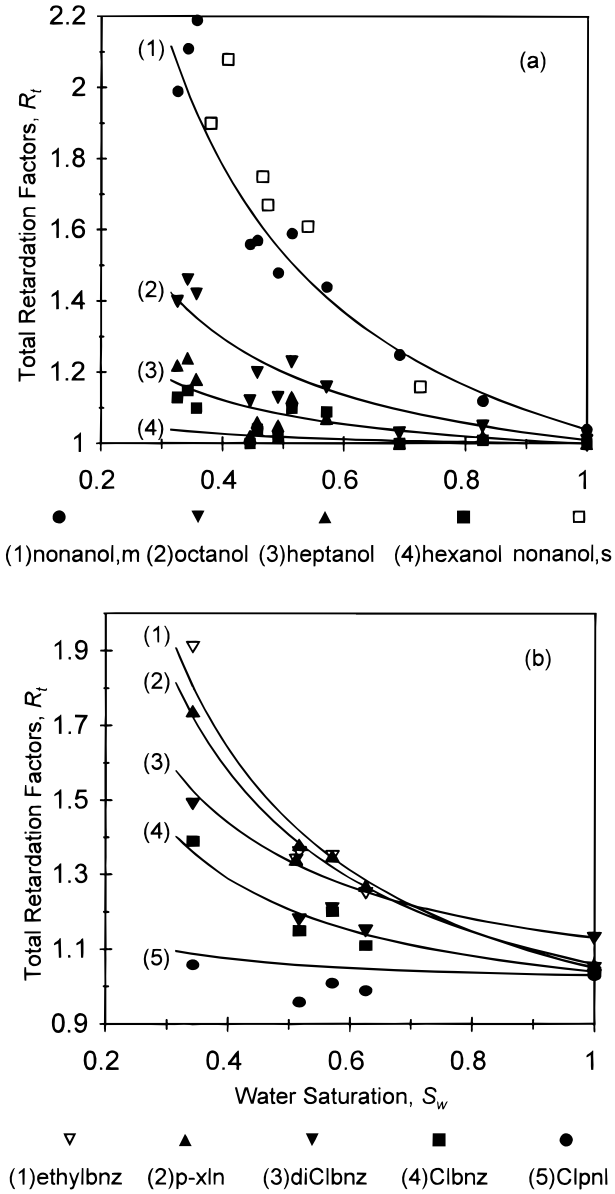

FIGURE 3. Effect of water saturation on the total retardation factors (R_t) of alcohols (a) and aromatic compounds (b). All the retardation sources (soil sorption, gaseous partitioning, and air−water interfacial adsorption) were taken into account for the predicted curves (solid lines); nonanol, m, alcohol mixture solution; s, single component solution; notation for aromatic compounds is the same as in Figure 2.

retardation factor (R_t) with increasing water saturation (S_w) was in good agreement with the experimental observations.

Since the Henry's constant (H) values for the n-alcohols are quite small, the partial contribution to the retardation factor due to gaseous partitioning, $\beta_a = H\theta_a/\theta_w$, is essentially negligible. However, large K_i values for the alcohols result in a significant contribution, $\beta_i = a_i K_i/\theta_w$, due to adsorption at the air−water interface (Table 1). For example, for the predicted $\beta_T = 0.99$ for n-nonanol at $\theta_w = 0.12$, the fractional contributions (f) of gaseous partitioning, soil sorption, and interfacial adsorption were 0.001, 0.12, and 0.88, respectively. Note that the K_i values for the n-alcohols decrease as the carbon chain length decreases. Accordingly, at a given water content and under the same experimental conditions, the retardation factors of the n-alcohols with longer carbon chains are larger than those of the alcohols with relatively short carbon chains.

The major factor contributing to the retardation of aromatic compounds investigated in this study is different from that of the n-alcohols described above. Due to relatively small air−water interfacial adsorption coefficients (K_i) and large gaseous partitioning coefficients (H), the retardation of chlorobenzene, ethylbenzene, and p-xylene is dominantly due to gaseous partitioning during the miscible displacement. For o-dichlorobenzene, with a relatively small H as compared to other aromatic compounds used in this study, the soil sorption is responsible for 70% of the observed retardation (Table 1). Even though the contribution of air−water interfacial adsorption of the aromatic compounds to the total retardation factors was not significant in this study, the effect of interfacial adsorption could have an important role in systems with a much larger specific air−water interfacial area. Similarly, for soils having a larger organic carbon content and larger K_d values, the contribution of soil sorption to retardation can be substantial.

Although the individual fractions (β) of predicted retardation factors were not listed in Table 1 for experiments conducted at higher water contents ($\theta_w > 0.12$), the results were consistent with those listed in the table for both aromatic compounds and alcohols.

The retardation factor of n-nonanol in a solution without any other organic compounds except sodium bromide is slightly larger than that of n-nonanol in a mixture of alcohols (Figure 3a). This effect of other alcohols in the solution on the surface excess of n-nonanol is caused by a combination of reasons. An alcohol in a mixture solution may have a different chemical activity from that in a pure aqueous solution, and more importantly, there may be a significant surface activity difference between an alcohol in a mixture and that in an aqueous solution with only the alcohol of interest. The predicted R_t values of aromatic compounds were based on K_i and H estimated from data for single-component solutions. However, the R_t values measured for multicomponent experiments do not deviate significantly from the predicted values (Figure 3b). This may not always be the case for other experimental systems. It is not clear whether the K_i value of an aromatic compound will change significantly due to other dissolved chemical species. In a water-unsaturated system with a relatively small quantity of air−water interfacial area (e.g., the sand used in this study), the fraction of the retardation factor due to interfacial adsorption will be still negligible unless a dramatic increase of surface excess is induced by other compounds (e.g., anionic surfactant with dissolved electrolytes). Henry's constant of an aromatic compound is known to be affected by other organic/inorganic compounds depending on their concentrations. When the retardation factor of an organic compound is substantially different from that predicted by the Henry's constant, a correction (for the aqueous activity coefficient change) will be necessary to obtain an accurate Henry's constant of the compound.

Mass recovery of aromatic compounds during unsaturated flow experiments varied from 60% to 100% depending on the sampling duration and the magnitude of Henry's constants. However, no mass loss was observed for alcohols under the same experimental conditions. Since alcohols (e.g., n-hexanol) are typically less resistant to microbial degradation than aromatic compounds, the mass loss of aromatic compounds is considered to be caused by volatilization. Under slow flow rate conditions, a longer sampling duration (collecting column effluent samples in open GC vials) was necessary to obtain a minimum quantity of sample (2 mL) for GC analysis. Assuming volatilization is the only source of mass loss and that the mass loss is directly proportional to the aqueous concentrations of aromatic compounds in samples, no correction for the R_t calculation is required. Note that while the mass recovery (zeroth moment) may not be

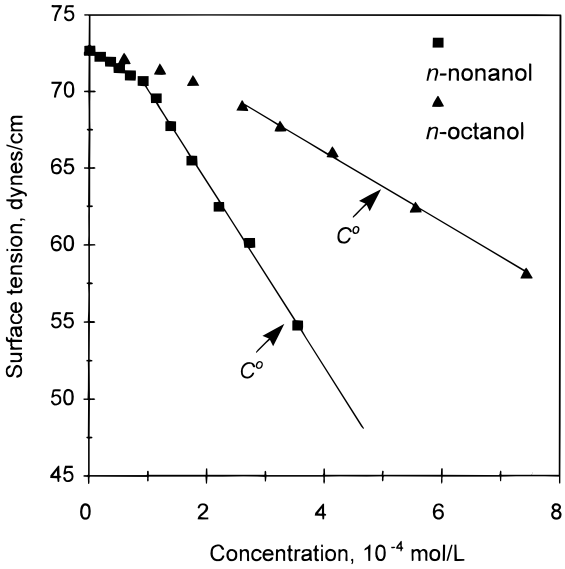

FIGURE 4. Measured surface tensions of *n*-octanol and *n*-nonanol; C^0 represents the influent alcohol concentration used during the column experiments.

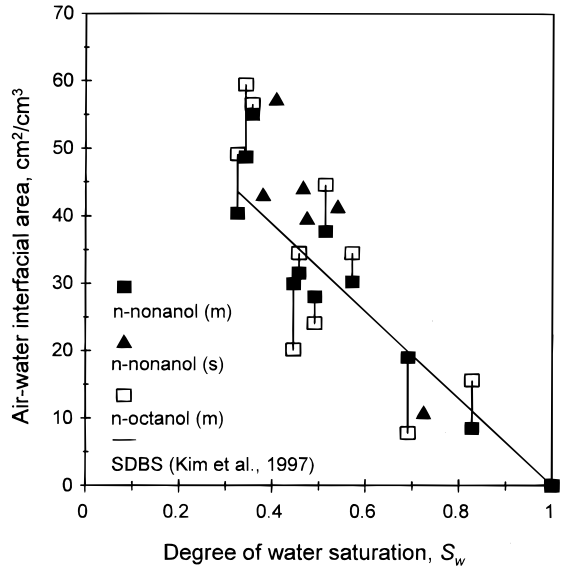

FIGURE 5. Correlation of the specific air−water interfacial areas (a_i) calculated from the retardation of *n*-octanol (in mixture) and *n*-nonanol [in mixture (m) and single-component solution(s)] with the degree of water saturation (S_w); an empirical curve from SDBS displacement experiments by Kim et al. (*15*) was overlaid for comparison; vertical lines represent data from one experiment with a suite of alcohols.

100% due to volatilization, the normalized first moment is not impacted. However, if most mass loss is due to microbial activity during the column experiments, a correction must be incorporated (*27*), which will increase the uncorrected R_t about 15−20% with about 40% mass loss.

Estimation of Air−Water Interfacial Area. Equation 4 can also be used to estimate the specific air−water interfacial area (a_i) accessible to an aqueous interfacial tracer during an unsaturated displacement. The surface tensions of *n*-octanol and *n*-nonanol aqueous solutions were measured over a range of alcohol concentrations (Figure 4), and the K_i values were calculated based on the Gibbs adsorption equation (eq 8). The surface tension−concentration curves for both alcohols are essentially linear ($r^2 > 0.99$) at the column input concentrations (C^0) used in the miscible displacement experiments. In our previous study (*15*), we used sodium dodecyl benzenesulfonate (SDBS) as the tracer to estimate the effective specific air−water interfacial areas as a function of water content for the same sand sample. An empirical equation (eq 12) derived based on the SDBS retardation data was used as a reference for the interfacial area calculation in this study. Only *n*-octanol and *n*-nonanol results were used to estimate the interfacial areas. The other alcohols did not provide retardation factors large enough to be statistically reliable for interfacial area estimation. However, a comparison between estimated and predicted retardation factors (using eq 12) at a volumetric water content of 0.12 was attempted for all the alcohols (Table 1).

The calculated specific air−water interfacial areas are consistent with the result from the SDBS experiments (Figure 5). Greater scattering in data points was observed for the interfacial areas estimated from *n*-octanol as compared to *n*-nonanol. This is due to the small total retardations that generated more relative errors in the interfacial areas. The air−water interfacial areas estimated from the experiments with the solutions containing only *n*-nonanol were slightly larger than those of aqueous solutions with alcohol mixture. On the basis of the assumption that a mixture of surface active compounds (e.g., *n*-alcohols) with different K_i values does not significantly change the adsorption characteristics of each compound, application of the mixture will provide a better opportunity to obtain adequate retardation factor(s) for at least one or more compounds when the air−water interfacial area is unknown. If more than one compound can be applicable for the air−water interfacial area determination, confirmation of the acquired air−water interfacial area by multiple compounds will be possible. A similar strategy of using multiple partitioning tracers to estimate residual NAPL (non-aqueous phase liquid) saturation in porous media has been used by Jin et al. (*28*).

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Supporting Information Available

Two figures showing the experimental setup and column configuration for unsaturated column experiments and one table showing the boundary conditions for the column experiments (3 pp) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the Supporting Information from this paper or microfiche (105 × 148 mm, 24× reduction, negatives) may be obtained from Microforms Office, American Chemical Society, 1155 16th St. NW, Washington, DC 20036. Full bibliographic citation (journal, title of article, names of authors, inclusive pagination, volume number, and issue number) and prepayment, check or money order for $12.00 for photocopy ($14.00 foreign) or $12.00 for microfiche ($13.00 foreign), are required. Canadian residents should add 7% GST. Supporting Information is also available via the World Wide Web at URL http://www.chemcenter.org. Users should select Electronic Publications and then Environmental Science and Technology under Electronic Editions. Detailed instructions for using this service, along with a description of the file formats, are available at this site. To down-load the Supporting Information, enter the journal subscription number from your mailing label. For additional information on electronic access, send electronic mail to si-help@acs.org or phone (202)872-6333.

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