Volatilization of Binary Nonaqueous Phase Liquid Mixtures in Unsaturated Porous Media

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ABSTRACT

This study examines the volatilization behavior of binary nonaqueous phase liquid (NAPL) mixtures consisting of styrene, and toluene or tetrachloroethylene (PCE). Residual NAPL saturations were emplaced in unsaturated (residual water saturation) soil columns packed with Wagner 50-80 sand. Initial column effluent concentrations were measured for the NAPL mixtures at several pore gas phase velocities. Rate-limited volatilization occurred at higher gas phase pore velocities, and mass transfer coefficients could be reasonably predicted with a correlation developed from single component NAPL volatilization data. Long-term volatilization studies for the binary NAPL mixtures were also conducted. The effluent concentrations for both NAPL components were observed to be initially proportional to their mole fractions. After the more volatile component became depleted, a rapid drop in the effluent concentration of this component was accompanied by an increase in the mole fraction and effluent concentration of the remaining constituent to near saturated values until the free phase NAPL was volatilized. The final stage of removal was associated with a dramatic decrease in effluent concentration, attributed to reduction in the gas-NAPL interfacial area, followed by low concentration tailing. The tailing and subsequent flow interruption behavior are likely a consequence of rate-limited desorption. Equilibrium and rate-limited simulations of the long-term volatilization experiments did not provide a satisfactory description of the data. A simulation that included a fixed concentration gradient and fitted activity coefficients provided a better characterization of the volatilization data. Various potential explanations for this "fixed gradient" volatilization behavior were considered, but additional research is needed to test these hypotheses.

N ONAQUEOUS PHASE LIQUIDS are typically released into the subsurface environment by accidental spills or improper storage and disposal practices. As a NAPL migrates through the soil, a residual portion is retained in the pore space due to capillary forces. In the unsaturated zone, a continuous water phase is generally assumed to coat the soil grains. In this case, the residual organic has been observed as thin films or wedges separating the water and gas phases (Wilson et al., 1990; Hayden and Voice, 1993). Residual NAPL saturations in the unsaturated zone typically range from 4 to 10% of the pore space (Wilkins et al., 1995). Due to the low volatility and solubility of most NAPLs, this residual saturation can serve as a persistent source of soil, water, and air contamination. Regulated exposure levels for many of these organic liquids are several orders of magnitude below their volatility and solubility values and, thus, NAPLs are of great environmental concern.

Soil vapor extraction (SVE) and bioventing (BV) have emerged as attractive in situ remediation technologies for unsaturated soils contaminated with volatile organic compounds (e.g., Crow et al., 1987; DiGiulio, 1992; Rathfelder et al., 1995). Soil vapor extraction and BV operations are conducted by forcing air through the contaminated unsaturated zone. The well configuration and pumping rates are designed to maximize volatilization during SVE, whereas the stimulation of indigenous microorganisms to transform contaminants is of primary concern in BV. Both technologies, however, are based upon interphase partitioning processes. Accurate knowledge of the volatilization behavior is therefore essential for the design and efficient implementation of SVE and BV.

Soil vapor extraction systems in the field typically exhibit large initial recovery rates, followed by a rapid decline in effluent concentrations to persistent low levels (e.g., Crow et al., 1987; DiGiulio, 1992). Following SVE shutdown, a temporary concentration rebound has been commonly observed when flow is reinitiated (McClellan and Gilham, 1992). This behavior has been attributed to field scale heterogeneities (Johnson et al., 1990a; Kearl et al., 1991); that is, diffusion from low to high permeability zones. Laboratory experiments, however, suggest that concentration tailing and rebound behavior may also result from a variety of pore-scale processes, including: NAPL volatilization rate limitations at higher flow rates (Wilkins et al., 1995; van der Ham and Brouwers, 1998); rate-limited volatilization of soluble organic components from the aqueous phase (Armstrong et al., 1994); desorption (Farrell and Reinhard, 1994); intra-aggregate diffusion (Brusseau, 1991; Gierke et al., 1992; Conklin et al., 1995); organic vapor sorption on the gas–water interface (Pennell et al., 1992; Hoff et al., 1993; Conklin et al., 1995); variable accessibility of gas to organic and aqueous phases as a result of pore-scale permeability variations (Ho and Udell, 1992); temporal changes in NAPL composition (Hayden et al., 1994; Fischer et al., 1996; Liang and Udell, 1999; Ng et al., 1999); and water saturation above residual level (Yoon et al., 2002).

Nonaqueous phase liquids found at contaminated waste sites are commonly composed of mixtures of several organic species (Powers et al., 1997). Examples of volatile organic mixtures include: gasoline; diesel fuel; petroleum products; and various chlorinated solvents used in industrial operations. The interaction of components in NAPL mixtures may create substantial differences in the mass transfer characteristics of a given component in comparison with the behavior of the pure

Abbreviations: BV, bioventing; NAPL, nonaqueous phase liquid; PCE, tetrachloroethylene; SVE, soil evaporation extraction.

compound (Banerjee, 1984). If ideal behavior of the organic phase is assumed, estimates of equilibrium partitioning behavior can be obtained according to a generalized form of Raoult's Law (Pankow and Cherry, 1996). This assumption is believed to be reasonable for NAPL mixtures composed of chemically similar components (Schwarzenbach et al., 1993; Adenekan et al., 1993). In some cases, however, low mole fraction components have been reported to exhibit deviations from ideal behavior (Hayden et al., 1994). The equilibrium concentrations and dissolution behavior of complex NAPLs in completely mixed batch reactors have also been observed to be inconsistent with ideal mixture theory (Mukherji et al., 1997). Differences between ideal and observed behavior have sometimes been ascribed to diffusional limitations within the NAPL mixture (Ortiz et al., 1999).

Interphase mass transfer of organic contaminants in porous media is often assumed to be controlled by diffusion of constituents through a boundary layer in one phase (see Rathfelder et al., 1991; Wilkins et al., 1995; Abriola et al., 1999). Diffusion of components through dual boundary layers (in aqueous and NAPL phases) has also been considered (Ortiz et al., 1999; Willson et al., 2000). A quasi-steady state approximation of Fick's first law of diffusion through a boundary layer, a linear driving force model, is commonly used in conjunction with equilibrium partitioning relations to describe interphase mass transfer. The mass transfer rate is the product of a lumped mass transfer coefficient and the concentration gradient across the interface boundary layer. One approach for estimating the lumped mass transfer coefficient is to develop correlations between relevant system parameters and experimentally determined lumped mass transfer coefficients (Pfannkuch, 1984; Parker et al., 1991; Miller et al., 1990; Powers et al., 1992; Guarnaccia et al., 1992; Imhoff et al., 1994; Wilkins et al., 1995). System specific values of the velocity, median grain size, grain-size distribution uniformity, and residual NAPL saturation are typically incorporated into these mass transfer correlations.

A limited number of studies have examined the volatilization behavior of several NAPL mixtures (Rathfelder et al., 1991; Ho et al., 1994; Hayden et al., 1994; Liang and Udell, 1999; Ng et al., 1999). These studies largely examined NAPL components that are found in gasoline and diesel fuel. In contrast to pure NAPLs, the volatilization of NAPL mixtures may be subject to nonideal equilibrium partitioning and diffusional limitations that depend on specific physical and chemical properties of the NAPL components. These volatilization mechanisms are also incompletely understood and quantified for a wide variety of NAPL mixtures. This manuscript reports on the volatilization behavior of several atypical binary NAPL mixtures entrapped within unsaturated porous media. A series of column experiments was undertaken to measure initial volatilization mass transfer coefficients at several gas phase velocities and to explore methods for the prediction of mass transfer coefficients. Additional experiments were conducted to examine the long-term volatilization behavior of residual NAPL mixtures. Long-term volatilization data were

Table 1. UNIFAC calculated activity coefficients (γ) for the binary NAPL mixtures.

Mixture (mole fraction)	Property	Styrene	Toluene	PCE
0.82 toluene/0.18 styrene	γ	0.931	0.996	–
0.53 toluene/0.47 styrene	γ	0.970	0.977	–
0.22 toluene/0.78 styrene	γ	0.995	0.937	–
0.39 PCE/0.61 styrene	γ	0.955	–	0.863

interpreted using a multiphase transport simulator that accounts for equilibrium or rate-limited mass transfer.

MATERIALS AND METHODS

The material and experimental protocols employed in this work were similar to those used in previous volatilization experiments using pure organic liquids (Wilkins et al., 1995; Abriola et al., 1999). Organic liquid components of the binary NAPL mixture consisted of various combinations of styrene (monomer inhibited), toluene (high pressure liquid chromatography grade [HPLC grade]), and PCE. These three compounds are on the 1999 Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) priority list for hazardous substances, are used in a wide variety of industrial applications, and encompass a range of densities, spreading coefficients (defined as $\sigma_{gw}-\sigma_{go}-\sigma_{ow}$; where σ is the surface or interfacial tension of the phases indicated with subscripts g, w, and o for gas, water, and organic, respectively) and vapor pressures.

Three binary mixtures of styrene and toluene and one binary mixture of PCE and styrene were prepared. On a mole fraction basis these were 0.53 toluene/0.47 styrene, 0.82 toluene/0.18 styrene, 0.22 toluene/0.78 styrene, and 0.39 PCE/0.61 styrene. Water has a very low solubility in PCE, toluene, and styrene (Demond and Lindner, 1993) and was not considered as a component of the NAPL mixtures. Activity coefficients for the NAPL components in the mixtures were estimated using the UNIFAC method (Fredenslund et al., 1975). Inclusion of water (solubility limit) in the NAPL mixtures had only a minimal influence on the estimated activity coefficients (<2%). The UNIFAC method assumes that a liquid mixture may be described as a solution of structural units from which the molecules are formed. The UNIFAC calculated activity coefficients for the various NAPL mixtures are given in Table 1. The water used in this study was distilled and filtered Milli-Q water (Nanopure filter, ion exchange system), which had been deaired by heating and aspiration. Relevant flow and transport properties for these fluids are presented in Table 2.

Wagner 50-80 sand was used in this investigation. This sand is typical of aquifer materials in the Michigan area and composed of very angular grains, representing a wide range of mineral components (including shale and quartz). Wagner sand has been used in previous dissolution (Powers et al., 1992, 1994) and volatilization (Wilkins et al., 1995) studies. Wagner 50-80 sand has a median grain size (d_{50}; units of length, L) of 0.024 cm and a grain-size uniformity index (U_i) of 1.31.

Wilkins et al. (1995) describes the experimental equipment and protocols that were employed herein for one-dimensional soil column volatilization experiments. The custom designed aluminum columns were 10 cm long and 5 cm in diameter. Endplates and Viton o-rings (DuPont Dow Elastomers L.L.C., Wilmington, DE) were used to form a tight seal at the top and bottom of the columns. The endplates contained perforated stainless steel plates and wire mesh to uniformly disperse fluid flow at the column inlet and outlet, and to retain the packed sand. All connections to the columns were plumbed with stainless steel or teflon tubing to minimize interaction with the organic compounds. The columns were dry packed with Wagner

Table 2. Nonaqueous phase liquid (NAPL) component characteristics.

Parameter	Styrene	Toluene	PCE
Molecular weight, g mol^{-1}†	104.1	92.1	166.0
Density at 25°C, g cm^{-3}†	0.906	0.867	1.623
Saturated gas concentration, mg L^{-1}†	40.1	140.5	162.3
Air–NAPL surface tension, dynes cm^{-1}†	32.0	32.8	31.7
NAPL–water interfacial tension, dynes cm^{-1}†	33.0	36.1	47.5
Gas diffusion coefficient in N, cm^2 s^{-1}†	0.076	0.085	0.088
Water solubility, mg L^{-1}‡	300	535	150
Henry's law constant, atm m^3 mol^{-1}‡	2.05×10^{-2}	6.37×10^{-3}	2.59×10^{-2}

† From Wilkins et al. (1995).
‡ From Mercer and Cohen (1990).

sand. Care was taken to ensure uniform packing by gradually adding small quantities of sand and then slowly vibrating the column for several seconds. The porosity (ε) was determined according to the method of Danielson and Sutherland (1986) using the measured soil bulk density and assuming a specific solid density of 2.65 g cm^{-3}. The column was then saturated by pumping water upwards at a rate of 1 to 2 mL min^{-1} for 25 to 30 pore volumes using a high pressure solvent delivery system.

Residual water saturation was attained in the column by displacing water with air. For this purpose, a suction of 115 cm of water was applied for 24 h to the bottom column endplate using a hanging water column in contact with filter paper (2.5-µm pore-size filter paper contacts the sand on one side and the endplate on the other side). Following desaturation, the filter paper at the bottom of the sample was replaced with a porous Teflon filter (DuPont Dow Elastomers L.L.C., Wilmington, DE) that serves as an organic-wet capillary barrier to the air and water phases. The air was then displaced from the column by injecting several pore volumes of a binary Nonaqueous phase liquid mixture into the bottom of the column at a rate of 1.5 mL min^{-1} using a syringe pump. Residual NAPL saturation was achieved by applying suction to the sample using a hanging NAPL column attached to the Teflon filter at the bottom of the column. Residual water and NAPL saturations were determined gravimetrically based on densities of the fluids and the difference in column weights before and after entrapment. Experiments were duplicated to establish the reproducibility of results. The average sand porosity, residual water, and residual NAPL saturations from replicate soil columns are 0.382, 0.146, and 0.111, respectively. The difference between replicate measures of column porosity, residual water saturation, and residual NAPL saturation was <2%. The uniformity of the residual saturation distributions obtained using this entrapment procedure was previously verified by Wilkins et al. (1995).

After residual water and NAPL saturations were achieved, the column was placed vertically within an isothermal chamber (70 by 40 by 35 cm cooler) for the volatilization study. Experiments were conducted at a constant temperature to minimize temperature-induced changes in the volatilization rates. The temperature was controlled in the chamber using 0.953 cm (or 3/8″) copper tubing, a small electric fan, and a recirculating water bath. The tubing was wound around the interior of the cooler and connected to the water bath, while the fan was positioned to provide air circulation inside the cooler. The instruments were adjusted to achieve a temperature of 24 ± 1°C inside the cooler. The column was equilibrated for 4 to 5 h in this chamber before initiating any volatilization experiment.

To minimize drying of the sand during the volatilization experiments, purified N$_2$ gas was bubbled through Milli-Q water to increase the relative humidity of the gas phase. No condensation of water vapor was observed in the tubing connected to the columns, indicating that the gas phase was not saturated with water vapor. This N$_2$ gas was then introduced into the column in an upflow mode. Effluent vapor phase concentration of the organic compounds were continuously monitored and analyzed with a gas chromatograph, equipped with a flame ionization detector. Effluent concentrations were determined by comparison of detector response and retention time to that obtained from standard solutions of binary NAPL mixtures dissolved in methanol.

Two types of volatilization experiments were conducted. Steady-state experiments examined the influence of various gas flow rates, ranging from 40 to 400 mL min^{-1}, on steady-state effluent gas concentrations. These flow rates correspond to interstitial or pore gas velocities of 0.12 to 1.2 cm s^{-1}, and were selected to be consistent with field SVE rates in the vicinity of injection or extraction wells. Gas pore velocities are typically <2 cm s^{-1} in field SVE systems (Johnson et al., 1990b). Each steady-state soil column experiment was run at approximately five velocities over this range (the order of the selected pore gas velocities was approximately 1.1, 0.22, 0.12, 0.44, and 0.67 cm s^{-1}). Effluent gas flow rates were monitored using a digital bubble flowmeter. Similar to other mass transfer studies (Powers et al., 1992; Wilkins et al., 1995), quasi-steady state or constant gas-organic interfacial area conditions were assumed when <15% of the residual NAPL mixture mass was recovered from the column effluent. Within this range of saturation reduction, the variance between effluent concentrations at a given flow rate has been reported to be independent of the NAPL saturation (Powers et al., 1992).

Transient (long-term) volatilization experiments were also performed. For these experiments, a low pore gas velocity of approximately 0.12 cm s^{-1} was maintained to achieve effluent concentrations near equilibrium. Effluent gas concentrations were measured until the free phase NAPL was nearly completely recovered; that is, component concentrations dropped and tailed at approximately two orders of magnitude below the saturated gas phase concentration of the pure organic liquid. Mass transfer limitations during the concentration tailing period (after free phase NAPL was removed) were subsequently examined using flow interruption techniques (see Pennell et al., 1993). Temporal changes in the column averaged NAPL component saturations were determined from mass balance considerations; that is, by subtracting the volatilized NAPL component mass determined by integrating the effluent concentration curve (Powers et al., 1994) from the initial NAPL component mass. Separate columns were used in steady-state and transient volatilization studies.

Conceptual and Mathematical Model

The pore-scale fluid distribution of gas, water, and NAPL in porous media is controlled by the wettability of the system. It is assumed that water is the wetting fluid, the NAPL is the intermediate wetting fluid, and the gas is the nonwetting fluid. Under such conditions, water is found coating the soil grains and occupies the smaller pore spaces, the residual NAPL will

tend to form continuous films, lenses, or wedges at the gas–water interface, and the gas will occupy the larger pores. Hence, the gas and aqueous phases are both in contact with the NAPL, whereas the solid phase only contacts the aqueous phase. This conceptual model is consistent with fluid distributions observed in etched glass micromodels (Wilson et al., 1990; Blunt et al., 1994) and in natural sands that were frozen and sectioned (Hayden and Voice, 1993). The gas and water phases are assumed to contact each other only after complete volatilization of the NAPL phase at a particular location.

In the experimental systems considered herein water and NAPL phases are at residual saturation levels and are therefore assumed to be immobile. The solid phase is also assumed to be immobile. No equations are needed to describe the movement of the gas phase because the permeability and porosity of the porous media in the columns are spatially homogeneous, and the gas phase moves at a constant Darcy velocity. Degradative activity of indigenous microorganisms and other chemical reactions are neglected because of the short experimental time scale. Changes in NAPL saturation are therefore assumed to result solely from interphase mass transfer, and the NAPL mass balance is written as:

$$\frac{\partial(\rho_o \theta_o)}{\partial t} = -\sum_i E_i^{go} - \sum_i E_i^{ow} \qquad [1]$$

where t (T) is time, ρ_o (M L^{-3}) is the NAPL mass density, θ_o (-) is the volumetric NAPL content, E_i^{go} (M L^{-3} T^{-1}) is the net rate of component i mass transfer between the gas and NAPL phases, and E_i^{ow} (M L^{-3} T^{-1}) is the net rate of component i mass transfer between the NAPL and water phases.

The composition of the fluid phases is subject to the following assumptions. The NAPL is considered to be a mixture of two organic components. The gas phase is assumed to be comprised of N$_2$, and both components of the NAPL when present. Simulations that considered N$_2$ and a single NAPL component in the gas phase, and neglected water vapor, provided an accurate description of observed volatilization behavior for pure NAPLs (Abriola et al., 1999). The aqueous phase is limited to components of the NAPL and water. The migration of individual components in the fluid α phase (α = g, o, and w for the gas, NAPL, or water phases, respectively) is represented by a general macroscopically averaged transport equation:

$$\frac{\partial(\theta_\alpha C_{\alpha i})}{\partial t} = -\nabla \cdot J_{\alpha i} + \sum_\beta E_i^{\alpha\beta} \qquad [2]$$

where $C_{\alpha i}$ (M L^{-3}) is the component concentration in the α phase, $J_{\alpha i}$ (M L^{-2} T^{-1}) is the component solute flux in the α phase, and β denotes the accessible phases for interphase mass transfer determined by the fluid distribution; that is, for α = g the value of β = o,w, for α = w the value of β = g,o,s, and for α = o the value of β = g,w. The value of J_{gi} consists of terms for the advective, dispersive, and diffusive solute fluxes. In contrast, the value of J_{wi} considers only the diffusive solute flux because the water phase is immobile. Macroscopic diffusive transport within the NAPL is assumed to be insignificant and, hence, J_{oi} equals zero. The solid phase mass balance equation for component i is given as:

$$\frac{\partial(\rho_b \omega_i)}{\partial t} = E_i^{sw} \qquad [3]$$

where ρ_b (M L^{-3}) is the soil bulk density, and ω_i is the concentration of component i on the solid phase. Nonequilibrium interphase partitioning is represented with a linear driving force expression:

$$E_i^{\alpha\beta} = \theta_\alpha k_i^{\alpha\beta} (C_{\alpha i}^{eq} - C_{\alpha i}) \qquad [4]$$

where $k_i^{\alpha\beta}$ (T^{-1}) is the lumped mass transfer coefficient of component i across the $\alpha\beta$ interface, and $C_{\alpha i}^{eq}$ (M L^{-3}) is the concentration of component i in the α phase in equilibrium with the β phase. Equation [4] is used to model volatilization and dissolution of entrapped NAPL, gas–water interchange of aqueous NAPL components, and sorption of the NAPL components. The mass transfer resistance and boundary layer concentration gradient in Eq. [4] is assumed to occur in the aqueous phase for NAPL dissolution, sorption, and component partitioning across the gas–water interface. In contrast, the mass transfer resistance and boundary layer concentration gradient is assumed to be in the gas phase during NAPL volatilization. Ortiz et al. (1999) found in dissolution experiments that the presence of a NAPL phase boundary layer only occurred in high viscosity NAPL mixtures.

The long-term volatilization experiments were examined using numerical modeling. A two-dimensional field scale SVE and BV simulator known as MISER, the Michigan SVE remediation model (Abriola et al., 1997; Rathfelder et al., 2000), was used for this purpose. The following description is restricted to those features of MISER utilized in the current work; for a complete description of MISER refer to Abriola et al. (1997) and Rathfelder et al. (2000). MISER solves the coupled nonlinear flow and transport equations given by Eq. [1] through [4] for a cross-sectional (x-z) domain with the Galerkin finite element method, using linear triangular elements and a modular set-iterative solution scheme. The transport equations are solved sequentially, first for the gas phase, second for the aqueous phase, and then for the organic phase. The solution of the organic liquid saturation equation follows after the solution of the transport equations. Decoupling is accomplished by lagging the coupling terms one iteration. These terms consist of the phase density and interphase mass transfer terms. Picard iterations are used to account for nonlinearities. The model has been verified using internal mass balance calculations, comparisons with one- and two-dimensional analytical solutions, and comparisons with other numerical models (Abriola et al., 1997). MISER has also been used to successfully simulate single component volatilization experiments (Abriola et al., 1999).

The transport properties used in the simulations are listed in Tables 1 and 2. The experimental columns were represented numerically using 400 elements, and a maximum nodal spacing of 0.1 cm. No flow boundary conditions were implemented along the sides of the column, a constant mass flux (third type) condition was specified at the inlet of the column and a zero diffusive/dispersive flux (second type) condition was specified at the outlet of the column.

RESULTS

Steady-State Mass Transfer

The influence of gas phase pore velocity and mixture composition on steady-state (constant interfacial area) NAPL volatilization is explored in this section. Nonaqueous phase liquid mixtures consisting of 0.82 toluene/0.18 styrene (mole fractions), 0.53 toluene/0.47 styrene, and 0.22 toluene/0.78 styrene were considered in the steady-state studies. Figure 1 presents normalized effluent component concentrations as a function of pore gas velocity (v_g, L T^{-1}) for a representative NAPL mixture, 0.82 toluene/0.18 styrene, entrapped in a particular soil column. The 95% confidence intervals (established from two to four replicate measurements) are also shown in this figure. Component concentrations (C_{gi}, M L^{-3})
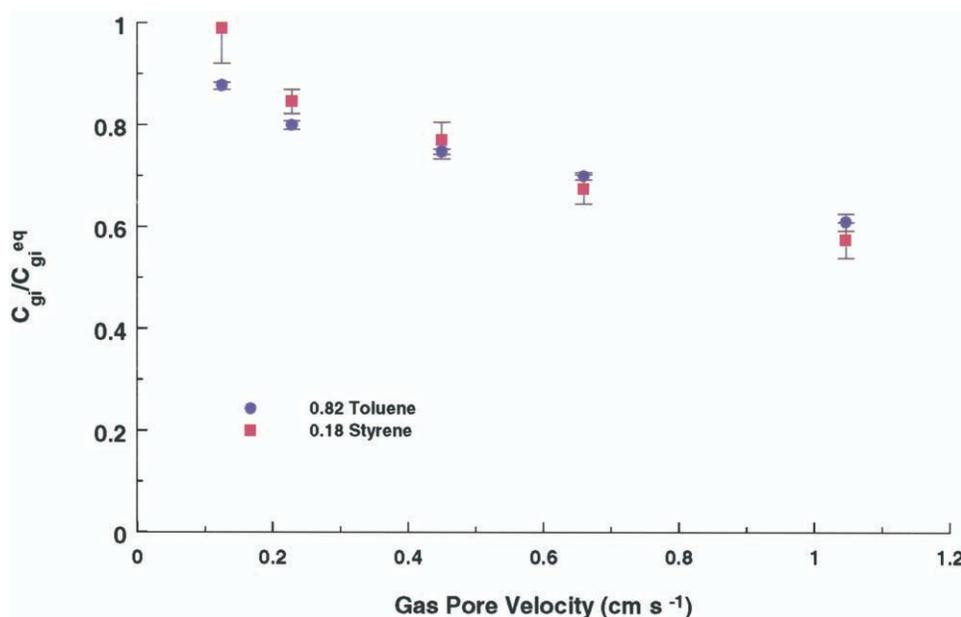
Fig. 1. Normalized (with respect to C_{gi}^{eq}) effluent component concentrations as a function of pore gas velocity for a representative NAPL mixture, 0.82 toluene/0.18 styrene.

are normalized to the equilibrium partitioning value (C_{gi}^{eq}, M L^{-3}):

$$C_{gi}^{eq} = \gamma_{oi}\, X_{oi}\, C_{gi}^{pure} \qquad [5]$$

where γ_{oi} (-) and X_{oi} (-) are the component activity coefficient and mole fraction in the NAPL phase, respectively, and C_{gi}^{pure} (M L^{-3}) is the pure organic component equilibrium vapor concentration. Equation [5] is based on the principle that the chemical potentials in each phase are equal at thermodynamic equilibrium, and assumes that the activity coefficient of component i in the gas phase is independent of X_{oi} and identical reference state fugacities for NAPL components. If ideal behavior is assumed ($\gamma_{oi} = 1$), then Eq. [5] reduces to Raoult's Law.

The normalized effluent concentrations for both styrene and toluene shown in Fig. 1 decline with increasing pore velocity. In general, normalized concentration values lower than unity are indicative of a rate-limited mass transfer process. These deviations from equilibrium increased with increasing velocity to a minimum concentration ratio of 0.57 at a gas pore velocity of 1.05 cm s^{-1}. Wilkins et al. (1995) observed a similar decrease in the normalized effluent concentration of pure organic liquids with increasing gas pore velocity.

To further explore steady-state volatilization rates, lumped mass transfer coefficients (k_i^{go}; T^{-1}) were calculated from the effluent component concentrations. Assuming quasi-steady state conditions and neglecting the diffusive/dispersive flux, the one-dimensional analytical solution of Eq. [2] for a zero concentration boundary condition at the inlet can be rearrange to give k_i^{go} (Wilkins et al., 1995):

$$k_i^{go} = -\frac{v_g \varepsilon}{L_c}\ln\!\left(1 - \frac{C_{gi}}{C_{gi}^{eq}}\right) \qquad [6]$$

where L_c (L) is the column length. Neglecting the diffusive/dispersive flux in Eq. [2] was previously found to

cause only minor errors in the estimated mass transfer coefficients (<10%) (Wilkins et al., 1995).

The parameters k_i^{go} and v_g are frequently presented in terms of dimensionless modified Sherwood (Sh$_i^{go}$) and Peclet (Pe) numbers, respectively, as:

$$Sh_i^{go} = \frac{k_i^{go}(d_{50})^2}{D_{gi}} \qquad [7]$$

$$Pe = \frac{v_g d_{50}}{D_{gi}} \qquad [8]$$

where D_{gi} (L^2 T^{-1}) is the component gas phase diffusivity given in Table 2. Figure 2 summarizes the steady-state volatilization data for the binary NAPL mixtures by presenting a plot of calculated Sh$_i^{go}$ versus Pe. Note that Sh$_i^{go}$ increases with increasing Pe, indicating that the mass transfer coefficient increases with increasing velocity. A similar dependence of the mass transfer coefficient on velocity has been reported in dissolution (Miller et al., 1990; Powers et al., 1992; Imhoff et al., 1994) and volatilization (Wilkins et al., 1995; van der Ham and Brouwers, 1998) studies.

Wilkins et al. (1995) calculated an empirical mass transfer correlation from pure organic compound (steady-state) volatilization data and system dependent variables:

$$Sh_i^{go} = 10^{-2.79}\, Pe^{0.62}\!\left(\frac{d_{50}}{0.05}\right)^{1.82} \qquad [9]$$

The Pe and d$_{50}$ for experiments reported herein fall within the range used to develop Eq. [9], allowing experimentally measured Sherwood numbers and those predicted by the pure-phase correlation of Wilkins et al. (1995) to be compared in Fig. 2. The coefficient of linear regression between the observed and predicted modified Sherwood numbers is equal to 0.80, indicating a reasonably good agreement. Other functional forms were tested to relate the experimental Sherwood numbers to compo-
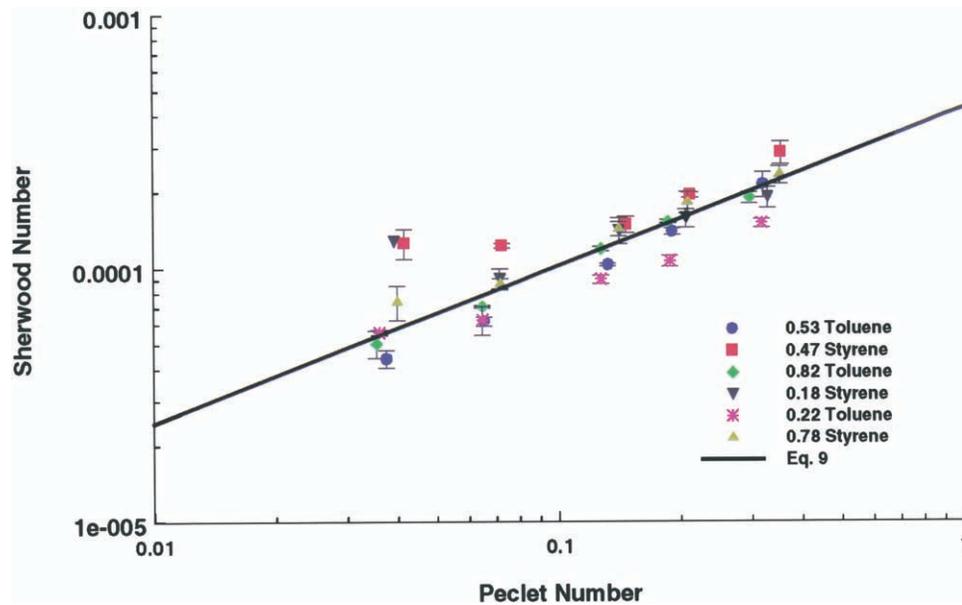
Fig. 2. A log plot of the Sherwood numbers versus the Peclet numbers obtained from the steady-state volatilization data. A plot of the predicted Sherwood numbers by the correlation of Wilkins et al. (1995) (Eq. [9]) is also shown.

nent mole or mass fractions, as well as Pe and d_{50}. Inclusion of power functions for the component mole or mass fractions in the mass transfer correlation did not significantly improve the description of the experimental data and were therefore not included.

Transient Mass Transfer–Data and Simulations

This section discusses the transient (long-term) volatilization behavior of binary NAPL mixtures entrapped in unsaturated Wagner 50-80 sand. Figure 3 presents observed and simulated effluent concentration curves for NAPLs composed of 0.82 toluene/0.18 styrene, 0.53 toluene/0.47 styrene, and 0.39 PCE/0.61 styrene, respectively. Here normalized component concentrations are (semi-log) plotted with respect to pore volumes of gas. In contrast to Fig. 1, the component concentrations are normalized here with respect to the saturated gas phase concentration of the pure organic liquid (C_{gi}^{pure}). At equilibrium this normalized concentration equals $\gamma_{oi} X_{oi}$ (Eq. [5]). The normalized concentrations in Fig. 3 therefore reflect temporal changes in NAPL composition (activity coefficient and mole fraction) that occur during transient (long-term) volatilization as well as mass transfer limitations.

Simulations are presented for both equilibrium (solid lines) and rate limited (dotted lines) mass transfer up to the first flow interruption. Condensation of NAPL components is included in the simulations (in Eq. [4] when $C_{gi} > C_{gi}^{eq}$). The equilibrium gas-NAPL mass transfer was obtained by selecting the mass transfer coefficient in Eq. [4] to produce equilibrium concentrations (95% over any one element). Gas-NAPL mass transfer coefficients used in rate-limited simulations were estimated using the correlation of Wilkins et al. (1995) (see Eq. [9]). The equilibrium gas phase concentrations used in Eq. [4] were adjusted for chemical activities (see Eq. [5] and Table 1) in the binary NAPL phase based upon

UNIFAC predictions. Water-NAPL, gas-water, and solid-water mass transfer coefficients were set to near equilibrium values based on the results of a sensitivity analysis showing that the simulated breakthrough curves did not depend upon the choice of these parameters. Water-solid mass transfer coefficients were set to fitted values obtained from previous work with similar single component NAPL experiments (Abriola et al., 1999).

In theory, the normalized concentration levels should be relatively close to equilibrium partitioning predictions (steady-state experiments were within 18% of equilibrium estimates at comparable velocities) because a low pore gas velocity (0.127–0.147 cm s^{-1}) was maintained during the experiments (see Fig. 1). An examination of the initial effluent concentrations shown in Fig. 3a (0.82 toluene/0.18 styrene mixture) indicates close agreement between the measured and equilibrium (Eq. [5]) values (within 18%). In contrast, the initial effluent concentrations shown in Fig. 3b and 3c indicate that measured concentrations are lower than equilibrium predictions for toluene and styrene, and higher for PCE. The 0.82 toluene/0.18 styrene experiment (Fig. 3a) was performed at a pore gas velocity (0.127 cm s^{-1}) that was approximately 14 (0.147 cm s^{-1}) and 8% (0.138 cm s^{-1}) less than the pore gas velocity used in the 0.53 toluene/0.47 styrene (Fig. 3b) and 0.39 PCE/0.61 styrene (Fig. 3c) experiments, respectively. The higher gas velocity may account for some of the deviation from equilibrium behavior observed in Fig. 3b, however it does not explain the apparent volatilization of PCE at concentrations above equilibrium in Fig. 3c. This deviation may be related to inaccuracies in our estimated PCE activity coefficient (UNIFAC). McCray and Dugan (2002) found large differences between measured and UNIFAC estimates of trichloroethene activity coefficients (measured values were as much as 15 times greater).

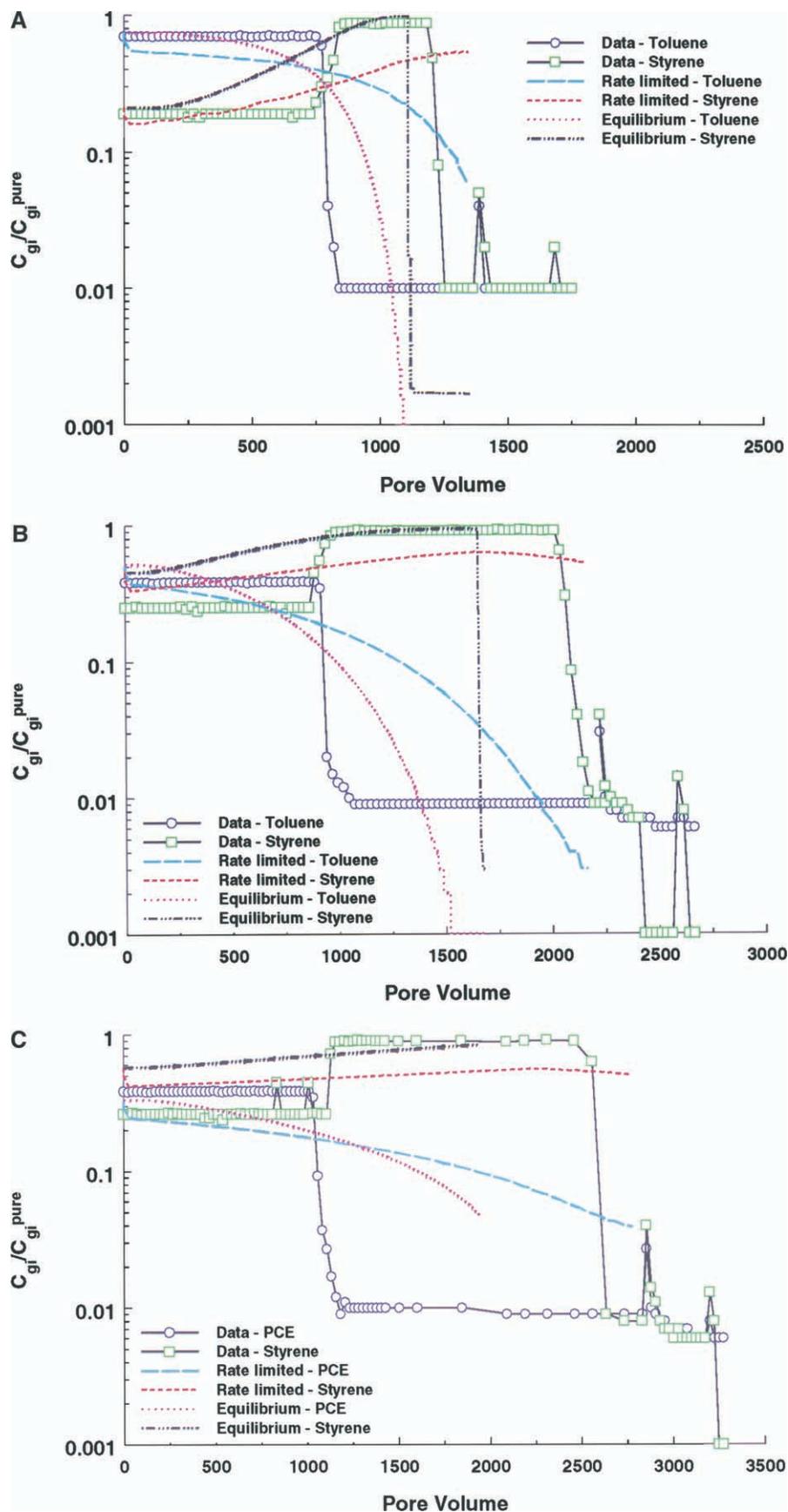In the early portion of the curves (Fig. 3), the relative

Fig. 3. Observed and simulated (equilibrium and rate-limited) effluent concentration curves for nonaqueous phase liquids (NAPLs) composed of 0.82 toluene/0.18 styrene (a), 0.53 toluene/0.47 styrene (b), and 0.39 PCE/0.61 styrene (c), respectively. Here normalized (with respect to C_{gi}^{pure}) component concentrations are (semi-log) plotted with respect to pore volumes of gas.

concentrations of both NAPL components are maintained over many pore volumes. This observation suggests a constant rate of mass transfer during this period. This result is quite surprising because a significant percentage (97%) of the more volatile component (toluene or PCE) mass is removed during this time period, and this mass removal is associated with significant changes in the component mole fractions. Changes in the component mole fraction alter the equilibrium concentration of this component (Eq. [5]), which in turn influences the concentration gradient that drives mass transfer (Eq. [4]). Simulated equilibrium or rate-limited effluent concentration curves exhibit significantly more curvature than the experimental data. The rate-limited simulations exhibit more curvature than equilibrium predictions, and therefore provide a less adequate description of the data.

As time (pore volume) progresses, the effluent concentration curves exhibit a rapid drop in the concentration of the more volatile component (Fig. 3a and 3b, toluene; Fig. 3c, PCE), which is simultaneously accompanied by an increase in concentration of the less volatile component (styrene) (Fig. 3). This observation is more consistent with equilibrium partitioning (see Eq. [5]), which predicts that a decrease in the mole fraction (concentration) of the more volatile component results in an increase in the mole fraction (concentration) of the remaining constituent. Consequently, the observed increase in styrene concentration is actually a result of a decrease in the mass of the more volatile component (toluene or PCE). The rate of concentration change, however, is more rapid than equilibrium or rate-limited simulations predict, and than has been observed in volatilization studies using other NAPL mixtures in porous media (Rathfelder et al., 1991; Hayden et al., 1994; Liang and Udell, 1999; Ng et al., 1999).

After depletion of the more volatile component, the effluent concentration of this component decreased to persistent low levels that were approximately two orders of magnitude below the component's saturated gas phase concentration (Fig. 3). In contrast, the effluent concentration of the remaining compound persisted near saturation for many pore volumes. This last observation was attributed to the presence of high interfacial area NAPL films during the course of volatilization experiment. Previous volatilization (Abriola et al., 1999) and dissolution (Bradford et al., 1999) studies support this hypothesis.

Eventually the majority of the remaining NAPL component mass was removed and a dramatic decrease in effluent concentration was observed (Fig. 3), which was also followed by low concentration tailing. This sharp decline in effluent concentration is believed to occur as a result of decreases in NAPL saturation (98–99% of the cumulative NAPL mass is removed) and, hence, a decrease in gas–NAPL interfacial area. In contrast, the similar rapid decrease in effluent concentration for the more volatile component occurred as a result of changes in NAPL composition.

Concentration tailing behavior occurred for both components in the latter stages of the effluent concentration curves (Fig. 3). To investigate rate limited mass transfer behavior in this tailing region the gas flow through the columns was temporally interrupted (stopped) and then reinitiated. Two shut-in equilibration periods of 6 to 8 h were performed during each experiment. Theoretically, if the separate phase of NAPL is still present in a column, the effluent concentration should rebound to near equilibrium levels when flow is reinitiated, provided that the flow interruption occurs for a sufficient duration (Pennell et al., 1993).

Observe in Fig. 3 that both components exhibit a concentration rebound following flow interruptions, the more volatile component (Fig. 3a,b toluene; Fig. 3c PCE) having a lower normalized concentration rebound than the less volatile constituent (styrene). Furthermore, following the second flow interruption, the component concentrations exhibit lower rebound levels after the first interruption. This observation can be explained by considering the time (number pore volumes) required to deplete the particular NAPL component and, hence, to initiate concentration tailing. The more volatile component is depleted more rapidly and, therefore, concentration tailing has occurred for a greater time. Note that the maximum normalized concentration rebound is only 4.9% of the saturated styrene concentration. This suggests that no separate phase NAPL exists in this tailing region.

Abriola et al. (1999) analyzed transient volatilization behavior of pure styrene in unsaturated Wagner sand. The concentration tailing for styrene was very similar to the behavior of the NAPL mixtures in Fig. 3. Mathematical modeling, measured sorption isotherms, and simple mass balance calculations of this pure volatilization data by these authors suggests that the remaining styrene mass resided primarily on the solid phase, and that the low concentration tailing was primarily due to rate limited desorption.

Transient Mass Transfer–Model Refinement

Inaccuracies in the UNIFAC estimated activity coefficients were examined as a potential explanation for the poor model description of the experimental data. Similar to Fig. 3b, Fig. 4 shows observed and simulated effluent concentration curves for the 0.53 toluene/0.47 styrene NAPL mixture. In this case, however, initial activity coefficient values were fitted to the experimental data. Toluene activity coefficients were 0.732 and 1.012 for the equilibrium and rate-limited simulations, respectively, whereas the UNIFAC estimate was 0.976. Styrene activity coefficients were 0.640 and 0.873 for equilibrium and rate-limited simulations, respectively, whereas the UNIFAC estimate was 0.969. Although the simulated volatilization behavior shown in Fig. 4 does provide an improved description of the data compared with Fig. 3b, it still does not accurately characterize temporal changes in effluent concentration curves. This suggests that inaccuracies in the UNIFAC estimated activity coefficients do not fully account for the poor model descriptions of the data.

The data in Fig. 3 suggests a constant rate of volatilization of both NAPL components until most of the more volatile component (Toluene or PCE) mass is recovered.
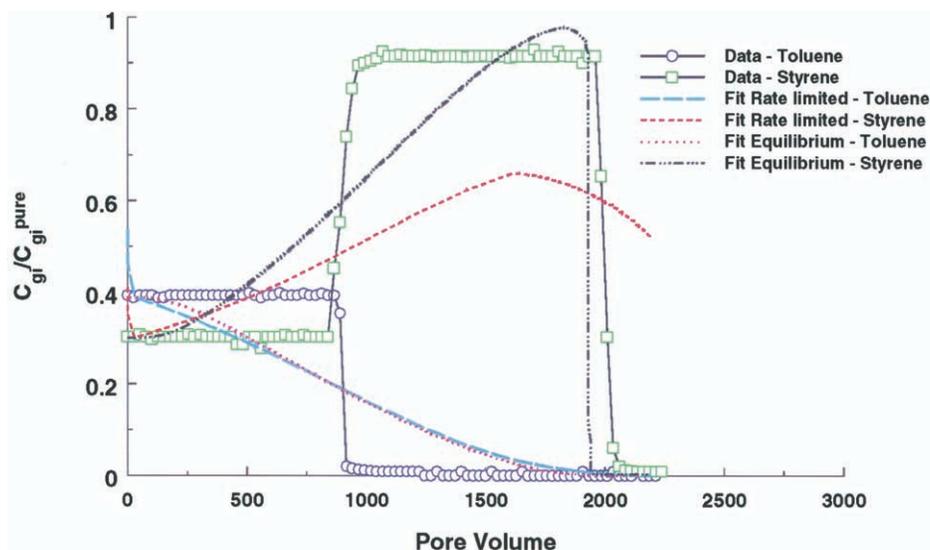
Fig. 4. Observed and simulated (equilibrium and rate-limited) effluent concentration curves for the 0.53 toluene/0.47 styrene NAPL mixture. The simulations utilized fitted initial component activity coefficients.

In an attempt to simulate this behavior, the value of $C_{\alpha i}^{eq}$ in Eq. [4] and [5] was set equal to a fixed value of $\gamma_{oi} X_{oi} C_{gi}^{pure}$, determined by initial conditions. When the mole fraction of the more volatile component in the NAPL mixture approached zero within the column, the value of $C_{\alpha i}^{eq}$ was set equal to 0 and C_{gi}^{pure} for the more and less volatile component, respectively. Condensation of NAPL components was not considered in this case, due to the assumption of a fixed concentration gradient. Figure 5 presents observed and simulated effluent concentration curves for the 0.53 toluene/0.47 styrene NAPL mixture. A rate-limited simulation is employed here using the fixed concentration gradient approach outlined above, a fitted gas–NAPL mass transfer coefficient (0.05 s^{-1}) and fitted activity coefficients (0.732 and 0.640 for toluene and styrene, respectively). This fixed gradient simulation provides a good description of the volatilization data.

Various explanations for this constant rate of volatil-ization were considered. Liang and Udell (1999) argued that NAPL film flow can be neglected in volatilization studies, because NAPL contamination of the gas–water interface lowers the surface tension and the spreading coefficient approaches zero or negative values (no spreading). Nonaqueous phase liquid film flow was therefore discounted as an explanation for the observed volatilization behavior. Additional simulations were conducted that considered equilibrium sorption of NAPL components to the gas–water interface, as well as the processes considered in Eq. [1] through [4]. Simulations were very similar to those shown in Fig. 3, suggesting that interfacial sorption does not provide a viable explanation for the observed behavior.

A third hypothesis concerns the distribution of components in the NAPL mixture. The mathematical model (Eq. [1]–[4]) assumes that the NAPL components are uniformly distributed throughout the mixture at a par-
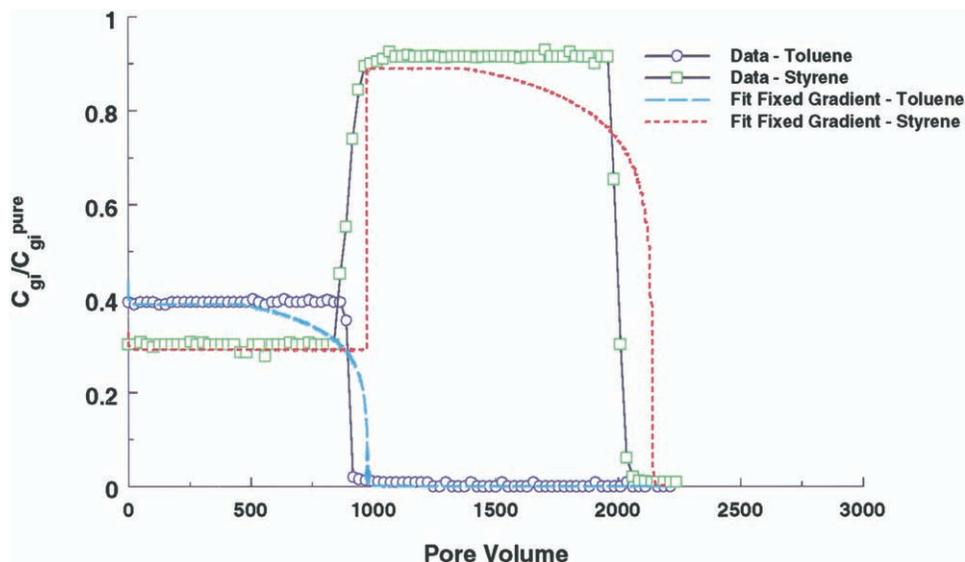

Fig. 5. Observed and simulated effluent concentration curves for the 0.53 toluene/0.47 styrene NAPL mixture. The simulation utilized fitted initial component activity coefficients, a fitted gas-NAPL mass transfer coefficient, and a fixed value of $C_{\alpha i}^{eq}$ in Eq. [4] determined by initial conditions.

ticular location and time. It is possible that variations in the mass transfer rates of the NAPL components at the water–NAPL and gas–NAPL (including condensation) interfaces produce boundary layers or nonuniform distributions of NAPL components within the mixture that are not accounted for by this model. Additional research is justified to further test this hypothesis, but is beyond the scope of the current investigation.

CONCLUSIONS

This work investigates the rate-limited volatilization behavior of binary NAPL mixtures entrapped at residual saturation in unsaturated porous media. Studies were conducted for both steady-state and transient volatilization conditions. In steady-state experiments, the NAPL saturation and composition does not change appreciably over the course of the experiment (<15%). In contrast, the transient experiments examined the nearly complete recovery of the NAPL mixture (long-term) and, hence, occur over significant ranges in NAPL composition and saturation.

In steady-state experiments, the component concentrations and mass transfer coefficients were determined at various gas phase pore velocities. The data indicate that significant deviations from equilibrium partitioning occur for higher gas phase pore velocities that are typical of soil vapor extraction operations in the vicinity of injection or extraction wells. A previously developed mass transfer correlation that was established from steady-state volatilization data of pure NAPLs (Wilkins et al., 1995) was found to provide a reasonable prediction of the NAPL component mass transfer coefficients.

Due to the low experimental pore gas velocity in the transient experiments, the initial component concentrations were proportional to their mole fractions. These concentrations were maintained for long periods. As the more volatile component became depleted, a sharp decrease in this constituent concentration occurred, followed by concentration tailing approximately two orders of magnitude below the saturated gas phase concentration of the pure organic liquid. The depletion of the more volatile component was simultaneously accompanied by a sharp rise in concentration and mole fraction of the remaining component to near saturated levels. High concentrations of the less volatile component were maintained until the separate phase NAPL was recovered and the interfacial area dramatically decreased. At this time, a sharp drop in the effluent concentration of the less volatile component was observed, followed by concentration tailing. The concentration tailing of both components and the observed component concentration rebounds following flow interruption, indicate that the persistence of separate phase NAPL was not likely responsible for this behavior. Experimental and modeling results from similar volatilization studies using pure NAPL suggests that rate-limited desorption was the process controlling this concentration tailing behavior.

Equilibrium and rate-limited volatilization simulations of the transient experiments did not provide a satisfactory description of the component effluent concentra-

tion curves. Inaccuracies in the estimated activity coefficients could not fully account for differences in the data and simulations. An equilibrium simulation that included a fixed concentration gradient and fitted gas–NAPL mass transfer and activity coefficients provided a reasonable characterization of the volatilization data. Nonaqueous phase liquid film flow and interfacial sorption of NAPL components onto the gas–water interface were discounted as possible explanations for this "fixed gradient" volatilization behavior. Small-scale spatial variability in the NAPL composition as a result of mass transfer was proposed as one potential explanation for this fixed gradient behavior. Additional research is needed to test this hypothesis.

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