

ABSTRACT

As immiscible organic contaminants migrate through the subsurface environment, a significant portion of non-aqueous phase liquids (NAPL's) is trapped by capillary forces and remains in the subsurface as immobile blobs or ganglia. Residual saturations of NAPL on the order of 0 - 30 percent have been observed in saturated subsurface systems. The NAPL can partition into the aqueous phase and serve as a long-term source of groundwater contamination. NAPL- aqueous mass transfer rates impact the distribution and the rate of movement of the contaminant within the subsurface. The mass transfer coefficient is a function of many variables including aqueous phase velocity and NAPL-aqueous interfacial area.

One-dimensional column experiments were performed in which the NAPL (toluene) is initially at residual saturation while the velocity of the aqueous-phase flow through the porous media (glass beads) is varied. Mass-transfer rates are quantified for the NAPL-aqueous phase system as a function of aqueous- phase velocity, porous media size, and percent NAPL saturation. Aqueous-phase velocities in the range of 0.1 to 35 m/d and NAPL saturations in the range of 2.5 to 21 percent are studied. The results of column experiments are shown in dimensionless form, and criteria are derived that show where the assumption of equilibrium between the NAPL and aqueous phase is appropriate. Initial solubility and mass transfer experiments were performed to determine the effect of humic acid and a cosolvent (ethanol) on NAPL-aqueous solubility and mass transfer characteristics.

The results of this research indicate that the rate of NAPL-aqueous interphase mass transfer increases as a function of increasing aqueous phase velocity and percent NAPL saturation. The data indicates that NAPL-aqueous equilibrium is a valid assumption under the experimental conditions addressed in this study.

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1 Introduction

1.1 Background

In the United States groundwater has become one of our most valuable natural resources. Groundwater supplies 25 percent of our nation's domestic, agricultural and industrial water and approximately 50 percent of our population's drinking water (Driscoll, 1986). Reliance on groundwater has increased greatly in past decades as our population has shifted to areas where surface water is not an abundant or reliable water source.

As our reliance on groundwater has increased, so too has our concern for groundwater quality. The United States Environmental Protection Agency considers groundwater pollution to be a major environmental issue in the 1980's (Hoag et al., 1986). Recent legislation including the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the Resource Conservation and Recovery Act (RCRA), has focused on groundwater contamination and remediation. Efforts have been made to greatly increase expenditures on site investigations, groundwater monitoring, and remediation. Despite these efforts to address groundwater contamination, it has been estimated that approximately one percent of all groundwater in the United States is currently contaminated and that further contamination will continue into the next decade (Hoag et al., 1986; Clark et al., 1988).

The need for better protection of our groundwater and for effective remediation technologies is evident. Presently there are few documented techniques for aquifer restoration, and there have been no examples of successful cleanups reported (Hunt et al, 1988b). Common remediation methods, such as "pump and treat" techniques, have proven to be very expensive due to slow dissolution rates of organic compounds. Cleanup costs for a single contaminated aquifer may cost as much as 10's of millions of dollars and the actual

remediation may take decades to complete (MacKay et al., 1989).

Threats to groundwater quality include point sources from various industries as well as non-point sources associated with agricultural pesticides and fertilizers. The most frequently occurring and most persistent contaminants found in groundwater are immiscible, organic compounds (MacKay et al., 1989). These compounds are most commonly found in the form of industrial solvents and aromatic hydrocarbons from the petroleum industry. Most groundwater contamination of this type is caused by leakage from underground storage tanks (UST) and associated piping. It has been estimated that as of 1986, as many as 100,000 UST's in the United States were leaking (Hoag et al., 1986).

Groundwater contaminated with partially-miscible organic compounds poses a particularly challenging problem with regard to containment and remediation. The time for complete dissolution of such fluids into the groundwater is extremely long due to low aqueous solubilities of these organics (typically on the order of hundreds of parts per million). Therefore, small volumes of a contaminant have the potential to pollute large quantities of flowing groundwater. Furthermore, drinking water quality standards for many organic contaminants require concentrations of less than 5-10 parts per billion, substantially less than the aqueous solubilities of many organic compounds.

As an organic contaminant is introduced into the subsurface, it will migrate downward under the influence of gravity. As a NAPL (Non-Aqueous Phase Liquid) moves through the unsaturated zone, a portion of the contaminant will be retained within the pores by capillary forces. This immobile NAPL is referred to as residual saturation. The extent of residual saturation left behind is a function of the pore distribution of the media, and the surface tension of the NAPL. If the volume of the contaminant spill is sufficiently large, the NAPL will eventually reach the water table. A low density (less than water) solute (Figure 1 - 1) will tend to spread laterally above the table creating a "pool" or "lens" of NAPL. Variations in the groundwater level, due to seasonal recharge, can carry a NAPL deeper into the aquifer, creating a zone of residual saturation within the saturated

zone. Wilson et al. (1986) report that the saturated zone has the potential to retain more hydrocarbons than the unsaturated zone due to the lesser magnitude of gravitational forces in the saturated zone.

As a DNAPL (Dense Non-Aqueous Phase Liquid), shown in schematic form by Figure 1-2, reaches the water table, it will continue to migrate downward into the saturated zone, leaving a region of residual saturation behind. Assuming that the spill is sufficiently large, the DNAPL will eventually be retarded by a region of low hydraulic conductivity. Here, the DNAPL can accumulate and form a pool, displacing the normal flow of groundwater. In both the case of low and high density contaminants, the residual saturation and the NAPL pool created will serve as a source of contamination.

Once the contaminant is introduced into the subsurface, a multiphase system exists that consists of an aqueous phase, a solid phase, a vapor phase, and a non-aqueous phase. Within this multiphase system, a complex series of interphase mass transfer processes occurs and with time the contaminant will exist in all phases.

In the unsaturated zone, the solute can transfer from the non-aqueous phase, present as residual saturation, to the vapor phase, to the solid phase or to the aqueous phase. Once present in the vapor phase, contaminant transport may occur by molecular diffusion, advection, and dispersion. The solute can also be transported to the groundwater via interphase mass transfer from the non-aqueous phase or solid phase to percolating water, which can originate from natural recharge or infiltration. Sorption of the solute to the porous media will retard the transport of contaminant as the solute is released back into the system at a relatively slow rate.

In the saturated zone, the solute can undergo interphase mass transfer from the non-aqueous phase, present as residual saturation and/or as a pool of NAPL, to the flowing groundwater. Once dissolved in the groundwater, the contaminant is transported through the aquifer by advection and hydrodynamic dispersion. As in the unsaturated zone, sorption in this region can also serve to retard contaminant transport.

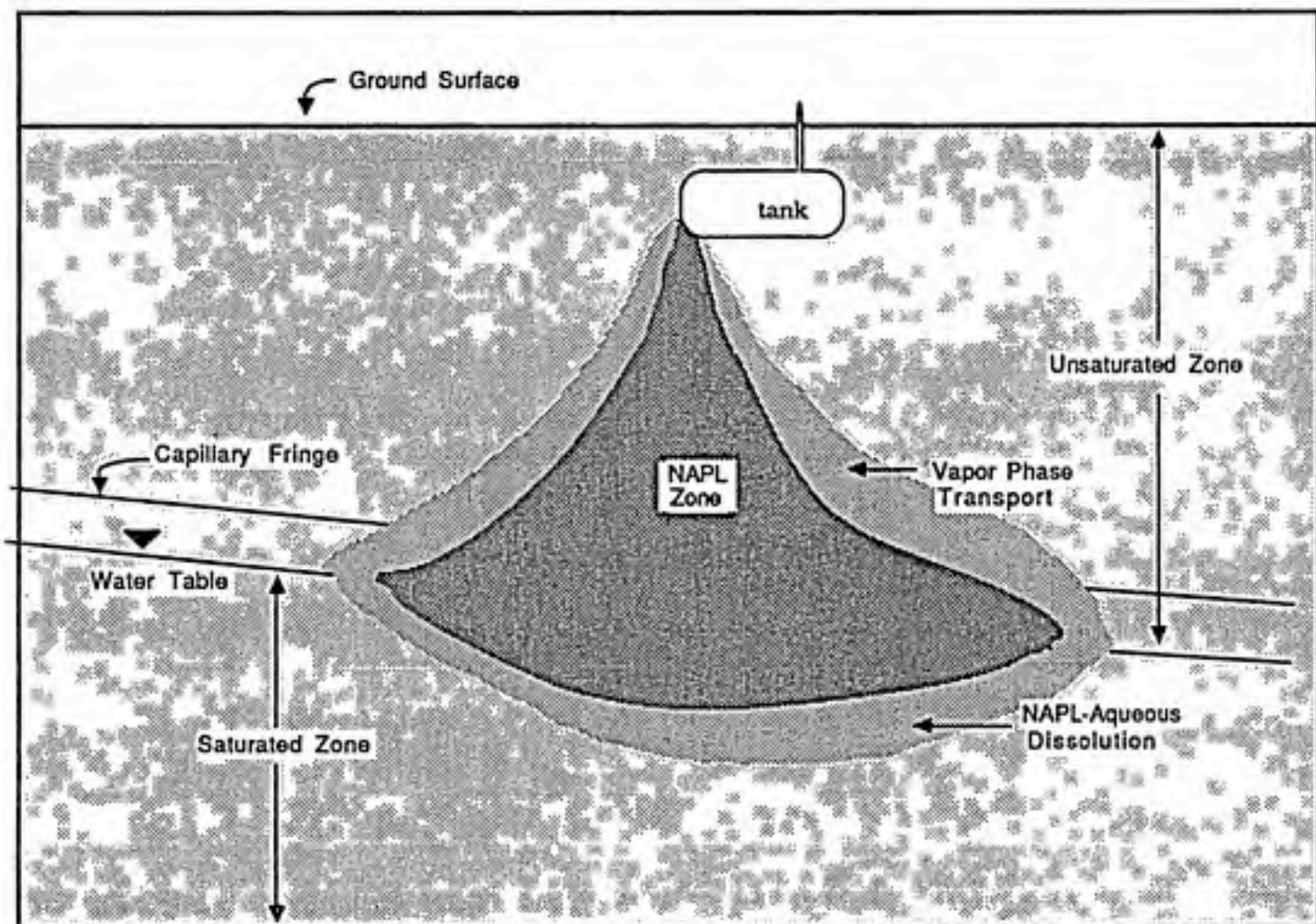


Figure 1-1. NAPL Subsurface Migration

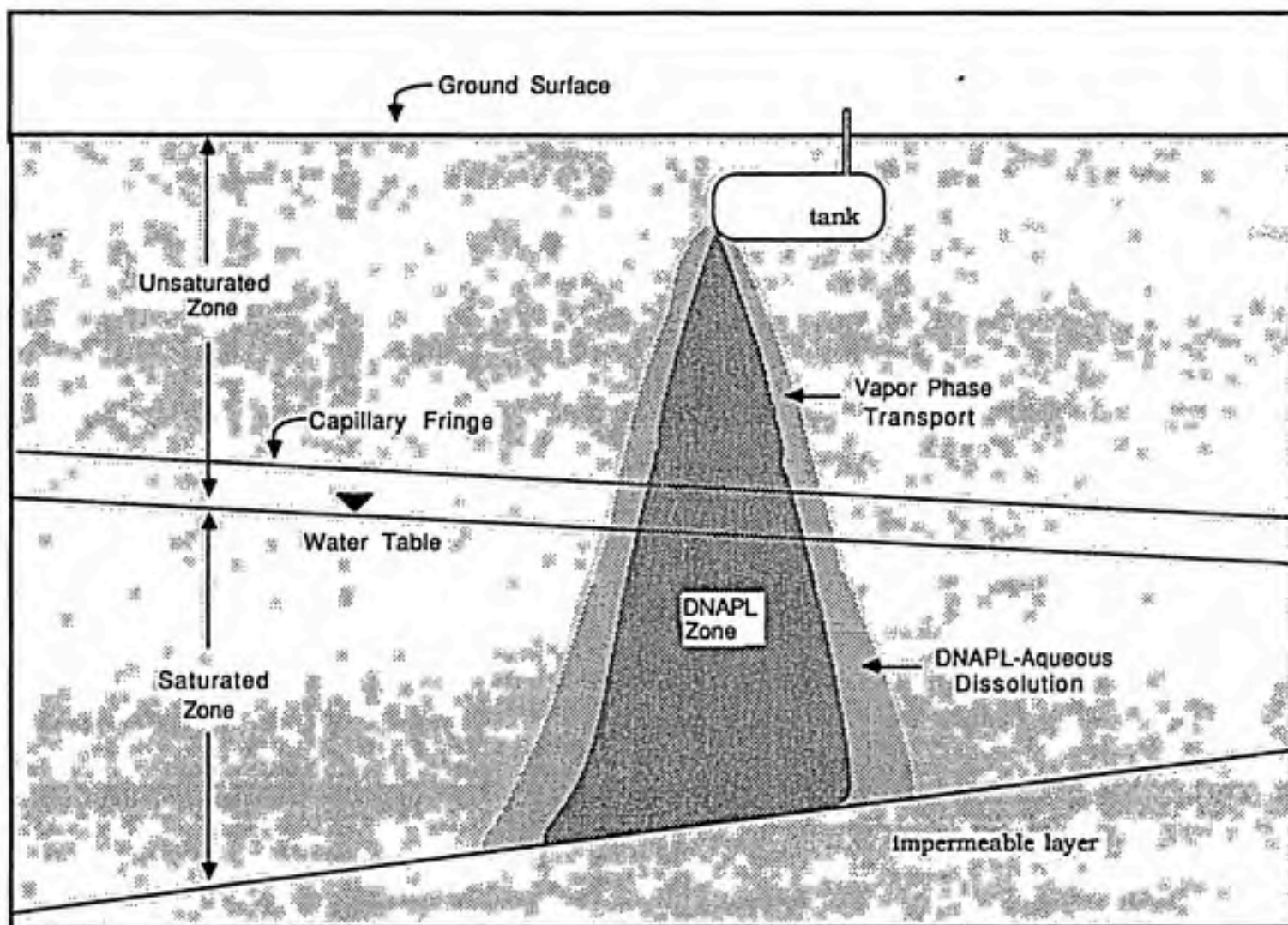


Figure 1-2. DNAPL Subsurface Migration

Mathematical models have been developed that describe multiphase flow and transport of organic chemical contaminants in the subsurface (Abriola, 1988). These models are an important tool for predicting the movement of contaminants in the subsurface as well as for assessing aquifer remediation efforts. An important assumption in many of the published multiphase models is that of local equilibrium between fluid phases (Abriola et al., 1985; Corapcioglu et al., 1987). The local equilibrium assumption implies that equilibrium exists between phases at all locations and at all times. While the assumption of local equilibrium is commonly made in multiphase modeling, there is little experimental or field data to suggest that this assumption is valid (Pfannkuch, 1984; Abriola, 1988). Furthermore, while chemical engineering literature describes numerous mass transfer processes, there has been little focus on mass transfer in porous media.

1.2 Research Objectives

This study focuses on interphase mass transfer between the aqueous phase and the non-aqueous phase in a saturated, multiphase porous media. The objective of this work is to gain a qualitative and quantitative understanding of the fundamental nature of the interphase mass transfer process through laboratory investigations. More specifically, the study is aimed at determining if and under what conditions the assumption of interphase local equilibrium is valid. The experiments focus on the relationship between mass transfer and four specific system parameters: velocity, media size, fluid saturation, and solvent characteristics. The findings of this study will lead to better understanding and more accurate modeling of contaminant transport in the subsurface.

2 Background

2.1 Multiphase Flow Equations

Many subsurface contaminant problems result in multiphase systems. Mathematical descriptions of multiphase systems have been developed in the literature and aid in the understanding of contaminant transport and fate in such systems.

The equations governing multiphase flow can be developed from mass and momentum balance equations. The mass balance equation for a given species, i , in a single phase, α , can be used as a starting point upon which to develop multiphase flow equations (Abriola, 1988). The equation is given as

$$\frac{\partial}{\partial t} (\epsilon_{\alpha} \rho^{\alpha} \omega_i^{\alpha}) + \nabla \cdot (\epsilon_{\alpha} \rho^{\alpha} \omega_i^{\alpha} \mathbf{v}^{\alpha}) + \nabla \cdot \mathbf{J}_i^{\alpha} = Q_i^{\alpha} + R_i^{\alpha} \quad (2-1)$$

where $\mathbf{v}^{\alpha}$ is the mass average velocity of the α phase, ω_i^{α} is the mass fraction of species i in the α phase, ϵ_{α} is the fraction of volume occupied by the α phase, ρ^{α} is the mass density of the α phase, $\mathbf{J}_i^{\alpha}$ is the non-advective flux of species i in the α phase, Q_i^{α} is the mass transfer of species i due to interphase diffusion or phase change, and R_i^{α} is an external source term.

The first term of 2-1 accounts for the accumulation of species i in the α phase. The second term accounts for the movement of species i due to advection of the α phase. The third term represents the movement of species i due to non-advective effects such as mechanical dispersion and molecular diffusion. The first term on the right hand side of the equation takes into account interphase mass transfer and the second term accounts for a change in mass due to chemical reaction and/or biological transformation. Based on 2-1 a mathematical description can be derived for fluid flow or contaminant transport for any

multicomponent, multiphase system.

Figure 2-1 depicts the classification of subsurface water. The subsurface can generally be divided into two areas: the vadose zone and the saturated zone. In the vadose zone, water tends to move downward under the influence of gravity. However, a significant volume of water is retained in the interstitial pores of the solid media due to molecular attraction and capillary forces. The vadose zone is also referred to as the unsaturated zone since the void spaces in the porous media are only partially water-saturated, although the capillary region of the vadose zone, directly above the water table, can be completely saturated. The saturated zone is the region below the water table in which the pore spaces of the soil are completely water-saturated.

Consider the cross-section of a porous media shown in Figure 2-2. This is a typical characterization of a contaminated groundwater site. Four phases are shown: a porous media phase (s), an aqueous phase (a), a vapor phase (v), and a NAPL phase (n). Typically, the NAPL phase is a multicomponent contaminant. In order to describe the interphase mass transfer and transport of a contaminant component within the entire system, it is convenient to write a species mass balance for the contaminant of interest, i , for each phase α .

For a component, i , in the aqueous phase, a , the following mass balance can be written

$$\frac{\partial}{\partial t} (\rho^a \epsilon_a \omega_i^a) + \nabla \cdot (\rho^a \epsilon_a \mathbf{v}^a \omega_i^a) + \nabla \cdot \mathbf{J}_i^a = Q_i^a + R_i^a \quad (2-2)$$

Similarly, for the vapor, NAPL, and solid phases the following equations can be written

$$\frac{\partial}{\partial t} (\rho^v \epsilon_v \omega_i^v) + \nabla \cdot (\rho^v \epsilon_v \mathbf{v}^v \omega_i^v) + \nabla \cdot \mathbf{J}_i^v = Q_i^v + R_i^v \quad (2-3)$$

$$\frac{\partial}{\partial t} (\rho^n \epsilon_n \omega_i^n) + \nabla \cdot (\rho^n \epsilon_n \mathbf{v}^n \omega_i^n) + \nabla \cdot \mathbf{J}_i^n = Q_i^n + R_i^n \quad (2-4)$$

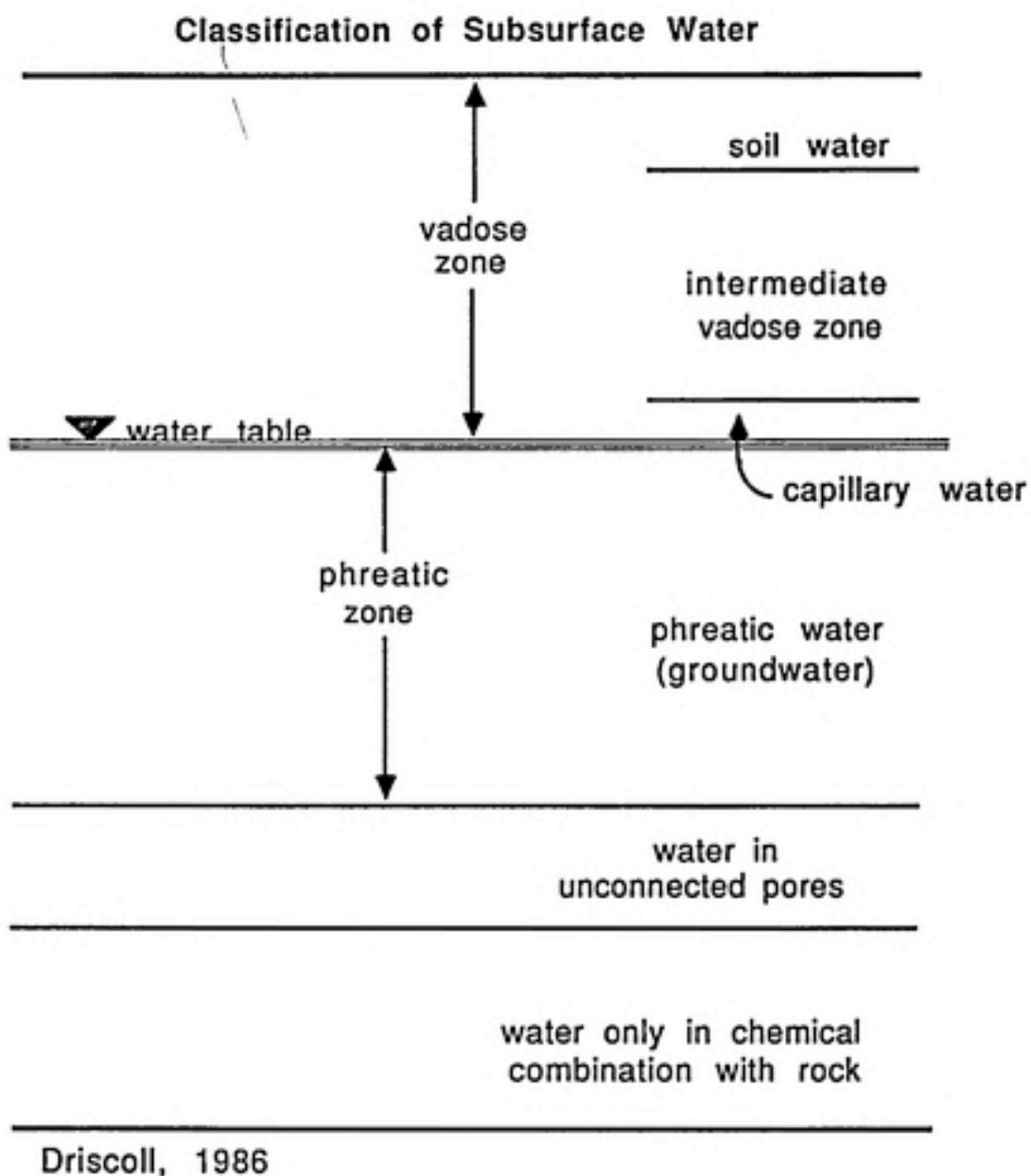


Figure 2-1. Classification of Subsurface Water

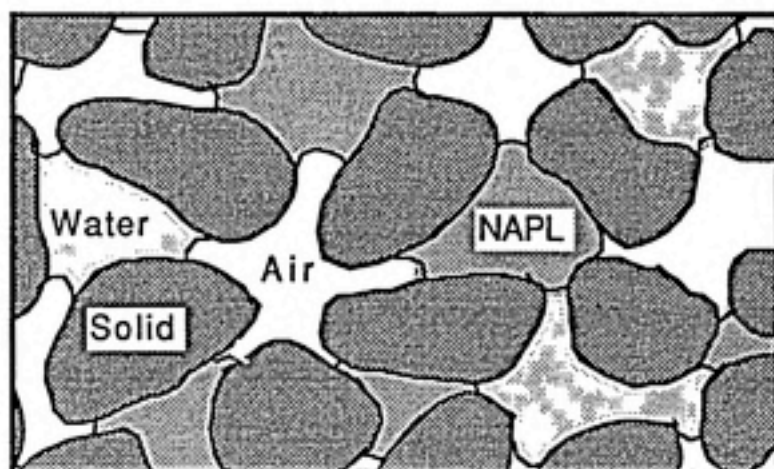


Figure 2-2. Microscopic View of Multiphase Porous Media

$$\frac{\partial}{\partial t}(\rho^s \epsilon_s \omega_i^s) + \nabla \cdot (\rho^s \epsilon_s \mathbf{v}^s \omega_i^s) + \nabla \cdot \mathbf{J}_i^s = Q_i^s + R_i^s \quad (2-5)$$

For a multicomponent system, phase mass balance equations must be written for each component. In order to describe the transport of a component i within the system, the mass balance equations for each phase must be solved simultaneously.

The general form of equations 2-2 to 2-5 can be reduced to describe multiphase flow in the phreatic or saturated zone. The vapor phase equation 2-3 can be completely eliminated since the vapor phase is not present in the saturated zone.

If the solid phase is considered to be immobile, the advective term of the solid phase equation 2-5 may be eliminated. For a system in which the sorption of the contaminant onto the solid phase is considered to be negligible, the solid phase terms for interphase mass transfer, diffusion, accumulation, and external sources are zero. Effectively, the entire solid phase equation is eliminated.

Consider the aqueous phase equation 2-2. If the contaminant i is considered to be chemically and biologically nonreactive, the last term of the aqueous phase equation is zero and the equation can be simplified to

$$\frac{\partial}{\partial t}(\rho^a \epsilon_a \omega_i^a) + \nabla \cdot (\rho^a \epsilon_a \mathbf{v}^a \omega_i^a) + \nabla \cdot \mathbf{J}_i^a = Q_i^a \quad (2-6)$$

The first term of 2-6 accounts for the accumulation of component i in the aqueous phase. The second and third terms account for the advective and dispersive movement of i in the aqueous phase, respectively. The term on the right side of the equation accounts for interphase mass transfer of i to the aqueous phase.

Consider the NAPL phase equation 2-4. If the NAPL phase is assumed to be a pure phase of component i , the diffusion term is zero. If the NAPL phase is considered to be at residual saturation, the phase is immobile and the advective term of the NAPL phase can be eliminated. Furthermore, if the contaminant i is chemically and biologically nonreactive

and in the absence of external sources R_i^n is zero. For a single component NAPL phase, $\omega_i = 1$. Incorporating all of these assumptions, the general form of the multiphase equation for the NAPL phase reduces to

$$\frac{\partial}{\partial t}(\rho^n \epsilon_n) = Q_i^n \quad (2-7)$$

Equation 2-7 states that the change in mass of the NAPL phase is due solely to interphase mass transport.

Thus far, the multiphase system has been simplified to an aqueous and a NAPL equation, 2-6 and 2-7. Neglecting all other sources of i , Q_i^n represents mass gained or lost to interphase transfer. It is evident that interphase mass transfer in this system occurs solely between the aqueous and NAPL phases. From the concept of conservation of mass, the mass of contaminant i transferred to the aqueous phase must equal to the mass of i transferred from the NAPL phase. Mathematically this can be expressed as

$$Q_i^a = -Q_i^n \quad (2-8)$$

A constitutive expression to describe this interphase mass transfer term is required. In order to develop a description of mass transfer processes, it is often necessary to make fundamental assumptions about the mechanisms of mass transfer and about the hydrodynamic conditions near the phase interface. Multiphase mass transfer models generally assume that the resistance to mass transfer is confined largely to a thin region adjacent to the phase interface (Sherwood et al., 1975). Resistance is defined as the ratio of the gradient of the potential to mass flux. The potential gradient serves as the driving force for mass transfer and is most often expressed as a concentration gradient. Concentration is considered to be a reasonable measure of potential since the mass flux approaches zero as the phase concentrations equalize and concentration is usually a known system parameter (Sherwood et al., 1975).

These models frequently employ a mass transfer coefficient that is defined as the ratio of mass flux to potential or one over a resistance. It follows that the rate of mass transfer is directly proportional to the mass transfer coefficient. This resistance type conceptual interphase mass transfer model is frequently cited in the literature and can be mathematically described as (Sherwood, 1975; Hunt, 1988b)

$$J_i = K_L (\Delta C_i) \quad (2-9)$$

where J_i is the mass flux ($M/L^2 \cdot T$) of species i across the phase boundary in the direction of the concentration gradient, K_L is the mass transfer coefficient with units of length per time, and ΔC_i is the difference in concentration across the phase interphase.

In order to incorporate 2-9 into the multiphase equations, it is necessary to express ΔC_i in terms of each single phase. This can be accomplished by incorporating stagnant film theory. Film theory assumes that there is no resistance to mass transfer at the phase interface. Based on boundary layer theory, the velocity of each phase is assumed to be zero at the phase interface. Therefore, it is assumed that equilibrium exists at the phase boundary and that the concentration at this location is equal to the aqueous solubility of the NAPL. Based on this assumption, equation 2-9 can be written to describe interphase mass transfer of species i to the aqueous phase

$$J_i^a = K_L (C_i^{a*} - C_i^a) \quad (2-10)$$

where C_i^{a*} is the aqueous solubility of species i , C_i^a is the concentration of i in the aqueous phase. It is evident from the definition of the concentration of species i in the α phase that $C_i^a = \rho^a \omega_i^a$. Substituting this expression into 2-10 yields

$$J_i^a = K_L (\rho^a \omega_i^{a*} - \rho^a \omega_i^a) \quad (2-11)$$

where ω_i^{a*} is the equilibrium mass fraction of species i in the a phase.

In order to preserve dimensional consistency, equation 2-11 must be multiplied by the volume fraction of the appropriate phase and the specific surface area, a . Specific surface area is defined as the interfacial surface area over the total volume of the phase and has units of inverse length. Substituting this interphase mass transfer expression into the multiphase aqueous equation 2-6 as a source term yields

$$\frac{\partial}{\partial t}(\rho^a \epsilon_a \omega_i^a) + \nabla \cdot (\rho^a \epsilon_a \mathbf{v}^a \omega_i^a) + \nabla \cdot \mathbf{J}_i^a = K_L a \epsilon_a (\rho^a \omega_i^{a*} - \rho^a \omega_i^a) \quad (2-12)$$

The sign convention used implies that mass is transferred from the NAPL phase to the aqueous phase.

Based on the conservation of mass, the mass of i gained by the aqueous phase must equal the mass of i lost by the NAPL phase. Mathematically this can be expressed by incorporating 2-11 into the multiphase NAPL equation 2-8 to give

$$\frac{\partial}{\partial t}(\rho^n \epsilon_n) = -K_L a \epsilon_a (\rho^a \omega_i^{a*} - \rho^a \omega_i^a) \quad (2-13)$$

The aqueous solubility of i can be expressed in terms of the NAPL phase by the use of a partition coefficient H where

$$H = \frac{\rho^a \omega_i^{a*}}{\rho^n \omega_i^n} \quad (2-14)$$

Substituting 2-14 into 2-13 yields

$$\frac{\partial}{\partial t}(\rho^n \epsilon_n) = -K_L a \epsilon_a (H \rho^n \omega_i^n - \rho^a \omega_i^a) \quad (2-15)$$

For a pure phase NAPL, $\omega_i^n = 1$. Therefore

$$\frac{\partial}{\partial t}(\rho^n \epsilon_n) = -K_L a \epsilon_n (H \rho^n - \rho^a \omega_i^a) \quad (2-16)$$

Equations 2-12 and 2-16 can be solved simultaneously to describe the transport of contaminant i in the system.

In order to solve these equations, an expression for the mass average velocity of the aqueous phase must be obtained. Darcy's law provides an expression for velocity and has been used extensively in the literature to model multiphase flow (Abriola, 1985). Darcy's law for a single fluid phase is given as (Bear, 1979)

$$\mathbf{v}^a = -K \text{grad} \left(\frac{P^a}{\rho^a g} + z \right) \quad (2-17)$$

where $\mathbf{v}^a$ is the fluid phase velocity, K is the hydraulic conductivity tensor, P^a is the fluid phase thermodynamic pressure, g is the acceleration due to gravity, and z is the elevation head. Based on empirical data, it has been determined that K can be expressed as (Bear, 1979)

$$K = \frac{k_a \rho^a g}{\mu_a} \quad (2-18)$$

where k_a is the intrinsic permeability, μ_a is the fluid dynamic viscosity.

For a multiphase fluid system the application of Darcy's Law becomes more complex. Based on experimental data, a modified Darcy's Law has been developed which incorporates a relative permeability function, k_{ra}

$$\mathbf{v}^a = -\frac{k k_{ra} \rho^a g}{\mu_a} \text{grad} \left(\frac{P^a}{\rho^a g} + z \right) \quad (2-19)$$

where

$$k_{r\alpha} = \frac{k_{\alpha}}{k}$$

The relative permeability of a fluid is a function of the fluid saturation which in-turn is a function of the fluid pressure and the saturation history of the system. The larger the portion of porous media occupied by the fluid, the greater the relative permeability. It should be noted that the intrinsic permeability, k , is usually assumed to be solely a function of the solid matrix and independent of fluid properties.

Substituting the mass average velocity expression into the aqueous phase equation 2-12, the following is obtained

$$\frac{\partial}{\partial t} (\rho^a \epsilon_a \omega_i^a) - \nabla \cdot \left[\rho^a \epsilon_a \omega_i^a \frac{k k_{ra}}{\mu_a} \text{grad} (P^a + \rho^a g z) \right] + \nabla \cdot \mathbf{J}_i^a = K_L a \epsilon_a (H \rho^n - \rho^a \omega_i^a) \quad (2-20)$$

The $\mathbf{J}_i^a$ term is the non-advective flux of species i in the aqueous phase. This term accounts for the motion of species i due to molecular diffusion and mechanical dispersion and is usually characterized by Fick's First Law (Abriola, 1988)

$$\mathbf{J} = -\rho^a \epsilon_a \mathbf{D}^a \cdot \nabla \omega_i^a \quad (2-21)$$

where $\mathbf{D}^a$ is a second rank dispersion tensor and is defined as

$$\mathbf{D}^a = \mathbf{D}_m^a + \mathbf{D}_d^{a*} \quad (2-22)$$

where $\mathbf{D}_m^a$ is a mechanical dispersion tensor and $\mathbf{D}_d^{a*}$ is the effective molecular diffusion tensor for species i in the α phase. The dispersion tensor accounts for hydrodynamic dispersion in the system or movement of the solute due to effects other than advection. Hydrodynamic dispersion is due to two phenomena: mechanical dispersion, and molecular diffusion.

Mechanical dispersion can be viewed as a microscopic process caused by three mechanisms: differential drag exerted on the fluid by the pore surfaces, differential molecular velocities due to differences in pore sizes along the flow path, and dispersion due to tortuosity and branching effects (Freeze and Cherry, 1979). A general form of the mechanical dispersion tensor can be written as

$$D_{ij} = \alpha_T \bar{v}^\alpha \delta_{ij} + (\alpha_L - \alpha_T) \frac{\bar{v}_i^\alpha}{\bar{v}_j^\alpha} \bar{v}^\alpha + D_d^{\alpha*} \quad (2-23)$$

where D_{ij} is the ij term of the dispersion tensor, $\bar{v}$ is the average magnitude of the α phase velocity, α_L is the longitudinal dispersivity, α_T is the transverse dispersivity, and δ_{ij} is the Kronecker delta function ($\delta_{ij} = 1$ for $i = j$ and $\delta_{ij} = 0$ for $i \neq j$).

Incorporating Fick's Law into 2-20 gives

$$\frac{\partial}{\partial t} (\rho^a \epsilon_a \omega_i^a) - \nabla \cdot \left[\rho^a \epsilon_a \omega_i^a \frac{k k_{ra}}{\mu_a} \text{grad} (P^a + \rho^a g z) \right] - \nabla \cdot (\rho^a \epsilon_a D^a \cdot \nabla \omega_i^a) = K_L a \epsilon_a (H \rho^n - \rho^a \omega_i^a) \quad (2-24)$$

The saturation of a phase α , S_α , is defined as the volume fraction of the phase α to the media void space. Thus, by definition $\epsilon_\alpha = S_\alpha n$. Substituting this relationship and $C_i^a = \rho^a \omega_i^a$ into the multiphase equations 2-15 and 2-24 yields

$$\frac{\partial}{\partial t} (S_a n C_i^a) - \nabla \cdot \left[C_i^a S_a n \frac{k k_{ra}}{\mu_a} \text{grad} (P^a + \rho^a g z) \right] - \nabla \cdot (S_a n D^a \cdot \nabla C_i^a) = K_L a S_a n (C_i^{a*} - C_i^a) \quad (2-25)$$

$$\frac{\partial}{\partial t} (n S_n \rho^n) = -K_L a S_a n (H \rho^n - C_i^a) \quad (2-26)$$

Assuming that ρ^a and n are constant with time leads to

$$\frac{\partial}{\partial t}(S_a C_i^a) - \nabla \cdot \left[C_i^a S_a \frac{k k_{ra}}{\mu_a} \text{grad} (P^a + \rho^a g z) \right] - \nabla \cdot (S_a D^a \nabla C_i^a) = K_L a S_a (C_i^{a*} - C_i^a) \quad (2-27)$$

$$\rho^n \frac{\partial S_n}{\partial t} = -K_L a S_a (H \rho^n - C_i^a) \quad (2-28)$$

Simplifying 2-27 to one-dimensional flow in the x direction yields

$$\frac{\partial}{\partial t}(S_a C_i^a) - \frac{\partial}{\partial x} \left[S_a C_i^a \frac{k_x k_{ra}}{\mu_a} \frac{\partial}{\partial x} (P^a + \rho^a g z) \right] - \frac{\partial}{\partial x} \left(S_a D_x^a \frac{\partial C_i^a}{\partial x} \right) = K_L a S_a (C_i^{a*} - C_i^a) \quad (2-29)$$

The aqueous phase fluid properties are assumed to remain constant despite the transfer of contaminant i into the aqueous phase. Equation 2-29 is referred to as the advective-dispersive-reactive equation and can be solved simultaneously with the NAPL phase equation 2-28 to describe the transport of species i in the system.

Simplifying the aqueous velocity term in 2-29, assuming a uniform NAPL saturation along x , and dropping the phase superscript a and the species subscript i yields

$$\frac{\partial}{\partial t}(S_a C) = -v_x S_a \frac{\partial C}{\partial x} + D_x S_a \frac{\partial^2 C}{\partial x^2} + K S_a (C^* - C) \quad (2-30)$$

Note that $K = K_L a$ where K is a mass transfer coefficient with units of inverse time. Assuming that the aqueous and NAPL saturations are constant with time yields

$$\frac{\partial C}{\partial t} = -v_x \frac{\partial C}{\partial x} + D_x \frac{\partial^2 C}{\partial x^2} + K (C^* - C) \quad (2-31)$$

Note that the NAPL phase equation 2-28 goes to zero with this assumption. The steady-state analytical solution to 2-31 can be derived using Laplace transformation methods and is given as

$$C(x) = C^* \left[1 - \exp \left(\frac{x \left(v_x - (v_x^2 + 4KD_x)^{0.5} \right)}{2D_x} \right) \right] \quad (2-32)$$

Rearranging to solve for the mass transfer coefficient K yields

$$K = \frac{\left[v_x - \frac{2D_x}{x} \ln \left(1 - \frac{C(x)}{C^*} \right) \right]^2 - v_x^2}{4D_x} \quad (2-33)$$

2.2 Mass Transfer Processes

Introduction

Mass transfer phenomena in multiphase systems are difficult to describe. Conditions near the phase interface are often unknown and are difficult to observe experimentally (Sherwood et al., 1975). It is therefore convenient to develop mathematical models of the mass transfer process. These models aid in the conceptual understanding of the process and can generate quantitative information about the system. The degree to which the model describes the physical system is an indication of the appropriateness of the model.

Mass Transfers Models

The complexity of multiphase mass transfer processes is compounded in the subsurface by the physical media. Flow through porous media involves complicated geometries and the hydrodynamics of the system is complex and difficult to characterize. A logical approach to describing mass transfer in porous media, therefore, is to begin by characterizing mass transfer in simpler, well-defined systems.

Most of the experimental and theoretical development of interphase mass transfer processes has been made in the field of chemical engineering. Although many of the

models have been directed toward gas-liquid and solid-liquid systems, much of the theory can be applied to liquid-liquid systems (Pfannkuch, 1984a).

Film Theory

Stagnant film theory was first proposed by Nernst in 1904 (Sherwood et al., 1975). This theory assumes that there is a single resistance to mass transfer at the phase boundary. Resistance is modeled as a stagnant film layer that is adjacent to the phase interface. This simplified conceptual model is derived from fluid mechanics in that as a fluid flows over a phase boundary, the velocity at the boundary approaches zero. Due to the absence of advective flow, the dominant mechanism for mass transport within the film is molecular diffusion.

Consider the mass transport of fluid *A* into fluid *B* (Figure 2-3a). The flux of mass through the film can be described using Fick's Law of diffusion

$$J_a = D_{ab} \frac{(C_a^* - C_a)}{\delta} \quad (2-34)$$

where J_a is the flux of mass *A* into fluid *B*, D_{ab} is the molecular diffusion of a dilute solution of fluid *A* in fluid *B*, C_a^* is the solubility of *A* in *B*, C_a is the concentration of *A* in the bulk fluid *B*, and δ is the film thickness. An important condition is this model is that the two phases are assumed to be at equilibrium at the interphase. Equation 2-34 can be written as

$$J_a = K_L (C_a^* - C_a) \quad (2-35)$$

where

$$K_L = \frac{D_{ab}}{\delta} \quad (2-36)$$

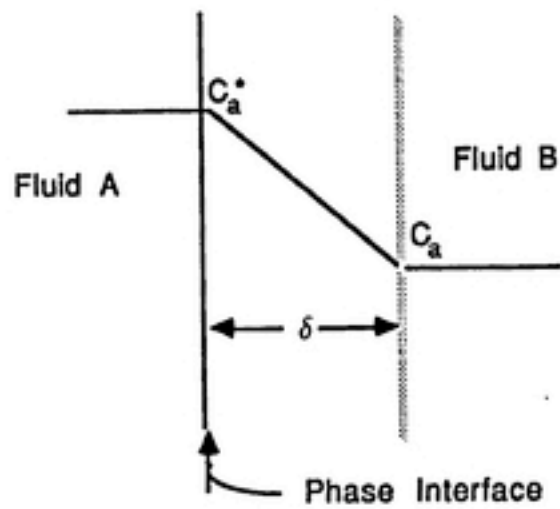


Figure 2-3a. Stagnant Film Theory

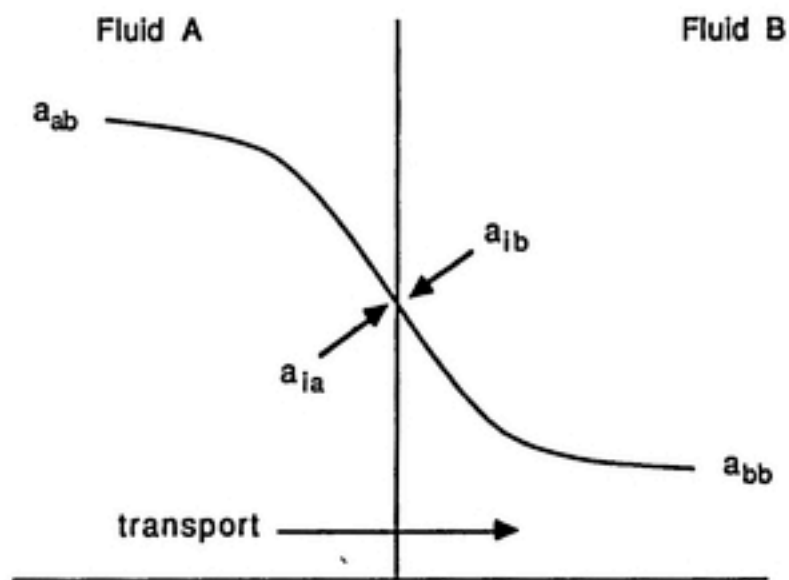


Figure 2-32b. Activity Gradients Near a Phase Boundary

K_L is the mass transfer coefficient for the system and is defined as the ratio of mass flux to the potential difference or driving force and has units of length per time.

It is evident that the mass transfer coefficient and hence the rate of mass transfer is inversely related to the film thickness, δ , and is directly related to the molecular diffusion, D_{ab} . Although the film thickness is employed in the model, it is difficult to obtain such a measurement in most systems. Film thickness, however, is a function of the flow conditions and can be characterized by the Reynolds Number, Re

$$Re = \frac{v_x l}{\nu}$$

where v_x is velocity, l is the characteristic length of the system, and ν is the fluid kinematic viscosity. At a high velocity or a high Reynolds number, fluid boundary layer profiles become flatter, creating a thinner film thickness thus increasing the mass transfer coefficient. It follows from this model that the rate of mass transfer is a function of velocity, characteristic length and fluid viscosity.

An extension to the stagnant film model is the two-film theory model. This model assumes that there are two resistances to mass transfer in the form of two stagnant films, one on either side of the phase boundary. The solute must first diffuse through its own fluid film to the interface and must then diffuse through the solvent film to the bulk fluid. Therefore, this theory is only meaningful for a multicomponent system. The model assumes that the resistance to mass transfer at the interface of the two films is negligible or that the phases are at equilibrium at the interface between the two films. The resistances are modeled in series and the overall resistance to mass transfer is simply the sum of the individual resistances in series.

Sherwood et al. (1975) describes two-film theory in its simplest form. Figure 2 - 3b illustrates the case where a solute is being transferred at a constant rate from the bulk fluid A to the bulk fluid B, each being well mixed. Assuming equilibrium at the interface,

the activity of each fluid at this point is equal.

From conservation of mass, the steady-state flux can be given as

$$J_a = K_a (a_{ab} - a_{ai}) = K_b (a_{bi} - a_{bb}) = K_L (a_{ab} - a_{bb}) \quad (2-37)$$

where a_{ab} and a_{bb} are the activities of the solute in the bulk fluid A and B, respectively. a_{ai} and a_{bi} are the activities of the solute within each respective fluid at the phase interface. The overall resistance to mass transfer is modeled as two resistances in series so that

$$\frac{1}{K_L} = \frac{1}{K_a} + \frac{1}{K_b}$$

This leads to an overall mass transfer coefficient for the system of

$$K_L = \frac{K_a K_b}{K_a + K_b} \quad (2-38)$$

An alternative and more rigorous approach to mass transfer is to consider the effects of advective fluid motion along the boundary interface. Solving this type of problem analytically, involves defining the boundary layer profile near the interface. This type of analysis has been done for fluid-solid and fluid-fluid systems that contain relatively simple velocity profiles, such as mass transfer from a single sphere (Bowman, 1961). However, as Pfannkuch (1984a) points out, analytical solutions for more complex liquid-liquid interfaces become difficult to develop due to complex velocity profiles at the interface.

Mass Transfer from a Single Sphere

Bowman et al. (1961) developed a theoretical description of mass transfer from a fluid or solid sphere at low Reynolds numbers. Bowman derived an analytical solution by solving the streamline function around a sphere in order to characterize the local velocity profile and concentration boundary layer (Pfannkuch, 1984a). The analytical solution

applies specifically to steady-state diffusion from a single sphere to a continuous, laminar flow. Through dimensional analysis using the Sherwood number (Sh) and Peclet number (Pe), Bowman develops an empirical description of mass transfer as a function of velocity.

The Sherwood number is a dimensionless form of mass transfer and is defined as

$$Sh = \frac{K_L l}{D_a^*}$$

The Peclet number is the ratio of advective mass transport to diffusive mass transport and is defined as

$$Pe = \frac{vl}{D_a^*}$$

where l is the characteristic length of the system, D_a^* is the effective molecular diffusivity, and v is the fluid velocity.

The results for solid and noncirculating fluid spheres indicate that mass transfer is independent of velocity for Peclet numbers less than 1. However, for Peclet numbers greater than 10, mass transfer varies with velocity and Peclet number to the one third power. Mathematically, this can be described as

$$\begin{aligned} Sh &= 2 & Pe < 1 \\ Sh &= 0.978 Pe^{0.33} & Pe > 10 \end{aligned}$$

This model has direct application to many two-phase contacting processes. Bowman develops a similar description of mass transfer for the case of circulating fluid spheres.

Other mass transfer correlations based on theoretical and experimental work have been developed for a variety of systems that are somewhat similar to NAPL-aqueous dissolution in porous media. These correlations are summarized in Table 2 - 1. The correlations are valid for different ranges of Re . it should be noted that varying amounts of scatter

have been reported in the experimental data. The correlations predict that the Sherwood number varies with the power of the Reynolds number in the range of 0.21 to 1.5.

Mass Transfer in Porous Media

Film theory and Bowman's analytical solution for mass transfer from a single sphere are derived for relatively simple systems. Based upon these theoretical analyses, mass transfer is generally dependent on fluid properties, interfacial areas, and flow hydrodynamics. Multiphase mass transfer in a porous media is much more complex. Heterogeneity in pore size will cause local velocity fluctuations, making the hydrodynamics of the system difficult to characterize. The shape and extent of the interfacial contact area is a function of the distribution of residual saturation, which is in-turn a function of porous media and fluid properties. Smaller pore spaces will contain smaller blobs of NAPL; thus the interfacial area in finer medias is higher for the same saturation. Interfacial surface area will increase with increasing NAPL saturation to a maximum level and will then decrease with increasing NAPL saturation until the interphase area is zero at 100 percent NAPL saturation (Pfannkuch 1984a). While it is possible to develop analytical models for relatively simple systems, it is difficult to accurately determine the geometric and process parameters, and mass transfer mechanisms in a porous media. A common approach to modeling complex systems, however, is to begin with and expand upon simplified models.

The general form of the mass transfer model described by equation 2 - 9 is

$$J_i = K(C_i^* - C_i)$$

All of the characteristics that affect the mass transfer process other than the concentration difference are lumped together in the mass transfer coefficient, K . In order to apply this model to a specific physical system, such as a porous media, one must determine which system parameters affect mass transfer. A mathematical or functional relationship between

Table 2-1 Mass Transfer Correlation Equations

Reference	Experimental System	Equation	valid range
Bowman et al. (1966)	Theoretical, flow around a single sphere	$Sh = 0.98 Re^{0.33} Sc^{0.33}$ $Sh = 2 + 9/16 Re Sc$	$Pe > 10$ $Pe < 1$ $+ 9/64 Re^2 Sc^2 + \dots$
Dwivedi et al. (1977)	Fixed and Fluidized beds; various fluid-solid systems (literature review)	$Sh = 1.1068 n^{-1} Re^{0.18} Sc^{0.33}$ $Sh = 0.4548 Re^{0.59} Sc^{0.33}$ $Sh = e^{-1} Sc^{0.33} (0.765 Re^{0.18} + 0.365 Re^{0.61})$	$Re < 10$ $Re > 10$ $0.01 < Re < 15000$
Kumar et al. (1977)	water, 60% propylene glycol-water, Benzoic acid pellets	$Sh = 1.12994 Re^{0.21} Sc^{0.33}$ $Sh = 0.5643 n^{-1} Re^{0.32} Sc^{0.42}$ $Sh = 4.2258 Re^{0.21} Sc^{0.33}$	$Re < 10$ $Re < 10$ $Re < 20$
Ohashi et al. (1985) from Roberts et al. (1985)	Various organic activated carbon	$Sh = 2 + 1.58 Re^{0.4} Sc^{0.33}$	$10^{-3} < Re < 5.8$
Pfannkuch (1984b) from Hoffman (1971)	light fuel oil soil	$Sh = 0.55 + 0.25 Pe^{0.67}$	$0.6 < Pe < 50$
Williamson et al. (1963)	Dissolution of benzoic acid spheres by water	$Sh = 2.4 e Re^{0.34} Sc^{0.42}$	$0.08 < Re < 125$ $150 < Sc < 1300$
Wilson & Geankoplis (1966)	Water and 60% propylene glycol-water benzoic acid	$Sh = 2.5 Re^{0.33} Sc^{0.33}$ $Sh = 1.09 e^{-1} Re^{0.33} Sc^{0.33}$	$0.0016 < Re < 55$ $0.0016 < e Re < 55$ $0.35 < e < 0.75$

the system parameters and mass transfer must also be known. Intuitively, multiphase mass transfer in a porous media is a function of the hydrodynamics of the system, the contaminant solubility, the interfacial contact area, and the extent of residual saturation (Pfannkuch, 1984a). The problem of characterizing the mass transfer process becomes one of determining the functional relationships between the mass transfer coefficient and these system parameters.

Dimensional Analysis

Dimensional analysis is a commonly used methodology for determining the functional relationships of a system (White, 1979). This approach involves forming dimensionless groups out of the parameters that affect the process and thereby reducing the number and complexity of experimental variables that affect the physical phenomena. Through the use of experimental data and dimensional analysis, empirical relationships can be developed to describe the mass transfer process. The use of dimensionless numbers also creates a means by which data from a wide variety of sources can be compared. Models, based on empirical methods, can be used to describe systems that may be too complex to describe analytically.

In the field of mass transfer and fluid mechanics, several dimensionless groups have been developed and are frequently applied (White, 1979). These include Reynolds number (Re), Sherwood number (Sh), Peclet number (Pe), and the Schmidt number (Sc).

The Reynolds number is a dimensionless group for velocity and is defined as

$$Re = \frac{v_x l}{\nu} \quad (2-39)$$

A dimensionless form of mass transfer coefficient is the Sherwood number. Sh is the ratio of the overall mass transfer and the mass transfer due solely to molecular diffusion

$$Sh = \frac{K_L l}{D_d} \quad (2-40)$$

The Sherwood number as defined in equation 2-40 has been defined for a system described by

$$J = K_L a (\Delta C)$$

where J is a mass volumetric flux with units of mass/volume-time, a is the specific surface area with units of inverse length, K_L is a mass transfer coefficient with units of length per time, and ΔC is the concentration gradient. The mass transfer coefficient K used in Equation 2 - 27, was developed with the specific surface area lumped into the coefficient and therefore

$$K = K_L a$$

Specific surface area is defined as interfacial area divided by total volume of the system. Since the interfacial surface area between the NAPL and aqueous phase is unknown, a cannot be determined and must remain lumped in with the mass transfer coefficient K . If K is to be represented by the Sherwood number, the Sh must be modified by a factor of length to remain dimensionless. If it is assumed that specific surface area is related to the characteristic length of a system, l can be incorporated into Sh to give

$$Sh^* = \frac{K l^2}{D_d} \quad (2-41)$$

The Peclet Number compares the advective mass transport to the transport due to molecular diffusion alone

$$Pe = \frac{v_x l}{D_d} \quad (2-42)$$

The Peclet Number can also be expressed as the ratio of advective mass transport to dispersive mass transport. Referring to equation 2 - 20, the dispersion coefficient for one-dimensional flow in the x direction can be expressed as

$$D_x = \alpha_L v_x + D_d^*$$

The dispersive Peclet Number, Pe^* is expressed as

$$Pe^* = \frac{v_x l}{D_x} = \frac{v_x l}{\alpha_L v_x + D_d^*}$$

If the molecular diffusion is small compared to the mechanical dispersion term then

$$Pe^* = \frac{l}{\alpha_L} \quad (2-43)$$

The Schmidt number, Sc , is defined as

$$Sc = \frac{\nu}{D_d^*} \quad (2-44)$$

where v_x is the velocity, l is the characteristic length of the system, D_d^* is the effective molecular diffusivity, K_L is a mass transfer coefficient with units of length per time, and ν is the fluid kinematic viscosity.

2.3 Research Overview

Introduction

Few experimental studies have been performed that focus on NAPL-aqueous mass transfer in porous media. Those that have been reported in the literature have yielded contradictory results regarding under what conditions equilibrium between the phases can be expected (Abriola, 1988). Experimental systems have varied greatly from study to study and parameters that may be important to mass transfer generally have not been controlled. These include the extent and distribution of residual saturation, the effects of sorption onto the solid media, the effects of NAPL interaction with the vapor phase, and the influence of multicomponent dissolution on aqueous solubilities (Pfannkuch, 1984a). In light of these inconsistencies, previously collected data has been difficult to interpret with certainty. Studies that have been performed, however, provide a starting point for continued investigations into interphase mass transfer in porous media.

Experimental

Van Der Waarden et al. (1971) conducted laboratory column experiments using a glass bead media. A mixture of hydrocarbons was injected at the top of a vertical column and the NAPL was allowed to redistribute within the unsaturated porous media. Water was then trickled down through the column and concentrations of the effluent were measured. The samples collected at the column effluent were observed to be at aqueous solubility. It is difficult, however, to draw conclusions about the nature or existence of NAPL-aqueous equilibrium from this experiment. The distribution of the NAPL, and therefore the interfacial contact area, varied along the column. It is also unclear if the NAPL phase was mobile or immobile or what effect of the vapor phase had on the results.

Zilliox and Muntzer (1974) performed laboratory experiments at the Institute of Fluid

Mechanics in Strasbourg to evaluate the nature of NAPL-aqueous dissolution in porous media. The mathematical relationship used to evaluate the data was

$$M = EAt \quad (2-45)$$

where M is the mass of the NAPL dissolved in the aqueous phase, A is the area of NAPL-aqueous phase interface, t is the contact time, and E is a constant exchange coefficient.

It is apparent that the exchange coefficient is a mass flux defined as

$$J = \frac{M}{At} = E \quad (2-46)$$

where J is mass per area per unit time. Three experiments were performed that brought a NAPL into contact with the aqueous phase. The first study brought moving water in contact with oil in the absence of porous media. The contact area in this study was known. The second experiment involved moving water in a porous media with NAPL floating on top. In the third experiment, the flow of water was through a porous media previously contaminated with NAPL. Although the conditions of the experiment are vague and it is unclear how the interfacial surface areas were calculated in the porous media, there was mention of a dependence of E on the flow velocity: as the velocity increased, the exchange coefficient increased. The investigators also noted a decrease in effluent concentration and in the exchange coefficient E over a period of time, all other experimental conditions remaining fixed. It was hypothesized that the interfacial contact area changed over time.

Additional experiments were also performed at Strasbourg and were published by Fried, et al (1979). Two types of vertical column experiments were performed. In the first study, the entire 1-meter column contained NAPL residual saturation and in the second study, only the top portion of the 0.5-meter column was contaminated. The columns were flushed with water at Darcy velocities in the range of 0.2 m/d to 30 m/d and samples were

collected at the bottom of the column and were analyzed for NAPL. The contaminants consisted of a toluene-isooctane mixture. The authors reported that equilibrium concentrations were reached within a few tens of centimeters. It is not clear, however, what the extent and distribution of residual saturation was. The presence of a vapor phase and its effect on the mass transfer process was not considered.

Large scale experiments were performed by Duffey et al. (1980) which involved a 90-cm by 90-cm by 106-cm column. Crude oil was spilled on the sand media and was allowed to distribute by natural infiltration. The system was then irrigated with water and samples were collected at the bottom of the column. It was reported that concentrations of the effluent compared well with the concentrations measured under a floating crude oil film in a beaker, leading one to conclude that the effluent concentrations were at solubility. It is not clear if the NAPL phase was mobile or immobile in these experiments.

Field scale experiments were performed by Dietz (1978) that utilized large, rectangular cement 2-m by 2-m columns filled with a sandy porous media. A slab of media, contaminated with a light fuel oil, was placed directly above the groundwater level. The columns were then put in the ground and exposed to natural rainfall, which created an estimated average downward velocity of 1-meter per year in the media. Samples collected beneath the contaminated slab were reported to be close to solubility.

Most recently, Hunt et al. (1988b) conducted experiments in a 91-cm long horizontal glass column packed with an aqueous-saturated sandy porous media. NAPL was injected into the centerline of the column and allowed to disperse naturally. The column was initially flooded with water at a relatively high rate of 15 m/d to check for NAPL displacement and mass transfer limited dissolution. The flow rate was then lowered to 1.5 m/d to check for a change in effluent concentration. The NAPLs used were TCE, a toluene-benzene mixture, and gasoline. The effluent concentrations were observed to be at aqueous solubility during the water flooding period. An average value for residual saturation was calculated to be 2.5 percent, however, the distribution of the NAPL was unknown.

Hunt et al. (1988a) theoretically estimated that at low velocities, NAPL mass transfer is diffusion or mass transfer limited. Based on the experimental studies, the authors concluded that since the column effluent was at equilibrium, the system was not mass transfer limited. Although the experimental results contradict the theoretical predictions, the authors attempt to explain this inconsistency. The authors speculate that the residual saturation was not uniformly distributed throughout the column and that an artificially high interfacial area caused the apparently high effluent concentrations.

Theoretical

Pfannkuch (1984b) extended Bowman's (1961) analysis of mass transfer from a single sphere to mass transfer in porous media. Pfannkuch recasted experimental data published by Zilliox (1973) and Hoffman (1969) in dimensionless form and developed an empirical description relating mass transfer coefficient and velocity. He compares the results of the experimental data to those derived from Bowman's analytical description of flow around a single sphere. The correlation models predicted from Bowman's work are shown in Table 2-1. The results based on the experimental work of Hoffman and Zilliox can be expressed as

$$Sh = 0.55 \quad Pe < 1$$

$$Sh = bPe^a \quad Pe > 10$$

where b and a are constants. Pfannkuch admits that a for both sets of experimental data is larger than 0.33, as Bowman predicted, but notes that in a porous media, velocity dependent mass transfer may be enhanced by close juxtaposition of the tortuous flow lines and mechanical dispersion and removal of the diffusion boundary layer (Pfannkuch, 1984b). Pfannkuch also notes that for $Pe < 1$, the experimental value for Sh of 0.55 differs considerably from Bowmans predicted value of 2.

However, the experimental results predict conclusions similar to the results from the

analytical approach and Pfannkuch concludes that at Peclet numbers less than 1, mass transfer in a porous media is diffusion limited and is independent of velocity and at Peclet numbers greater than 10, mass transfer is velocity dependent.

3 Experimental Methods

3.1 Introduction

A one-dimensional column apparatus and experimental procedure was developed to study the nature of mass transfer between the aqueous phase and a non-aqueous phase liquid (NAPL) in a porous media. The experiment was performed by pumping water through a column packed with glass beads. At the beginning of the experiment, the column contained toluene at residual saturation. The experiments were repeated varying the aqueous-phase velocity, bead size, percent residual saturation, and packed bed length. These variations allowed for comparison of mass transfer coefficients using parameters such as velocity, media size, and NAPL saturation. Packed bed length variations allowed for confirmation of the experimental effectiveness and reproducibility. Efforts were made to perform each experiment using exact procedures in order to produce consistency, reproducibility, and comparability among all the experimental runs.

Fluoride tracer tests were performed on the experimental systems in order to characterize the hydrodynamics of the packed beds used in the mass-transfer experiments with and without NAPL saturation. Tracer tests were also performed on the inlet/outlet portions of the system.

3.2 Materials

Chemicals

A lighter than water contaminant, toluene, served as the NAPL for the experiments. A spectranalyzed grade hexane was used as the extraction solvent for the analysis of toluene

and iso-octane was used as an internal standard for the gas chromatography analysis. Ethanol was used as a co-solvent in some of the mass-transfer experiments. All of the chemicals were purchased from Fisher. The chemical properties and solubilities of the chemicals are given in Table 3 - 1.

The de-ionized water used in all the experimental and analytical methods was distilled by a Corning Water Purifier LD-2A. The water was cooled to room temperature before use.

Packed Bed Media

To preclude the effects of NAPL sorption onto the porous media and to preserve a pure NAPL-aqueous system, the column was packed with a glass bead media. The experiments were run with two different sizes of beads, each differing in mean particle diameter and porosity. The bead characteristics and sources are summarized in Table 3 - 2.

The bead size distribution and mean particle diameter were determined by sieve analysis. The particle density, bulk density, and porosity were determined for each bead size based on techniques found in Black (1965).

The particle density was calculated from the mass of the sample and its volume. The weight of a dry 100-ml volumetric flask was measured and approximately 50 grams of air-dried beads were added to the flask. The flask was then filled approximately half full with deionized water. The water was boiled for several minutes to remove trapped air in the bead sample. The flask and contents were cooled to room temperature and deionized water was added to the flask for a total volume of 100 ml. The mass of the flask and contents were measured on a Mettler H20 balance. The bead sample was then emptied from the flask and the mass of the flask filled with 100 ml of deionized water was measured. The particle density was calculated as follows:

Table 3-1. Chemical Properties

Chemical	Density* (g/ml)	Vapor** Pressure 20° C (mm)	Aqueous Solubility 25° C (mg.l)
Toluene	0.867	22	515**
Hexane	0.663	120	9.5***
Iso-octane	0.688		0.56**
Ethyl Alcohol	0.789	44	miscible

* Manufacturer

** Mackay & Wolfe, 1973

*** Verschueren, 1983

Table 3-2. Packed Bed Media Characteristics

Mean Particle Diameter (μ m)	Diameter Range (μ m)	Particle Density (g/cm ³)	Bulk Density (g/cm ³)	Porosity	Source
400	351 - 495	2.43	1.48	0.39	Coming
650	595 - 710	2.98	1.74	0.42	Ferro

$$\rho_p = \frac{\rho_w(M_s - M_a)}{(M_s - M_a) - (M_{sw} - M_w)} \quad (3-1)$$

where ρ_w is the density of water at 25°C in grams per cubic centimeter, M_s is the mass of the flask plus bead sample, M_a is the mass of the flask filled with air, M_{sw} is the mass of the flask filled with the bead sample and water, and M_w is the mass of the flask filled with water.

The bulk density of the bead sample was calculated as the ratio of the mass of the sample to the macroscopic volume of the sample. A Mettler H20 balance was used to measure a given mass of beads. The sample was then saturated with deionized water and slurried into a 25-ml volumetric cylinder. The volume of the saturated sample was measured in milliliters and the bulk density was calculated as:

$$\rho_b = \frac{M_b}{V_b} \quad (3-2)$$

where M_b is the mass of the bead sample and V_b is the saturated volume of the sample.

The porosity was calculated from the experimentally determined particle and bulk densities as follows:

$$n = \left(1 - \frac{\rho_b}{\rho_p}\right) \quad (3-3)$$

The beads were cleaned and soaked with acetone and a 10 percent nitric acid solution prior to use to remove any organic materials, which may have affected mass transfer or caused sorption.

Humic Acid Solution

The humic solution that was used in the solubility experiments was prepared from humic acid purchased from Aldrich. The solution was prepared by dissolving 200 mg of

humic acid in 500 ml of deionized water. The pH of the solution was raised to 11.5 by the addition of sodium hydroxide. In order to assure maximum dissolution, the humic solution was mixed with a magnetic stirrer for 15 hours. The solution was then adjusted to a pH of 7 by the addition of hydrochloric acid and diluted to 1 liter. The solution was filtered through a 0.45 micron MetriceI membrane filter to remove particulate matter. The total organic carbon (TOC) content was then determined by TOC analysis.

3.3 Solubility Experiments

Introduction

Experiments were performed to determine and verify the solubility of toluene in the aqueous systems that were studied. These systems included a deionized water, deionized water with dissolved humic acid, and a deionized water-ethyl alcohol solution. The solubilities measured in these experiments were used in the calculation of mass-transfer coefficients.

Experimental Procedure

The same solubility experimental method was used to measure the solubility of toluene in all of the solutions. The method consisted of placing 50 ml of the test aqueous-sample into a 60-ml glass centrifuge bottle. Approximately 2 to 3 ml of toluene were added to the bottle, which was then sealed with a Teflon-coated septa cap, leaving a head space of approximately 7 to 8 ml. The bottle and contents were then mixed on a mechanical shaker for a period of 24 hours at 25°C. Insulation was placed between the bottle and the machine to avoid heating of the sample. To separate the toluene phase from the aqueous phase, the bottle was then centrifuged at 2300 rpm for 30 minutes on a Damon CRU-5000 centrifuge. The bottle was centrifuged upside down so that the lighter-than-water toluene was on top of the aqueous layer and the aqueous layer was against the septa cap.

The bottles were carefully removed from the centrifuge upside down, and a 3-ml sample was pulled through the septa with a syringe. The aqueous sample was immediately injected into a 20-ml vial containing 10 ml of hexane and was sealed with a Teflon-coated septa cap. The centrifuge bottle was centrifuged again and a second sample was taken in the same manner. The samples were analyzed by UV-spec as described in Section 3 - 7.

A stock solution of 60 mg/l humic acid was prepared as described in Section 3 - 2. The stock solution was diluted with deionized water to prepare humic solutions of 0, 2, 10, 20, 30, 40, and 50 mg/l. The solubility of toluene in each of these solutions was then measured.

A UV-spec scan of hexane that had been extracted with a humic acid solution, was performed to verify that the humic acid would not interfere with the analysis of toluene. The results of the scan showed that extraction with a humic-aqueous solution had no affect on the hexane UV-absorbance. There was no indication that humic material in the aqueous solution was extracted into the hexane.

A 50 percent stock solution of ethyl alcohol was prepared by making a 1:1 dilution with deionized water. The stock solution was diluted with deionized water to prepare ethyl alcohol solutions of 0, 10, 20, 30, 40 and 50 percent. The solubility of toluene in these solutions was then measured.

A UV-scan of hexane that had extracted a 50 percent ethyl alcohol solution was performed to determine the effect that the absorbance of the ethyl alcohol would have on the toluene analysis. It was found that the absorbance increased by 0.02 absorbance units. This corresponds to 3.7 mg/l increase in the calculated toluene concentration. Since a 50 percent solution was the highest ethyl alcohol concentration used (i.e., 3.7 mg/l was the largest error which was introduced), the error introduced by the ethyl alcohol was considered negligible. This decision was also based on the goal of these solubility test, which was to measure approximate changes in toluene solubilities based on ethyl alcohol concentrations.

3.4 Experimental Apparatus

Experiments were conducted in a vertical glass "Adjusta-Chrom" column manufactured by Ace Glass, Inc. A schematic description of the experimental apparatus is shown in Figure 3 - 1. The column was 90-mm long with an inside diameter (ID) of 25-mm and was equipped with two Teflon plungers to allow for adjustment of the packed bed length. The plungers were fitted with a coarse glass frit disc, which served to retain the porous media without restricting flow. After passing through the glass disc, the flow was funneled into 2-mm ID Teflon tubing. The tubing was valved at the inlet and outlet of the column with stainless steel/Teflon Omnifit two-way connectors. At the column outlet, 2-mm Teflon tubing served as the sampling port.

The samples were collected directly into an extraction solvent in order to minimize NAPL losses to volatilization. The sample containers were 20-ml or 40-ml glass vials sealed with Teflon-coated septa caps. The room temperature was monitored during each experiment and from experiment to experiment. The temperature varied from 25° to 26° C. All of the experiments were run upflow with the column in a vertical position.

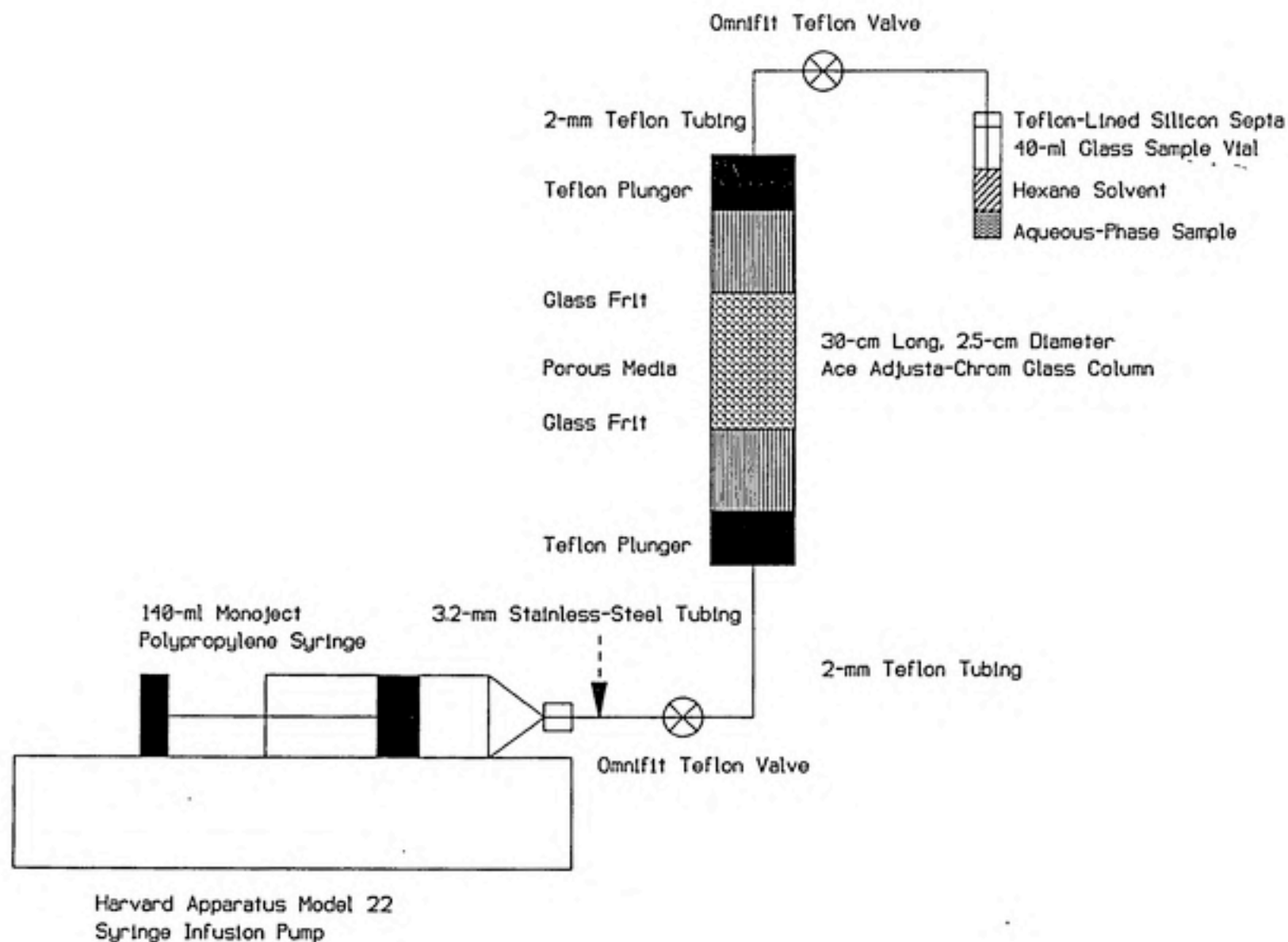
A Harvard Apparatus Model 22 syringe infusion pump was used to pump the aqueous solution through the column. The pump was rated for ± 1 percent accuracy and ± 0.1 percent reproducibility. A Sherwood- Monject 140-ml polypropylene syringe was used to feed the aqueous solution. All tubing and connections from the syringe to the column were made from Teflon or stainless steel.

3.5 Mass-Transfer Experiments

Experimental Apparatus

The column apparatus, previously described in Section 3 - 4, was used in the mass-transfer experiments. The first step in preparing the packed bed consisted of packing,

Figure 3-1. Experimental Apparatus



saturating, and bringing the porous media to a level of residual saturation. The following procedure was used consistently for each of the experimental runs:

1. For each experiment a given mass of glass beads was measured on a Mettler H20 balance. This mass of beads remained constant for each experimental run of a given bead size. A mass of 9.0 g and 7.5 g was used for the 650 μm and 400 μm bead sizes, respectively. The beads were poured into a dry, vertically-upright column with the bottom plunger in place. The aqueous phase was pumped up through the porous media until complete saturation was reached.
2. A predetermined volume of NAPL, based on the targeted residual saturation, was added to the media through a microliter syringe. The media was thoroughly stirred with a stainless steel spatula in order to achieve uniform distribution of NAPL in the packed bed.
3. The top Teflon plunger was put into place and the packed bed length was measured. The packed bed length was chosen based on the maximum length which produced effluent concentrations less than solubility. The bed length varied among experimental runs with the majority of the runs having a length in the range of 0.010 m to 0.011 m.
4. To assure a state of residual saturation, the aqueous phase was pumped through the column at a relatively high interstitial velocity, approximately 23 m/d for 30 minutes. The top plunger and sample port tubing was then removed and flushed with acetone and deionized water in order to remove any NAPL that may have been mobilized and trapped during the flushing period.
5. The top plunger and sample port was replaced and the aqueous-phase was pumped until the entire system was filled. The inlet and outlet valves were then closed until the experiment began.

Experimental Procedure

The experiment consisted of pumping deionized water through the column and sampling the effluent at a variety of velocities. A minimum of one bed volume of the aqueous phase was allowed to pass through the packed bed before samples were taken. This procedure allowed steady-state dissolution to be achieved. To increase accuracy of the data, two to three samples were collected for each velocity. One of the assumptions made for each experimental run was that the residual saturation of the packed bed remained constant during the course of the experiment. To minimize the NAPL mass lost to aqueous dissolution in the packed bed during the experimental run, the effluent was sampled at a maximum of five different interstitial velocities. Calculations showed that this procedure minimized the change in residual saturation during an experimental run to 10 percent or less.

Since toluene and hexane are very volatile compounds, precautions were taken to minimize losses due to evaporation. The aqueous samples were collected in 20-ml or 40-ml vials, sealed with Teflon-coated septa caps. Prior to sampling, the vials were filled with 5 to 10 ml of hexane. The exact volume of the hexane was determined through mass measurements made on a Mettler H20 balance and known chemical density which are tabulated in Table 3 - 1. The column sampling port or Teflon tubing was inserted down through a Teflon-coated septa cap, which was screwed onto the vial during sampling. A stainless steel tube with an ID of < 0.5 -mm was placed through the cap to allow for atmospheric pressure equalization. To further decrease toluene losses during sampling, the Teflon tubing was immersed directly into the hexane. At the end of the sampling period, the sample volume was measured using mass differencing and the density of water. The sample vials were shaken by a mechanical sieve shaker or by hand for a two minute period. In order to minimize the change in residual saturation during the experiment, samples of 1 ml or less were collected. This produced an extraction ratio (volume of solvent/volume

of sample) of five to ten. In the majority of experimental runs, the samples were analyzed within 24 hours of the experiment. When storage was necessary, samples were stored upside down at 4°C to minimize sample volatilization.

Test vials containing hexane were carried along with actual sample vials to measure the volatilization losses of hexane during the sampling period. These vials were treated in the same manner as the sample vials, including replacing the storage caps with the sampling caps for the duration of a sampling period. This procedure verified that there was no significant loss of the solvent during the sampling period.

At the end of each experiment, the ending residual saturation for that run was calculated using a extraction technique. The top plunger and sampling apparatus was removed and 10 ml of hexane was pipetted into the column. The solvent was then thoroughly mixed into the porous media, which extracted the remaining NAPL in the packed bed. A sample of the hexane was then placed in a Teflon-sealed vial and was later diluted 0.1:10 and analyzed with the effluent samples. This measurement, combined with porosity and packed bed volume data, allowed for calculation of the ending residual saturation.

An estimate of the NAPL lost to aqueous dissolution during the course of each experiment was made based on sample volumes and concentrations collected during the experiment. This data, combined with the calculated ending residual saturation, allowed for a back calculation of the beginning residual saturation. The interstitial velocities were computed by

$$v = \frac{Q}{\pi r^2 n S_a} \quad (3-4)$$

for

$$S_a = 1 - S_n$$

where v is the interstitial velocity, Q is the volumetric flow rate, n is the porosity of the

packed bed, r is the radius of the packed bed, S_a is the percent aqueous phase saturation, and S_n is the percent NAPL saturation.

All of the glassware used in the experiments was soaked in a fifty percent nitric acid bath and rinsed with deionized water between runs to remove any organic material. The plungers, valves, and Teflon tubing were rinsed with acetone and deionized water to remove any trapped toluene.

3.6 Tracer Experiments

The column apparatus described in Section 3-4 was used to perform the tracer tests. The packed bed was prepared in the same manner as described in Section 3-5. Tests were performed for both the 650 μm and 400 μm media diameter bead sizes. In order to determine the effect of residual saturation, tests were performed with and without toluene present in the packed media. Sodium fluoride was added to the feed solution of deionized water and the solution was introduced into the system as a step input (continuously fed at $t > 0$). The fluoride solution was pumped through the system and aqueous samples were collected at the column effluent. The samples were then analyzed for fluoride. The time at which the fluoride was introduced to the system and the time at which each sample was taken was recorded.

Volumetric flow rates of 2 and 3 ml/hr were used during the runs. The samples were collected in 20-ml vials at approximately 10-minute intervals during the breakthrough period. Sample volumes were measured by mass differencing using a Mettler H20 balance. At the end of the run, the NAPL was extracted from the packed bed, and the residual saturation was calculated as discussed in Section 3-6.

In order to estimate the dispersion in the packed bed, the residence time of the inlet and outlet flow portions of the system were subtracted from the recorded sampling times. To measure the volume of the inlet and outlet portions of the system, the column was prepared without a packed bed (i.e., the plungers were placed flush together). Deionized

water was pumped through the system and the residence time of the fluid was calculated. The volume was back calculated from the time and the flowrate.

In order to distinguish dispersion in the packed bed from dispersion in the rest of the system, a dispersion test was performed on the inlet/outlet portion. Both plungers were put in place with the glass frits flush together and the test was performed as described above.

3.7 Analytical Methods

Specific Ion Electrode Method

An analytical method, based on Part 413 B in APHA (1985), was used to measure fluoride concentrations in the column effluent. The method utilized a fluoride selective-electrode and a double-junction reference electrode, both manufactured by Fisher. A Fisher Accumet potential meter was used to measure millivolts.

A stock fluoride solution was prepared, which served as the column feed solution. The stock solution was prepared by adding 1.31392 g of sodium fluoride to 0.25 l of deionized water to obtain a 2378.04 mg/l fluoride solution. A standard solution of 546.95 mg/l fluoride was prepared by diluting the stock solution. Additional standards of 54.7, 5.47, 0.55 0.88, and 0.33 mg/l were prepared from successive dilutions the 546.95 mg/l standard solution.

The calibration curves produced for the fluoride-selective electrode analysis were linear in the region of calibration (i.e. 0.33 ppm to 2378.04 ppm). A linear regression produced an $R^2 = 0.9997$. The slope of the calibration curves were within the manufacturers limits of -59 ± 4 millivolts. A typical calibration curve is shown in Figure 3 - 2.

An Orion brand Total Ionic Strength Adjustment Buffer (TISAB) was added to the standard solutions and samples in the amount of 5-ml TISAB to a 50-ml sample. The TISAB served to provide a uniform ionic strength background.

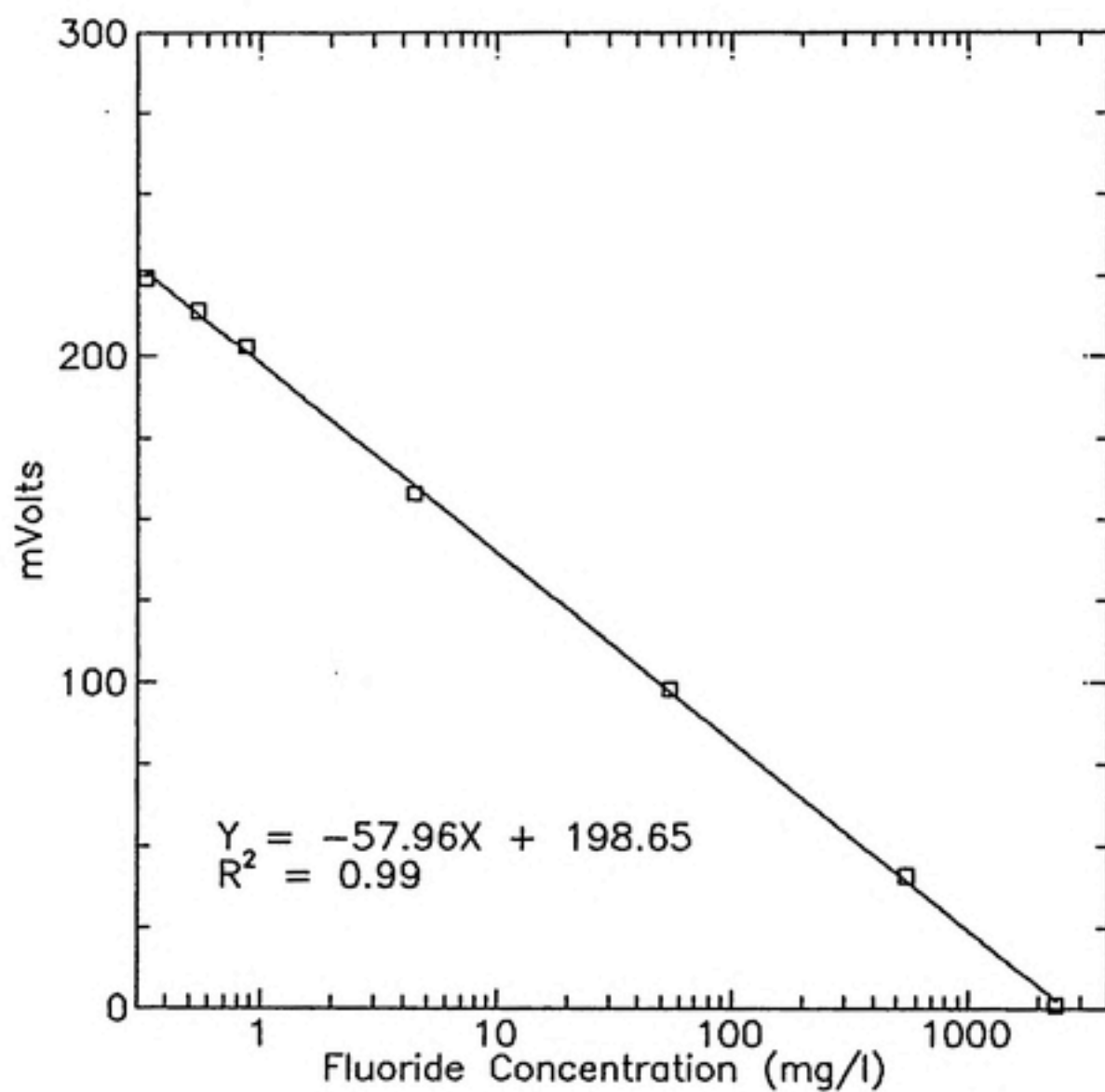


Figure 3-2. Fluoride Selective Electrode Calibration Curve

The aqueous effluent samples were collected in 20-ml vials containing the aqueous-TISAB solution. The sample volumes were calculated by mass differencing using a Mettler H20 balance. After collection, samples were diluted to 25 ml.

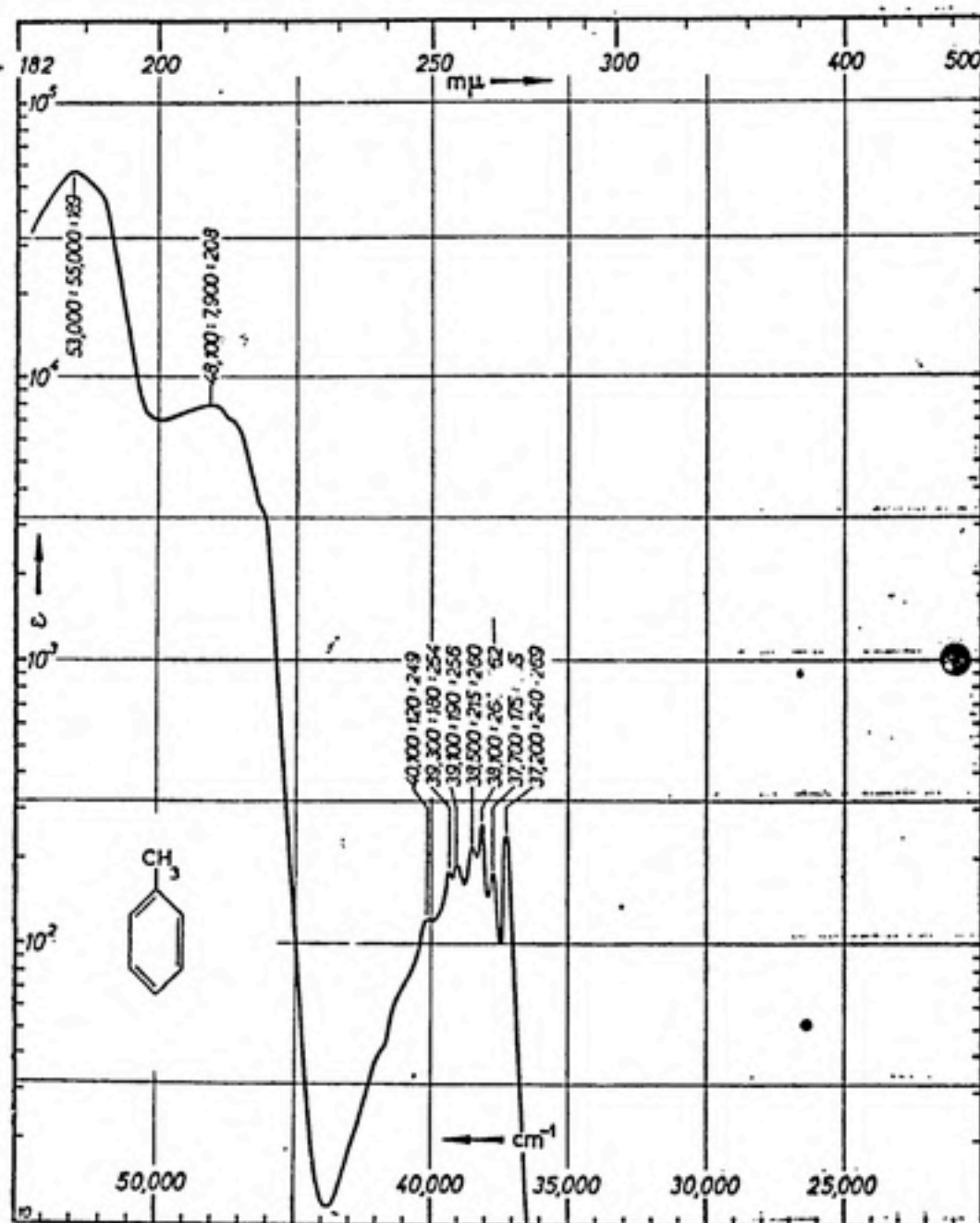
The electrodes were immersed in the sample and equilibrium was established while the solution was stirred with a magnetic stir bar for approximately three minutes. A piece of cardboard was placed between the magnetic stirrer and the sample beaker to minimize solution heating. The sample temperature was monitored and millivolt readings were recorded at a temperature of 25°C. Between sample measurements, the electrodes were rinsed with deionized water and blotted dry. The potential meter was calibrated every 30 minutes with a standard solution at 25°C to insure accuracy of the sample measurements.

Ultra-Violet Spectrophotometry

An analytical method was required to measure the toluene concentration in the aqueous phase column effluent. The method used for all of the mass-transfer experiments was one in which the toluene was extracted from the aqueous phase by a hexane and the sample was then analyzed by ultra-violet spectrophotometry (UV-spec).

The hexane samples were analyzed for toluene on a Cary 219 spectrophotometer manufactured by Varian, using 1-cm path length Fisherbrand spectrophotometer cells. A wavelength scan of toluene and hexane was performed and verified by a comparison to a published scan (Atlas of Organic Compounds, 1966). The toluene scan is shown in Figure 3-3. All analysis were made at a wavelength of 262 nanometers in order to maximize absorbance levels.

A calibration curve was produced from standard concentrations of toluene in hexane. Two standard curves were run each time the UV-spec was used—once at the beginning and once at the end of the sample analysis. A typical calibration curve is shown in Figure 3-4. Each sample was analyzed once on the UV-spec. Standards were made from a stock solution of 1040.0 mg/l toluene, made by diluting 120 μ l of toluene in 100 ml of hexane.



The stock solution was diluted 1:50, 6:50, 3:10 to obtain standards of 20.8 mg/l, 124.8 mg/l and 312.0 mg/l, respectively. Standards were stored in volumetric flasks with a parafilm sealed stopper at 4°C. A new stock solution was made every three weeks. Comparison of new and old standards typically showed a difference of 0.010 absorbance units. The toluene concentration was linearly proportional to absorbance and all calibration curves correlated with the a regression $R^2 > 0.9999$.

Gas Chromatography

The accuracy of the UV-spec method was verified by analyzing a set of samples by gas chromatography in addition to UV-spec. The analysis was made on a Hewlett Packard 5890A gas chromatograph equipped with a flame-ionization detector and a 5 meter DB5 capillary column with 0.25 mm I.D. and a 0.25 film thickness. Nitrogen was used as the carrier gas. The samples were run iso-thermally at a column temperature of 75°F and injector and detector temperatures of 225 and 300°F, respectively. Automatic injection of a 2- μ l sample was performed in duplicate by a Hewlett Packard auto-injector. The auto-injector used 2-ml sample vials sealed with a Teflon-coated caps.

Iso-octane was used as an internal standard because of its chemical similarity to toluene and sufficient peak resolution. The chemical properties of iso-octane can be found in Table 3 - 1. The internal standard was added to the stock solution of hexane prior to sample collection. A stock solution of 99.8 mg/l iso-octane was prepared by diluting 580 μ l of iso-octane into 4 l of hexane. A standard curve was run at the beginning and end of the sample analysis and were linear in the range of calibration. A typical calibration curve is shown in Figure 3 - 5. The same standard solutions of toluene in hexane that were used for the UV-spec analysis were used in the GC analysis.

Although the standards and samples contained 99.8 mg/l iso-octane during the UV-spec analysis as well during the GC analysis, a UV-spec scan was performed to analyzed for iso-octane absorbance. It was noted that iso-octane, present at 99.8 mg/l in hexane,

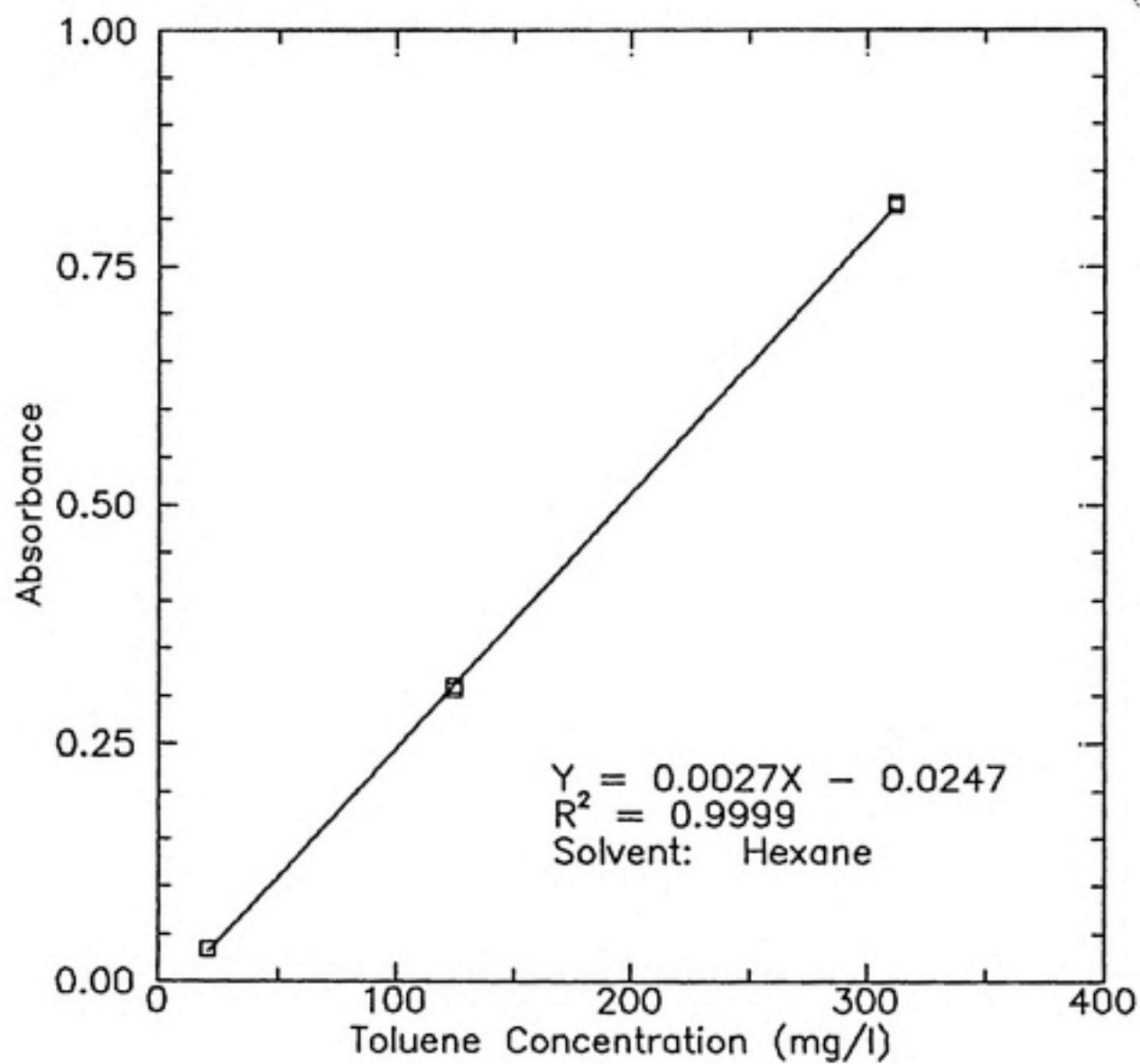


Figure 3-4. UV-Spec Toluene Calibration Curve

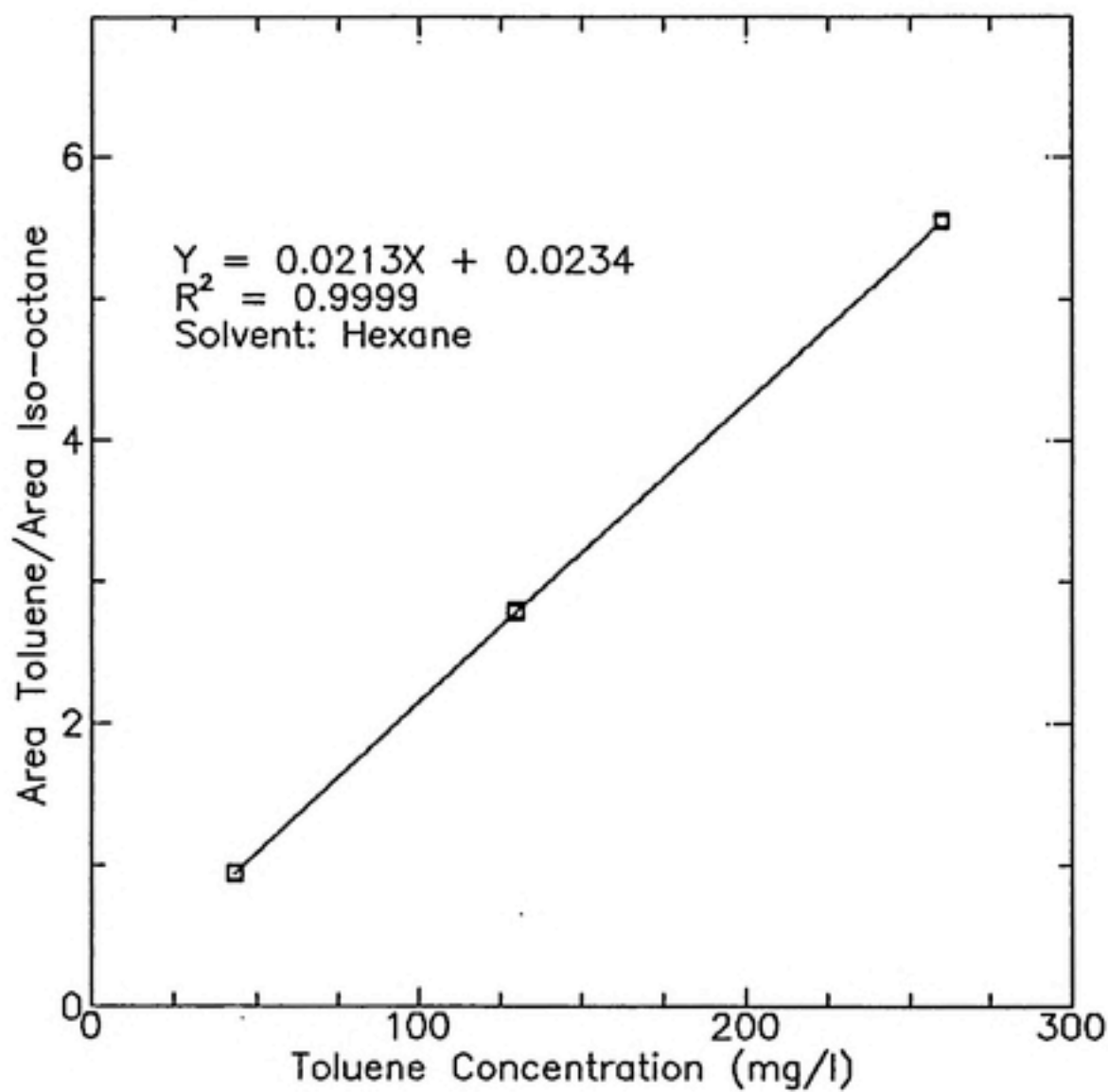


Figure 3-5. Gas Chromatography Toluene Calibration Curve

did not absorb at significant levels.

Total Organic Carbon Analysis

The stock humic acid solution, used in some of the mass transfer experiments, was analyzed for Total Organic Carbon (TOC) on a TOC Analyzer Model 700, manufactured by the OI Corporation. The analyzer oxidizes the TOC to CO_2 with sodium persulfate and analyzes the CO_2 with an infrared detector.

4 Results and Discussion

4.1 Tracer Studies

Introduction

Fluoride tracer studies were performed in order to estimate hydrodynamic dispersion through the packed bed media. A dispersion coefficient was estimated for each size media using sodium fluoride experimental breakthrough curves. Based on the estimated dispersion coefficient, advective velocity, degree of NAPL saturation and the molecular diffusion of fluoride through the column, a dispersivity for each size media was calculated. The dispersivity was used in conjunction with the other system parameters to characterize the hydrodynamic dispersion of NAPL during the mass transfer experiments.

Experimental Results

Tracer studies were performed for each size media with and without NAPL contamination. A tracer test was also performed to determine the significance of dispersion through the inlet and outlet portion of the column apparatus.

The breakthrough curves were adjusted to reflect dispersion through the packed bed media by subtracting the residence time of the inlet/outlet system from the sample times. The theoretical residence time based on the advective velocity through the column was calculated from the volumetric flowrate, the porosity, the percent residual saturation, and the length and cross-sectional area of the packed bed. Theoretically, the residence time of the column should correspond to the time when approximately 50 percent of the tracer's feed concentration arrives at the effluent. In tests where the complete volume in the inlet and outlet portions of the system could not be accounted for, the curves were shifted so

that the true residence time of the column corresponds to the approximately 50 percent breakthrough.

A tracer test was performed on the inlet/outlet portion of the system, in order to determine if significant dispersion occurred through the valves and fittings of the apparatus. The breakthrough curve for the inlet/outlet section is shown in Figure 4 - 1. The sharp front on the curve indicates that the flow through this portion approaches plug flow. Based on the shape of the breakthrough curve, the dispersion in the inlet/outlet portions of the system was assumed to be negligible.

Estimation of Dispersion Coefficients

The fluoride ion is considered to be a nonreactive or conservative tracer since it is not subject to any chemical changes, interactions, or reactions. The movement of a conservative tracer through a packed bed is affected only by the hydrodynamics of the system and is therefore governed by the advective-dispersive (AD) equation. Given a source function and initial and boundary conditions of a system, many analytical solutions to the AD equation can be found in the literature (Bear, 1979).

The tracer study was assumed to follow the initial and boundary conditions

$$C(x, 0) = 0 \quad x > 0$$

$$C(0, t) = C_0 \quad t > 0$$

$$C(\infty, t) = 0$$

Solving the AD equation subject to these conditions, the following one-dimensional analytical solution can be derived (Bear 1979):

$$C/C_0 = \frac{1}{2} \left[\operatorname{erfc} \left(\frac{x - v_x t}{2(D_x t)^{1/2}} \right) + \exp \left(\frac{v_x x}{D_x} \right) \operatorname{erfc} \left(\frac{x + v_x t}{2(D_x t)^{1/2}} \right) \right] \quad (4-1)$$

where erfc is the complementary error function, x is the distance along the flowpath, and

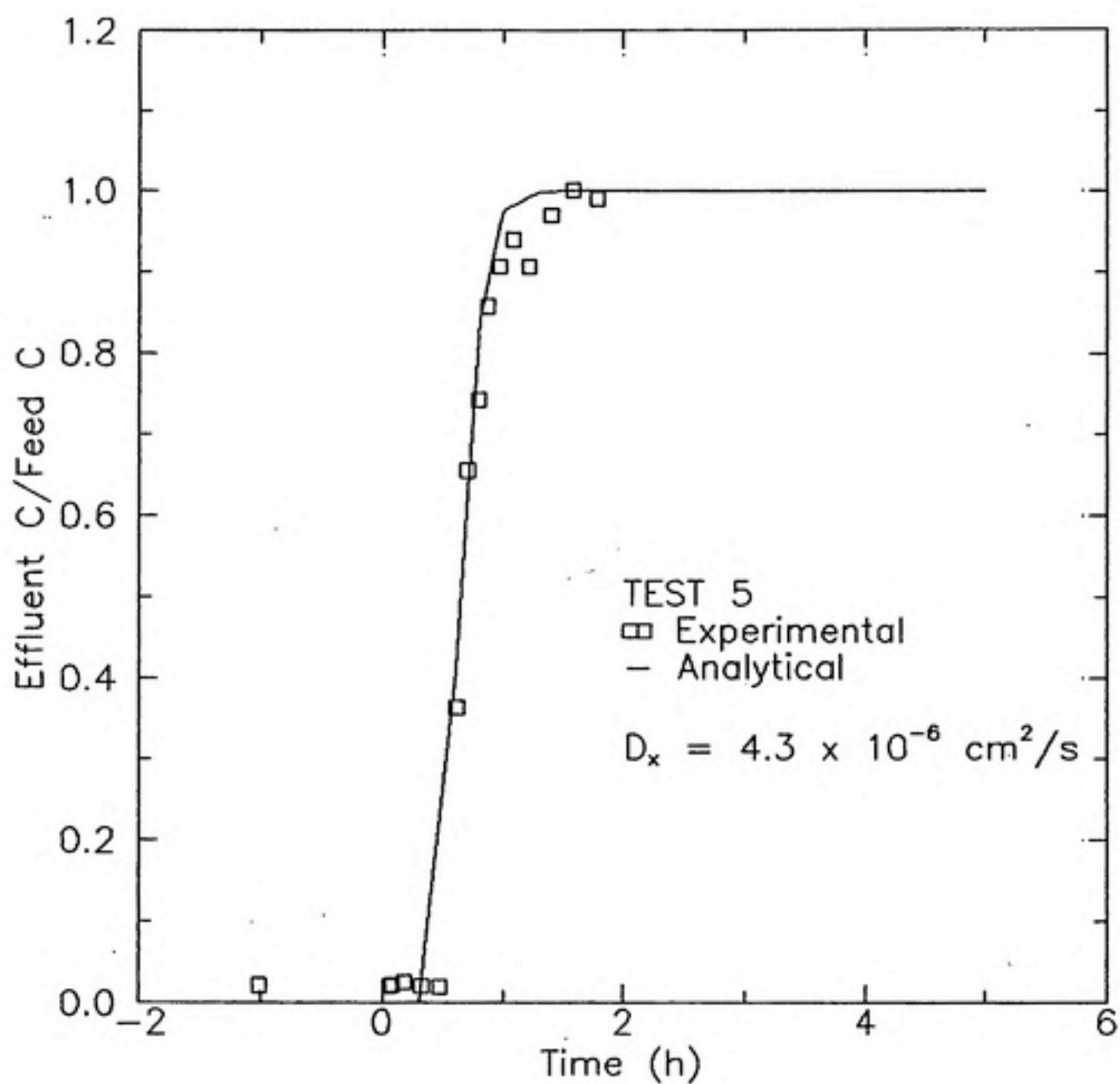


Figure 4-1. Fluoride Breakthrough Curve for Test 5

v_x is the average linear velocity in the x direction, t is the time, D_x is the dispersion coefficient in the x direction, C/C_0 is the normalized concentration at x .

By minimizing the sum of the square error between the predicted effluent concentrations and the experimentally measured effluent concentrations for a wide range of dispersion coefficients, a best fit dispersion coefficient D_x was determined. The experimental breakthrough curves and the best fit curves predicted by the analytical solution are shown in Figures 4-3 through 4-6. The best fit dispersion coefficients are listed in Table 4-1.

Mathematical Description of Dispersion

As previously discussed in Section 2.1, hydrodynamic dispersion describes the degree to which the NAPL movement deviates from advective flow. This deviation is due to two phenomena: mechanical dispersion, and molecular diffusion. For one-dimensional flow, the dispersion coefficient, D_x , can be described as (Bear, 1979)

$$D_x = \alpha_L v_x + D_d^* \quad (4-2)$$

where α_L is the longitudinal dispersivity of the porous media, v_x is the advective velocity in the x direction, and D_d^* is the effective molecular diffusion through the porous media.

The $\alpha_L v_x$ term accounts for mechanical dispersion, and the D_d^* term accounts for molecular diffusion. It is evident from equation 4-2 that at high velocities, diffusion is due primarily to mechanical mixing and at low velocities, diffusion is the dominant dispersive process.

Mechanical Mixing

The $\alpha_L v_x$ term in Equation 4-2 describes the movement of a solute due to mechanical dispersion and is a function of velocity, v_x , and longitudinal dispersivity, α_L . The dispersivity is an empirical coefficient that accounts for the mixing of the solute due to

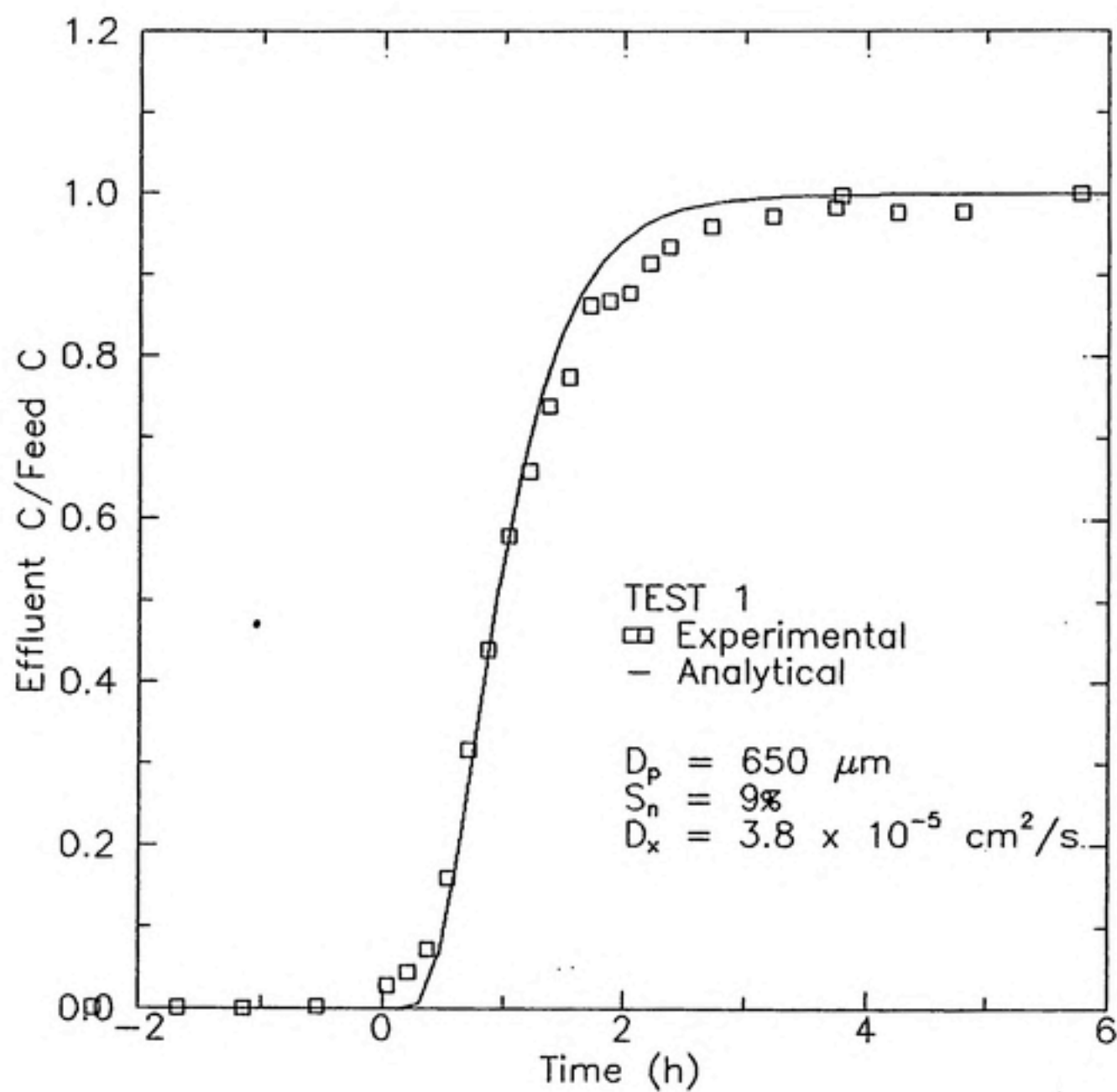


Figure 4-2. Fluoride Breakthrough Curve for Test 1

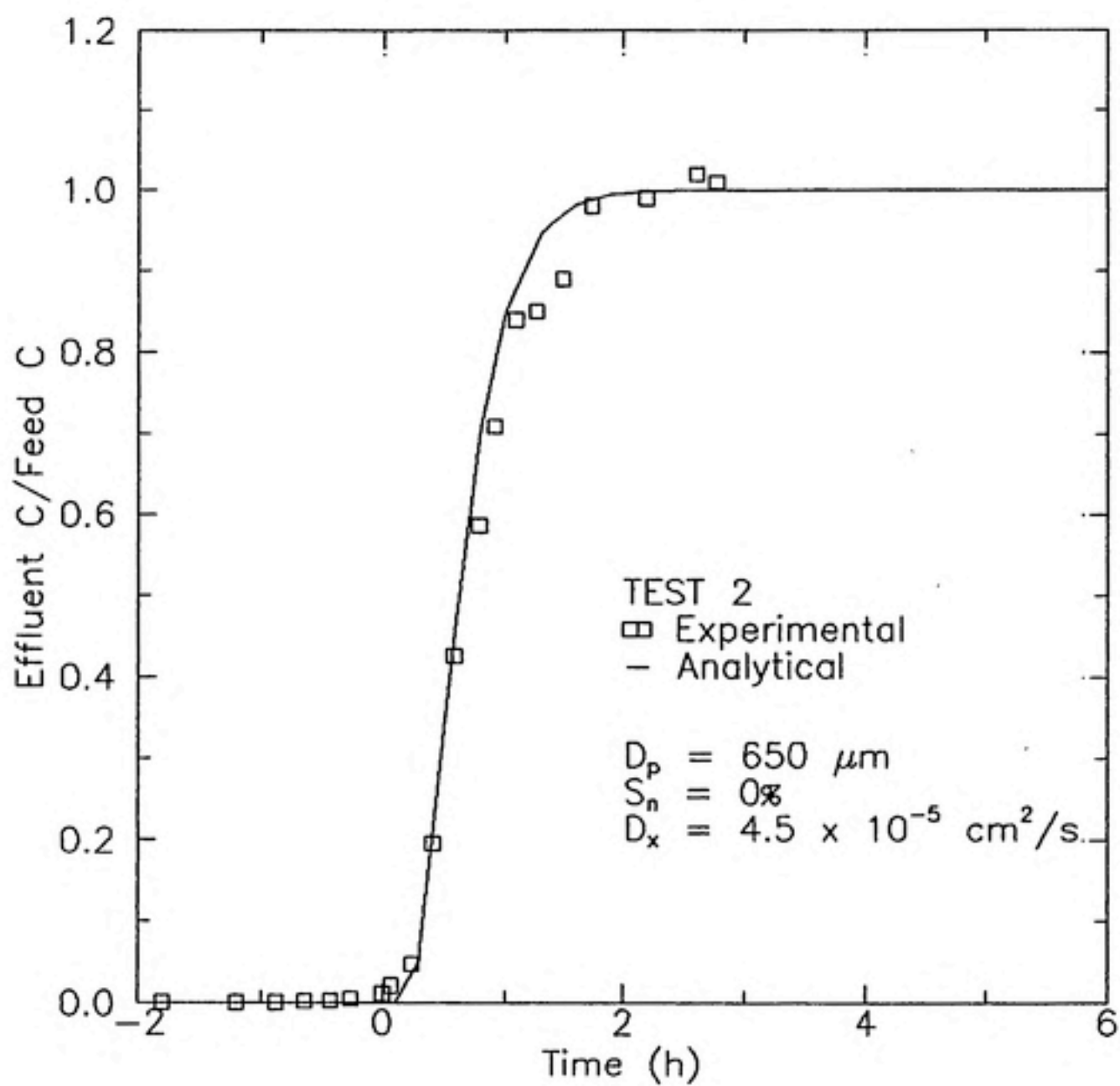


Figure 4-3. Fluoride Breakthrough Curve for Test 2

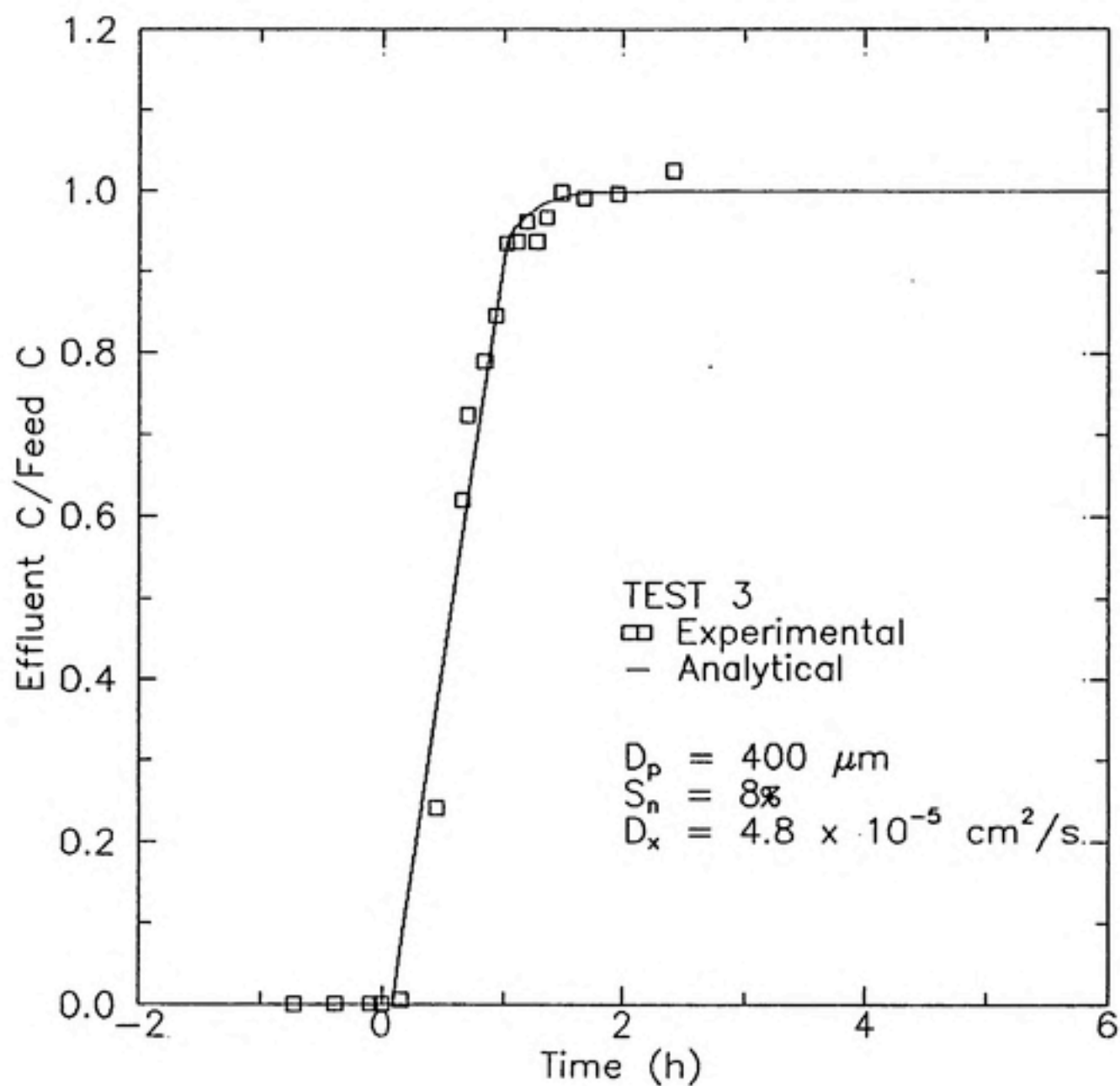


Figure 4-4. Flouride Breakthrough Curve for Test 3

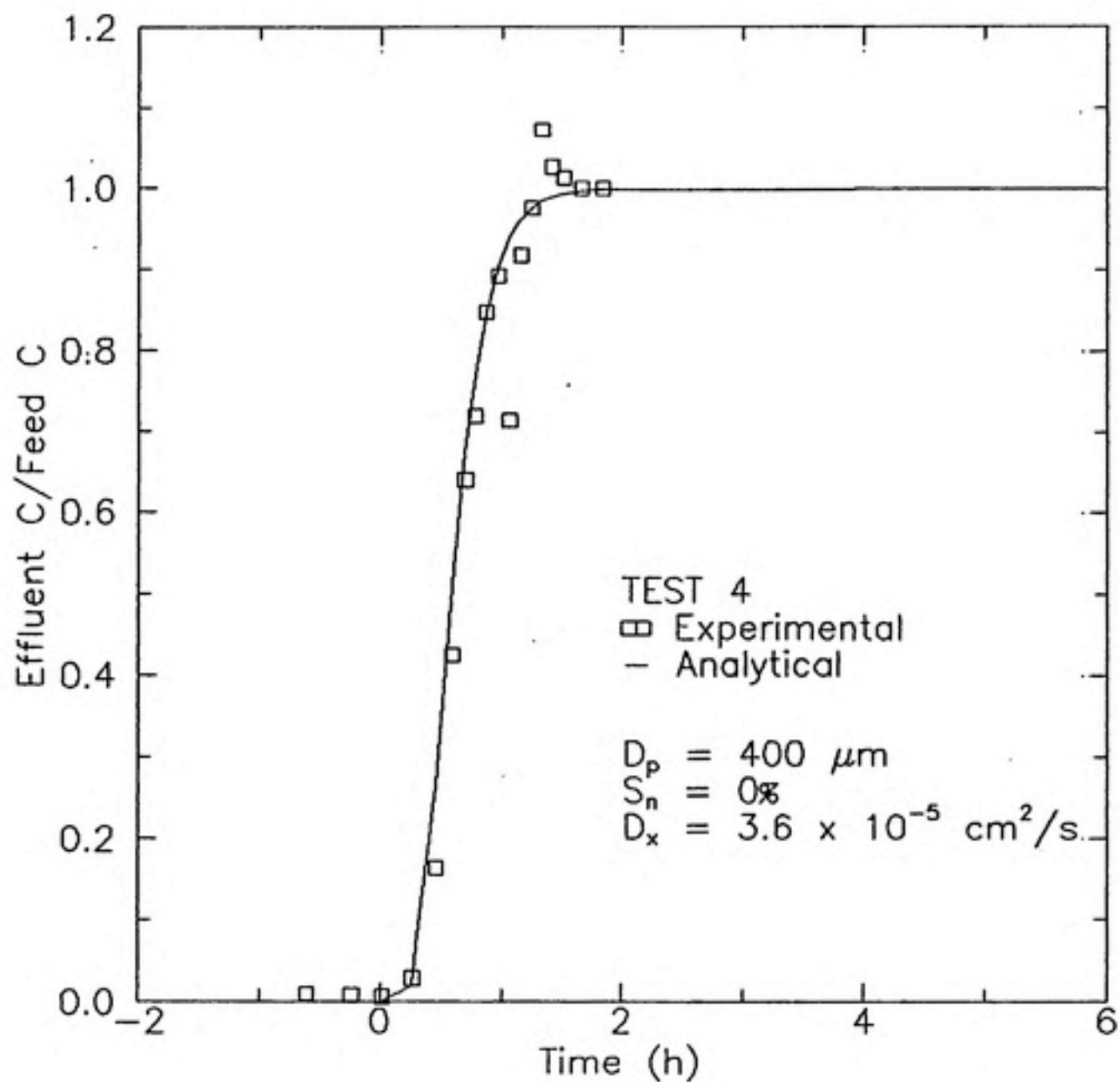


Figure 4-5. Fluoride Breakthrough Curve for Test 4

Table 4-1. Tracer Test Results

Test	Media Size (μm)	NAPL Saturation	Velocity (cm/s)	$e t^*$	Molecular Diffusion (cm^2/s)	Dispersion Coefficient (cm^2/s)	Dispersivity (cm)
1	650	9	2.9×10^{-4}	0.23	1.09×10^{-5}	3.8×10^{-5}	0.12
2	650	0	4.0×10^{-4}	0.32	1.09×10^{-5}	4.5×10^{-5}	0.1
3	400	8	4.8×10^{-4}	0.22	1.09×10^{-5}	4.8×10^{-5}	0.09
4	400	0	4.4×10^{-4}	0.29	1.09×10^{-5}	3.6×10^{-5}	0.07
5	inlet/outlet	---	4.4×10^{-4}	----	1.09×10^{-5}	4.3×10^{-6}	----

e = effective porosity

t^* = Millington-Quirk tortuosity

the presence of the porous media. Dispersivity is solely a function of the media geometry (Bear, 1979).

Molecular Diffusion

Molecular diffusion is a process whereby a solute moves under the influence of kinetic activity in the direction of a concentration gradient (Freeze and Cherry, 1979). Diffusion occurs in the absence of advective flow and can be described by Fick's first law

$$J_m = -D_d \frac{\partial C}{\partial x}$$

where J_m is the mass flux, $\partial C / \partial x$ is the concentration gradient, and D_d is the free molecular diffusion coefficient. In a porous media, the apparent molecular diffusion is less than the free molecular diffusion. This phenomena is due to the tortuous diffusional path length that is caused by the presence of the media particles as well as to a decreased cross-sectional area through which diffusion can occur. The effective molecular diffusion through a porous media, D_d^* , can be described as

$$D_d^* = \tau^* D_d$$

where τ^* is a tortuosity term less than one, and D_d is the free molecular diffusion (Bear, 1979). Tortuosity is an empirical term that takes into account the effect of the porous media on diffusion (Freeze and Cherry, 1979).

Geankoplis (1978), describes molecular diffusion through a porous media as

$$D_d^* = n_e \tau D_d$$

where n_e is the effective porosity of the media, τ is a tortuosity term, and D_d is the free-phase molecular diffusivity. The effective porosity accounts for the decreased cross-

sectional area through which diffusion can take place and the tortuosity term accounts for the increased diffusional path length due to the pore geometry.

Several models of tortuosity through a porous media have been applied in the literature (Bear, 1972; Geankopolis, 1978; Jury et al., 1983; Parker et al., 1987). A commonly used estimate of tortuosity is the Millington-Quirk model which was empirically developed for air-gas diffusion in partially saturated soil (Millington and Quirk, 1961). This model has also been applied to water-liquid diffusion in soil in the form (Jury et al., 1983)

$$D_d^* = \tau_m D_d$$

where

$$\tau_m = \frac{\epsilon_a^{10}}{n^2}$$

where τ_m is the Millington-Quirk tortuosity, ϵ_a is the volumetric water content and D_d is the free-phase molecular diffusion. For multiphase porous systems, the volumetric water content can be expressed as nS_a , where n is the porosity of the media and S_a is the aqueous-phase saturation. By substituting for the volumetric water content and rearranging the terms of τ_m to separate the effects of diffusional area and path length, an analogy to the Geankopolis model can be made

$$\tau_m = \frac{(nS_a)^{10}}{n^2} = nS_a \left(n^{\frac{1}{3}} S_a^{\frac{7}{3}} \right) = n_e \tau \quad (4-3)$$

where $n_e = nS_a$ and $\tau = n^{\frac{1}{3}} S_a^{\frac{7}{3}}$. This model states that tortuosity is a function of the NAPL saturation, S_n , since $S_a = 1 - S_n$. NAPL saturation is defined as the volume fraction of NAPL in the solid media pore space. The model predicts that as the NAPL saturation increases, tortuosity through the media decreases thereby decreasing the effective molecular diffusion.

Free Molecular Diffusion Calculations

Values for the free molecular diffusion of fluoride and toluene in water are required to calculate hydrodynamic dispersion. The molecular diffusion of fluoride in water was estimated by an electrolyte estimation method (Treybal, 1951). For concentrated solutions of electrolytes, the diffusion in water was calculated as

$$D_c = D_d \left(1 + \frac{m \ln \gamma_{\pm}}{m} \right) \left(\frac{u_b}{c_B V_B \mu} \right)$$

where

$$D_d = \frac{R' T U^+ U^-}{U^+ + U^-} \left(\frac{1}{Z^+} + \frac{1}{Z^-} \right)$$

where m is the molality of the solution, $\gamma_{\pm}$ is the mean ionic activity coefficients, V_B is the partial molal volume of water in solution in $\text{cm}^3/\text{g-mole}$, c_B is the number of gram moles of water per cm^3 of solution, μ_b is the viscosity of water, μ is the viscosity of the solution, R' is the gas constant, T is temperature, U^+ and U^- are absolute velocities of the cation and anion, and Z^+ and Z^- are the valences of the cation and anion. Based on this method, the molecular diffusion of sodium fluoride in water is calculated to be $1.09 \times 10^{-5} \text{ cm}^2/\text{s}$.

The free molecular diffusivity of toluene in water was calculated using the Hayduk and Laudie method (Lyman, 1982)

$$D_{bw} = \frac{(13.26)(10^{-5})}{\mu_w^{1.14} V_B^{0.589}}$$

where μ_w is the viscosity of water at a given temperature, and V_B is molar volume cm^3/mol . The LeBas Method (Lyman, 1982) was used to calculate V_B . The free molecular diffusivity of toluene in water at 25°C is calculated to be $9.1 \times 10^{-6} \text{ cm}^2/\text{s}$.

Dispersivity Calculations

Rearranging equation 4-2, the dispersivity for each media was calculated as

$$\alpha_L = \frac{D_r - D_d^*}{v_r}$$

The dispersion coefficients were obtained from the tracer studies and the tortuosity was calculated based on the Millington-Quirk model (1961). The calculated dispersivities for each media are listed in Table 4 - 1.

The free molecular diffusion of fluoride in water is relatively high compared to the mechanical dispersion at the operating velocity and thus played a significant role in the dispersion process during the tracer studies. Overall, the dispersivities for both medias are small compared to typical values measured in the field. Freeze and Cherry (1979), indicate that dispersivities obtained from column tests invariably yield values in the range of 0.01 cm to 2 cm. Dispersivities under field conditions are generally larger due to the effects of heterogeneity in macroscopic flow. Since the porous media used in the experiments are relatively homogeneous, small dispersivities are expected.

Higher values of dispersivity were calculated for the media containing NAPL residual saturation for both bead sizes. There is little theoretical or experimental work addressing the effect of NAPL contamination on dispersivity in a NAPL contaminated porous media. However, since dispersivity is a function of the pore geometry, intuitively, one would expect that the presence of a NAPL would change the flow geometry and the hydrodynamic flow conditions. Whether the effect of NAPL contamination is to increase or decrease the dispersivity would most likely depend on the shape of the physical NAPL at the microscopic level. Due to the limited data obtained in this study, it is not clear if the presence of a NAPL significantly affects the dispersivity. Since the calculated values of dispersivity with and without NAPL residual are on the same order of magnitude, the value for 0 percent residual saturation was used in all subsequent calculations.

Dispersivity was ultimately used in equation 2-33 to calculate mass transfer coefficients of toluene in porous media. The accuracy of the mass transfer calculations is dependent on the accuracy of the dispersivity calculations. A sensitivity analysis was performed to determine the effect of dispersivity on the mass transfer coefficient, K . Figure 4-6 shows K in dimensionless form as a function of dimensionless dispersivity for several values of C/C^* .

It is apparent that K is insensitive to dispersivity for values of α_L/x less than 1.0 and increasingly sensitive for greater values. The range of α_L/x values calculated for the experimental media with and without NAPL contamination is on the order of 7.0×10^{-2} to 1.2×10^{-1} and falls within the insensitive range. Although the dispersivity of the media will change from experiment to experiment as a function of NAPL saturation, the sensitivity analysis predicts that for the media used, this variation is not of significance when calculating K . Therefore, dispersivity was not expressed as a function of NAPL saturation in this study.

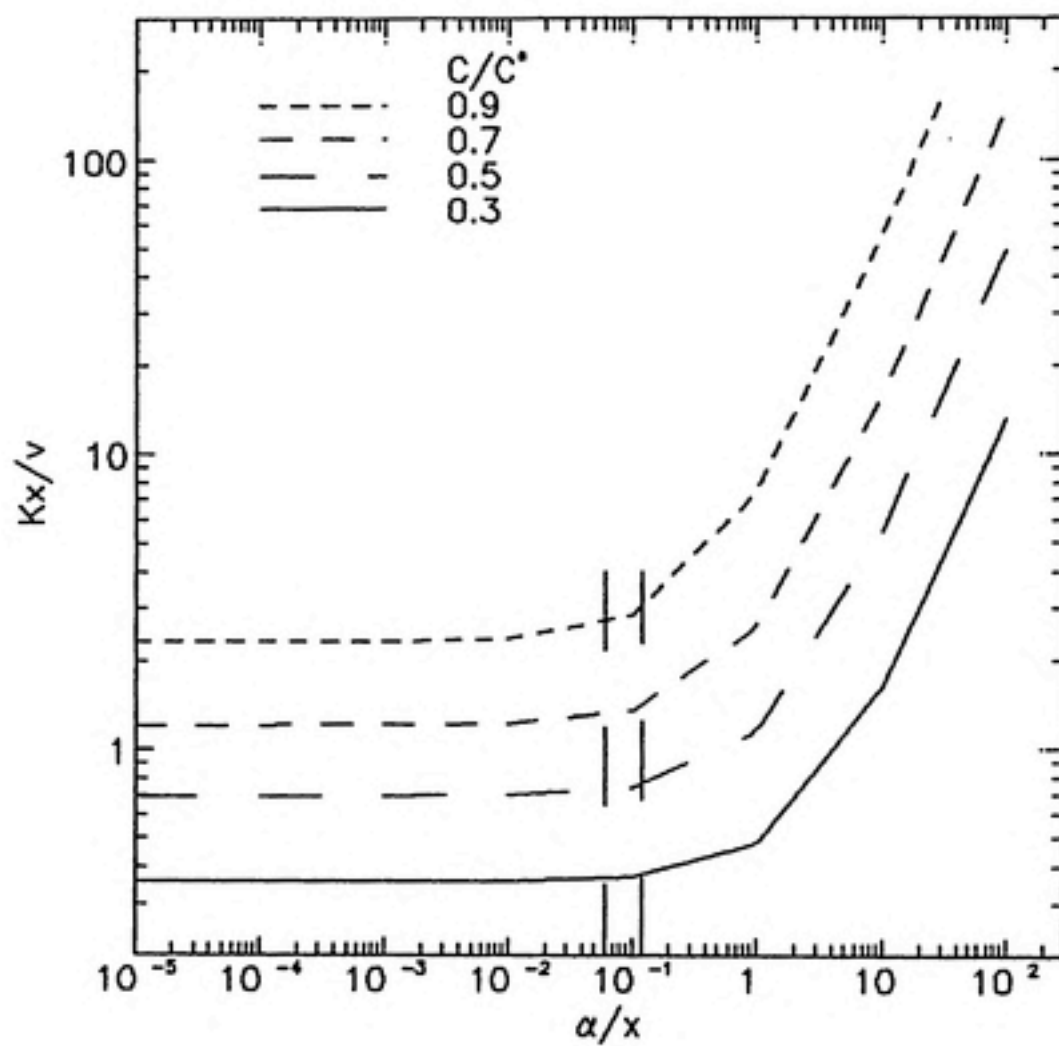


Figure 4-6. Sensitivity of Mass Transfer Coefficient to Dispersivity

4.2 Mass Transfer Experiments

Introduction

The data from the column experiments was analyzed to determine qualitative and quantitative information about NAPL-aqueous phase mass transfer in porous media. Data was collected for a wide range of NAPL- aqueous saturations and aqueous phase velocities typically observed in the field. The data was correlated using dimensionless groups to incorporate the effect of the physical media and NAPL saturations on mass transfer. The results were then interpreted in light of the NAPL- aqueous phase local equilibrium assumptions typically made in the development of groundwater contaminant fate and transport models.

Experimental Measurements and Sensitivity Analysis

Based on the analytical solution to the multiphase equations developed in Section 2-1, the NAPL-aqueous phase mass transfer coefficient can be described by Equation 2-33 as

$$K = \frac{\left[v_x - \frac{2D_x}{r} \ln \left(1 - \frac{C(r)}{C^*} \right) \right]^2 - v_x^2}{4D_x} \quad (4-4)$$

The following assumptions are made in the development of the system equations and thus apply to the analytical solution for K :

1. Steady-state NAPL aqueous dissolution
2. One-dimensional aqueous phase flow
3. No sorption of the NAPL onto the porous media
4. A single component NAPL
5. An immobile, uniformly distributed NAPL phase
6. No vapor phase present

7. No chemical or biological reactions

The experimental procedure was designed to conform to the above assumptions, thus allowing the calculation of mass transfer coefficients from Equation 4-4.

Under steady-state conditions, the aqueous phase concentration at every location x along the column is constant and independent of time. In order to achieve steady-state dissolution within the experimental column, at least one bed volume of deionized water was allowed to pass through the column before effluent samples were taken. Steady-state was verified in that concentrations of samples taken consecutively over a period of 0.05 to 1 hour at a given velocity did not vary significantly. Glass beads were used as the porous media in order to prevent sorption of the NAPL onto the media. The beads were washed with nitric acid and acetone to remove any organic material associated with the beads. The absence of a vapor phase was achieved in the column by filling the porous media with deionized water upflow, thereby allowing trapped air to escape. The media was also stirred when the NAPL was added to allow further removal of air and to assure a uniformly distributed NAPL. The column was flushed with water at a relatively high rate after NAPL was added to the media to assure that the NAPL was immobile at each sampling velocity. Biodegradation was not a concern in these experiments since the experimental runs lasted a maximum of four hours.

The experimentally measured parameters used in estimating K were interstitial velocity, column length, hydrodynamic dispersion, effluent concentration, and the NAPL-aqueous solubility. The error in estimating K is a function of the experimental error in measuring these parameters. Analyses were performed to determine the sensitivity of K to these parameters.

NAPL Saturation

Interstitial velocity is defined as

$$v_x = \frac{Q}{A\epsilon_a}$$

where Q is volumetric flow rate, A is cross-sectional area of flow, and ϵ_a is the fraction of volume occupied by the aqueous phase. Since $\epsilon_a = n(1 - S_n)$, the interstitial velocity for each experiment was calculated as

$$v_x = \frac{Q}{An(1 - S_n)} \quad (4-5)$$

The NAPL residual saturation was measured using a mass-balance technique. At the end of each experimental run, the remaining NAPL was extracted from the packed bed with a solvent and analyzed for NAPL using UV-spec. The NAPL lost from the column during the experimental runs was estimated based on the concentration and volume of the effluent collected during the runs. Based on the analytical method and allowing for solvent and NAPL volatilization losses, it is estimated that the error in measuring residual saturation is less than 0.5 percent. Mass transfer is a function of residual saturation, S_n , since the interfacial area for mass transfer is a function of S_n . Therefore, the experimental error in S_n will lead to an error in K . The sensitivity of K to S_n due to interfacial area is not known because there is no available mathematical description of interfacial area as a function of S_n . Based on 4-4, interstitial velocity is also a function of S_n and therefore, an error in S_n will produce an error in K . This error can be quantified since the relationship between S_n and v_x is known (4-5). Figure 4-7 shows the sensitivity of the mass transfer coefficient expressed as the Sherwood number to saturation for a constant volumetric flow rate of 16 ml/hour and $C/C^* = 0.76$. This figure shows that a 0.5 percent change in residual saturation will produce a change in K equal to 0.02 1/d.

During the course of one experimental run, the column was sampled at several velocities, each velocity producing one data point. All of the data points produced from a single run were assumed to represent the same residual saturation. Theoretically, the

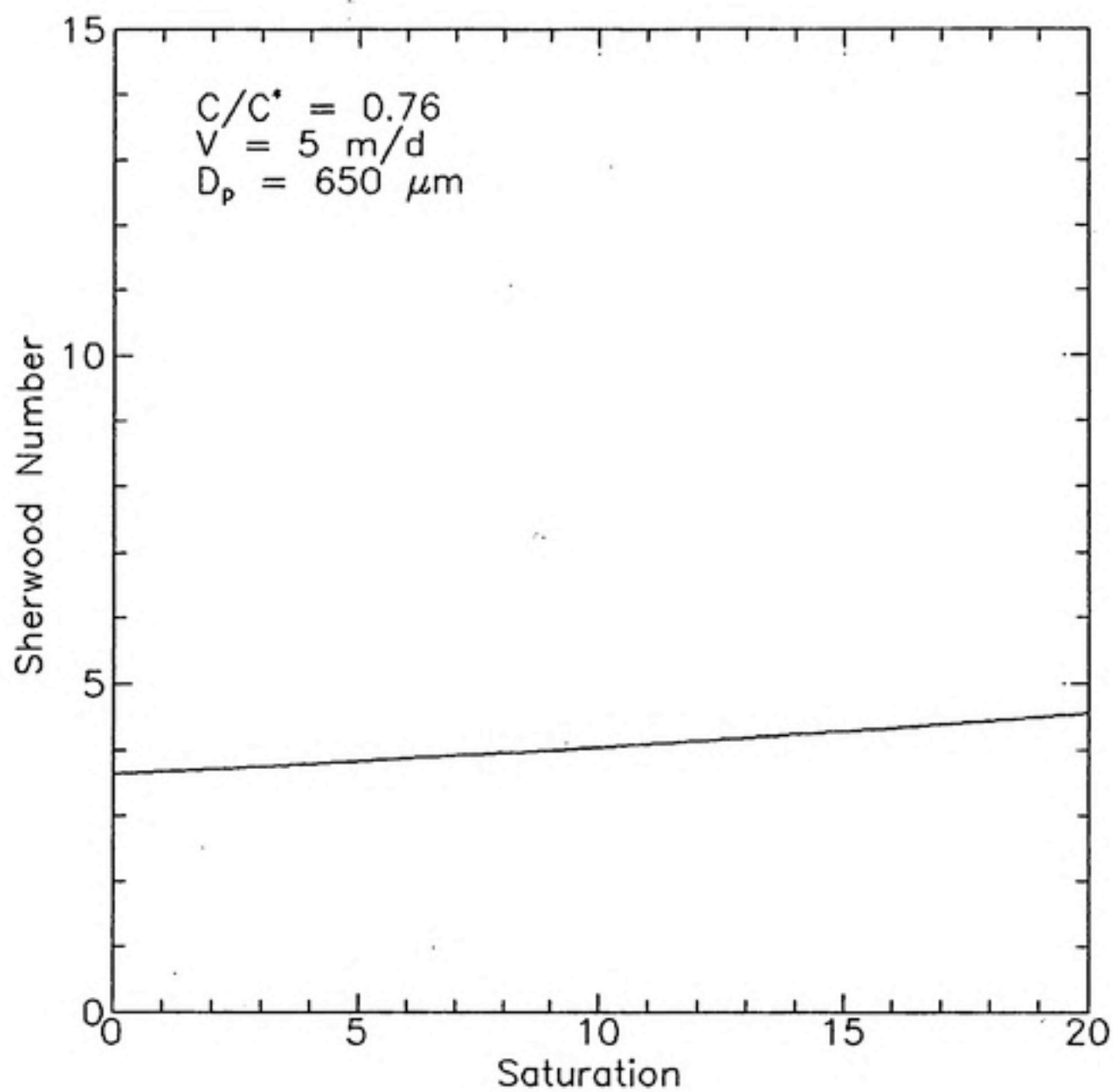


Figure 4-7. Sensitivity of Mass Transfer Coefficient to Changes in Interstitial Velocity due to Changes in Residual Saturation

NAPL residual saturation changed continuously during each experiment as NAPL dissolution occurred. The amount of mass lost to dissolution is significantly affected by the total volume of aqueous phase that flows through the column during a run. Therefore, the total volume of aqueous phase used in an experiment was controlled to limit the change in residual saturation during the run to less than 10 percent. This was accomplished by taking small samples (approximately 1 ml) and by minimizing the bed volumes passed through the column between sampling and velocity changes. For runs with low residual saturations (less than 5 percent), only one sample was taken for each velocity. Data were discarded for column runs in which more than 10 percent of the original mass was lost.

Effluent Concentration Measurements

For experiments with NAPL residual saturation greater than 5 percent, effluent concentrations were calculated as the average of three samples. Scatter in the analytically determined effluent concentrations varied from run to run. The 95 percent confidence intervals for effluent concentrations were calculated for the best and worst cases of scatter and are shown in Figure 4 – 8. For the case of greatest scatter among effluent concentrations, the outer limits of the intervals are on the average within 5 percent of the mean concentration. Figure 4 – 9 shows the sensitivity of the mass transfer coefficient to the percent error in concentration for several values of C/C^* . The mass transfer coefficient is expressed in dimensionless form. Mass transfer is insensitive to changes in effluent concentration for C/C^* less than 0.7. As C/C^* increases, mass transfer becomes increasingly sensitive. It should be noted that most of the data was collected for C/C^* in the range of 0.7, thereby minimizing error in the estimate of K .

Hydrodynamic Dispersion

The hydrodynamic dispersion was calculated using an experimentally measured dispersivity (Section 4 – 1), a theoretically estimated molecular diffusion coefficient (Section 4 – 1), and the interstitial velocity. As discussed in Section 4 – 1, mass transfer is insensitive to hydrodynamic dispersion within the range of the experimental parameters.

In order to estimate K , the column effluent concentration must be lower than solubility. It is evident from Equation 4 – 4 that as the effluent concentration approaches the aqueous solubility limit, the error in estimating the mass transfer coefficient increases. The effluent concentration is a function of the mass transfer and the length of the column, x . Trial and error experiments using column lengths ranging from 6.0 cm to 0.5 cm were performed to determine the ideal column length for the velocity and NAPL saturation range of interest. It was determined that a length of 1 cm produced effluent concentra-

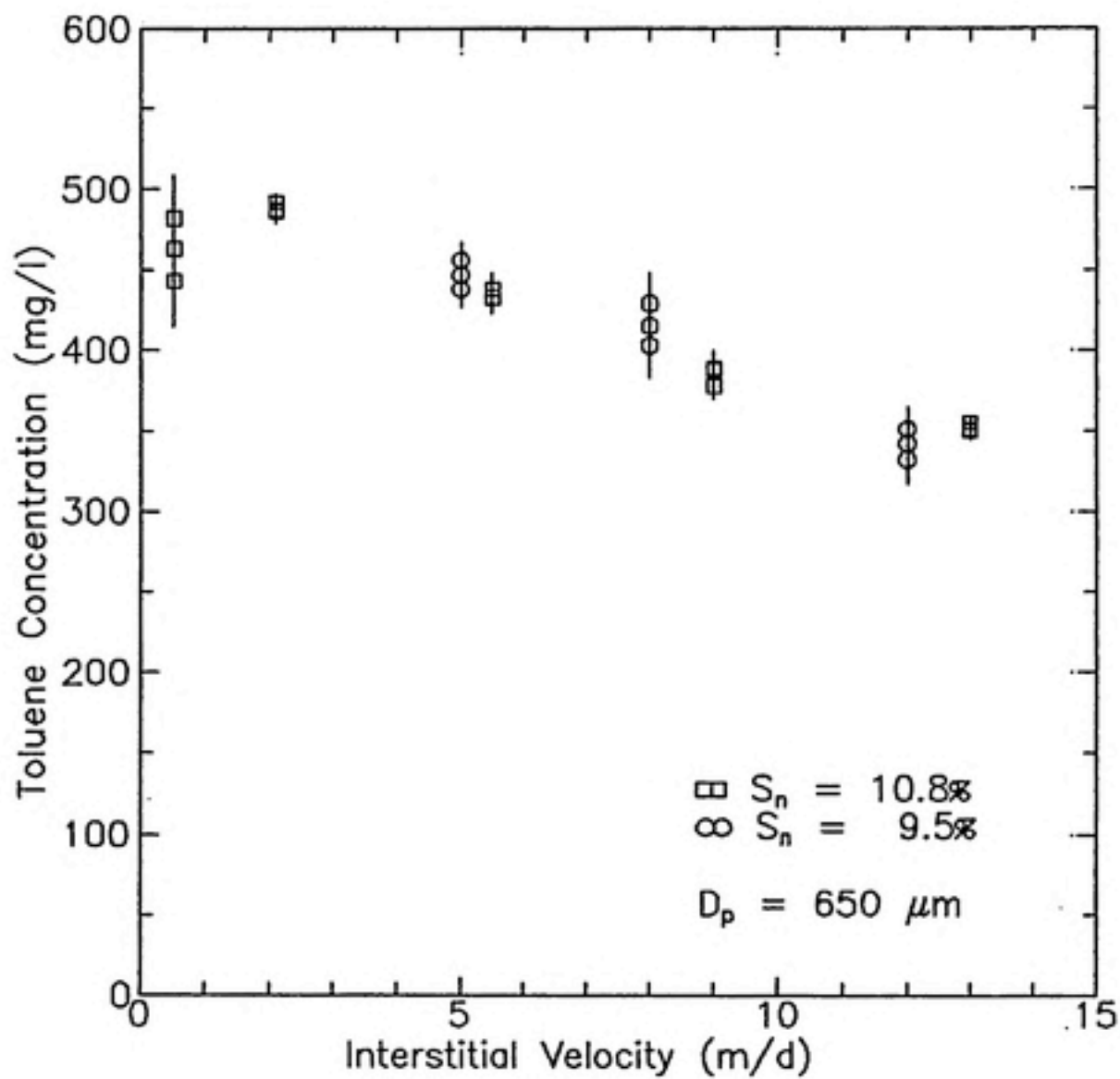


Figure 4-8. 95 Percent Confidence Intervals for Effluent Concentration Measurements

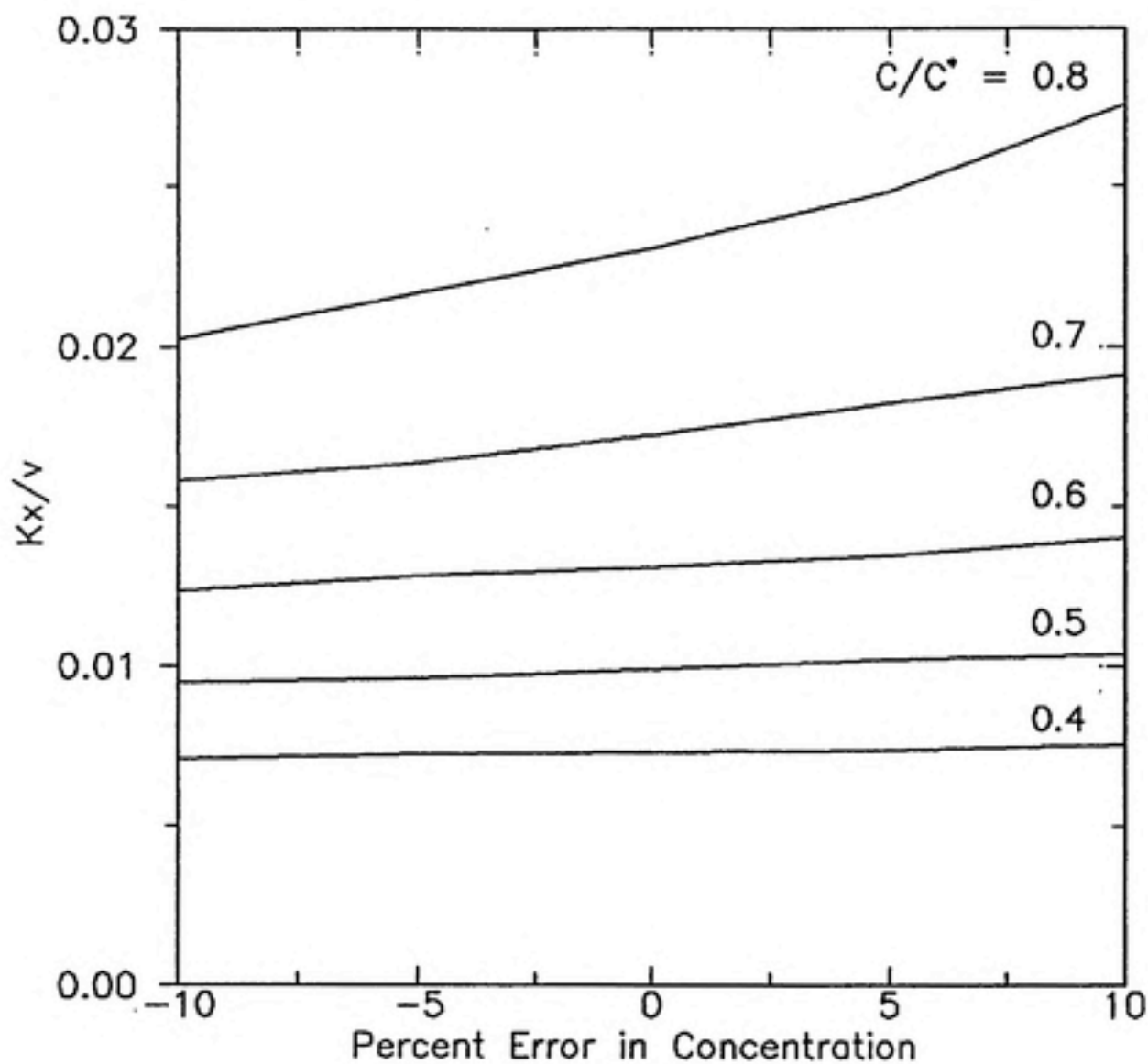


Figure 4-9. Sensitivity of Mass Transfer to Percent Error in Effluent Concentration

tions less than solubility for the range of velocities and residual saturations used in this study. The column length was measured in millimeters for each experimental run. In order to minimize the error in K , all data points within two percent of solubility were discarded.

Experimental Results

Twenty-five column experiments were performed for two media sizes and a wide range of NAPL residual saturations and velocities. The experiments yielded 103 data points representing effluent concentrations less than 98 percent of the aqueous phase solubility for toluene. For the 650- μm media, residual saturations ranging from 3.9 percent to 12.3 percent were obtained. Residual saturations in the range of 4.3 percent to 21 percent were obtained for the 400- μm media. Residual saturations in this range have been reported by other researchers (Hunt et al., 1988).

One of the most fundamental results obtained from the column experiments is the relationship between NAPL-aqueous phase mass transfer and aqueous phase velocity. Figures 4-10 and 4-11 present mass transfer coefficient versus Reynolds number for nine independent experimental runs. The Reynolds number is analogous to velocity in this case since the data shown in each figure is from systems with the same molecular diffusion and characteristic length. Figure 4-10 shows data collected from 650- μm media at four different NAPL saturations. Each curve represents one column run at a constant NAPL saturation. Note that although each run was sampled at the same volumetric flow rate, the interstitial velocities vary slightly due to the difference in residual saturation. For the same flow rate, interstitial velocity is higher at a greater residual saturation. Mass transfer coefficients in the range of 100 1/d to 2000 1/d were obtained for velocities on the order of 0.5 to 13 m/d. The data for each run indicates that mass transfer increases as a function of velocity. At low velocities, mass transfer is more sensitive to velocity and the slope of the curve is steep. At higher velocities, mass transfer is less sensitive to velocity as indicated by the relatively flat portion of the curve. Figure 4-11 shows data collected from

400- μm media at five residual saturations. This data indicates a trend in mass transfer as a function of velocity similar to the 650- μm data. The slope of the curves increase with increasing NAPL saturation indicating that the sensitivity of mass transfer to velocity increases with increasing S_n . Note that the data sets for 13.3 percent and 21 percent are incomplete since at the intermediate velocities, the effluent concentrations were within 2 percent of solubility and were discarded. The data is shown in Figures 4 - 12 and 4 - 13 representing a log-log relationship between mass transfer and velocity.

Data representing a wider range of interstitial velocities is shown in Figure 4 - 14. This figure is a plot of effluent concentration normalized by the NAPL-aqueous solubility versus the interstitial velocity of the aqueous phase. The data was obtained from three independently performed experiments with similar residual saturations. The parabolic shaped curve represents a trade off between NAPL-aqueous contact time and mass transfer. At low velocities the effluent concentration is limited by the rate of mass transfer and at high velocities the concentration is limited by the residence time in the column. The continuity of the curves indicates that the experiments are repeatable and that consistent results can be obtained.

Mass transfer coefficients generated from these data are shown in Figure 4 - 15 as a function of velocity. The mass transfer-velocity trend is consistent with the data shown in Figures 4 - 10 and 4 - 11. Mass transfer is very sensitive to velocity in the range of 0.1 to 20 m/d and is relatively insensitive to velocity at velocities over 20 m/d.

The phenomena of increasing mass transfer with increasing velocity is also predicted by stagnant film theory that was developed in Section 2 - 2. This theory models mass transfer as a product of a mass transfer coefficient and a concentration gradient. The mass transfer coefficient is defined as molecular diffusivity over the thickness of a theoretical stagnant film located at the phase boundary. As the film thickness or diffusional length decreases, the model predicts that the rate of mass transfer increases. Film thickness is a function of the hydrodynamics of the system and can be characterized by the Reynolds

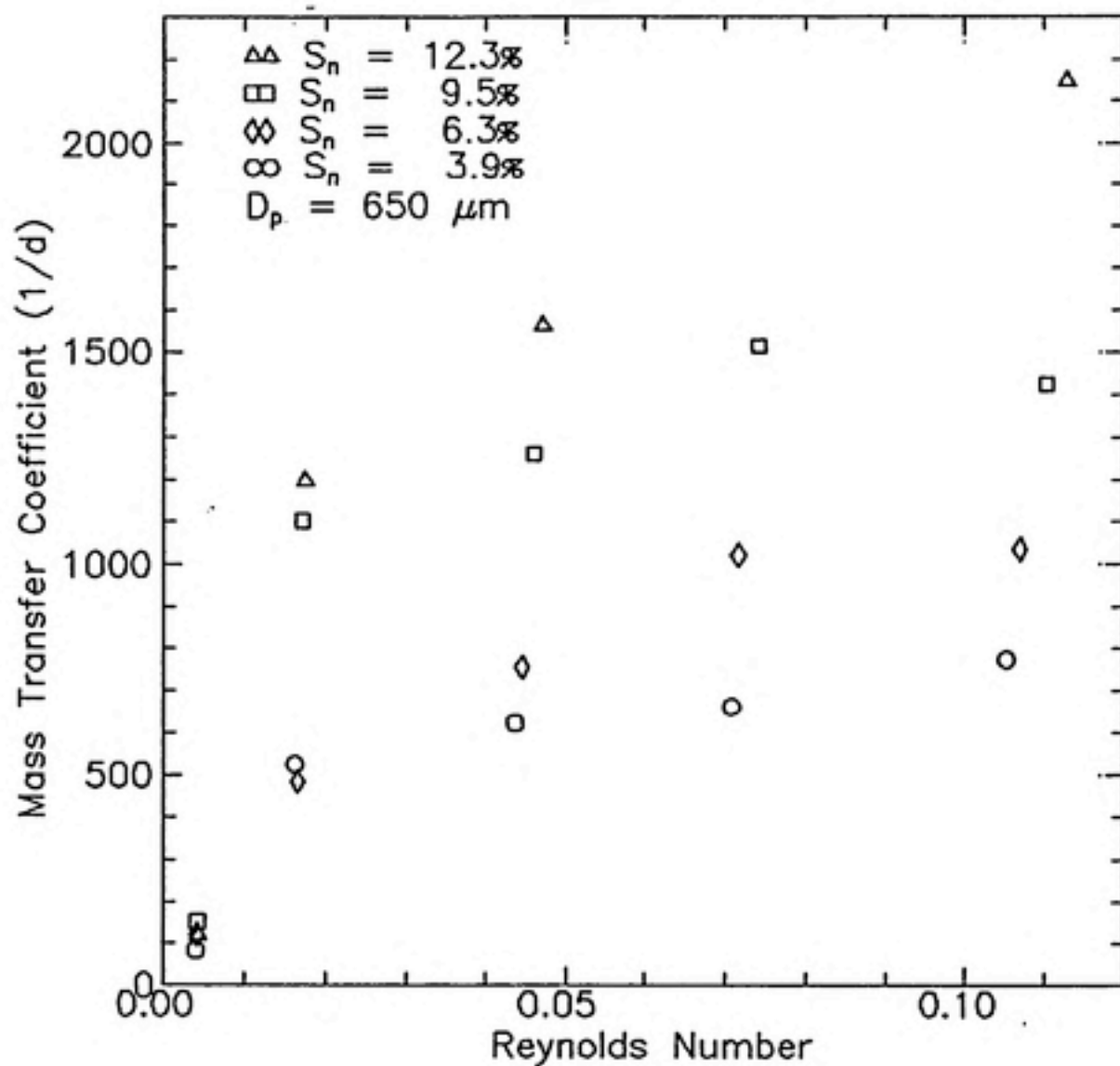


Figure 4-10. Mass Transfer Coefficient Versus Reynolds Number as a Function of NAPL Saturation for 650- μm Media

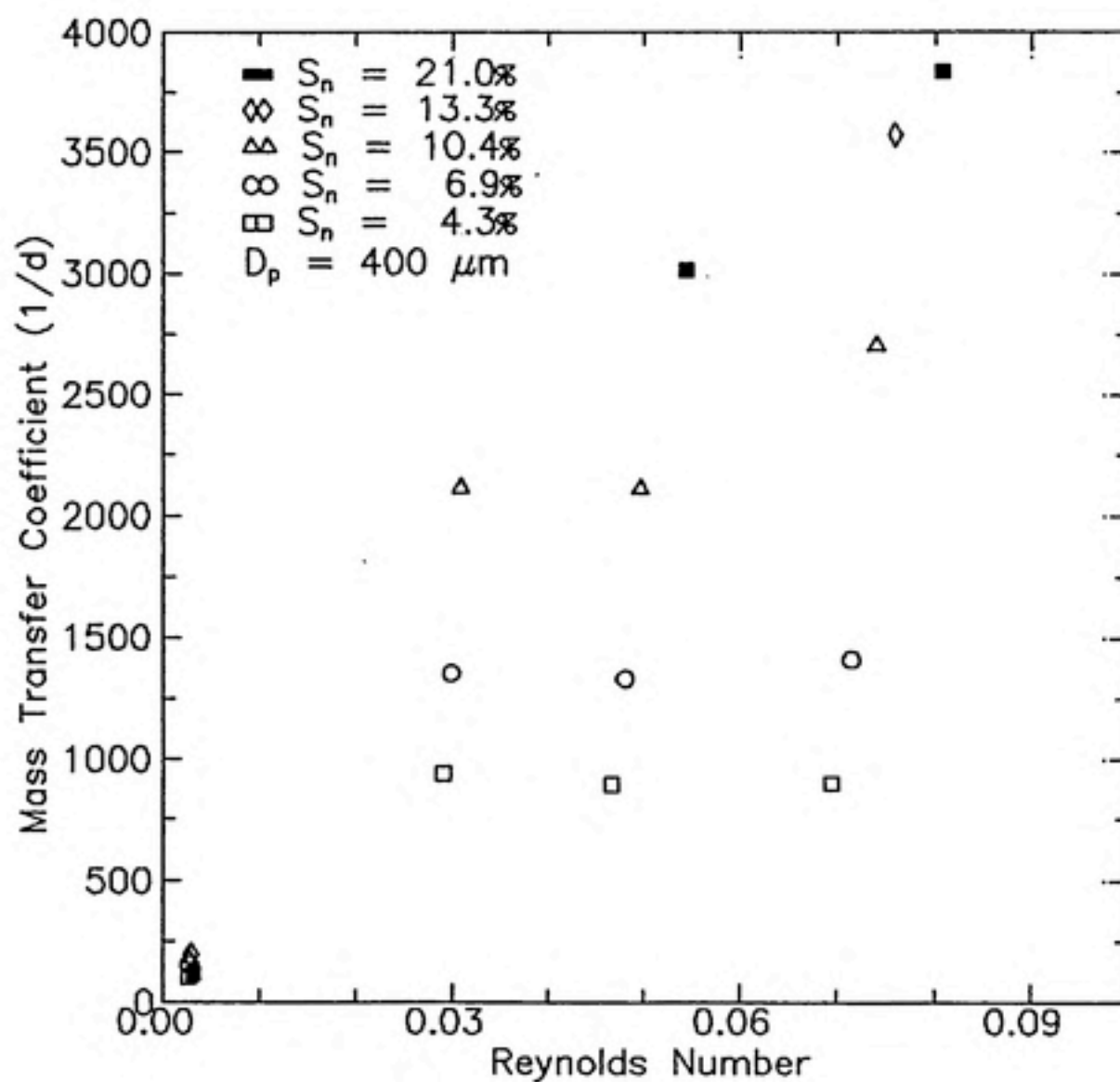


Figure 4-11. Mass Transfer Coefficient Versus Reynolds Number as a Function of NAPL Saturation for 400- μm Media

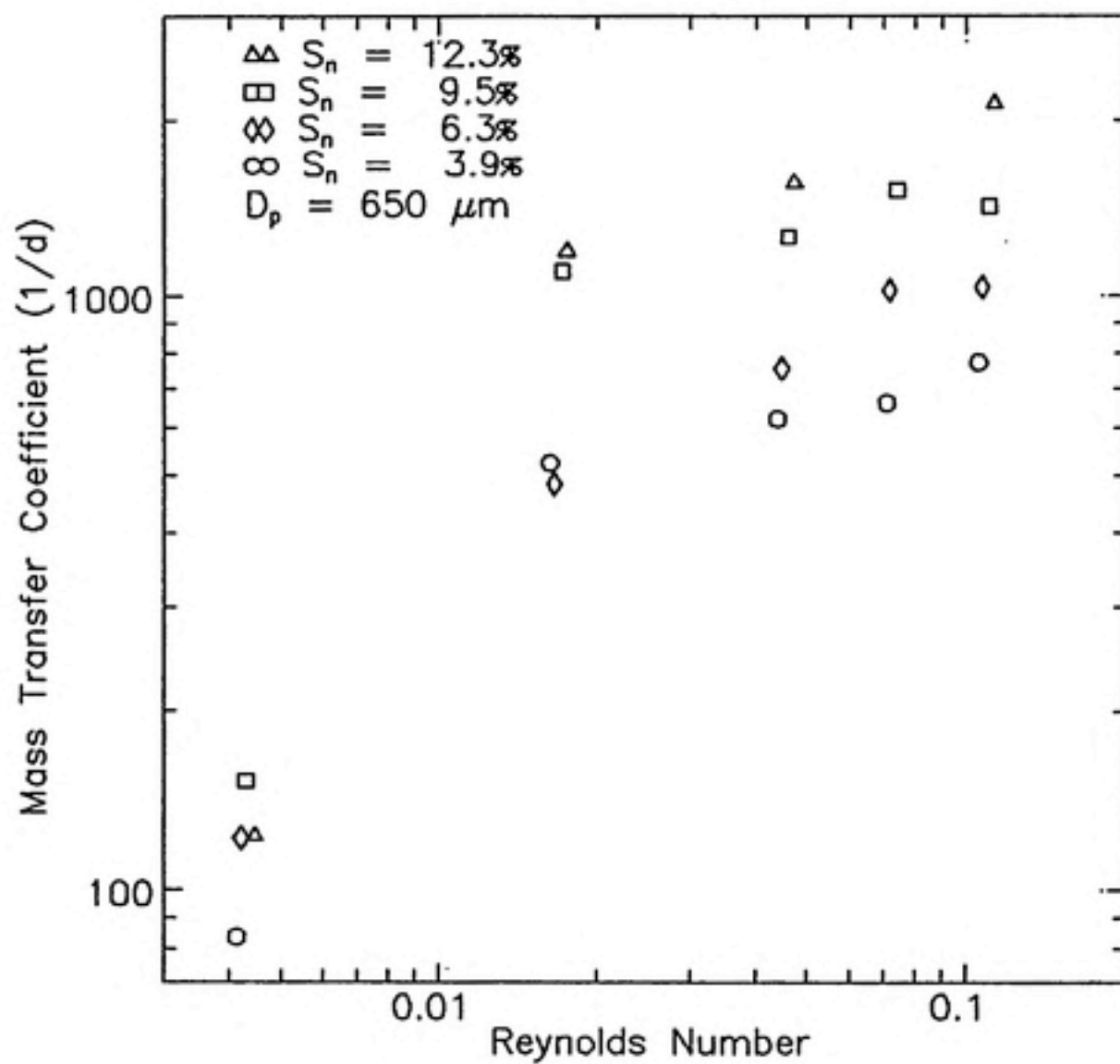


Figure 4-12. Log Mass Transfer Coefficient Versus Log Reynolds Number as a Function of NAPL Saturation for 650- μm Media

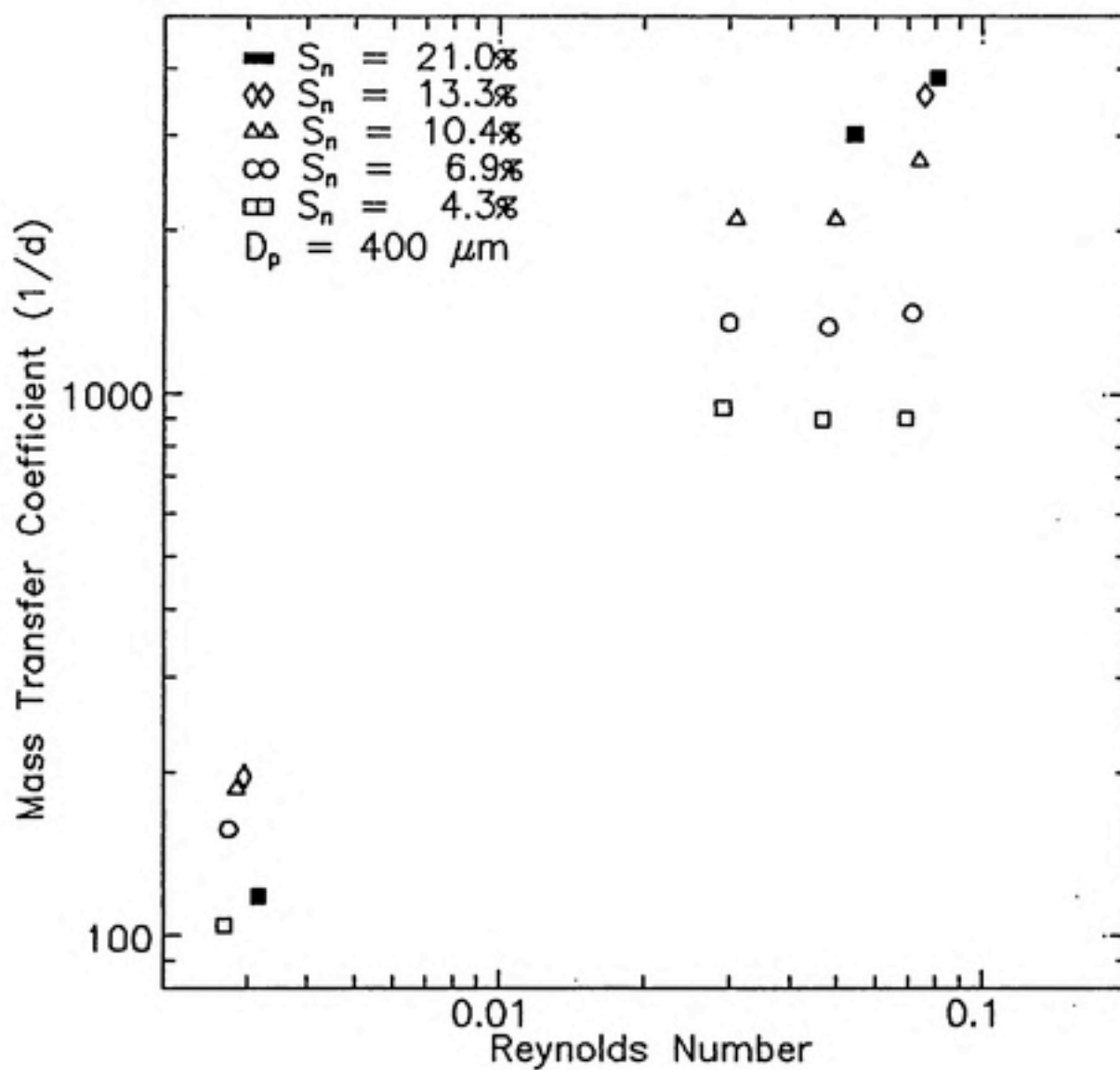


Figure 4-13. Log Mass Transfer Coefficient Versus Log Reynolds Number as a Function of NAPL Saturation for 400- μm Media

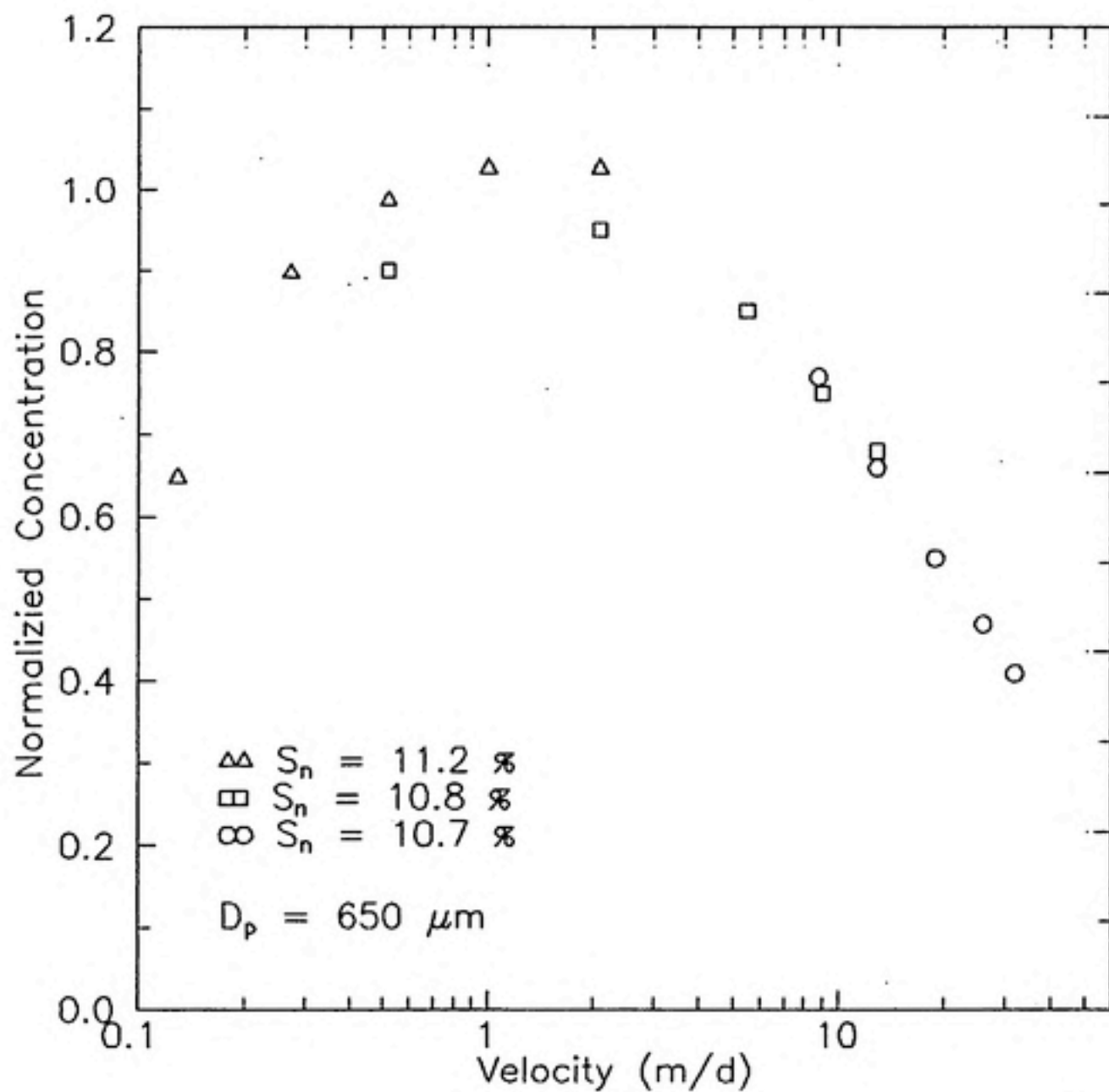


Figure 4-14. Normalized Effluent Concentration as a Function of Interstitial Velocity for 650- μm Media

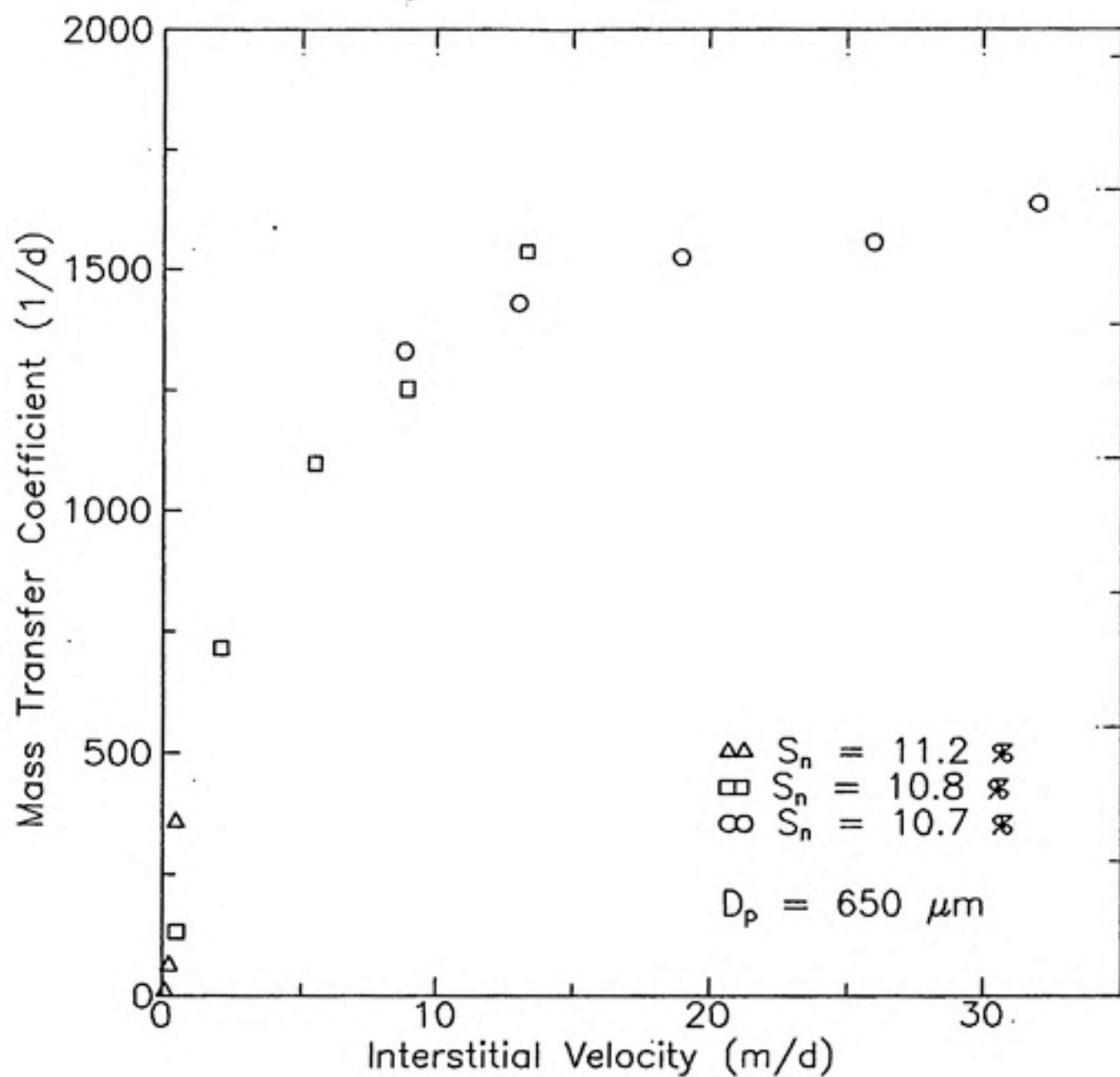


Figure 4-15. Mass Transfer Coefficient as a Function of Interstitial Velocity for 650- μm Media

number; as Reynolds number increases, the film thickness decreases. In reality however, a velocity profile exists at the phase boundary (Bowman, 1961).

Figures 4 - 10 and 4 - 11 show a qualitative relationship between mass transfer and percent NAPL saturation. The results from the experiments using both 650- μm and 400- μm media sizes consistently indicate that systems with a greater percentages of residual saturation have higher mass transfer rates. This phenomenon may indicate that a larger NAPL-aqueous phase interfacial area is present at higher residual saturations thus increasing the rate of mass transfer.

The relationship between mass transfer and percent NAPL saturation is also shown in Figures 4 - 16 and 4 - 17 for flow through 650- μm and 400- μm media, respectively. Each curve represents an average aqueous phase velocity. For NAPL saturations less than approximately 10 percent, the data clearly indicates that mass transfer increases as a function of residual saturation. Above 10 percent the effect of saturation on the mass transfer coefficient is less apparent; in some cases the mass transfer appears to level off or decrease. As described in Section 2 - 2, interfacial surface area will increase with increasing NAPL saturation to a maximum level and will then decrease with increasing NAPL saturation until the interphase area is zero at 100 percent NAPL saturation. Thus, interfacial area plotted against percent NAPL saturation will produce a parabolic shaped curve. However, due to the lack of data at high saturations it is not clear if mass transfer or interfacial area is increasing, decreasing or leveling off. In other words, it is not clear where the system is located along the interfacial area versus percent NAPL saturation curve. The data does indicate however, that the sensitivity of mass transfer to residual saturation decreases with increasing percent NAPL saturation at low saturations. Data at higher residual saturations is required to confidently describe mass transfer as a function of residual saturation at higher saturations. It should be noted that interfacial surface area is largely dependent on the pore geometry and NAPL shape and can not be characterized from the results of these experiments.

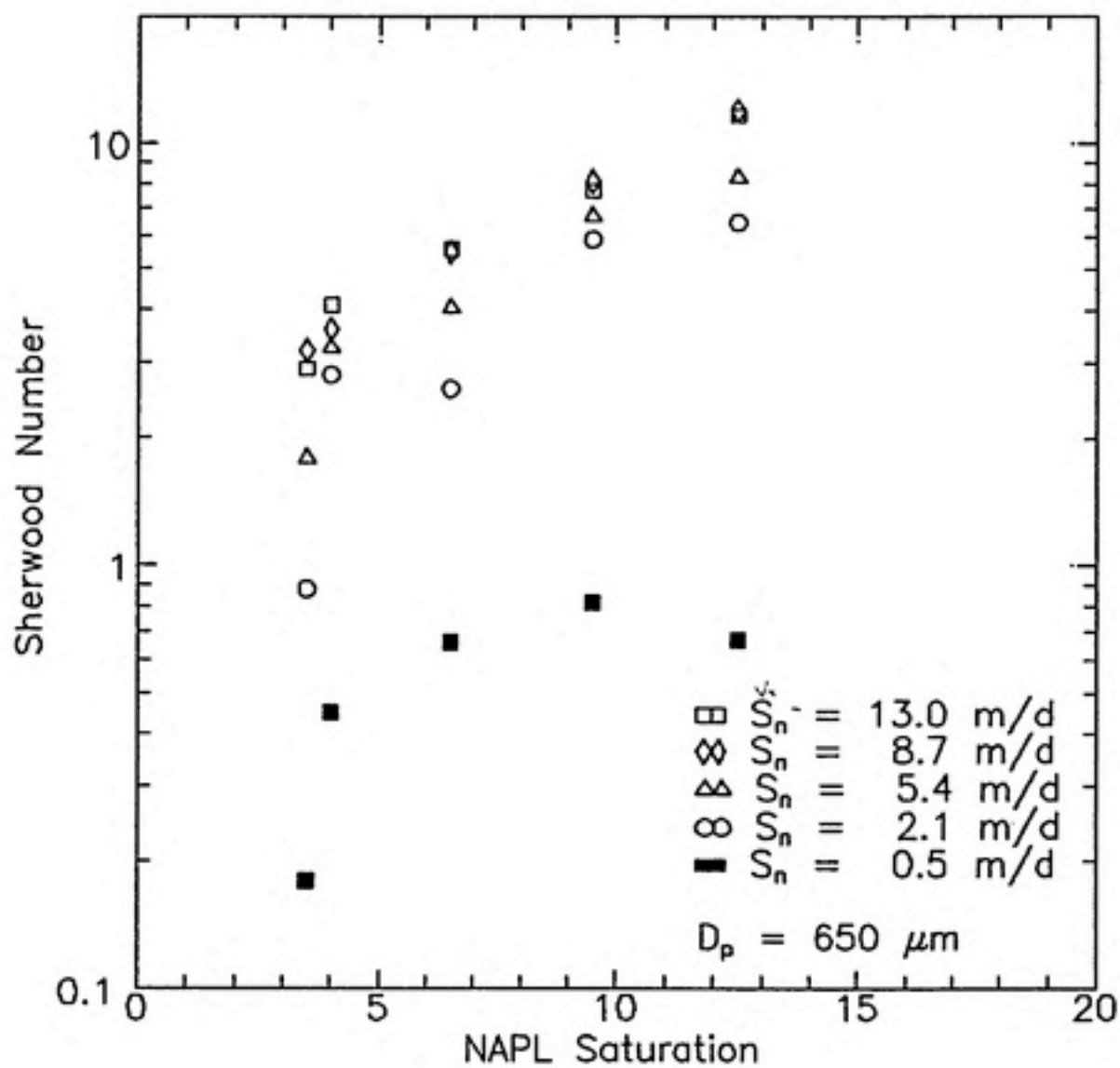


Figure 4-16. Mass Transfer Coefficient as a Function of NAPL Saturation for a Constant Velocity for 650- μm Media

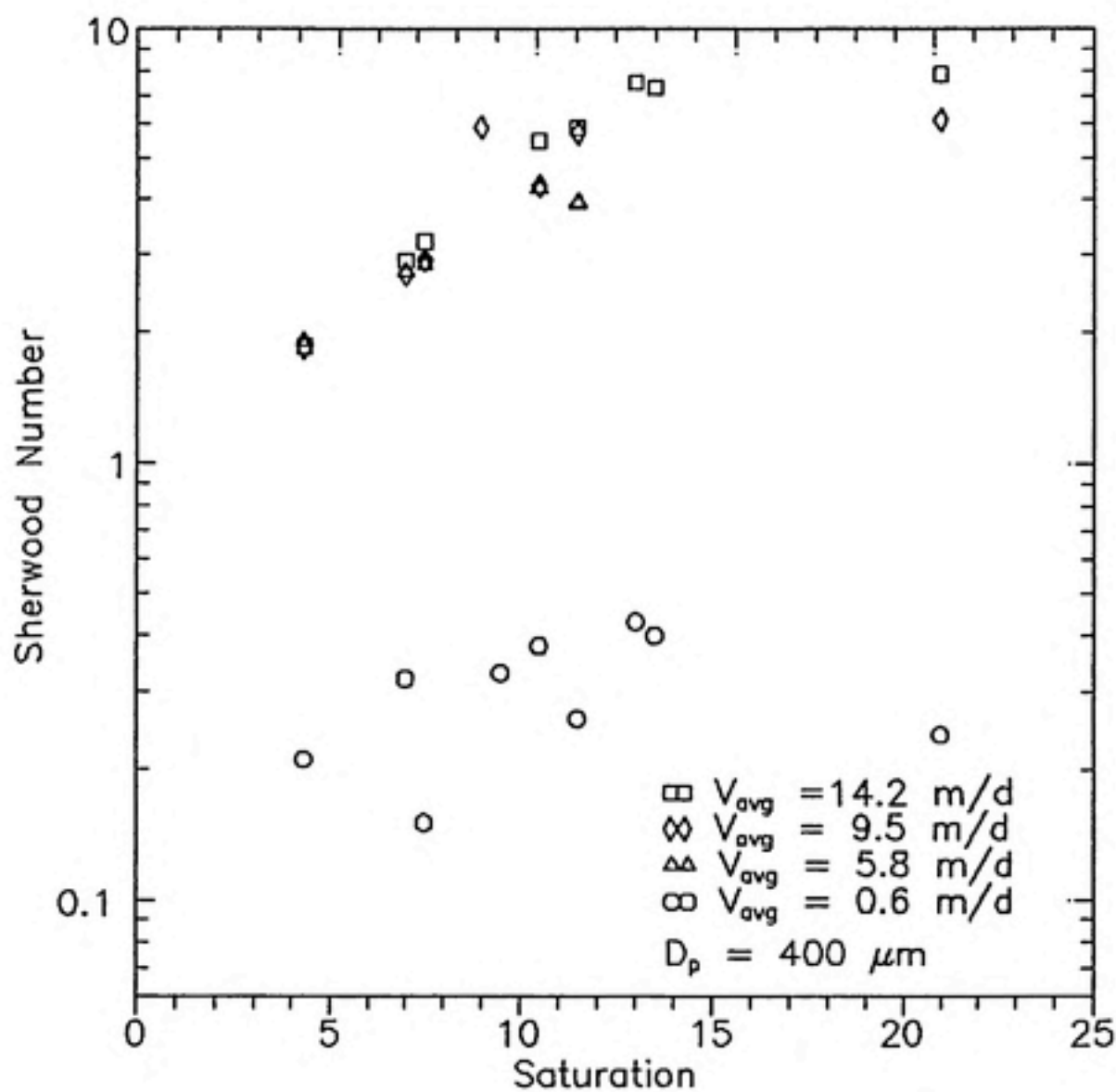


Figure 4-17. Mass Transfer Coefficient as a Function of NAPL Saturation for a Constant Velocity for 650- μm Media

In the previous section, only qualitative results based on mass transfer for a given media size were discussed. Based on the data from an experimental run, a model can be developed to quantitatively describe mass transfer as a function of velocity and percent residual saturation for a given media size. However, a more general model that is valid for any media or NAPL is sought. Dimensionless groups, such as those described in Section 2.2, can be used to formulate correlations between mass transfer and system parameters. The dimensional groups incorporate the influence of media and fluid properties (particle diameter, viscosity, molecular diffusivity) as well as flow characteristics (hydrodynamics). Since only one NAPL was used in these experiments, a correlation based on fluid properties can not be validated from the data. However, the data from both media sizes at different NAPL saturations can be compared and correlated.

Figure 4 - 18 and 4 - 19 are plots of the modified Sherwood number, Sh^* , developed in Section 2 - 2 versus Reynolds number, Re . Figure 4 - 18 shows four independent experimental runs from both media sizes at two similar residual saturations. The Sherwood number and Reynolds number represent mass transfer and velocity, respectively. The mean particle diameter of the media is used as the characteristic length, l , in the calculation of Sh^* and Re . This substitution is typically made for packed bed systems (Dwivedi et al., 1977). Theoretically, data collected at the same Reynolds number should produce the same Sherwood number, independent of media size, all other system parameters being equal. Therefore, the runs shown in Figures 4 - 18 and 4 - 19 with approximately the same NAPL saturation for the two media sizes should produce the same data, within experimental error. It appears that this is not the case for these runs. Figure 4 - 19 shows data from runs with smaller percentages of residual saturation. Again, the curves representing the same residual saturations appear to differ significantly. In all of the cases, the 650- μ m media produced higher Sherwood numbers at a given Reynolds number.

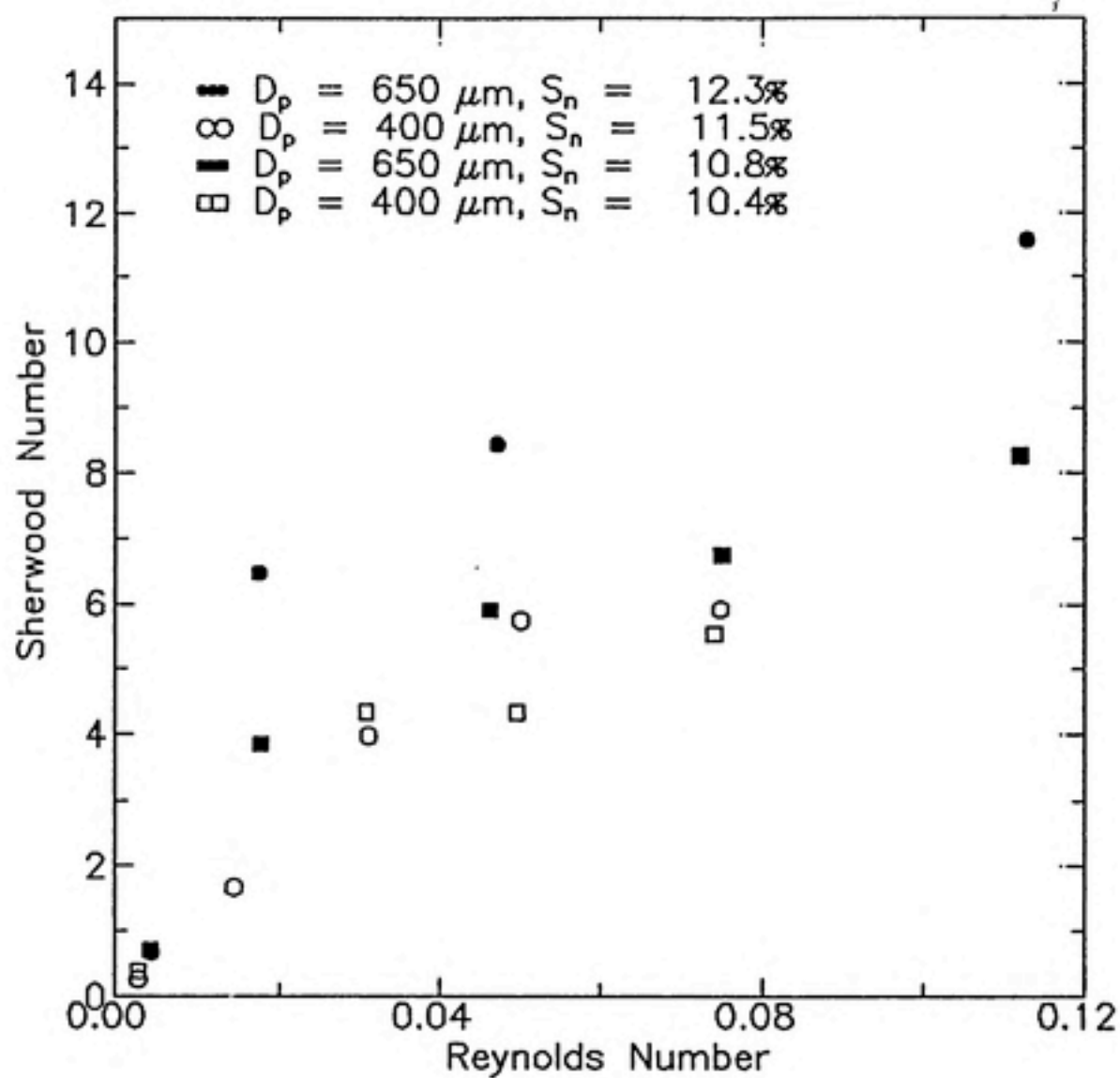


Figure 4-18. Sherwood Number as a Function of Reynolds Number for 650- μm and 400- μm Media at High Residual Saturations

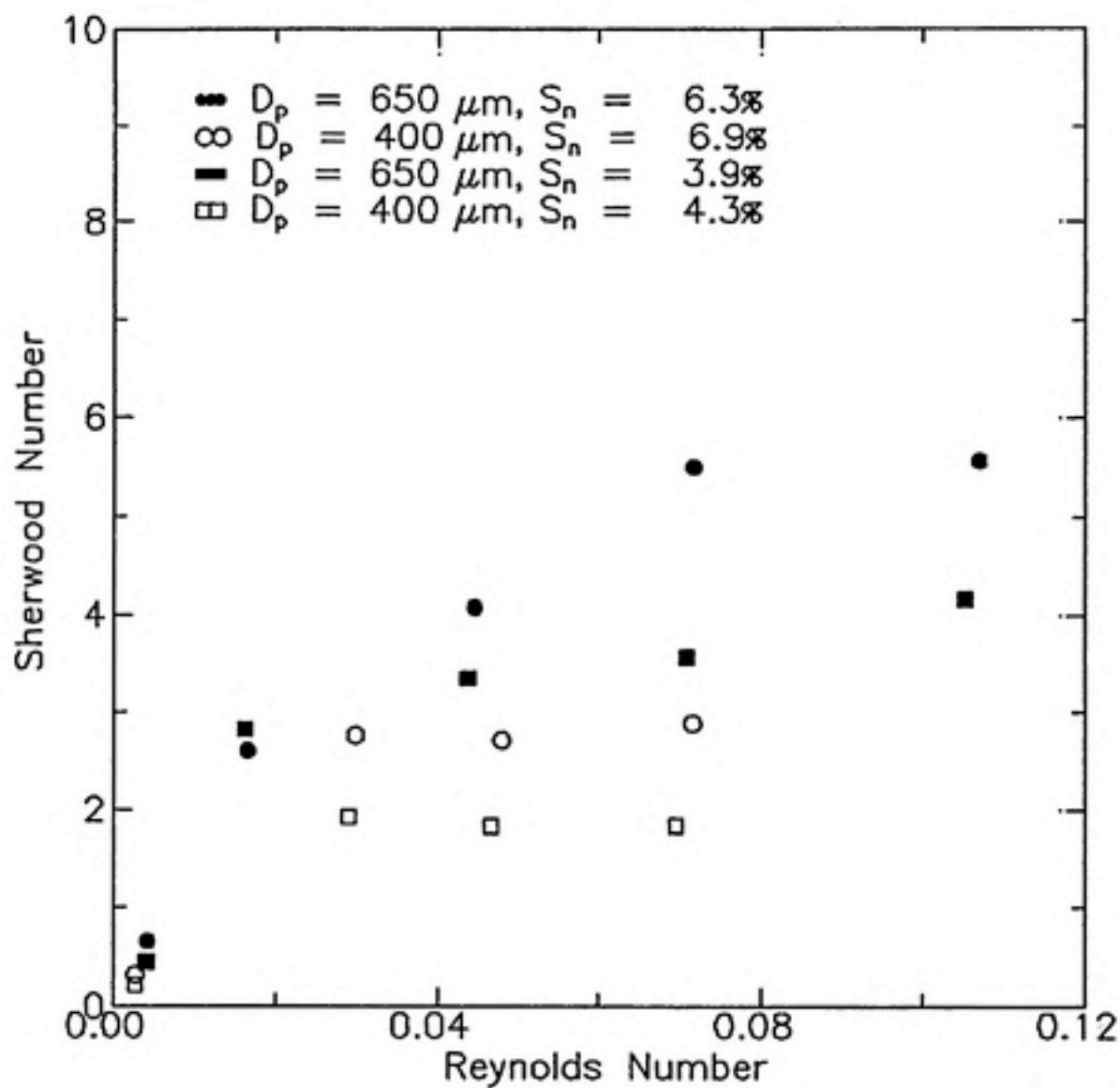


Figure 4-19. Sherwood Number as a Function of Reynolds Number for 650- μm and 400- μm Media at Low Residual Saturations

Some of the difference in Sherwood numbers versus Reynolds number for similar NAPL saturations can be explained by experimental error. Error in calculating the mass transfer coefficients and error in calculating residual saturation could contribute to this discrepancy. The lack of agreement between the curves could also suggest that the particle diameter is not a representative measure of characteristic length.

In order to compare all of the experimental data quantitatively, model fitting is employed. The object of model fitting is to obtain the simplest model that will fit the data well and that can be used for predictive purposes. Power functions that incorporate dimensionless groups have been used frequently to correlate experimental data from mass transfer studies (Dwivedi et al., 1977; Pfannkuch, 1984; Roberts et al., 1985). Table 2 - 1 lists several models that have been developed for a variety of mass transfer systems. It is evident from these models that the Sherwood number or dependent variable is often written in terms of Reynolds number and Schmidt number or independent variables. Since only one NAPL was used in these experiments, the Schmidt number is constant for all of the experimental data and is therefore not required in these correlations. However, since the specific surface area is not known in the NAPL-aqueous system, the percent saturation of each data point must be included in the correlation model. The following expression is used as a model to describe the data collected in this study

$$Sh^* = bRe^c S_n^d \quad (4-6)$$

where Sh^* is a modified Sherwood number, Re is the Reynolds number, S_n is the NAPL phase saturation, and b , c , and d are constants. A multiple regression analysis using the least squares method was used to fit this model to the entire data set. In addition, the model was fit separately to the 650- μm and 400- μm data. The results of the regression analysis are shown in Table 4 - 2.

For the entire data set, the model predicts that the Sherwood number varies with

Table 4-2. Parameter Estimation Results

Model	Data Set	Coefficient Estimate	Standard Error	Percent Standard Error	95% Confidence Interval
$Sh = bRe^c S_n^d$	All	b 3.91	0.61	16	2.26 - 5.57
		c 0.46	0.03	7	0.39 - 0.53
		d 0.72	0.04	6	0.57 - 0.88
$\log Sh = \log b + c \log Re + d \log S_n$	All	b 2.52	0.29	12	2.00 - 3.03
		c 0.36	0.01	3	0.33 - 0.39
		d 0.36	0.05	14	0.28 - 0.44
$Sh = bRe^c S_n^d$	400 μm	b 6.57	3.42	52	1.90 - 11.2
		c 0.64	0.08	13	0.47 - 0.80
		d 0.63	0.14	22	0.44 - 0.81
$Sh = bRe^c S_n^d$	650 μm	b 1.36	0.45	33	0.40 - 2.31
		c 0.37	0.03	8	0.31 - 0.43
		d 1.13	0.13	12	0.84 - 1.41

approximately the 0.46 power of the Reynolds number and with the 0.72 power of the NAPL saturation. Referring to Table 2 - 2, the exponent of the Reynolds number falls within the range of reported Mass transfer-velocity correlations for other systems. The model was also fit to data from each size media separately. As shown in Table 4 - 2, the models differ significantly from each other and from the overall model. For the 650- μm data, the model predicts that Sherwood number varies to the 0.37 power of the Reynolds number and to the 1.13 power of saturation. For the 400- μm media, the model predicts that the Sherwood number varies to the 0.64 power of the Reynolds number and to the 0.63 power of saturation. Figure 4 - 20 is a plot of the predicted models for typical values of Reynolds number and NAPL saturation.

Table 4 - 2 lists the standard error associated with each parameter estimate. The standard errors are calculated as a percent of the estimated parameter in order to determine which model fits the data best. The most important parameters for determining the fundamental relationships in the mass transfer process are c and d since these are related to Reynolds number and NAPL saturation. Overall, the data correlates well to these parameters as indicated by the low standard error and small confidence intervals. The case in which the model was fit to all of the data indicates the data fit Re and S_n equally well based on the error as a percent of the coefficient estimate. Overall the log transformation model fit the data with less error and correlated better to Re than to S_n . In both of the cases that the model was fit to data from one media size, the data correlated better to the Reynolds number than to the NAPL saturation.

It should be noted that the true mass transfer relationship for a single media size cannot be determined independently of a , the specific surface or interfacial area, since the mass transfer coefficient measured in the experiments is the lumped product of K_L and a . It is assumed in the development of the modified Sherwood number that a is directly related to the characteristic length of the system, or in this case the mean particle diameter of the media. The discrepancy between the predicted model for the 650- μm and 400- μm

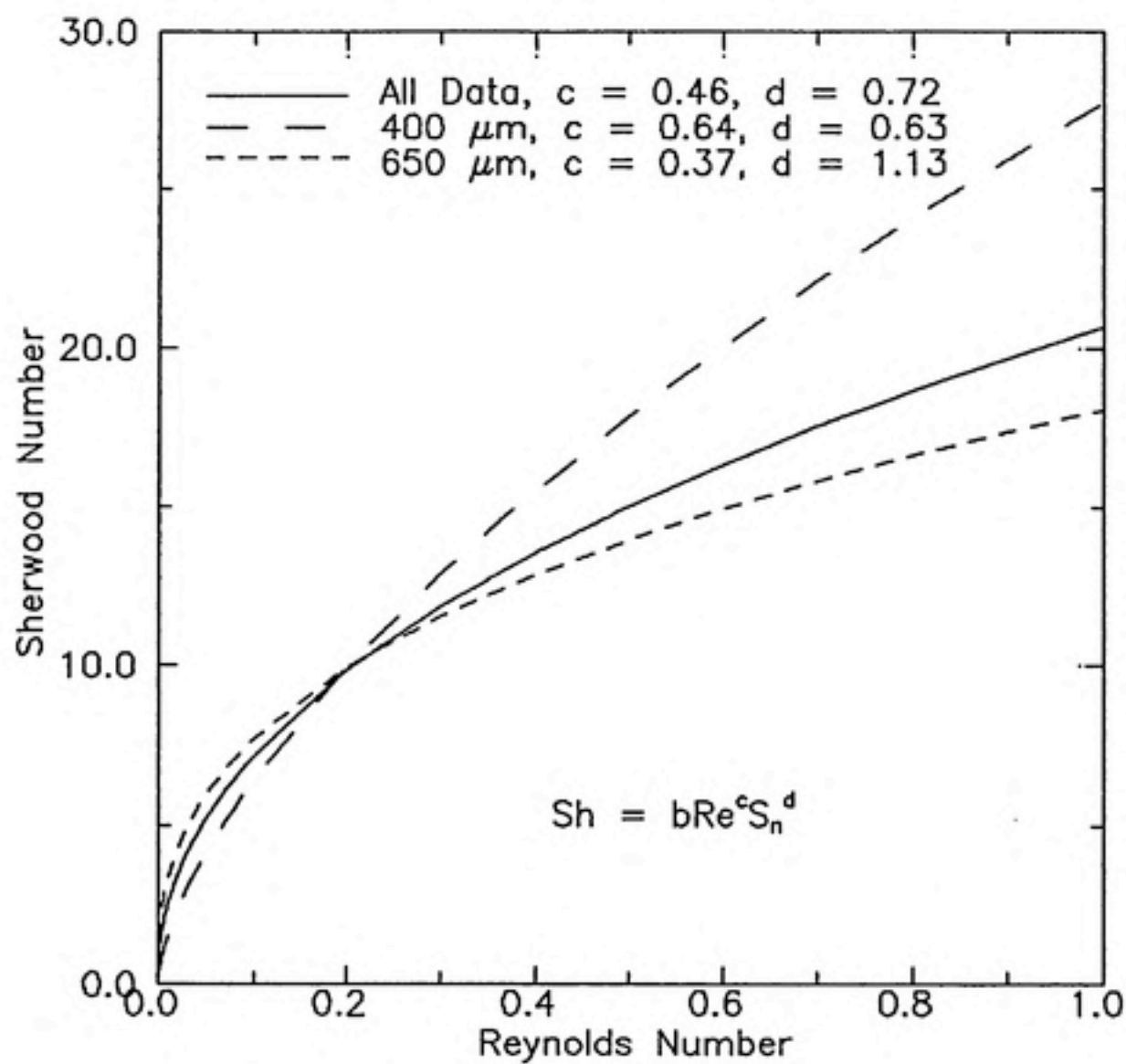


Figure 4-20. Best-Fit Mass Transfer Correlations for Selected Experimental Data

media could be explained if the characteristic length of the media is not a good pseudo parameter for NAPL-aqueous interfacial area. The characteristic length of the system may need to be modified by some shape factor in order to better describe interfacial area as a function of NAPL saturation. A similar technique was used by Roberts, et al. (1984) to correct for deviations from ideal spherical geometry in the study of external mass transfer rates of fixed bed adsorption.

A final factor that may explain the poor comparisons of correlations between the 650- μm and 400- μm media is related to the experimental procedure. After the media was contaminated with the NAPL, the column was flushed with deionized water at a high flow rate for approximately 30 minutes to assure that the NAPL was present at residual or immobile conditions. In the process of flushing the column it is suspected that a significant portion of NAPL was removed at the inlet side of the column creating a non-uniform NAPL distribution. This phenomenon would produce artificially low effluent concentrations and cause low estimates of mass transfer coefficients. It should be noted that the true mass of NAPL in the column runs are known since the measurement was made at the end of each experiment. However, the assumption of a uniformly distributed NAPL saturation may be violated. Initial estimates based on 30 minutes of flushing and an effluent concentration of 300 mg/l indicate that as much as 14 percent of NAPL may have been removed due to dissolution during the flushing period.

In order to test this hypothesis, two column runs were performed using a modified procedure. In lieu of flushing the column with deionized water, the column was flushed with a NAPL-saturated solution. Theoretically, only free NAPL would be removed from the column since NAPL-aqueous dissolution would not occur into a NAPL saturated solution. The results of the runs are shown in Figure 4 – 21. The normalized effluent concentration versus velocity are shown for both modified and unmodified runs. As expected, the modified runs produced relatively high effluent concentrations compared to those observed in previous runs. Figure 4 – 22 compares Sherwood number as a function of Reynolds

number for the runs using the modified experimental method to runs using the unmodified method with similar NAPL saturations. The data using the unmodified experimental method indicate that the actual mass transfer coefficients are higher than those calculated from the unmodified runs. This data makes sense if indeed a nonuniform distribution of NAPL was present for the unmodified runs. It should be noted that the results from runs using the unmodified experimental method produced conservative results with regard to the assumption of NAPL-aqueous equilibrium. However, violation of the assumption of uniformly distributed NAPL could significantly affect the mass transfer correlations.

4.3 Solubility Enhancement Experiments

Humic Acid

Background

Humic substances make up 50 to 75 percent of the dissolved organic carbon found in natural aquatic systems. These organic molecules are present in groundwaters at concentrations of 0.03 to 0.1 mg/l (Thurman, 1985). Studies have shown that at very low concentrations, humic material may influence the fate and transport of organic chemicals in the environment by enhancing the apparent solute aqueous-solubility (Wershaw et al., 1969; Hassett et al., 1979; Haas et al., 1985; Chiou et al., 1986). The mechanisms of interaction between humics and organic compounds are not well understood. It has been suggested by Chiou, et al. (1986) that a partition-like interaction of the solute with the microscopic environment of dissolved humic molecules may explain the solubility enhancement. Wershaw, et al. (1969) studied the effect of humics on the aqueous-solubility of DDT and concluded that humics influenced the organic in two ways: (1) the humic material interacted directly with the DDT through sorption, and (2) the humics increased the solvency of the DDT by decreasing the surface tension of the water.

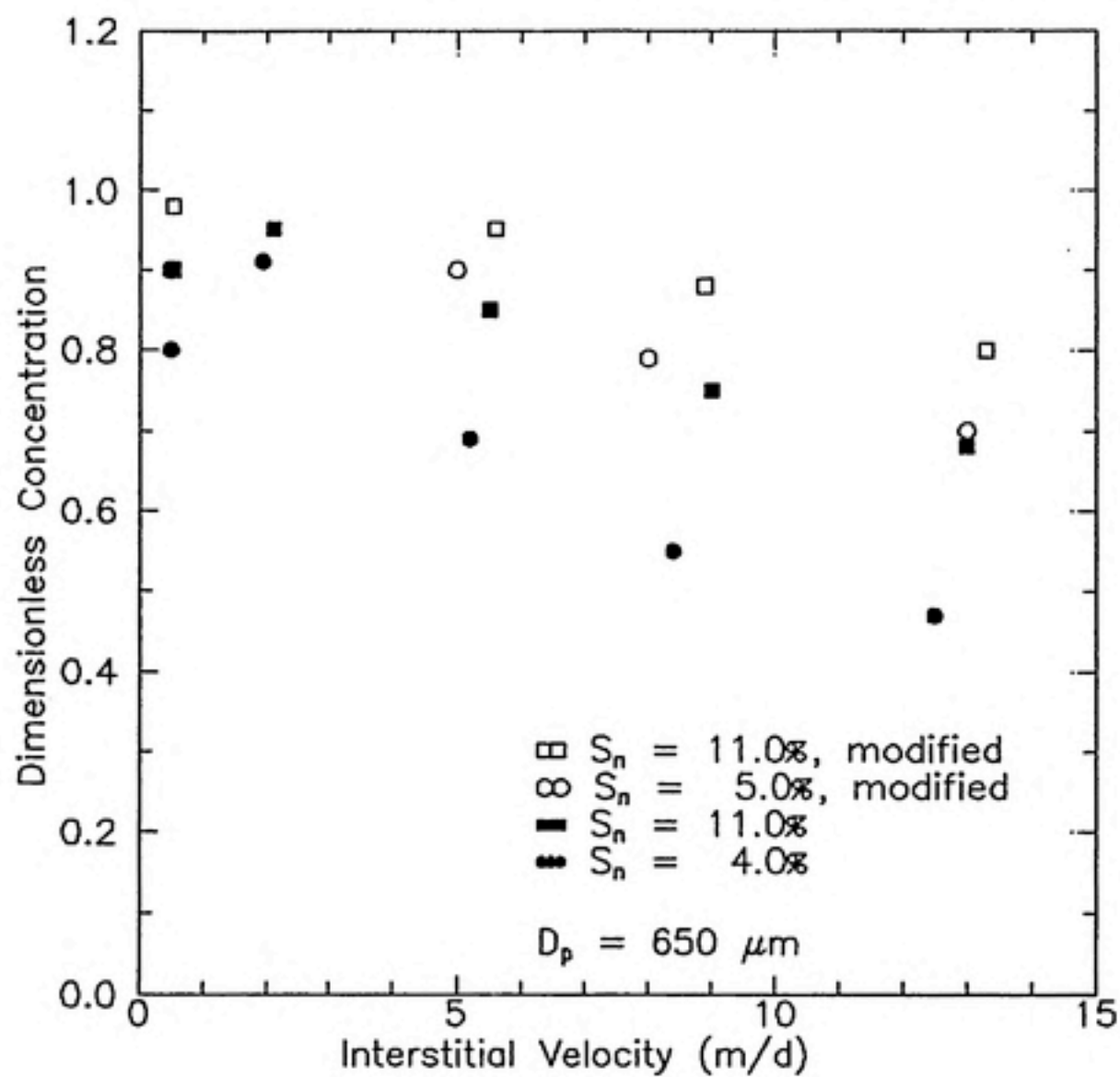


Figure 4-21. Dimensionless Effluent Concentration as a Function of Interstitial Velocity for Modified and Unmodified Experiments

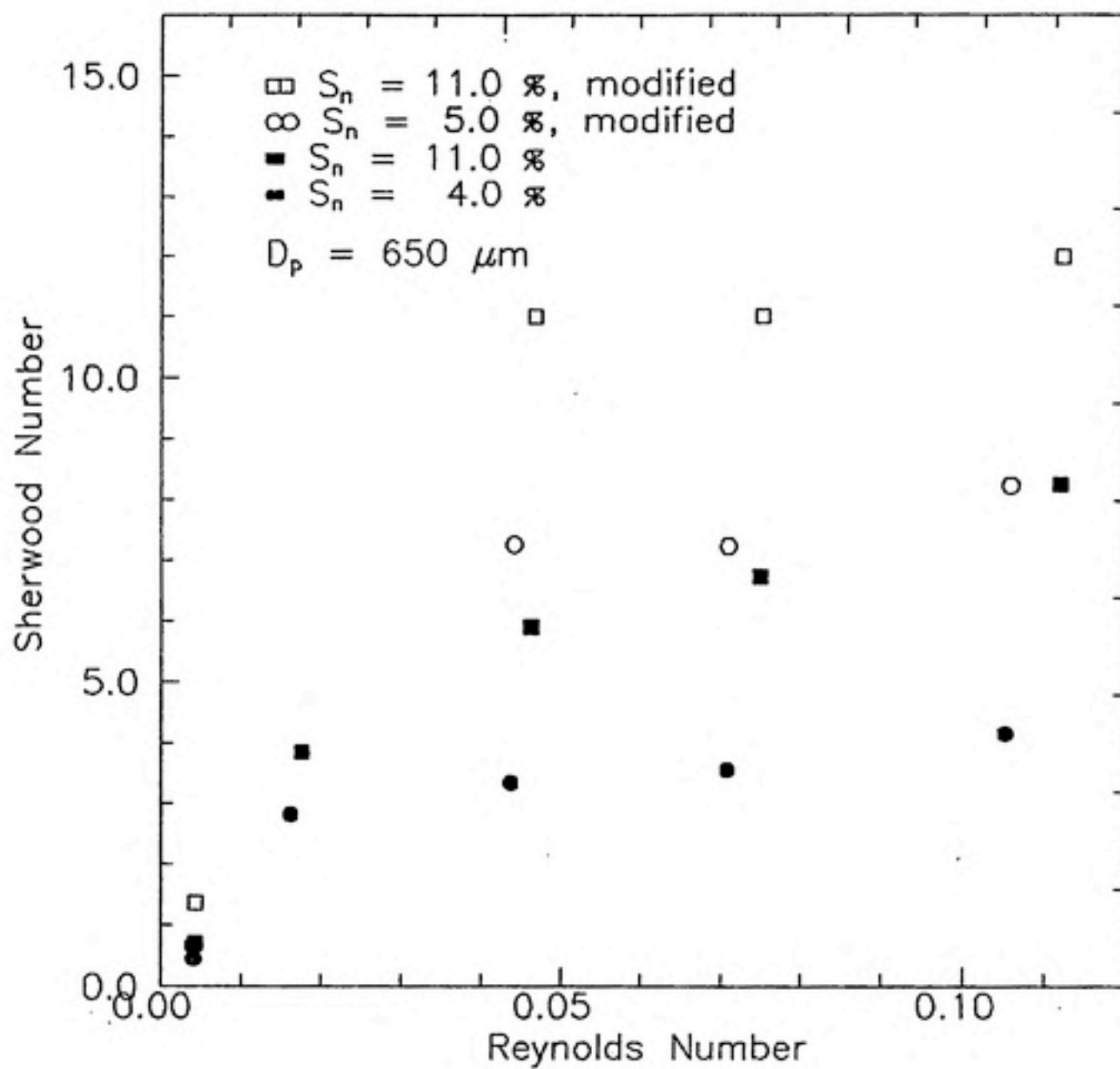


Figure 4-22. Sherwood Number as a Function of Reynolds Number for Modified and Unmodified Experiments

Based on these studies, the effect of naturally occurring humic material in groundwater on the fate and transport of organic contaminants is of concern. Initial solubility studies were performed to determine the effect of humic acid on the aqueous phase solubility of toluene.

Results

Figure 4 - 23 shows the experimentally measured aqueous solubility of toluene as a function of humic acid concentration. These results indicate that humic acid did not significantly enhance the aqueous solubility of toluene, especially at low humic concentrations found in natural groundwater systems. The largest increase of toluene solubility was 5.1 percent, which occurred in the presence of a 40 mg/l humic acid solution. At higher humic concentrations, the solubility of toluene began to decrease. The data compares well to studies described by Haas, et al. (1985) in which a maximum 8 percent increase in toluene solubility occurred in the range of 0 to 70 mg/l humic acid. Haas suggest that the decrease in toluene concentration at higher humic concentrations could have occurred due to the formation of micelles. While the results of this experiment show that humic materials enhance toluene solubility, the effect of this enhancement on toluene transport in the environment seems to be fairly limited.

It should be noted that previous studies focused on the solubility enhancement of fairly insoluble organic chemicals. Chiou et al. (1988) suggests that large solubility enhancements by dissolved co-solutes in relatively dilute concentrations would be largely restricted to solutes that are themselves extremely insoluble in water. In light of this observation, the lack of solubility enhancement of toluene is not surprising since toluene is relatively soluble in water at 515 mg/l.

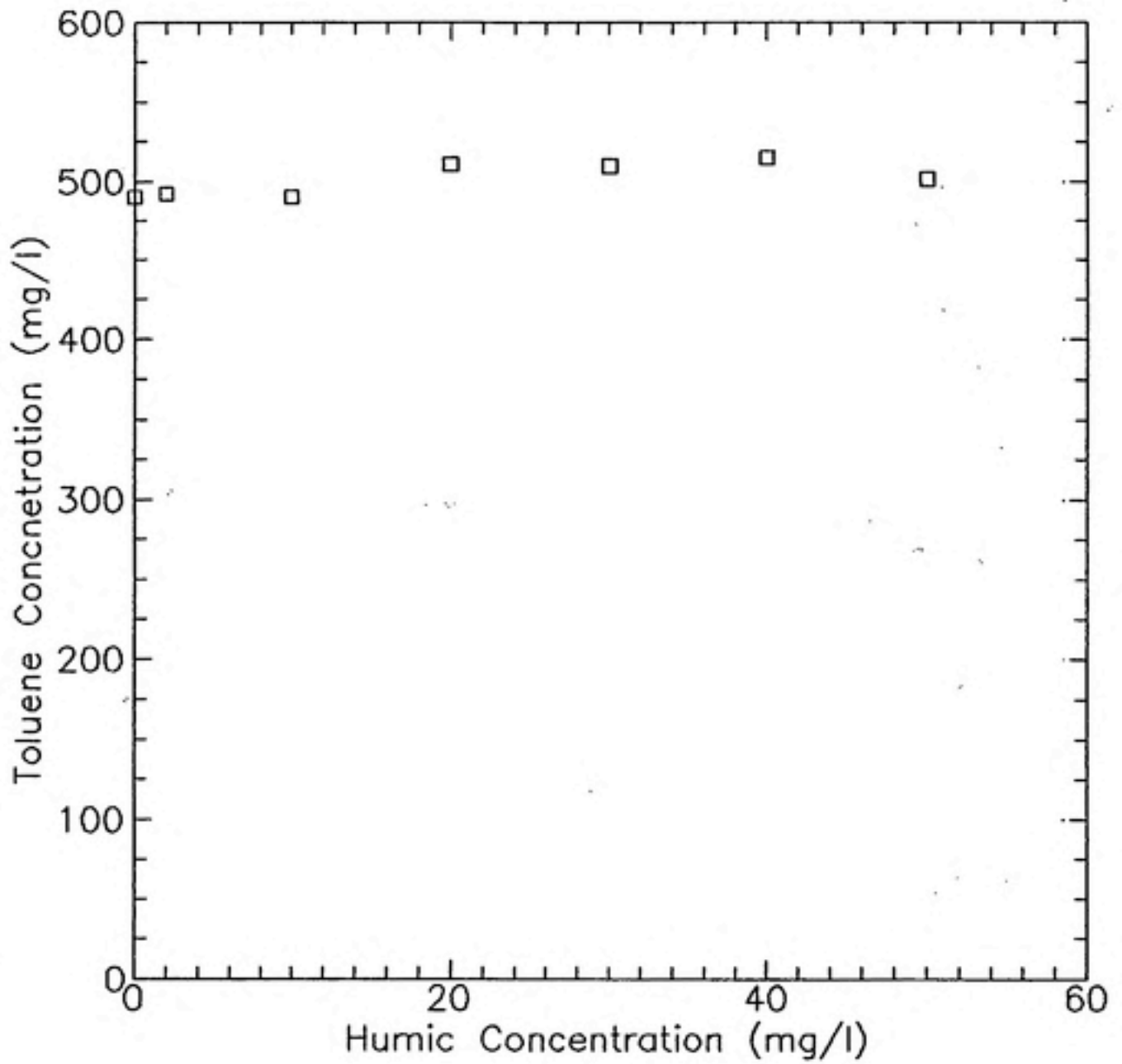


Figure 4-23. Toluene Concentration as a Function of Humic Acid Concentration

Background

Most remediation of contaminated groundwater sites is based on pump and treat methods (Mackay and Cherry, 1988). These methods usually involve pumping contaminated water from the ground and treating the water on-site. This technology has proven to be expensive and ineffective rehabilitating a contaminated aquifer. Organic contaminants tend to have low aqueous solubilities and therefore removal of contaminants by dissolution requires large quantities of water to be pumped and treated. Practical experience indicates that this type of cleanup process can take decades and is expensive, particularly for contaminants in the saturated zone (Mackay and Cherry, 1988). At best, pump and treat options can be used as a tool for hydraulically controlling the migration of NAPL once a spill has occurred. From a technological and economical standpoint, it is clear that there is a need for more efficient aquifer remediation technologies.

The use of cosolvents in groundwater remediation is a technology that has not been widely studied or applied in the field to date. There has been considerable research on the effect of solubility enhancement of solutes in cosolvent systems. Furthermore, it has been experimentally shown that the presence of a cosolvent in an aqueous phase has the effect of increasing hydrocarbon solubility (Yalkowsky 1974, Fu et al., 1986, Groves, 1988).

Fu and Luthy (1985) studied the solubility of aromatic organic compounds in aqueous solutions containing miscible polar solvents. Experimental data was compared to several theoretical models that estimate solute solubility in miscible solvent-aqueous systems. The results of the experimental work showed that solute-aqueous solubility can be enhanced significantly in the presence of a cosolvent. It was generally observed that a semi-logarithmic increase in solute solubility occurred with an increasing volume fraction of cosolvent. The study predicted that the log-linear approach holds for systems in which the solubility

parameter of the solute is at least three units less than that of the solvent.

The use of cosolvents is routinely used as an aid in solubilizing drugs and has been a focus of cosolvent solubility enhancement research. Yalkowsky points out that although it has been shown that cosolvents can enhance solute solubility by orders of magnitude, it is also possible that a cosolvent can have little or no effect or can actually decrease solute solubility. Yalkowsky has found that the effectiveness of solubility enhancement by a cosolvent is dependent on the polarity of the solute with respect to the cosolvent and the aqueous phase. He uses the octanol-water partition coefficient, PC , of the solvents and solutes as a measure of polarity. The most effective means of increasing solute solubility is to have a nonpolar solute. A nonpolar solute is defined as a solute that is less polar than the aqueous phase or cosolvent based on the PC s. Yalkowsky derived an expression for nonpolar solutes that relates the solute solubility in the cosolvent-aqueous solution to the volume fraction of cosolvent present in the aqueous-phase

$$\log S_m = \log S_w + \sigma f_c \quad (4-7)$$

where

$$\sigma = \log PC_{o/w} - \log PC_{o/c}$$

where S_m is the solute solubility in the cosolvent-aqueous solution, S_w is the solute solubility in the pure aqueous-phase, f_c is the volume fraction of cosolvent in the aqueous-phase, $PC_{o/w}$ is the solute octanol-water coefficient, and $PC_{o/c}$ is the octanol-cosolvent partition coefficient of the solute. Equation 4-7 predicts an exponential increase in $\log S_m$ with increasing cosolvent composition.

Initial solubility and mass transfer experiments were performed to determine the effect of a cosolvent on the solubility and mass transfer characteristics of toluene in porous media systems.

Results

Figure 4 - 24 shows the experimentally measured aqueous solubility of toluene as a function of percent ethanol in the aqueous phase. The results indicate that a 50 percent solution of ethanol enhances toluene aqueous solubility by a factor of 25. However, the relationship between solubility and percent ethanol is not log or semi-log as has been reported by other researchers (Yalkowsky, 1974; Fu et al., 1986).

Mass transfer column experiments were performed using an ethanol- aqueous feed solution to determine the effect of ethanol on mass transfer. The results of the experiment are shown in Figures 4 - 25 and 4 - 26. Figure 4 - 25 compares the results of 650- μm media runs using 10 percent and 25 percent by volume ethanol solutions with a run with a similar NAPL saturation using a 0 percent ethanol solution. The results indicate that mass transfer in the presence of ethanol decreases the rate of mass transfer. Figure 4 - 26 compares data from 400- μm runs. This data suggests that the rate of mass transfer is unaffected by the presence of ethanol. These inconsistencies suggest that more data is needed to come to a conclusion regarding the effect of ethanol on NAPL-aqueous mass transfer.

The results of this initial investigation indicate that the use of a cosolvent, such as ethanol, incorporated into a pump and treat remediation scheme may offer an effective means of aquifer cleanup. An increase in the aqueous solubility of toluene by a factor of 25 implies that the use of a cosolvent may significantly decrease the remediation time and volume of waste water generated when compared to normal pump and treat methods. However, any cosolvent used in a remediation scheme should not cause additional risk to the migration of the contaminant or to the quality of the groundwater. A cosolvent such as ethanol is highly biodegradable and should not be of concern. However, as indicated by the experimental results, ethanol acts to remobilize the NAPL and thus there is risk of spreading the contaminant to previously uncontaminated areas. Based on the results of

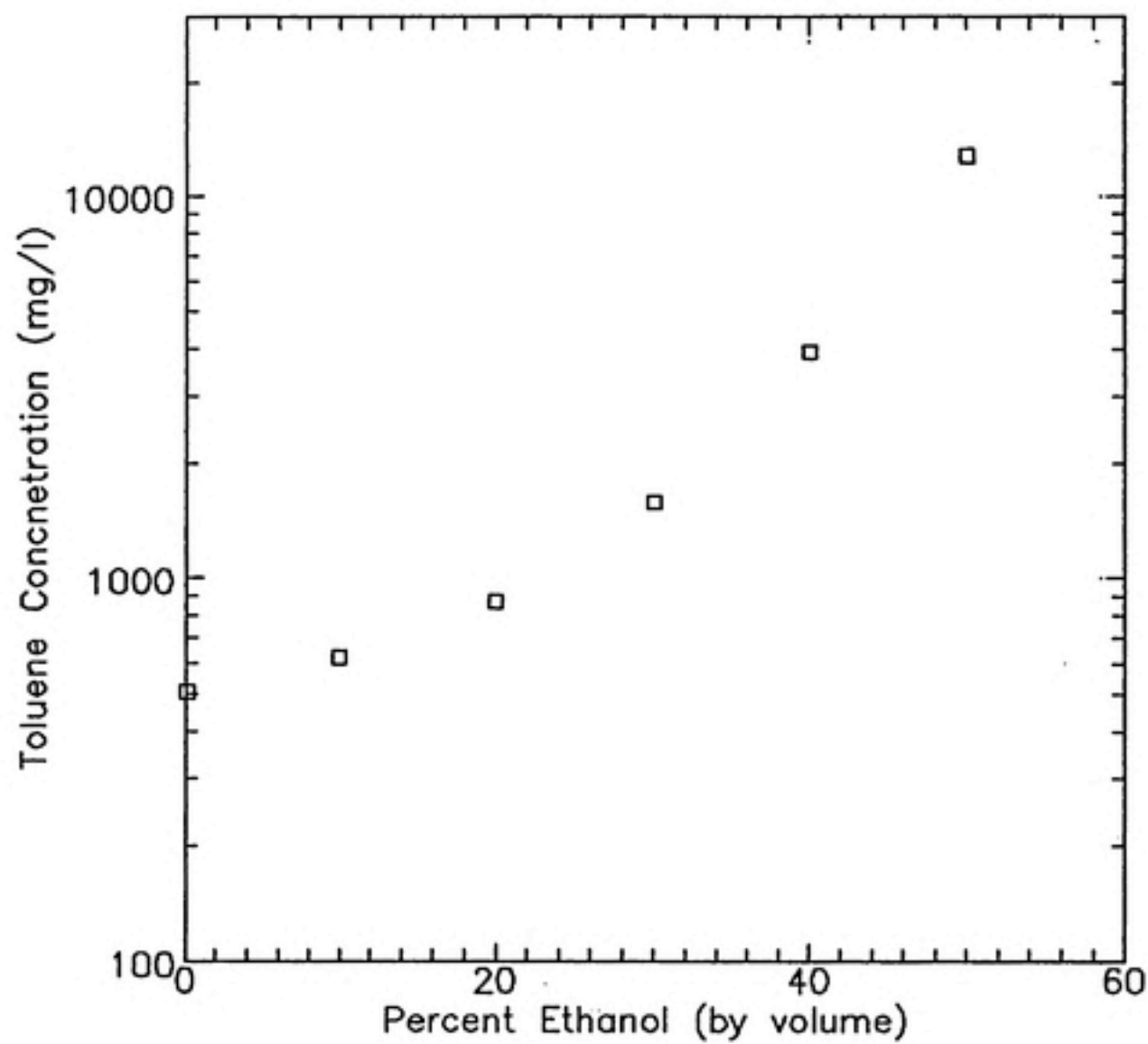


Figure 4-24. Toluene Concentration as a Function of Percent (by volume) Ethanol Solution.

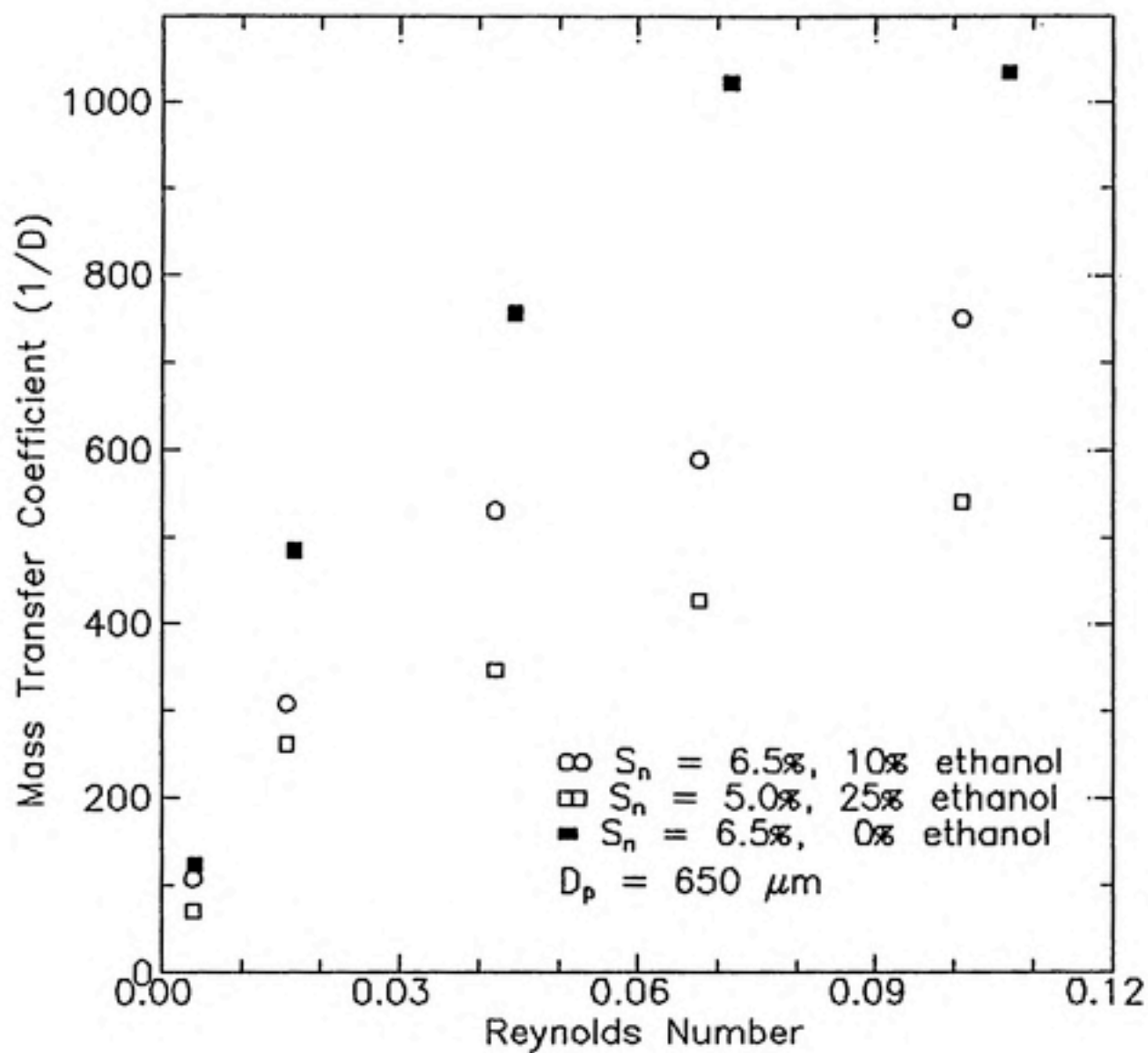


Figure 4-25. Mass Transfer Coefficient as a Function of Reynolds Number for 0, 10, and 25 Percent (by volume) Ethanol Solutions in 650 μm Media

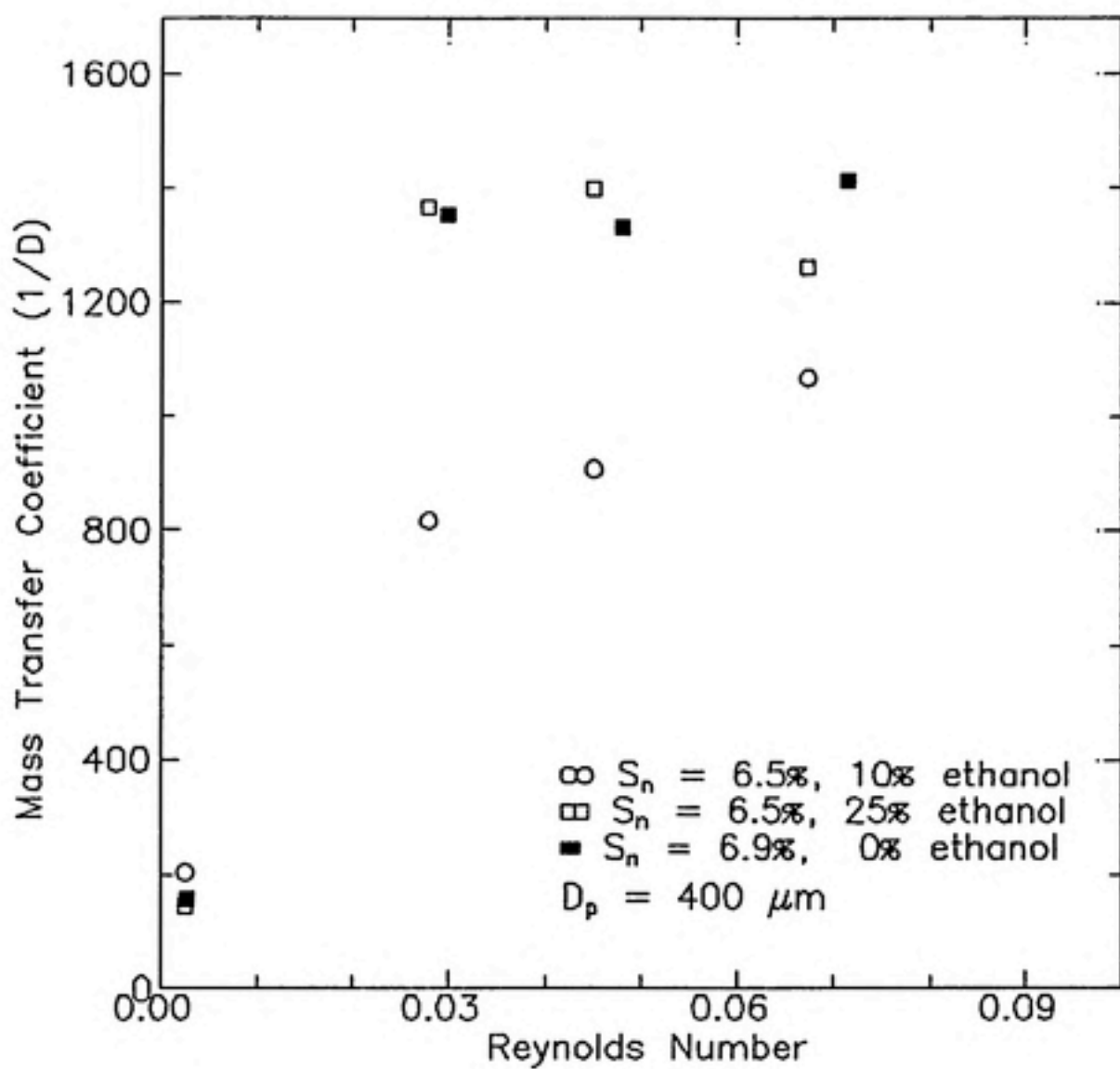


Figure 4-26. Mass Transfer Coefficient as a Function of Reynolds Number for 0, 10, and 25 Percent By Volume Ethanol Solutions in $400\mu\text{m}$ Media

this study, further investigation into the use of cosolvents is needed.

5 Conclusions

5.1 Conclusions

The results of the mass transfer experiments yield both quantitative and qualitative information about NAPL-aqueous dissolution in porous media. It is stressed that these results apply only to the type of system addressed in this study, namely, saturated flow in the velocity range of 0.1 m/d to 32 m/d and for uniform or nearly uniform NAPL (toluene) saturations in the range of 2.5 percent to 21 percent. Sorption and biodegradation have been neglected.

Qualitatively, the results of this study indicate that NAPL-aqueous mass transfer increases with aqueous phase velocity. Mass transfer is more sensitive to velocity at lower velocities and becomes increasingly less sensitive as velocity increases.

The data also indicates that mass transfer increases as a function of increasing residual saturation. At low NAPL saturations, mass transfer is very sensitive to changes in saturation and becomes increasingly less sensitive as saturation increases. This trend is consistent with NAPL-aqueous interfacial area as a function of NAPL saturation. Theoretically, NAPL-aqueous interfacial area increases at a decreasing rate as NAPL saturation increases to a maximum level. The interfacial surface area then decreases as the NAPL saturation approaches zero. However, it is not clear at what NAPL saturation the interfacial area and therefore the rate of mass transfer reaches a maximum.

Correlations based on the $Sh^* = bRe^c S_n^d$ model indicate that mass transfer increases to the c power of velocity and the d power of NAPL saturation where c is in the range of 0.4 - 0.6 and d is in the range of 0.6 to 1.1.

One of the major motivations for this study is to determine if and under what conditions the assumption of local equilibrium is valid. The qualitative data from this research

indicates that mass transfer coefficients are fairly high under all of the experimental conditions (velocities in the range of 0.1 m/d to 32 m/d and NAPL saturations in the range of 2.5 percent to 21 percent). High mass transfer coefficients imply that NAPL-aqueous solubility is attainable in a short period of time or, more importantly in groundwater contaminant problems, within a short distance of groundwater flow.

It should be noted that the rate of mass transfer as well as the NAPL-aqueous contact time determine the NAPL-aqueous concentration at any location x . This phenomena is important with regard to pump and treat remediation techniques. In designing a remediation plan, a tradeoff exists between the time required to completely remove NAPL from the subsurface, and volume of aqueous phase that is required to be pumped and treated. At low flow rates, a NAPL-saturated aqueous phase can be removed from the subsurface and at higher flow rates, a less than NAPL-saturated aqueous phase may be observed. The data in Figures 4 - 27 and 4 - 28 illustrate this phenomena. These data show a simulation of the concentration of the aqueous phase verses distance x through the porous media based on experimentally measured mass transfer coefficients. The data in Figure 4 - 27 shows data for a NAPL residual saturation equal to 2.5 percent and the data in Figure 4 - 28 shows data for a saturation of 12.5 percent. At a relatively low aqueous phase velocity of 0.5 m/d, equilibrium is attained in a shorter distance than for aqueous flow at 13 m/d. However, for all of the cases shown, equilibrium is attained in a very short distance of less than 0.3 meters. With regard to aquifer remediation this suggests that NAPL saturated water can be removed for a wide range of flow rates. Contaminant plumes extending from 0.5 to 5 kilometers have been reported in the literature (Mackay and Cherry, 1989). Based on the magnitude of the areal extent of these plumes, it appears that NAPL-aqueous local equilibrium is a reasonable assumption to make in modeling fate and transport of contaminants under the conditions studied. As expected, equilibrium is attained in a shorter distance at a higher residual saturation.

Results of initial humic studies indicate that humic acid, at naturally occurring con-

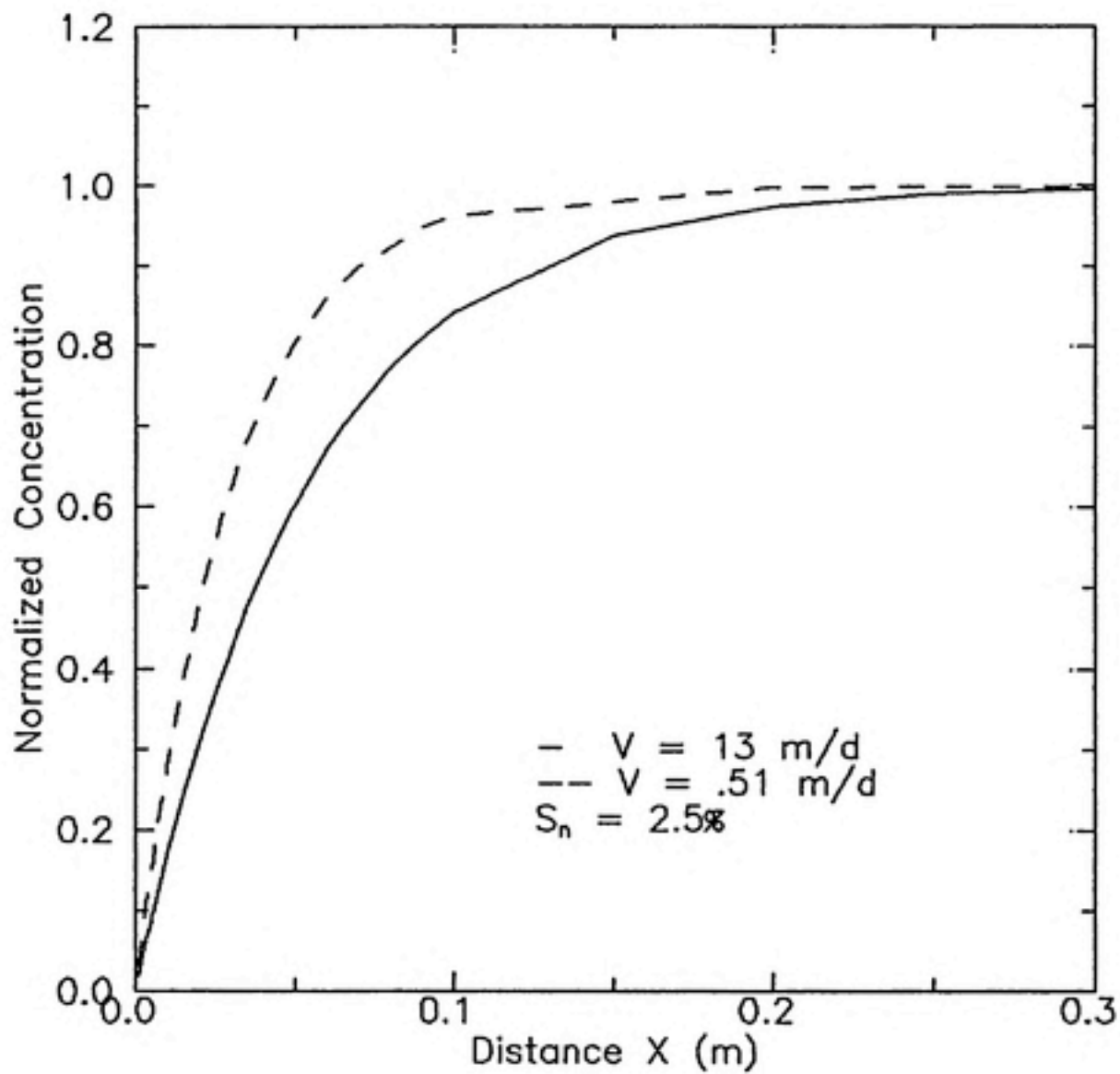


Figure 5-1. Predicted Aqueous Phase Concentration as a Function of Location X for $S_n = 2.5$ Percent as a Function of Velocity

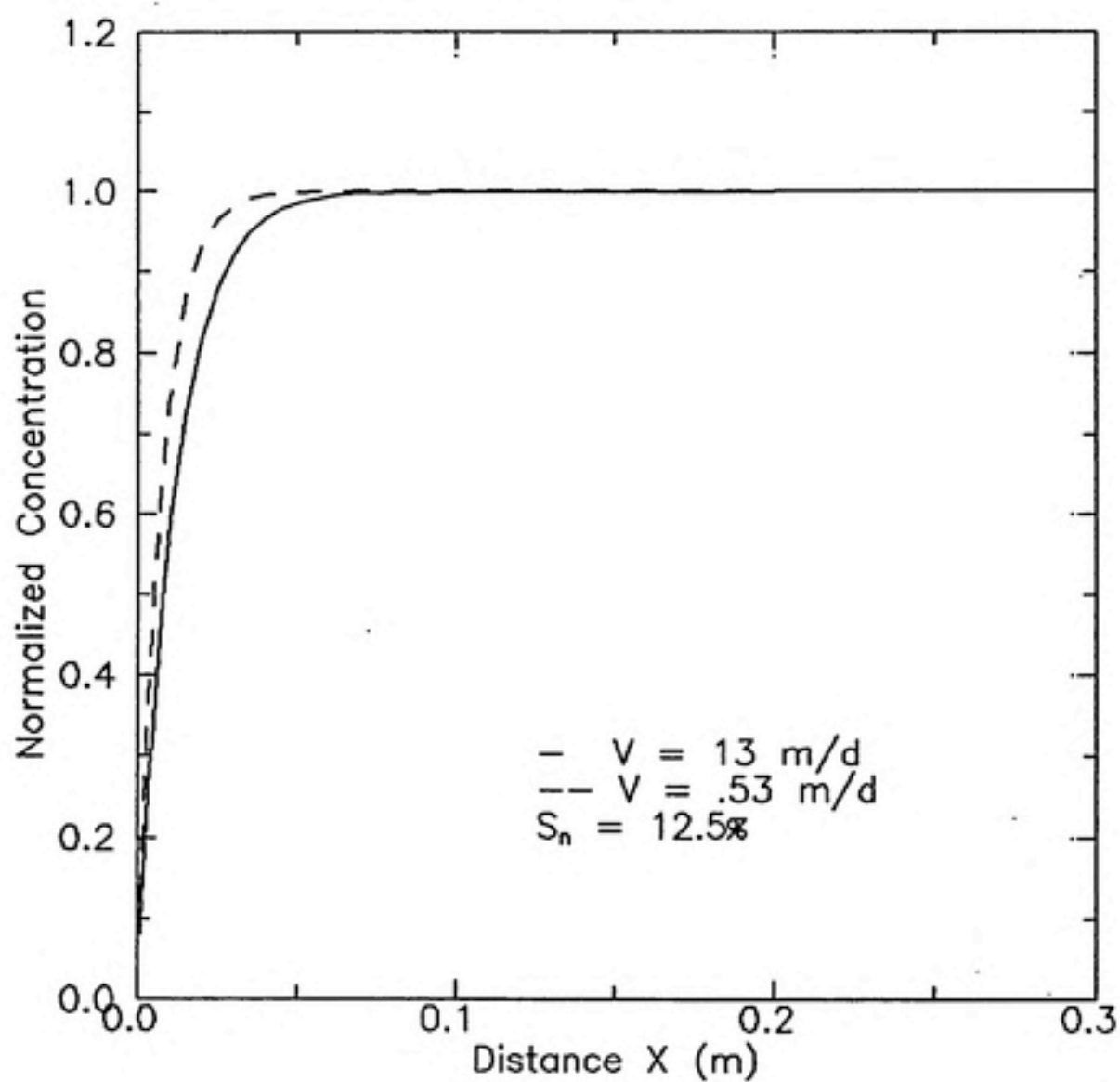


Figure 5-2. Predicted Aqueous Phase Concentration as a Function of Location X for $S_n = 12.5$ Percent as a Function of Velocity

centrations, does not significantly enhance the solubility of toluene. This may be due to the relatively high aqueous-solubility of toluene. Based on this study it appears that naturally occurring humic acids do not play a large role in the transport of organic contaminants chemically similar to toluene.

The results of the ethanol solubility experiments indicate that ethanol significantly enhances the solubility of toluene. However, the results regarding the effect of ethanol on NAPL-aqueous mass transfer rates are inconclusive. Overall, the ethanol studies indicate that the use of cosolvents in aquifer remediation warrants further investigation.

5.2 Recommendations

As indicated by the mass transfer results obtained using the modified experimental method described in Section 4 - 2, it appears that significant mass was lost to dissolution during the initial flooding stages. It is therefore recommended that experiments be performed using the modified experimental method to determine to what extent the assumption of a uniformly distributed NAPL phase was violated in the presently performed experiments. It is expected that the results will show that the mass transfer coefficients presented in this report are artificially low. However, this finding would strengthen the validity of the NAPL-aqueous mass transfer local equilibrium assumption.

The extent and shape of residual saturation within the subsurface is a function of the geometry of the pore network, fluid-fluid properties such as interfacial tension, density ratio and viscosity ratio, and fluid-soil properties (Wilson et al., 1986). Therefore, residual saturation can exist as both isolated blobs of NAPL within individual pore spaces and as a continuum or lense of NAPL occupying many pore spaces (Hunt et al., 1988a). The shape of the NAPL saturation will influence the geometry of the aqueous phase flow as well as the NAPL- aqueous interfacial area. Mass transfer characteristics in NAPL contaminated porous media are expected to vary as a function of the NAPL configuration within the media. This study has considered the case of residual saturation present as uniformly

distributed NAPL blobs within individual pore spaces. Further research is needed to characterize NAPL-aqueous interfacial area and NAPL shape as a function of porous media and fluid properties.

From this study it appears that very low NAPL saturations may prove to be the most persistent source of contamination and the most difficult to remove. Experiments should be performed for NAPL saturations less than 2.5 percent in order to validate equilibrium assumptions under these conditions.

Mass transfer correlations based on NAPL fluid properties were not addressed in this study. Experiments using other NAPL's, including DNAPL's, should be performed in order to develop a more general description of NAPL-aqueous mass transfer in porous media.

6 Notation

a	activity.
A	area (L^2).
b	constant in equation 4-6.
c	constant in equation 4-6.
c_B	number of gram moles of water per cm^3 of solution (ML^{-3}).
C_i^α	concentration of species i in the α phase (ML^{-3}).
C_i^*	equilibrium concentration of species i in α phase (ML^{-3}).
d	constant in equation 4-6.
D_α	dispersion coefficient (L^2t^{-1}).
D_c	molecular diffusion of concentrated species in water (L^2t^{-1}).
D_d	free molecular diffusion (L^2t^{-1}).
$D_d^{\alpha*}$	effective molecular diffusion of species i in the α phase (L^2t^{-1}).
D_d	molecular diffusion of dilute species in water (L^2t^{-1}).
D_{ij}	molecular diffusion of species i in fluid j (L^2t^{-1}).
D_m^α	mechanical dispersion coefficient (L^2t^{-1}).
D_x	x component of the dispersion coefficient (L^2t^{-1}).
f_c	volume fraction of cosolvent in aqueous phase (<i>dimensionless</i>).
F	volumetric flow rate (L^3t^{-1}).
g	gravity vector (Lt^{-2}).
J_i	mass flux of species i ($ML^{-2}t^{-1}$).
J_i^α	mass flux of species i to or from the α phase ($ML^{-2}t^{-1}$).
k	permeability (L^2).
k_r^α	relative permeability (<i>dimensionless</i>).
K	second order tensor (L^3tM^{-1}).

K	mass transfer coefficient (t^{-1}).
K_a	mass transfer coefficient (Lt^{-1}).
K_b	mass transfer coefficient (Lt^{-1}).
K_L	mass transfer coefficient (Lt^{-1}).
l	characteristic length (L).
L	length.
m	molality.
M_a	Mass of air filled flask (M).
M_s	Mass of bead filled flask (M).
M_{sw}	Mass of bead and water filled flask (M).
M_w	Mass of water filled flask (M).
n	porosity or volume of void per total volume (<i>dimensionless</i>).
PC	octanol-water coefficient (<i>dimensionless</i>).
P^α	thermodynamic pressure of α phase ($ML^{-1}t^{-2}$).
Pe	Peclet number (<i>dimensionless</i>).
Q_i^α	interphase mass transfer of species i to or from α phase ($ML^{-3}t^{-1}$).
R'	gas constant ($L^2t^{-1}T^{-1}$).
Re	Reynolds number (<i>dimensionless</i>).
R_i^α	external source of species i to or from α phase ($ML^{-3}t^{-1}$).
Sc	Schmidt number (<i>dimensionless</i>).
Sh	Sherwood number (<i>dimensionless</i>).
Sh^*	modified Sherwood number (<i>dimensionless</i>).
s_α	saturation of α phase or volume α phase per void volume (<i>dimensionless</i>).
S_m	solute solubility in cosolvent system (ML^{-1}).
S_w	solute aqueous solubility (ML^{-1}).
t	time.
T	temperature.

v	velocity (Lt^{-1}).
v^α	velocity of the α phase (Lt^{-1}).
V_B	partial molal volume of water in solution ($\text{cm}^3\text{g-mole}^{-1}$).
U^+	absolute velocity of cation.
U^-	absolute velocity of ion.
Z^+	valence of cation.
Z^-	valence of ion.
α_L	longitudinal dispersivity (L).
α_m	dispersivity (L).
α_T	transverse dispersivity (L).
δ_{ij}	Kronecker delta function (<i>dimensionless</i>).
δ	film thickness (L).
ϵ	volume fraction (<i>dimensionless</i>).
$\gamma_\pm$	mean ionic activity coefficient.
μ	dynamic viscosity ($\text{ML}^{-1}\text{t}^{-1}$).
μ_B	dynamic viscosity of water ($\text{ML}^{-1}\text{t}^{-1}$).
ν	kinematic viscosity (L^2t^{-1}).
ω_i^α	mass fraction of species i in α phase (<i>dimensionless</i>).
ρ^α	mass density of the α phase (ML^{-3}).
ρ_b	bulk density (ML^{-3}).
ρ_p	particle density (ML^{-3}).
ρ_w	density of water at 25°C (ML^{-3}).
σ	solubilizing power of cosolvent (<i>dimensionless</i>).
τ	tortuosity (<i>dimensionless</i>).
τ^*	tortuosity (<i>dimensionless</i>).
τ_m	Millington-Quirk tortuosity (<i>dimensionless</i>).

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