Determination of Hindered Diffusivities for Nonadsorbing Pollutants in Muds

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Rejuvenation of polluted stream beds or muds is important not only for bringing a once healthy stream back to life, but also for the aquatic life and humans that directly or indirectly are exposed to it. The study reported here deals with an experimental study of diffusivities through soils and calculation of hindrance factors. Such information provides a basis for predicting rejuvenation rates of polluted muds.

BACKGROUND

The general area of measuring solute diffusivities is either limited to complex experimental methods such as those of Stokes (1951), Harned and Nuttall (1949), and Gosting (1950), or limited to theoretical and semi-empirical techniques that prove to have limited application to diffusing electrolytes. In summing up the most accurate experimental methods for determining liquid diffusivities, Robinson and Stokes (1970) list the three most reliable methods. These are the conductimetric method of Harned and Nuttall (1949), the Gouy interference method as discussed by Gosting (1950), and the diaphragm-cell method. Both the Gouy and the conductimetric methods are absolute methods. The diffusivities can be calculated directly from the data collected in the experiment. Because the diaphragm must be calibrated by using the results of an absolute method, the diaphragm-cell method is a relative method.

A number of works have been published concerning transport processes through porous media, such as those by Satterfield (1970), Slattery (1972), and Neale and Nader (1973, 1974). Most of the experimental approaches to measuring diffusivities have been specifically tailored to meet the specific research need. In view of most of the published experimental approaches, it was found most convenient in this work to use the approach of Pommersheim (1973) and to extend the quasi steady state theory for gas diffusivities to the liquid state.

GOVERNING EQUATIONS

The ultimate goal of the investigation reported here is to estimate the hindrance factor H and hence the rate of diffusion through different types of stream bed media. On this basis, the hindrance factor is defined in our work as

$$D_{AE} = \frac{D_{AB}}{H} \qquad (1)$$

This factor can be described in many forms, as noted by Geankoplis (1972), and primarily relates to particle shape, tortuosity, and bed void fraction. In the above relationship, it is presumed that the hindrance factor is independent of the concentration of the diffusing species. This will be true whenever no chemical or physical interactions exist, that is, for nonsorbing pollutants. For the purpose of this study, it was assumed that negligible adsorption of the pollutant occurs on the particle surface. Of course this is not always the case (Greskovich, 1974); however, it can provide a basic model which can be extended. Because the pore size in the bed is usually much larger than the molecular diameter of the diffusing species, a hindrance factor based on one diffusing species will be accurate also for other species of similar molecular diameter that exhibits the same effects with the muds.

The theoretical analysis for unhindered diffusion is based on the form of Fick's first law in terms of N_A, the molar flux of the diffusing species relative to stationary coordinates, as detailed by Ghia et al. (1973).

The diffusion cell used in this research is typically referred to as a *Stefan cell.* Potassium chloride was used as the diffusing species for the determination of hindrance factors. This was accomplished by placing a solid salt phase with a porosity of ϵ_1 under the test diffusion zone which contains water during unhindered studies or the appropriate sand, mud, or clay being evaluated during hindered studies. Unlike the case of stagnant film diffusion, the flux of B does not equal zero. There is a small flux of water down the tube to partially fill the space left when the potassium chloride diffuses away from the salt interface. The flux ratio N_B/N_A is easily obtained by making volume and mass balances at the interface, taking into account the mud porosity ϵ_2. Thus

$$N_B/N_A = \frac{\epsilon_2 C_{B2}^*}{\epsilon_2 C_{A2}^* - C_{A1}^*} \qquad (2)$$

The concentrations in Equation (2) represent the equilibrium values of components A and B in phases 1 and 2. For the system studied here, these concentrations are the saturation values for potassium chloride and water in the salt phase and mud layers (diffusion zone), respectively. By assuming quasi steady state at the interface and by accounting for accumulation of solute as the interface moves, the following solution was obtained:

$$t = \frac{(C_{A1}^* - C_{A2}^*)(1 - \epsilon_1)}{2\, D_{\text{int}}\, C_{A2}^*} (z_i^2 - z_1^2) \qquad (3)$$

Equation (3) relates the interface movement as a function of time in the Stefan cell. D_{int} is the corrected integral diffusivity of the solute. Further details are presented by Pommersheim et al. (1974).

Since this study deals specifically with hindered diffusion of solutes through muds, the diffusion zone within the Stefan cell is filled with various soils comprising the

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mud. Hence, diffusion of the dissolved salt takes place between the solid salt-mud interface to the top of the diffusion cell at the mud-water interface. By observing the descending salt interface below the mud, the fluxes in the mud phase can be evaluated, and then values for the hindered diffusivity can be found. (During any experiment reported here, the maximum distance the salt interface moved was approximately 1.0 cm. In this period, the cell was maintained full by adding very small amounts of hindering medium to the cell.) The analogue of Equation (3) for hindered diffusion becomes

$$t = \frac{(C_{A1}^* - \epsilon_2 C_{A2}^*)(1 - \epsilon_1)}{2\, D_{\text{int}}\, C_{A2}^*} (z_i^2 - z_1^2) \qquad (4)$$

where ϵ_2 is the void fraction in the diffusion zone through which hindered diffusion is taking place. In addition D_{int} in Equation (4) is now the hindered integral diffusivity of the solute.

It is reasonable to assume that the hindrance factor H can relate both the unhindered and hindered integral diffusivities, so that Equations (3) and (4) can be combined with Equation (1) to yield

$$H = (\Delta z^2/t)_{\text{Un}}/(\Delta z^2/t)_{\text{Hin}} \times \left[\frac{(C_{A1}^* - C_{A2}^*)}{C_{A1}^* - \epsilon_2 C_{A2}^*}\right] \times \left[\frac{2\,000 - \left(V_A^* + \left[\frac{C_{B2}^* - C_{B1}^*}{C_{A2}^* - C_{A1}^*}\right] V_B^*\right) C_{A2}^*}{2\,000 - (V_A^* + N_B/N_A\, V_B^*) C_{A2}^*}\right] \qquad (5)$$

The last term in Equation (5) makes use of an accurate approximation (0.1% error) presented by Pommersheim et al. (1974) for the integral diffusivity. In order to obtain hindrance factors for the solute, it is only necessary to compare $(z_i^2 - z_1^2)$ vs. time data for the unhindered and hindered diffusion. Local saturation concentrations, specific volumes at the interface, and the porosity of the hindering medium are parameters. Equation (2) is used to find the flux ratio.

EXPERIMENTAL APPARATUS AND PROCEDURE

The apparatus consisted of four principal items; the temperature control system, a deionized water source, a cathetometer, and the diffusion cells.

The constant temperature bath was maintained at 25°C ± 0.1°C at all times and was approximately 18.75 l capacity. By submerging the diffusion cells, made from 0.417 cm I.D., thin-wall glass tubing into the bath, both temperature and bath concentrations (maintained at zero) could be carefully controlled. After several hours were allowed for the quasi steady state concentration profiles to develop in the diffusion cell, the cathetometer was fixed on the initial salt-mud interface (Z_1), and the movement of this interface down the tube with time was recorded as Z_i. The tubes were approximately 15 cm long. Since the cell diameter was uniform, these data yielded values for the salt flux.

RESULTS

Based on the slopes of the $(z_i^2 - z_1^2)$ vs. time plots, as depicted in Figure 1, the hindered diffusivities or hindrance factors for potassium chloride through various test media were obtained by Kenner (1973). The error in the plots varied from 1.7% to a maximum of 3.5%. These values are presented in Table 1. Also reported are values for the porosities of both phases. The hindrance factors determined in this study are dependent on both the void fraction and the tortuosity of the different beds. The results presented here indicate that the diffusion rates differ greatly for various bed types with different packing characteristics and different particle compositions. The hindrance factors shown in Table 1 vary from 3.04 for fine sand to 1.58 for loosely packed stream bed silt. In analyzing the results, it is seen that the H value for the (0.0147 to 0.0208)-cm diameter sand run is some what lower than expected. Aside from experimental error, this result may be attributable to incomplete separation of the sand in the Tyler sieve shaker. It should be noted that owing to the difficulty of measuring ϵ_2 in the last three runs in Table 1, the values of H presented there were calculated by using Equation (5) with the last two terms set equal to 1.0. This should not create exceptional error (~5%), since the product of these two terms equals approximately 0.95 for the first three runs in Table 1.

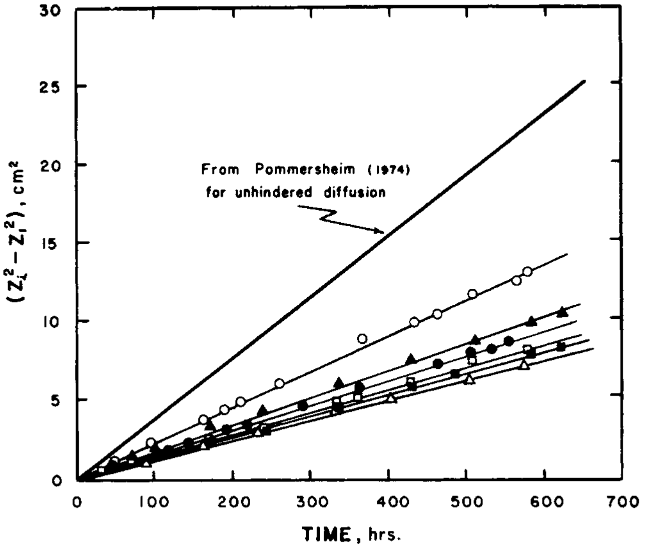

Fig. 1. Δz^2 vs. time data for hindered diffusion of potassium chloride through test media. ○—fresh stream bed silt, ▲—clayey—silt soil, ●—dried stream bed silt, □—(0.0147 to 0.0208)—cm sand, ■—(0.0417 to 0.0589)—cm sand, △—(0.0208 to 0.0295)—cm sand.

Table 1. Experimental Hindrance Factors and Void Fractions for Test Media

Medium	Particle diameter, cm	Average values ϵ_1	ϵ_2	H^*
Sand	0.0147-0.0208	0.383	0.491	2.82
Sand	0.0208-0.0295	0.399	0.507	3.04
Sand	0.0417-0.0589	0.358	0.510	2.70
Clayey-silt soil	~50% <0.0035	0.367	—	2.24†
Dried stream bed slit	~70% <0.0147	0.427	—	2.46†
Fresh stream bed slit	~50% <0.0020	0.409	—	1.58†

* Calculated from Equation (5).

† Calculated from Equation (5) by assuming last two terms equal 1.0.

It can be noted from Figure 1 that the ΔZ^2 vs. time plots were surprisingly linear, indicating no sorption on the hindering medium. There are few data in the literature to compare the hindrance factors with; however, by using the predictions of Neale and Nader (1973), values of H can be calculated for the first three sand runs in Table 1. These calculated values are 2.55, 2.46, and 2.44, respectively. This comparison is fairly good, especially when we recognize the experimental difficulties and the assumption that the particles are spherical.

CONCLUSIONS

The finite Stefan cell operating at quasi steady state with a moving interface has been shown to be a simple, convenient, and accurate method of determining hindrance factors for nonsorbing species in stream beds. In operation it serves as a close physical analogue for the process it models.

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NOTATION

A = subscript that refers to potassium chloride
B = subscript that refers to water
C = total molar concentration, moles/cm^3
C_A, C_B = molar concentration, moles/cm^3
D_{AB} = diffusivity of potassium chloride through water, cm^2/s
D_{AE} = effective diffusivity of potassium chloride through a settled soil slurry, cm^2/s

$$D_{\text{int}} = \frac{1}{C_{A2}^* - C_{A0}} \int_{C_{A0}}^{C_{A2}^*} \frac{D_{AB} dC_A}{1 - \left[V_A + \frac{N_B}{N_A} V_B \right] C_A}$$

H = hindrance factor
N_A, N_B = molar flux of A and B, moles/cm^2, s
$\tilde{V}_A$, $\tilde{V}_B$ = partial molar volume of A and B, cm^3/g mole
X_A, X_B = mole fraction
X_A^* = mole fraction potassium chloride at saturation
Z = distance in the vertical direction, cm
ϵ_1 = void fraction in the salt phase
ϵ_2 = void fraction of settled soil slurry bed
$*$ = superscript that refers to saturation at solid salt interface
o = subscript referring to cell entrance

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Generalized Prediction of Isothermal Compressibilities and an Isothermal Equation of State for Liquid Mixtures

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For design and analysis of liquid systems under high pressures, knowledge of the equation of state is necessary to obtain values of densities and thermodynamic properties. While liquids are not very compressible, at pressures above 100 bar, the density and its derivative, the compressibility, and thermodynamic properties such as enthalpy and entropy can be appreciably different from that at low pressures. Previously (Brelvi and O'Connell, 1972), we had established a corresponding states correlation for pure component compressibilities using only the density