r_p = radius of primary stream tube (Figures 1–3) instantaneous radial location of particles
t = time
u_p, v_p, w_p = instantaneous components of the particle velocity
u', v', w' = fluctuating components of gas velocity
$\tilde{u}, \tilde{v}, \tilde{w}$ = instantaneous components of the gas velocity
w, r, θ = directions of a cylindrical polar system
z = distance from chamber inlet

Greek Letters

α = defined by Eq. 4
ρ = gas density
ρ_p = particle density
$\mu_{\text{eff}}, \mu, \mu_t$ = effective, laminar and turbulence viscosities
ϵ = rate of dissipation of turbulence energy
ϕ = normally distributed random number
τ = lifetime of a fluid eddy
$\sigma_k, \sigma_\epsilon$ = constants in the turbulence model

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Comments on the Paper, "Gas Transport through Polyethylene Membranes"

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In "Gas Transport through Polyethylene Membranes," [*AIChE J.*, 28, 474 (1982)] Soles et al. described a procedure for determining both the Henry's Law Constant, H, and the diffusivity, D, which characterize gaseous transport through a polymer membrane. In their experiments, a polymer membrane (either high- or low-density polyethylene) was placed between two reservoirs containing a pure gas initially at different pressures. By assuming one-dimensional diffusion through the membrane, uniform mixing within the reservoirs and equilibrium at the gas-polymer interface, a relationship was derived between D and H and the temporal variation in pressure drop across the membrane. The objectives of their study were threefold:

1) Find a solution to the one-dimensional diffusion equation with the pressure in both reservoirs allowed to vary with time.

2) Find a solution to the one-dimensional diffusion equation for their experimental conditions in which the pressure in one reservoir was essentially constant.

3) Demonstrate a procedure for employing the latter solution to estimate H and D for gaseous transport through a polymer membrane. Soles et al. (1982) determined H and D for the transport of Argon through high- and low-density polyethylene.

Soles et al. (1982) were unable to find a general solution to the problem of one-dimensional diffusion between well-mixed reservoirs and instead reported a solution valid only for short times ($Dt/L^2 \ll 1$). However, solutions for all time are available (Spacek and Kubin, 1967; Shair and Cohen, 1969). The experimental analysis of Soles et al. (1982) was based on the assumption that the pressure in the larger reservoir (the high-pressure reservoir) was essentially constant. While the author's assumption was apparently valid for their experiments, this assumption is not required for analysis of the data. Reible and Shair (1982) employed the solution developed by Shair and Cohen (1969) to determine diffusivities in porous media in an apparatus similar to that employed by Soles et al. (1982). This approach can also be applied to evaluate both H and D in diffusion through polymer membranes and would not be subject to the limitations of the approach by Soles et al. (1982). The objective of the present paper is to outline the application of the solution of Shair and Cohen (1969) to this problem.

PROCEDURE

It is assumed that at time zero a pressure difference is applied across a polymer membrane of length, L, and cross-sectional area, A. The difference in pressure is measured in well-mixed reservoirs of volume V_1 and V_2, on each side of the membrane. At any time, the concentration of the dissolved gas at the edge of the polymer membrane, $C_m(0,t)$ [or $C_m(L,t)$], is in equilibrium with the reservoir pressure, P_1 [or P_2], according to the following relationships

$$P_1(t) = RTC_1(t) = RTHC_m(0,t) \tag{1}$$

$$P_2(t) = RTC_2(t) = RTHC_m(L,t) \tag{2}$$

where H is a Henry's law constant.

In addition, at time zero the dissolved gas concentration throughout the membrane is assumed to be in equilibrium with the pressure in V_2 as given by Eq. 2. Without loss of generality, this pressure can be taken to be zero and the pressure in V_1 taken to represent a differential pressure between V_1 and V_2.

Under these conditions, the applicable diffusion equation can be written

$$\frac{\partial C_m(x,t)}{\partial t} = D\,\frac{\partial^2 C_m(x,t)}{\partial x^2} \tag{3}$$

with the boundary conditions

$$HV_1\,\frac{\partial C_1(t)}{\partial t} = AD\,\frac{\partial C_m(0,t)}{\partial x} \tag{4}$$

$$HV_2\,\frac{\partial C_2(t)}{\partial t} = -AD\,\frac{\partial C_m(L,t)}{\partial x} \tag{5}$$

Adapting the solution of Shair and Cohen (1968), the solution of Eq. 3, subject to Eqs. 4 and 5 can be written

$$\begin{aligned} C_m(x,t) = C_{m\infty} + 2\,\frac{C_1(0)}{H}\sum_{n=1}^{\infty}\Big[\cos\lambda_n\Big(1-\frac{x}{L}\Big) &- \delta_2\lambda_n\sin\lambda_n\Big(1-\frac{x}{L}\Big)\Big] \\ &\cdot\frac{\delta_1\exp\{-\lambda_n^2Dt/L^2\}}{\{(1+\delta_1+\delta_2-\delta_1\delta_2\lambda_n^2)\cos\lambda_n-(\delta_1+\delta_2+2\delta_1\delta_2)\lambda_n\sin\lambda_n\}} \end{aligned} \tag{6}$$

where,

$$\delta_i = V_iH/AL \tag{7}$$

and

$$\tan\lambda_n = -\frac{(\delta_1+\delta_2)\lambda_n}{1-\delta_1\delta_2\lambda_n^2} \tag{8}$$

Thus $P_1(t)$ is

$$\begin{aligned} P_1(t) = HRTC_m(0,t) = HRTC_{m\infty} &+ 2RTC_1(0)\sum_{n=1}^{\infty} \times(\cos\lambda_n-\delta_2\lambda_n\sin\lambda_n) \\ &\cdot\frac{\delta_1\exp\{-\lambda_n^2Dt/L^2\}}{\{(1+\delta_1+\delta_2-\delta_1\delta_2\lambda_n^2)\cos\lambda_n-(\delta_1+\delta_2+2\delta_1\delta_2)\lambda_n\sin\lambda_n\}} \end{aligned} \tag{9}$$

and $P_2(t)$ is

$$\begin{aligned} P_2(t) = HRTC_m(L,t) = HRTC_{m\infty} &+ 2RTC_1(0)\sum_{n=1}^{\infty}\delta_1\exp\{-\lambda_n^2Dt/L^2\} \\ &\cdot\frac{1}{\{(1+\delta_1+\delta_2-\delta_1\delta_2\lambda_n^2)\cos\lambda_n-(\delta_1+\delta_2+2\delta_1\delta_2)\lambda_n\sin\lambda_n\}} \end{aligned} \tag{10}$$

Thus in terms of the dimensionless pressure difference between the two reservoirs,

$$\begin{aligned} \frac{\Delta P(t)}{\Delta P(0)} = \frac{P_1(t)-P_2(t)}{P_1(0)} &= 2\sum_{n=1}^{\infty}\delta_1\exp\{-\lambda_n^2Dt/L^2\} \\ &\cdot\frac{\{\cos\lambda_n-\delta_2\lambda_n\sin\lambda_n-1\}}{\{(1+\delta_1+\delta_2-\delta_1\delta_2\lambda_n^2)\cos\lambda_n-(\delta_1+\delta_2+2\delta_1\delta_2)\lambda_n\sin\lambda_n} \end{aligned} \tag{11}$$

Given $\Delta P(t)$, the values of the parameters H and D can be estimated from this relationship, e.g., using optimization routines such as the direct search method of Hook and Jeeves as employed by Soles et al. (1982).

Further simplification is possible, however, by considering, as did Soles et al. (1982), only long experiment times. Examination of Eq. 6 indicates that $\lambda_1 \ll \pi$ and $\lambda_n \geq (n-1)\pi$ for typical values of δ_1 and δ_2 ($\delta_1\delta_2 > 1$). Because of the exponential term in the infinite series, after relatively short periods of time the second and subsequent terms of the series are negligible. The dimensionless pressure difference between the two reservoirs can than be written

$$\frac{\Delta P(t)}{\Delta P(0)} = \frac{2\delta_1\exp\{-\lambda_1^2Dt/L^2\}\{\cos\lambda_1-\delta_2\lambda_1\sin\lambda_1-1\}}{(1+\delta_1+\delta_2-\delta_1\delta_2\lambda_1^2)\cos\lambda_1-(\delta_1+\delta_2+2\delta_1\delta_2)\lambda_1\sin\lambda_1} \tag{12}$$

or, alternatively,

$$ln\,\{\frac{\Delta P(t)}{\Delta P(0)}\} = ln\,K - \lambda_1^2\,\frac{Dt}{L^2} \tag{13}$$

where,

$$K = \frac{2\delta_1\{\cos\lambda_1-\delta_2\lambda_1\sin\lambda_1-1\}}{(1+\delta_1+\delta_2-\delta_1\delta_2\lambda_1^2)\cos\lambda_1-(\delta_1+\delta_2+2\delta_1\delta_2)\lambda_1\sin\lambda_1} \tag{14}$$

The latter indicates that a plot of *ln* $\{\Delta P(t)/\Delta P(0)\}$ vs. t should be a straight line (for long times) and that the slope of the line is related to D (and through λ_1 to H) while the "y-intercept" is a function of H only (through $\delta_1,\delta_2,\lambda_1$). The linear relationship between the logarithm of the pressure difference and time can also be deduced from Eq. 26 of Soles et al. (1982) which assumes a linear concentration gradient in the membrane. Soles et al. (1982) observed the linearized relationship given by Eq. 12 for times greater than 1,400 s in their experiments in which $\delta_1 = 725{,}000$ and $\delta_2 = 4{,}200$. As the parameters δ_1 and δ_2 are decreased, the time required for linearization to be valid increases. Reible and Shair (1982) found, however, that even for $\delta_1 = \delta_2 \cong 10$, this linearized relationship was observed within 3,600 s. Thus Eqs. 11, 12 or 13 could be used to evaluate D and H over a wide range of the parameters δ_1 and δ_2.

The work of Soles et al. (1982), however, is limited to the case of $\delta_1 \gg \delta_2$. If $\delta_1 \gg \delta_2$, (for $\delta_1, \delta_2 > 1$), λ_1 approaches $1/\delta_2$ and K in Eq. 13 approaches 1. The experimental pressure drop data is then relatively insensitive to the value of δ_1 and δ_2, from which H is determined. Under these conditions it is difficult to unambiguously determine the Henry's law constant, H, with even a moderate amount of experimental uncertainty. The relationships of Soles et al. (1982) also exhibit this behavior. Equations 11, 12 and 13, however, can be applied to cases where $\delta_1 \sim \delta_2 \sim 1$ and thus the determination of H can be made less sensitive to experimental uncertainties. Even with thin polyethylene membranes when $\delta_1 \sim \delta_2 \sim 1$ may be difficult to achieve this analysis allows δ_1 and δ_2 to be very much less than $10^3 \rightarrow 10^6$ as in Soles et al. (1982).

NOTATION

A = cross-sectional area of membrane
$C_m(x,t)$ = dissolved gas concentration within the membrane
$C_{m\infty}$ = steady state membrane concentration of dissolved gas
C_1,C_2 = gas concentration in reservoir at each end of polymer membrane
$C_1(0)$ = initial gas concentration in reservoir 1
D = effective diffusivity of gas in the membrane
H = Henry's law constant, defined by Eqs. 1 and 2
K = $f(\delta_1,\delta_2,\lambda_1)$ defined by Eq. 14
L = thickness of polymer membrane
P_1,P_2 = pressure of pure gas in reservoirs
ΔP = difference in pressure between reservoir 1 and 2
R = ideal gas constant
T = absolute temperature
t = time variable
V_1,V_2 = volumes of reservoirs
x = distance in direction of diffusion in membrane

Greek Letters

δ_i = dimensionless reservoir volumes, V_iH/AL
λ_n = roots of $\tan \lambda_n = -(\delta_1 + \delta_2)\lambda_n/(1 - \delta_1\delta_2\lambda_n^2)$

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Mathematical Modelling of the Ligand Exchange Process

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INTRODUCTION

Ligand exchange is a process in which a substance is removed from solution by complexing with a metal ion held on an ion exchange resin. For example, ammonia can be removed from water solution by complexing with Cu(II) ion held on a cation exchange resin. The term, ligand exchange, was coined by Helfferich (1962a,b,c) who studied the process extensively. The process has potential applications in pollution control. Where applicable it can reduce the concentration of a pollutant to a very low level. Because of the specificity of complex formation it offers the possibility of selectively removing specific pollutants. Dawson (1964) and Dobbs (1975, 1976) developed a process for removing ammonia from water by complexing with Cu(II) ion held on a hydrous zirconium oxide ion exchanger. Jeffrey (1977), in this laboratory, studied various metal ion-organic resin combinations for ammonia removal. Of the systems studied the Cu(II)-carboxylic acid type resin combination gave the best results.

The objective of this paper is to apply an ion-exchange-type mathematical model to ligand exchange conducted in a fixed bed of resin. It will be seen that the model gives a good fit to experimental data using plausible values of model parameters.

THE MODEL

Ligand exchange is mathematically analogous to adsorption or ion exchange with a highly nonlinear equilibrium curve. For this reason the Thomas model (Thomas, 1944) for fixed-bed ion exchange on a bed of granular solid was chosen. A material balance on the fluid phase in the bed gives

$$\epsilon \frac{\partial c}{\partial t} + \rho_B \frac{\partial q}{\partial t} + \epsilon v \frac{\partial c}{\partial x} = 0 \qquad (1)$$

The Thomas model uses a chemical reaction type expression for the adsorption rate at a point in the bed,

$$\rho_B \frac{\partial q}{\partial t} = ka\left[c\left(1 - \frac{q}{q_m}\right) - \frac{1}{K}(C_o - c)\frac{q}{q_m}\right] \qquad (2)$$

where k is a kinetic rate constant and K is the adsorption equilibrium constant. The rate expression of Eq. 2 is consistent with an equilibrium relation of Langmuir type,

$$\frac{q}{q_m} = \frac{K(c/C_o)}{1 + (K - 1)c/C_o} \qquad (3)$$

The Cu(II)-NH$_3$ system considered here forms labile complexes-the coordinated ammonia exchanges rapidly with other ligands. It is reasonable therefore to treat the exchange rate as mass transfer controlled. An effective value of the rate constant was calculated as described by Sherwood, Pigford and Wilke (Sherwood et. al., 1975). This procedure involves adding mass transfer resistances for the fluid phase and the resin phase, then correcting for the effect of the nonlinear equilibrium curve.

$$\frac{1}{k} = \frac{1}{b}\left[\frac{1}{k_f} + \frac{C_o}{k_p q_m \rho_B}\right] \qquad (4)$$

The correction factor b was obtained from a graph given by Sherwood et al. (1975). The Thomas solution takes the form

$$\frac{c}{C_o} = \frac{J(n/K,nT)}{J(n/K,nT) + [1 - J(n,nT/K)]\exp[(1 - K^{-1})(n - nT)]} \qquad (5)$$

with

$$n = \frac{kax}{v\epsilon} \qquad (6)$$

and

$$T = \frac{v\epsilon C_o t}{q_m \rho_B X} \qquad (7)$$

for the range of parameters in this paper the functions $J(n/K,nT)$ and $J(n, nT/K)$ reduce to 1.0 and 0.0 respectively so the solution is

$$\frac{c}{C_o} = \frac{1}{1 + \exp[(1 - K^{-1})(n - nT)]} \qquad (8)$$