$\overline{V}_0$ = characteristic velocity in Equation (3), cm./sec.
V_s = slip velocity, cm./sec.
V^o_s = slip velocity at zero holdup, cm./sec.
V^*_s = slip velocity at equilibrium, cm./sec.

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Influence of Resin Selectivity on Film Diffusion-Controlled Ion Exchange

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An analytic solution of the Nernst-Planck equations is derived which applies to a selective resin when film diffusion controls. The selectivity has a marked effect on the rate of exchange for a wide range of diffusivities. The unit-selectivity solution of Schlögl and Helfferich is included as a special case of the more general solution.

Ion exchange in solid-liquid systems is usually regarded as a double replacement reaction which may be written for monovalent cation exchange:

$$A^+Y^- + B^+R^- \rightleftharpoons B^+Y^- + A^+R^- \qquad (1)$$

A^+ and B^+ are the exchanging ions called *counterions,* Y^- is the accompanying ion in solution called the *coion,* and R^- is the fixed charged group on the exchanger matrix which ionically bonds with the counterions.

Since the activities of the reacting species are not readily determined (particularly in the exchanger), it is not convenient to describe this reaction in terms of a true equilibrium constant. Frequently another parameter is employed, called the selectivity coefficient α^A_B defined for reaction (1) as

$$\alpha^A_B = (\bar{C}_A\, C_B/\bar{C}_B\, C_A) \qquad (2)$$

where C is concentration. The superscript bar indicates the exchanger and the subscripts apply to the counterions.

Since the selectivity coefficient is defined in terms of concentrations, it is not necessarily independent of exchanger or solution composition. Pieroni and Dranoff (*1*) have shown that for the exchange of two monovalent ions, α^A_B is independent of total solution or exchanger concentration but is dependent on the mole fractions of A^+ and B^+ in both phases. It has been shown experimentally, however, that in many systems the equilibrium may be described adequately in terms of a constant selectivity coefficient.

It is generally accepted that the exchange rate is controlled by the diffusion of the reacting species through the solid and/or solution phases. Earlier diffusion models are based on a simple Fick's law approach in which the ex-

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change flux (or rate) is dependent on a concentration driving force and a constant diffusivity. These theories are applicable to isotope exchange, or the exchange of ions of equal mobility. If the counterions have different diffusivities, more than a simple concentration driving force is present, because an electrical field is generated which couples the fluxes of the exchanging ions.

This diffusion potential is a result of the charge carried by the ions. During the exchange process, the counterions are moving in opposite directions. There is a tendency for the more mobile ion to migrate at a higher rate. An accumulation of charge results in the system which retards the faster ion and accelerates the slower. Only a relatively small number of ions need be rearranged in this manner to establish a strong enough electric field to prevent further deviation from electroneutrality (2).

Recent ion exchange theory includes the effect of the diffusion potential. The Nernst-Planck equation expresses the diffusion flux in terms of a concentration driving force and an electric field. Schlögl and Helfferich (3) solved the equation analytically to obtain resin concentration as a function of time for the special case of film diffusion controlled exchange on a nonselective exchanger immersed in a solution of infinite volume. Helfferich and Plesset (4) solved the Nernst-Planck equation numerically for particle diffusion controlled exchange involving a selective resin. Only limited experimental verification of theories based on the Nernst-Planck flux equation is presented in the literature and its application is at present somewhat controversial. Helfferich (5) obtained reasonable agreement between predicted and observed exchange rates. Also the difference between forward and reverse rates was explained.

Hering and Bliss (6) studied particle-controlled exchange of six pairs of cations. They were able to correlate their data with either a Fick's law model or a Nernst-Planck model. The latter was preferred since it predicts the dependence of the overall diffusivity on the direction of exchange. Smith and Dranoff (7) studied sodium-hydrogen exchange with DOWEX 50W-X8 in a stirred tank. By assuming a film control mechanism, they were able to fit a Nernst-Planck model to their data.

The Nernst-Planck equation applies to all transferring ions in a given system for an externally applied field or for an internally generated field. It is restricted to ideal solutions, however, since the effect of activity coefficients has been neglected. Also, convection and pressure gradients have been neglected (2, 8).

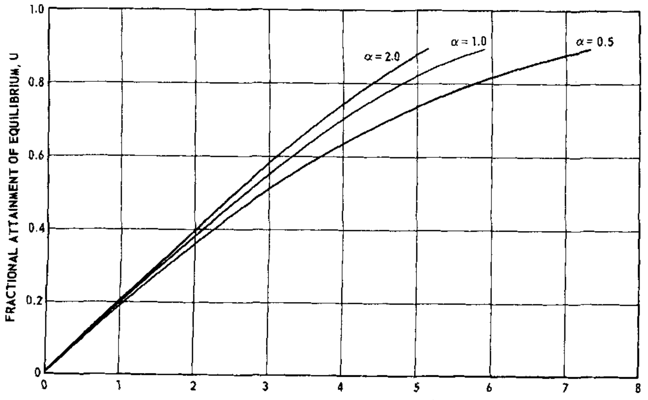

Fig. 1. Film-controlled exchange, $D_B/D_A = 7.0$.

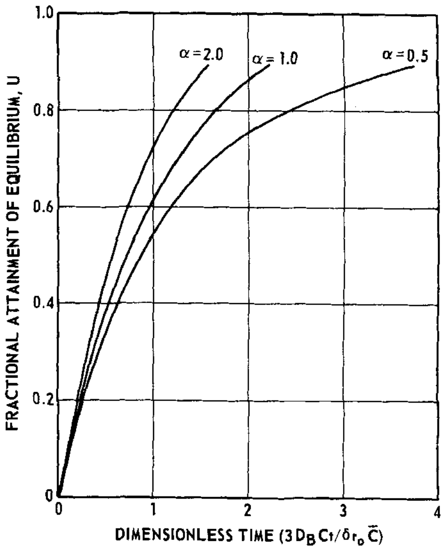

Fig. 2. Film-controlled exchange $D_B/D_A = 1.0$.

In the Nernst-Planck film model, the ion exchange is assumed to be a quasisteady state process, that is, the rate of change of conditions at the film boundaries is much slower than across the film. It is further assumed that concentration and field gradients occur only in the one direction. For each mobile monovalent ion, the flux is given by

$$J_i = -D_i \left[\frac{dC_i}{dx} + C_i \frac{df}{dx} \right] \tag{3}$$

where $f = F\phi z/RT$ and $i = A, B$, and W.

In addition the following conditions apply:

$$J_A + J_B = J_W = 0 \quad \text{No net current} \tag{4}$$

$$C_A + C_B = C_W \quad \text{Electroneutrality} \tag{5}$$

When we assume that an infinite volume of solution is present, the concentration of B in the liquid is zero at all times and the concentration of A equals the solution concentration C. Integration of Equation (3) from $x = 0$ at the solution side to any plane within the film gives

$$(C_A + C_B)\ (D_A C_A + D_B C_B) = D_A C^2 \tag{6}$$

For A replacing B on the resin, combining, integrating, and rearranging as was done by Schlögl and Helfferich (3) with the boundary conditions

$$x = 0, \quad C_A = C, \quad C_B = 0$$

and

$$x = \delta, \quad C_A = C'_A, \quad C_B = C'_B$$

we have

$$J_A = -\frac{2D_B D_A C}{\delta(D_B - D_A)} \left[\frac{1}{Y} - 1\right] \tag{7}$$

where

$$Y = \frac{D_A C'_A + D_B C'_B}{D_A C} \tag{8}$$

If the liquid at the surface is in equilibrium with the exchanger

$$C'_B = \frac{\alpha^A_B \bar{C}_B C'_A}{\bar{C}_A} \tag{9}$$

When Equations (6) and (9) are applied, Equation (8) becomes

$$Y = \left[\frac{1 + \dfrac{D_B}{D_A} \alpha^A_B \dfrac{\bar{C}_B}{\bar{C}_A}}{1 + \alpha^A_B \dfrac{\bar{C}_B}{\bar{C}_A}} \right]^{1/2} \tag{10}$$

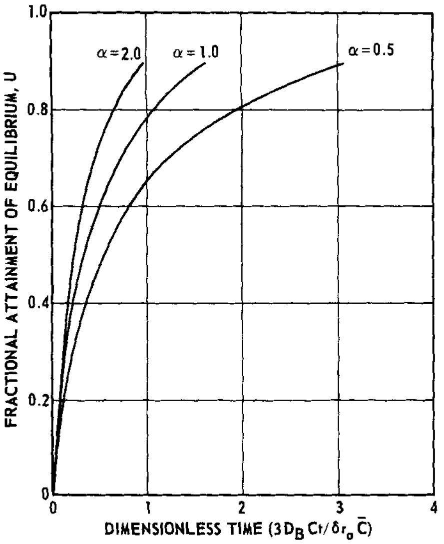

Fig. 3. Film-controlled exchange, D_B/D_A = 0.14.

For the infinite solution volume condition and for A replacing B, the fractional attainment of equilibrium is

$$U(t) = \frac{\bar{Q}_A(t)}{Q} \tag{11}$$

By material balance

$$\bar{Q}_A(t) = V\,\bar{C}_A(t) = \int_0^t J_A a\,dt, \quad \text{and} \tag{12}$$

$$\bar{Q} = V\,\bar{C} \tag{13}$$

Combination of Equations (11), (12), and (13) yields

$$U(t) = \frac{\int_0^t J_A a\,dt}{V\,\bar{C}} \tag{14}$$

If V is constant, and the particles are spheres

$$U(t) = \frac{3}{r_0\,\bar{C}} \int_0^t J_A\,dt \tag{15}$$

Differentiation with respect to time gives

$$\frac{dU}{dt} = \frac{3}{r_0\,\bar{C}} J_A \tag{16}$$

Alternatively, Equation (11) may be written for constant V:

$$U(t) = \frac{\bar{C}_A}{\bar{C}} \tag{17}$$

Substitution for $\bar{C}_A$ from Equation (10) gives

$$U = \frac{\alpha^A_B\left(\frac{D_B}{D_A} - Y^2\right)}{\alpha^A_B\left(\frac{D_B}{D_A} - Y^2\right) + (Y^2 - 1)} \tag{18}$$

Differentiating with respect to time and rearranging, we obtain

$$\frac{dU}{dt} = 2\left(1 - \frac{D_B}{D_A}\right)(\alpha^A_B) \frac{Y}{\left[\left(1 - \alpha^A_B\frac{D_B}{D_A}\right) + (\alpha^A_B - 1)\,Y^2\right]^2} \frac{dY}{dt} \tag{19}$$

Combination of Equations (7) and (16) yields

$$\frac{3\,D_BD_AC}{\delta\,\alpha^A_B\,r_0\,\bar{C}\,(D_A - D_B)}\,dt = \left(1 - \frac{D_B}{D_A}\right)\left[\frac{Y^2}{\left[\left(1 - \alpha^A_B\frac{D_B}{D_A}\right) + (\alpha^A_B - 1)\,Y^2\right]^2(1 - Y)}\right]dY$$

This equation is integrable under the boundary conditions

$$\text{at}\quad t = 0,\ Y = \left(\frac{D_B}{D_A}\right)^{1/2}$$

$$\text{at}\quad t = t,\ Y = Y$$

The integration of Equation (19) is cumbersome and is not included here. The process involves expanding the right-hand side into partial fractions. Each of the resulting simpler terms is easily integrated with the aid of a table of integrals. The result is

$$\begin{aligned}
\frac{3D_BC}{r_0\delta\bar{C}}\mathrm{t} = &-\frac{\left(1 - \frac{D_B}{D_A}\right)}{2(\alpha^A_B - 1)} \\
&\left[\frac{(\alpha^A_B - 1)\,Y - \left(1 - \alpha^A_B\frac{D_B}{D_A}\right)}{(\alpha^A_B - 1)\,Y^2 + \left(1 - \alpha^A_B\frac{D_B}{D_A}\right)} - \frac{(\alpha^A_B - 1)\left(\frac{D_B}{D_A}\right)^{1/2} - \left(1 - \alpha^A_B\frac{D_B}{D_A}\right)}{(\alpha^A_B - 1)\frac{D_B}{D_A} + \left(1 - \alpha^A_B\frac{D_B}{D_A}\right)}\right] \\
&+ \frac{(1)}{2\,\alpha^A_B}\ln\left[\frac{\left(1 - \alpha^A_B\frac{D_B}{D_A}\right) + (\alpha^A_B - 1)\,Y^2}{\left(1 - \alpha^A_B\frac{D_B}{D_A}\right) + (\alpha^A_B - 1)\frac{D_B}{D_A}}\right] \\
&- \frac{1}{\alpha^A_B}\ln\left[\frac{1 - Y}{1 - \left(\frac{D_B}{D_A}\right)^{1/2}}\right] + \left(\frac{1}{\alpha^A_B}\right)\left[(\alpha^A_B - 1) - (\alpha^A_B/2)\left(1 - \frac{D_B}{D_A}\right)\right] F\ (Y)
\end{aligned} \tag{20a}$$

Case I: For $\alpha_B^A < 1$ and $(D_B/D_A) > (1/\alpha_B^A)$ or $\alpha_B^A > 1$ and $(D_B/D_A) < (1/\alpha_B^A)$, then

$$F\ (Y) = \frac{1}{\left[(\alpha_B^A - 1)\left(1 - \alpha_B^A \frac{D_B}{D_A}\right) \right]^{1/2}} \left\{ \tan^{-1} \left\{ \left[\frac{\alpha_B^A - 1}{1 - \alpha_B^A \frac{D_B}{D_A}} \right]^{1/2} Y \right\} - \tan^{-1} \left[\frac{(\alpha_B^A - 1)\frac{D_B}{D_A}}{\left(1 - \alpha_B^A \frac{D_B}{D_A}\right)} \right]^{1/2} \right\}$$

Case II: For $\alpha_B^A < 1$ and $(D_B/D_A) < (1/\alpha_B^A)$ or $\alpha_B^A > 1$ and $(D_B/D_A) > (1/\alpha_B^A)$

$$F\ (Y) = \frac{1}{2\left[(1 - \alpha_B^A)\left(1 - \alpha_B^A \frac{D_B}{D_A}\right) \right]^{1/2}} \cdot$$

$$\ln \left\{ \frac{\left[(\alpha_B^A - 1)\ Y - \left\{ \left(1 - \alpha_B^A \frac{D_B}{D_A}\right)(\alpha_B^A - 1) \right\}^{1/2} \right]}{\left[(\alpha_B^A - 1)\ Y + \left\{ \left(1 - \alpha_B^A \frac{D_B}{D_A}\right)(\alpha_B^A - 1) \right\}^{1/2} \right]} \cdot \frac{\left[(\alpha_B^A - 1)\left(\frac{D_B}{D_A}\right)^{1/2} + \left\{ (1 - \alpha_B^A)\left(1 - \alpha_B^A \frac{D_B}{D_A}\right) \right\}^{1/2} \right]}{\left[(\alpha_B^A - 1)\left(\frac{D_B}{D_A}\right)^{1/2} - \left\{ (1 - \alpha_B^A)\left(1 - \alpha_B^A \frac{D_B}{D_A}\right) \right\}^{1/2} \right]} \right\}$$

For $(D_B/D_A) = (1/\alpha_B^A)$, Equation (20*a*) becomes

$$\frac{3 D_B C}{r_0 \overline{C}} t = \frac{1}{\alpha_B^A} \left[\ln \left(\frac{Y(\alpha_B^{A\ 1/2} - 1)}{1 - Y} \right) - Y + \left(\frac{D_B}{D_A} \right)^{1/2} \right] \qquad (20b)$$

Equation (20) will reduce to the relationship derived by Schlögl and Helfferich (3) for the case of unit selectivity coefficient (9).

$$-\frac{3 D_B C}{r_0 \delta \overline{C}} t = \ln \left[\frac{1 - Y}{1 - \left(\frac{D_B}{D_A} \right)^{1/2}} \right] + Y - \left(\frac{D_B}{D_A} \right)^{1/2} + (1/2)\left(Y^2 - \frac{D_B}{D_A} \right) \qquad (21)$$

Equation (20) is the general solution for film diffusion control and illustrates the role of selectivity. A series of numerical computations with Equation (20) used was carried out to establish the significance of both α_B^A and D_B/D_A. The results are shown in Figures 1, 2, and 3. The range of α_B^A and D_B/D_A values are generally those met in practice. For example when hydrogen ions replace sodium $D_B/D_A = 7.0$ and for the reverse case $D_B/D_A = 0.145$ and many resins exhibit selectivities between 0.5 and 2.0. The special case of $\alpha = 1$ corresponds to the Schlögl and Helfferich (3) solution and serves to illustrate the effect of diffusivity alone.

The electric field that develops across the film is given by (9)

$$\Delta E = \frac{RT}{2F} \ln Y \qquad (22)$$

For sodium replacing hydrogen the potential difference across the film is about 30 mv. and for the reverse case it is −7.7 mv. Despite the seemingly large potential difference, the deviation from electroneutrality is very small (9) and the assumption of electroneutrality is well justified.

NOTATION

a = surface exchanger, sq.cm./cc. exchanger
C = concentration, meq./cc.
D = diffusivity, sq.cm./sec.
ΔE = voltage across diffusion film
f = $F\phi/RT$
F = Faraday's electrochemical equivalent constant, 96,500 coulomb/eq.
J = ionic flux, meq./(sq.cm.) (sec.)
Q = amount of ionic species, meq.
r_0 = particle radius, cm.
T = absolute temperature, °K.
t = time
U = fractional attainment of equilibrium
V = volume, cc.
x = distance from film/solution boundary toward exchanger surface, cm.
Y = parameter
α_B^A = selectivity coefficient
δ = film thickness, cm.
ϕ = electrostatic potential, v.

Subscripts

A = counterion A
B = counterion B
0 = initial value
W = coion Y
∞ = equilibrium
$'$ = resin-film interface
— = resin phase

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