

Greek Letters

β	= constant exponent Equation (15)
δ	= slope increment
η	= viscosity
$[\eta]$	= intrinsic viscosity $[\eta] = (\eta - \eta_s)/c\eta_s$, limit as c and shear rate approach zero
η_e	= elongational viscosity
η_o	= initial viscosity of undegraded solution
η_s	= solvent viscosity
η_{sp}	= specific viscosity, $(\eta - \eta_s)/\eta_s$
ν	= kinematic viscosity, $\nu = \eta/\rho$
ρ	= density
τ	= shear stress
τ_o	= wall shear stress, $(-\Delta P)D/4L$

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Mass Transfer Characterization of Donnan Dialysis

Donnan dialysis is a relatively new ion exchange process using ion exchange membranes to permit continuous operation. Potential applications exist in many areas where traditional columnar ion exchange, requiring a regeneration cycle, is currently used. A mathematical model was developed. Mass transfer parameters for the model were determined from laboratory data and correlated with the system operating variables.

Donnan dialysis is a continuous ion exchange membrane process based on the Donnan equilibrium equation (Don-

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nan, 1924) applied to permselective membranes. These membranes have fixed charges incorporated into their structure and are permeable to ions of the opposite charge (counterions) while excluding ions of the same charge (coions). The significant aspect of the Donnan relationship is that concentration ratios are the important factors in

determining equilibrium, not concentration differences. For example, if a solution containing a low concentration of cesium nitrate is placed on one side of a cation transport membrane, while a second solution containing a high concentration of nitric acid is placed on the opposite side, both cesium and hydrogen ions will diffuse through the membrane until the Donnan equilibrium equation is satisfied. The result is that the large concentration gradient of the hydrogen ions will effectively pump the cesium ions across the membrane into the second solution until it reaches a concentration substantially higher than its origi-

nal value. At the same time, the cesium concentration in the first solution is reduced.

This has obvious potential for use in concentrating valuable materials in ionic form from dilute solutions and in stripping undesired ionic species from process or waste streams. Both types of applications have received the attention of several investigators. While these studies represent a great deal of laboratory investigation which has confirmed the potential of the Donnan dialysis process, relatively little effort has been directed toward obtaining a quantitative understanding and characterization of the mass transfer processes involved.

CONCLUSIONS AND SIGNIFICANCE

A mathematical model of Donnan dialysis was developed which includes series mass transfer resistances located in the feed channel boundary layer and in the membrane. Resistance to mass transfer in the strip channel was neglected. In order to separate the feed channel and membrane resistance, continuous flow, stirred cell experiments were used to independently determine the membrane counterion mass transfer coefficient (K_{mA}). The feed channel counterion mass transfer coefficient (K_{fA}), along with the coion leakage coefficient (K_N) and the solvent permeability constant (K_o), were determined from operating data on a parallel channel counterflow dialyzer.

The K_{mA} values applicable to the dialyzer were determined to be approximately one third the magnitude of those measured in the stirred cells. With this adjustment, the K_{fA} values for all systems investigated were adequately correlated by

$$N_{Sh} = 0.181 N_{Re}^{0.65} N_{Sc}^{0.40}$$

The K_N and K_o values were found to depend only on temperature and total ionic strength.

Several significant conclusions were drawn from this work. First, the basic mass transfer model did successfully correlate the laboratory data and proved useful for design calculations. Second, the model indicated that while univalent feed ions (sodium, potassium) exhibited evidence of both feed boundary layer and membrane resistances (with boundary-layer resistance generally predominant), a bivalent feed ion (calcium) was strongly membrane resistance controlled. Finally, the reduction in the effective membrane coefficient for the dialyzer as compared to the stirred cells indicates the presence of an additional mass transfer resistance, hypothesized to be a strip channel boundary-layer resistance.

BACKGROUND

Initial efforts to model binary transport in ion exchange resins used an equation developed by Helfferich and Plesset (1958) based on the Nernst-Planck equation (Helfferich, 1962) for resin (or membrane) phase diffusion. The coefficient of this nonlinear analogue of Fick's first law of diffusion is often referred to as the interdiffusion coefficient. Brooke and Rees (1968, 1969) and Barrer et al. (1973) found the Helfferich-Plesset equation unreliable when interdiffusion coefficients were computed from ionic self-diffusion coefficients. Sharma et al. (1970) demonstrated that physical changes with ionic content (principally swelling) were the source of this difficulty in organic resins. Tombalakian et al. (1967) determined the interdiffusion coefficient for several ion pairs in membrane systems.

The Nernst-Planck equation, and thus the Helfferich-Plesset equation, considers only the primary (electrical) coupling of the ionic fluxes in this multicomponent diffusion problem. The linear flux relations of Onsager (1965) provide a rather complex framework encompassing coupling of all fluxes in the system. A series of experiments in idealized systems to evaluate these couplings was proposed by Speigler (1958). Several authors (Mackey and Meares, 1959; Caramazza et al., 1963; Lightfoot and Scattergood, 1965; Scattergood and Lightfoot, 1968) have performed the experiments and have concluded that the interactions are not always negligible.

An appreciable amount of experimental work has been

done by Wallace (1967, 1969) in the stripping and concentration of dilute cations, mainly uranyl (UO_2^{++}) ions, in a Donnan dialyzer. Work on a similar system with recycle was done by Davis et al. (1971). Smith (1970, 1971) studied sodium-calcium exchange for water softening applications experimentally and presented a reaction kinetic (rather than diffusional) model based on the Donnan equilibrium equation. Melsheimer et al. (1973) applied a diffusional model with a constant membrane diffusivity along with the Donnan equilibrium equations for both membrane interfaces to uranyl-hydrogen and sodium-hydrogen exchange in a dialyzer. The model yielded satisfactory results for uranyl but was inadequate for sodium systems.

The above models assume all counterion resistance to be in the membrane phase. Van Brocklin and David (1972) made a computer investigation of mass transfer with the liquid film controlling using film penetration and boundary-layer models to relate transfer rates of electrolytes to the conventional nonelectrolyte system. Helfferich (1962) also discussed partial and complete liquid phase controlling, again with no experimental data.

THEORETICAL DEVELOPMENT

The mathematical model consists of overall and component mass balances, mass transfer rate equations, equilibrium relations and electroneutrality constraints, and thermodynamic equations for the system state properties. The system for which these equations are developed is the thin parallel channel Donnan dialyzer shown sche-

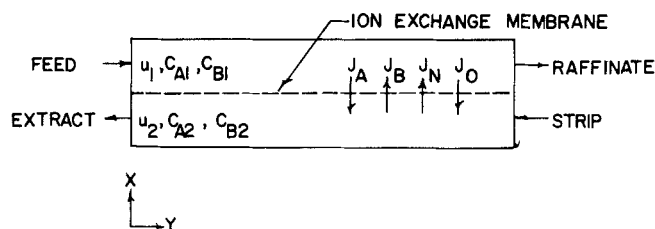


Fig. 1. Schematic of a countercurrent Donnan dialyzer.

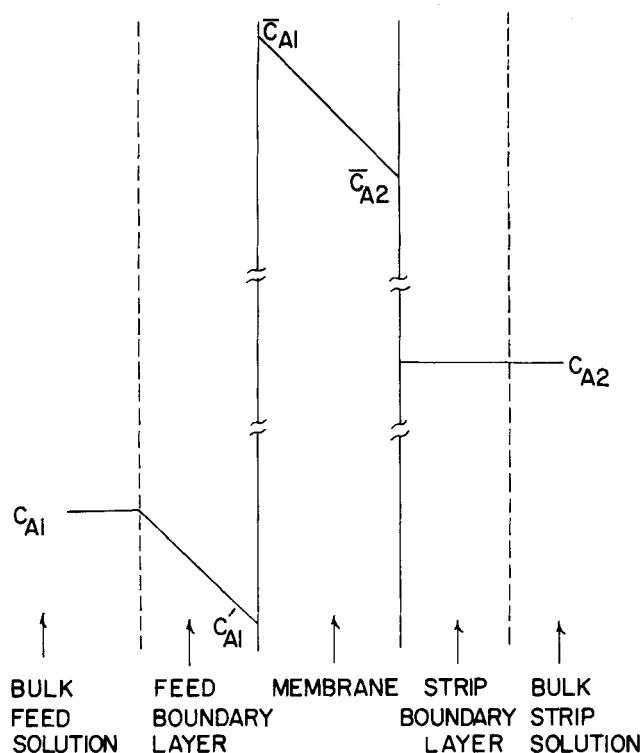


Fig. 2. Qualitative illustration of cross-sectional concentration profile of counterion A.

matically in Figure 1. The development of mass transfer rate equations to adequately describe the counterion, coion, and osmotic fluxes in the dialysis process was the primary object of this study.

The differential mass balances are

$$\frac{du_k}{dx} = - \frac{\sum J_i (MW_i) + J_o (MW_s)}{\rho_k h_k} \quad (1)$$

$$\frac{d(C_{ik}u_k)}{dx} = J_i/h_k \quad (2)$$

Assumptions made in formulating these equations were:

1. Countercurrent flow of feed stream ($k = 1$) and strip stream ($k = 2$).
2. Steady state operation.
3. Plug flow in the channels.
4. Constant density and temperature in each stream.

Electroneutrality requirements lead to the following relations between fluxes and the concentrations of the various ions in each stream:

$$\sum Z_i C_{ik} = 0 \quad (3)$$

$$\sum Z_i J_i = 0 \quad (4)$$

In the development that follows, the additional assumption is made that only two counterions [the feed counterion (A) and the strip counterion (B)] and one coion (N) are present in the system. Equation (3) may then be used to eliminate the component mass balances for the coion and Equation (4) to eliminate the flux of counterion B from the component mass balance equations for ions A and B.

The input concentrations of ions A and B in each stream, plus the input velocities of the strip and feed streams, provide the necessary boundary conditions. In data analysis problems, the process outputs are also known, and the mathematical model is used to solve for the mass transfer parameters of the flux equations by use of a nonlinear regression scheme.

The model recognizes mass transfer resistances in the feed channel boundary layer and in the membrane and neglects the strip channel boundary-layer resistance indicated by previous studies to be insignificant. Coion absorption by the membrane was also neglected in the initial formulation. Further, coupling of the fluxes is allowed only through the electroneutrality constraints. Direct flux cross coupling, while not always insignificant, is generally a secondary effect and is omitted to obtain a tractable and determinable model.

Figure 2 illustrates the concentration profiles of the dialysis system with these assumptions. The counterion, coion, and solvent flux equations are

$$J_A = K_{mA}(\bar{C}_{A1} - \bar{C}_{A2}) \quad (5)$$

$$J_A = K_{fA}(C_{A1} - C'_{A1}) \quad (6)$$

$$J_B = K_{fB}(C_{B1} - C'_{B1}) \quad (7)$$

$$J_N = K_N(C'_{N1} - C_{N2}) \quad (8)$$

$$J_o = K_o[(P_1 - P_2) - (\phi_1 - \phi_2')] \quad (9)$$

The two film transport coefficients are related by

$$\frac{K_{fA}}{K_{fB}} = \left[\frac{D_{AN}}{D_{BN}} \right]^{0.6} \quad (10)$$

Equation (10) expresses the relationship implicit in the film coefficient correlation equation obtained in this study, Equation (14).

The Donnan equilibrium equation is the thermodynamic relation for ionic equilibrium across permselective membranes. In the present case, this equation applies at each fluid-membrane interface and may be written at the strip as

$$\left[\frac{\bar{a}_i}{a_i} \right]^{1/z_i} = \left[\frac{\bar{a}_j}{a_j} \right]^{1/z_j} = \dots \quad (11)$$

On the feed stream side of the system, the Donnan equation is written to express equilibrium between the film and membrane concentrations:

$$\left[\frac{\bar{a}_i}{a'_i} \right]^{1/z_i} = \left[\frac{\bar{a}_j}{a'_j} \right]^{1/z_j} = \dots \quad (12)$$

An electroneutrality constraint also applies to the membrane phase concentrations and includes a term to account for the membrane fixed charge concentration:

$$\sum Z_i \bar{C}_i = \bar{X} \quad (13)$$

Equations (1) to (13) constitute the mathematical model of the dialyzer. Equations (1) and (2) are integrated over the length of the dialyzer, with Equations (3) to (13) solved algebraically at each integration step to evaluate the counterion, coion, and solvent fluxes.

EXPERIMENTAL

The mathematical model contains four transfer coefficients. The membrane counterion coefficient K_{mA} should not depend on the fluid boundary layers within the Donnan dialyzer and was isolated and determined separately with continuous overflow, well-stirred cell experiments. The remaining coefficients (K_{fA} , K_N , and K_o) were evaluated using data taken with a countercurrent, single-membrane dialyzer. Coefficients were determined which minimized the sum of squares of the deviations between the experimental and computed dialyzer effluent concentrations and flows. The experimental systems and procedures used are outlined in the following sections. Details are given in Lake (1975).

Stirred Cells

A set of Plexiglas cells as shown in Figure 3 was equipped with two high speed, three-bladed impeller stirrers. A section (19.7 cm²) of Nafion120® membrane (1200 equivalent weight, 10 mils nominal thickness) was sandwiched between the two cells and gasketed by a layer of silicone rubber on each cell face. The plan was to increase the stirring rate until a transfer plateau was reached, indicating that the boundary-layer resistance had been eliminated. However, the practical upper limit of the stirrers was reached prior to the plateau, making an extrapolation technique necessary. Stirred-cell experiments were made at 25°, 50°, and 70°C using a one and three molar nitric acid strip solution for each of the ions studied (sodium, potassium, and calcium). A range of feed ion concentrations was studied.

Countercurrent Dialyzer

Using the membrane counterion coefficient from the stirred-cell experiment, the remaining coefficients were calculated from the model as applied to the experimental dialyzer of Figure 4. The feed containing a single, dilute nitrate salt (sodium, potassium, or calcium) was passed countercurrently to a concentrated nitric acid strip stream with a flow about two orders of magnitude less than the feed flow.

The flow channels of each stream were created by a stainless steel wire screen with a silicone rubber gasket (0.12 mm thick on each face of the screen) defining the transfer area (5.08 cm × 82.2 cm). The screens used were 20 mesh, 0.356 mm diameter wire or 40 mesh, 0.169 mm wire, depending on the channel height desired. The system was operated with the strip pressure higher than the inlet feed pressure such that the membrane was pressed against the feed channel screen throughout the dialyzer. The feed channel height was twice the diameter of the wire of the spacer, and the strip channel height was twice the wire diameter plus the height of the combined compressed gaskets (approximately 0.32 mm). The effective channel height used in the calculations accounted for the wire volume of each spacer.

For each ion, the effect of the following parameters on the transfer coefficients was studied: strip flow (0.015 to 0.25 cm³/s), feed flow (0.800 to 12.5 cm³/s), strip stream acid concentration (1 and 3 kmole/m³), feed stream salt concentration (0.002 to 0.04 kmole/m³), feed stream acid concentration (0 to 10 times the feed salt concentration), temperature (25°, 50°, and 70°C), and channel height (0.169 and 0.356 mm wire spacers). For sodium, sufficient data were taken to study the interrelations of the parameters.

Measurements

After the system was allowed sufficient time (2 to 4 hr) to insure steady state operation, data from the run were taken. Outlet flow rates were measured by collecting timed samples in volumetric flasks, while inlet flow rates were determined from timed volumes (stirred cells) or rotameters (dialyzer). Temperatures were measured by thermometer or thermocouple recorder (dialyzer inlets). Pressures were measured with gauges, and the stirred cell stirring rates were determined stroboscopically.

Determination of hydrogen ion concentrations of the inlet and outlet stream samples was by titration to a phenolphthalein end point. Metal ion concentrations were determined by atomic absorption spectrophotometry.

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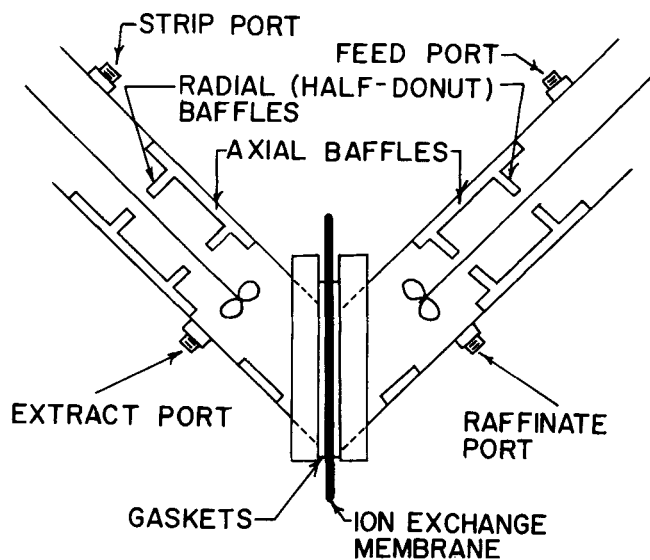


Fig. 3. Stirred-cell dialyzer.

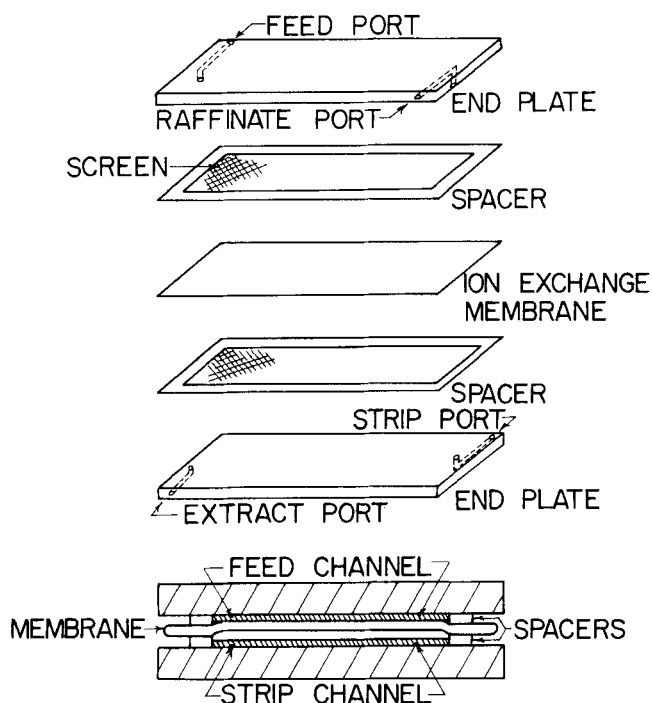


Fig. 4. Countercurrent thin channel dialyzer.

RESULTS AND DISCUSSION

The data and results for the stirred-cell and dialyzer experiments are voluminous. Consequently, only selected results which support the following discussion are presented in condensed form. Lake (1975) gives the complete data and results of this study.

Stirred-Cell Experiments

The K_{mA} values were computed using a single resistance, membrane controlling, flux model. This is simply Equation (5), with the Donnan equilibrium equation at both interfaces written in terms of bulk fluid properties rather than boundary-layer values.

The volumetric concentration of the fixed charges in the duPont Nafion 120® membrane was determined from an empirical equation presented by Grot et al. (1972) to be

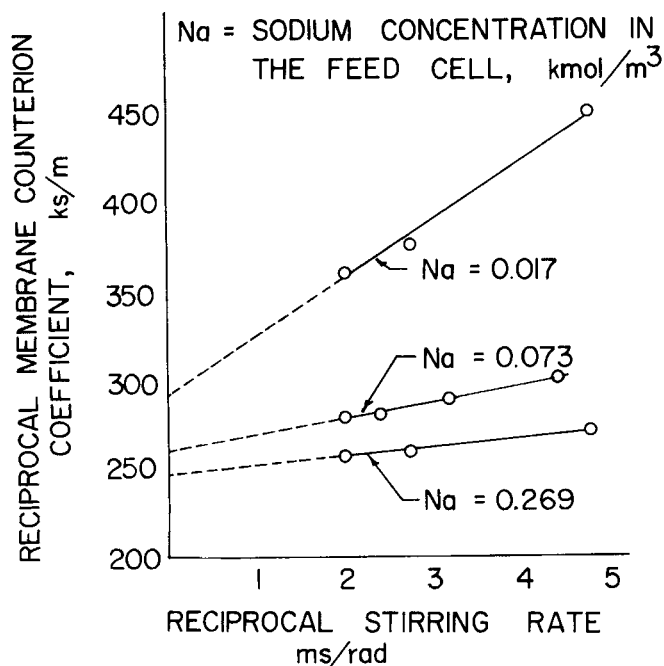


Fig. 5. Modified Wilson plot of stirred-cell data.

approximately 1.0 kequiv/m³. This value was used for all results presented in this paper.

The intended method for evaluating K_{mA} was to increase the stirring rate until all fluid phase resistance was eliminated. However, the highest stirring rate, 500 rad/s, was inadequate to accomplish this. Therefore, an extrapolation technique, illustrated in Figure 5, was utilized to estimate the K_{mA} value at infinite stirring rate. The data points generally lay on a straight line, lending credence to the technique.

The feed ion concentrations affect the value of the extrapolated membrane coefficient as may be seen in Figure 5. As the sodium concentration is increased, the slope of the curves in Figure 5 is decreased, and the extrapolated value of the membrane coefficient approaches a limiting value. The slope is indicative of the strength of the film resistance; the greater the slope, the greater the film resistance relative to the membrane resistance. For the lower sodium concentrations, the stirring rate is insufficient to reduce the film resistance to the region where the membrane resistance controls. As the supply of sodium on the feed side of the membrane increases at higher concentrations, the system more quickly approaches the point at which the rate of transport through the membrane is limiting. Thus, at higher sodium concentrations, the coefficient of the controlling membrane resistance may be extrapolated with greater accuracy. The convergence of the extrapolations at higher sodium concentrations indicates that the extrapolated value of K_{mA} , within limits, is independent of the sodium concentration.

Table 1 summarizes the stirred-cell data taken with sufficiently high feed ion concentrations to produce accurate extrapolations. Note that for the bivalent ion, calcium, the concentration required was much lower than for the univalent ions (sodium, potassium). This indicates a higher degree of membrane control for bivalent ions.

The acid concentration also affects the K_{mA} values significantly. This is attributed to the change in membrane state, especially swelling, with large changes in the ionic environment of the membrane. This variation of K_{mA} with acid concentration was taken into account in the model with a simple linear fit to the data. Temperature,

TABLE 1. MEMBRANE COUNTERION COEFFICIENTS FROM STIRRED-CELL EXPERIMENTS EXTRAPOLATED TO INFINITE STIRRING RATE

Counterion, A	Temp., °C	Concentration of A in the feed cell, kmole/m ³	Concentration of hydrogen ions in the strip, kmole/m ³	Extrapolated membrane counterion coefficient $\bar{X} = 1.0$ kequiv/m ³ , $\mu\text{m/s}$
Sodium	25	0.073	1.01	3.53
	25	0.268	1.95	4.25
	25	0.073	3.03	5.11
	50	0.252	0.89	6.29
	50	0.286	3.09	6.73
	70	0.244	0.89	8.33
	70	0.233	3.08	9.52
	70	0.071	0.95	4.88
Potassium	25	0.066	1.95	5.72
	25	0.065	3.04	7.14
	50	0.061	0.93	7.97
	50	0.071	2.87	11.50
	70	0.054	0.92	12.60
	70	0.048	2.87	15.90
	25	0.012	0.99	2.37
	25	0.010	1.99	2.87
Calcium	25	0.010	3.00	3.17
	50	0.009	0.94	3.75
	50	0.007	2.97	5.08
	70	0.006	0.94	5.13
	70	0.010	2.92	7.07

as may also be observed in Table 1, has the expected strong effect on the membrane coefficient.

While K_o and K_N are membrane properties that should be determinable from stirred-cell data, the solvent and anion fluxes in the stirred-cell system were too small for accurate measurement. Consequently, these parameters were computed from the countercurrent dialyzer data.

Countercurrent Dialyzer

Several versions of the model were investigated before the final formulation was derived. For each version, correlation of the K_{fA} values with system operating conditions was sought and graphs similar to Figures 6 to 8 produced. The consistency of the K_{fA} values (as repre-

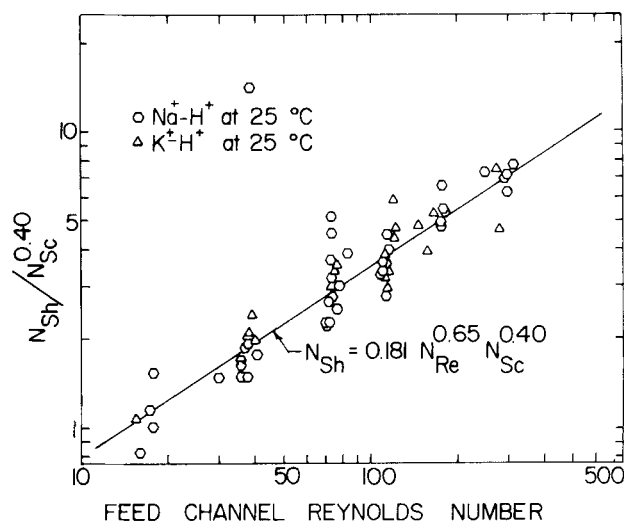


Fig. 6. Correlation of feed boundary-layer coefficients of sodium and potassium exchange with hydrogen at 25°C.

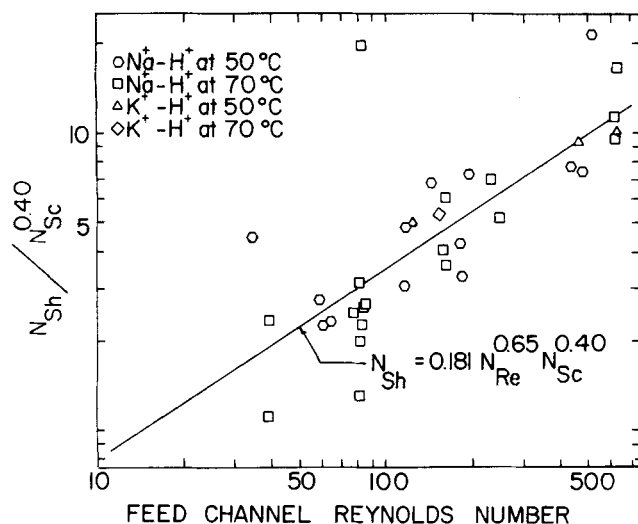


Fig. 7. Correlation of feed boundary-layer coefficients of sodium and potassium exchange with hydrogen at elevated temperatures.

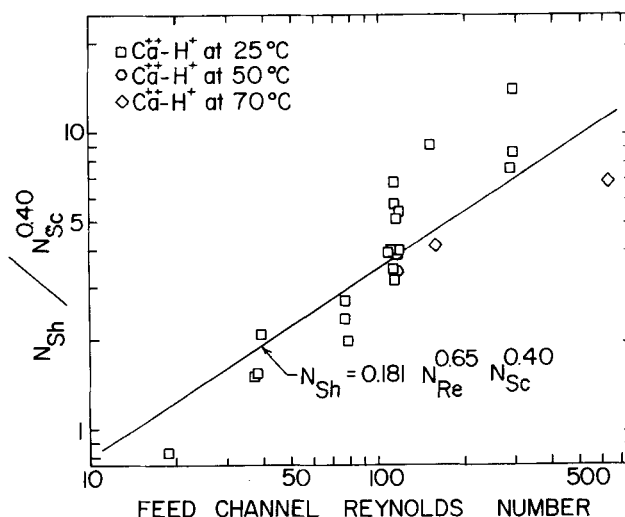


Fig. 8. Correlation of feed boundary-layer coefficients of calcium exchange with hydrogen.

sented by the Sherwood number) was the principle criterion for evaluation of the various model formulations.

To evaluate the activities in the Donnan equilibrium Equations (11) and (12), activity coefficient correlations (Bromley, 1972; Meisner and Kusik, 1972; Meisner et al. 1972) were used. While significant nonidealities were computed, the ratio form of the Donnan equation caused the model predictions to be altered very little from an ideal solution assumption. Owing to the appreciable advantage in computer time consumption which resulted, the ideal solution assumption was retained.

At the interface with the very concentrated strip solution, the assumption of negligible coion absorption is suspect (Helfferich, 1962). The model was modified to incorporate this effect, but no improvement was observed in the transport coefficient correlations. However, this phenomenon may bear further study, since significant alterations in internal concentration profiles were predicted.

The dialyzer studies with the bivalent feed ion, calcium, showed the feed channel coefficient (K_{fA}) values to have very little effect on the fit of the model predictions to the dialyzer data. These results indicated its transport to

be strongly membrane controlled, reinforcing earlier observations from the stirred cell experiments. Further evidence on this point was obtained by using the single resistance model (membrane controlling) of Melsheimer et al. (1973) to analyze the dialyzer data for calcium-hydrogen exchange. The apparent membrane coefficient (K_{mA}) values determined were nearly independent of the feed channel velocity. However, the apparent K_{mA} values for calcium as determined from dialyzer data were about one third the magnitude of the actual K_{mA} values from the stirred cell experiments. As the strip solution in the stirred cells was highly agitated, while very slight agitation exists in the strip channel of the dialyzer, this was taken to be evidence of a very significant (albeit nearly constant) resistance to mass transfer in the dialyzer strip channel.

If this hypothesis were true, similar effects should be observed with the univalent systems (sodium, potassium) studied. The stirred cell K_{mA} values for the univalent system were reduced by comparable amounts and the K_{fA} values redetermined. The best overall fit was obtained with adjustment factors of 0.30 for calcium, 0.33 for

TABLE 2. CONCENTRATION PROFILES CALCULATED AT THE AXIAL MIDPOINT OF THE COUNTERCURRENT DIALYZER

Temperature = 25°C

Feed concentration ≈ 0.01 kmole/m³ nitrate salt

(Except run 154 ≈ 0.02 kmole/m³; run 155 ≈ 0.04 kmole/m³)

Strip concentration ≈ 3.00 kmole/m³ nitric acid

Spacer wire diameter = 0.356 mm

Feed flow ≈ 5.0 cm³/s

Strip flow ≈ 0.05 cm³/s

System	Run number	Concentrations of counterion A					Normalized gradients	
		C_{A1}	C'_{A1}	\bar{C}_{A1}	\bar{C}_{A2}	C_{A2}	$\frac{C_{A1} - C'_{A1}}{C_{A1}}$	$\frac{\bar{C}_{A1} - \bar{C}_{A2}}{\bar{X}/Z_A}$
		kmole/m ³					Boundary layer	Membrane
Na ⁺ — H ⁺	153	0.0079	0.0038	0.361	0.060	0.155	0.52	0.30
	154	0.0177	0.0117	0.565	0.101	0.258	0.34	0.46
	155	0.0381	0.0314	0.756	0.142	0.366	0.18	0.61
	130	0.00630	0.00265	0.270	0.072	0.179	0.58	0.20
K ⁺ — H ⁺	118	0.00848	0.00683	0.440	0.025	0.155	0.19	0.83

TABLE 3. AVERAGE COION AND SOLVENT FLUX COEFFICIENTS

Temperature, °C	Approximate strip H ⁺ concentration, kmole/m ³	Coion flux coefficient, nm/s	Water flux coefficient, nmole m ² · s · Pa
25	1.0	45.4	2.45
25	3.0	66.5	1.87
50	1.0	66.9	3.50
50	3.0	77.8	2.83
70	1.0	96.1	4.16
70	3.0	125.0	3.58

sodium, and 0.40 for potassium. In each case, the apparent K_{mA} is approximately one third the actual K_{mA} the lower value accounting for the additional resistance hypothesized to be in the strip channel. With this adjustment, the equation

$$N_{Sh} = 0.181 N_{Re}^{0.65} N_{Sc}^{0.40} \quad (14)$$

was found to correlate all K_{fA} data on the systems studied.

Figures 6, 7, and 8 show the data correlated by this model. The overall scatter of the data was significantly improved by the adjustment of the membrane coefficients. This appears to substantiate the hypothesis of a strip boundary-layer resistance. Fortunately, over the strip stream flow range studied, there was little evidence of variation in this strip side resistance in that no systematic variation of K_{fA} with the strip stream velocity was discernible. Thus, the adjustment of the K_{mA} values adequately accounts for the strip boundary-layer resistance.

Further insight into the relative importance of the membrane and feed film resistances may be obtained from the computed concentration profiles across the dialyzer given in Table 2 for selected runs. This table also gives values of the concentration gradients in the feed film and membrane normalized with respect to the maximum possible gradient in each case. Thus, a higher value of the normalized gradient indicates a higher resistance to mass transfer, with values near unity indicating complete dominance by one resistance. The first three runs listed for sodium-hydrogen exchange clearly show the effect of the feed ion concentration on the relative gradients. At lower concentrations (run 153) the boundary-layer resistance

was more significant, while the membrane resistance clearly dominates at higher concentration levels (run 155). Under conditions where membrane resistance predominates, a moderate error in the value of K_{mA} would lead to a major discrepancy in the value of K_{fA} determined by regression on dialyzer data. This is the primary cause of the largest deviations in the data presented in Figures 6 to 8. The other univalent feed ion, potassium, behaved in much the same fashion as sodium.

The bivalent feed ion, calcium, displayed strong membrane dominated behavior at all concentration levels studied, as typified by run 118 of Table 2. There are three principal reasons for this: first, the calcium ionic diffusivity in the membrane phase is appreciably lower; second, the Donnan equilibrium equation predicts a much greater membrane affinity for bivalent ions; and third, the maximum membrane phase concentration of bivalent ions is half that of univalent ions ($\bar{X}/2$ rather than \bar{X}). Thus, the membrane transport ability saturates at lower external concentrations. The membrane controlled behavior of calcium in the dialyzer is consistent with the stirred-cell results in which the effect of stirring rate was much smaller for calcium than for the univalent ions at comparable concentrations.

The coion (K_N) and solvent (K_o) transport coefficients were found to exhibit systematic variation only with temperature and the strip acid concentration. No dependence on fluid channel hydrodynamics was observed, and variation with the different feed counterions was too small to be given any significance. This supports the assumption that K_N and K_o are membrane properties, dependent only on the membrane state and the species being transported. Values of K_N and K_o for the range of conditions studied are given in Table 3.

These values, along with Equation (14), the K_{mA} values of Table 1, and the K_{mA} adjustment factors complete the model for design application. This design model has been tested against the laboratory data and found to be adequate over the range of the experimental conditions. A sample of the design program predictions is given in Table 4. The poorest agreement with the experimental results was observed for run 15 and was only about 10% in error. The K_{fA} value determined for this run deviated over 400% from the correlation of Equation (14), a result of the membrane phase resistance controlling the counterion transport under conditions of high feed ion

TABLE 4. COMPARISON OF EXPERIMENTAL DATA WITH VALUES CALCULATED FROM A DESIGN PROGRAM

$K_{fA} = 0.181 N_{Re}^{0.65} N_{Sc}^{0.40} \left(\frac{D_{AN}}{h_1} \right) \text{m/s}$ $K_N = 66.5 \text{ nm/s}$ $K_o = 1.87 \text{ nmole water/m}^2 \cdot \text{s} \cdot \text{Pa}$						
Parameters used in design program						
	Concentration of A in the extract		Concentration of H ⁺ in the extract		Velocity of the extract	
Run number	Experimental kmole/m ³	Calculated % error	Experimental kmole/m ³	Calculated % error	Experimental mm/s	Calculated % error
Ca ⁺⁺ — H ⁺ Exchange at 25°C						
89	0.213	0.0%	2.06	1.0%	1.90	0.3%
94	0.299	−4.3%	1.71	0.8%	1.68	9.8%
103	0.297	0.0%	1.70	1.4%	1.84	4.6%
114	0.293	−5.8%	1.84	0.0%	1.46	1.0%
Na ⁺ — H ⁺ Exchange at 25°C						
15	0.726	−10.2%	1.39	6.3%	2.26	0.0%
16	0.556	−5.4%	1.56	5.6%	2.41	−2.3%
85	0.333	0.6%	1.84	−0.8%	1.50	1.2%

concentration. The conditions of run 15 were similar to those of run 155 in Table 2, differing somewhat in feed stream velocity. Similarly, in the case of calcium, the design predictions are in good agreement with the experimental results, despite appreciable discrepancies in the K_{fA} values.

While the overall level of accuracy illustrated by Table 4 would be satisfactory for most design purposes, the model has not been tested for ionic systems or membranes other than those described within, and the model validity for such cases is unknown. In any event, application with other systems or membranes requires further work to evaluate the membrane transport parameters.

Investigation is under way on the identification of the additional mass transfer resistance represented by the K_{mA} adjustment factor used in this model, presently hypothesized to be a strip channel resistance. Another area receiving study is the extension of modeling capability to include systems with more than two counterions.

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NOTATION

- a_i = activity, mole/ m^3
 C_{ik} = concentration, mole/ m^3
 h_k = flow channel height, m
 D_{ij} = diffusivity of salt ij , m^2/s
 J_i = molar flux of ion i , mole/ $m^2 \cdot s$
 J_o = osmotic (solvent) flux, mole/ $m^2 \cdot s$
 K_{fi} = feed channel counterion i transport coefficient, m/s
 K_{mi} = membrane phase counterion i transport coefficient, m/s
 K_N = coion leakage transport coefficient, m/s
 K_o = osmotic flux coefficient, mole/ $m^2 \cdot s \cdot Pa$
 MW_i, MW_s = molecular masses of ion i and solvent, respectively, g/mole
 N_{Sh} = Sherwood number of the feed stream, $K_{fA}h_1/D_{AN}$
 N_{Sc} = Schmidt number of the feed stream, $h_1u_1\rho_1/\mu_1$
 N_{Re} = Reynolds number of the feed stream, μ_1/ρ_1D_{AN}
 P = hydrostatic pressure, Pa
 u_k = stream velocities, m/s
 x = axial distance from feed stream inlet, m
 \bar{X} = concentration of fixed charges in the membrane, equiv/ m^3
 Z_i = valence of ion i
 μ_1 = viscosity of the feed stream, Pa $\cdot s$
 ρ_k = density, kg/ m^3
 ϕ_k = osmotic pressure, Pa

Subscripts

- i = ionic species i
 k = flow channel k (1 = feed, 2 = strip)
 s = solvent
 A, B = feed (A) and strip (B) counterions
 N = coion N

Superscripts

- ' = external solution property at the membrane interface
 $-$ = membrane phase property at the solution interface

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