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"Mathematical Modeling of Donnan Dialysis,
A Continuous Ion Exchange Membrane Process"

Submitted by

Stephen S. Melsheimer
Associate Professor
Clemson University
Clemson, South Carolina 29631

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SUMMARY

During this period of research the mathematical model of Donnan dialysis was extended to include 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 resistances, 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

$$N_{Sh} = 0.201 N_{Re}^{0.62} N_{Sc}^{0.40}$$

where the dimensionless groups are the Sherwood Number, Reynolds Number, and Schmidt Number, respectively. The K_N and K_O values were found to depend only on temperature and total ionic strength.

The model is programmed in Fortran and utilizes the Hooke-Jeeves Pattern Search algorithm for identifying the parameters by nonlinear regression. The efficiency of solution is significantly improved over earlier single resistance models programmed in CSMP with a Partan regression algorithm for both data analysis and design applications.

The research project met all primary goals set in the initial research proposal, and with expenditures closely following those outlined in the cost

estimate budget. 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 the univalent feed ions (sodium, potassium) exhibited both feed boundary layer and membrane resistances, with boundary layer resistance generally predominant, the 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 strongly indicates the presence of a significant mass transfer resistance in the strip channel of the dialyzer.

BACKGROUND

Donnan dialysis is a continuous ion exchange membrane process based on the Donnan equilibrium equation (Donnan, 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 factor 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 original 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. The former application has been studied by Wallace (1967, 1969) and by Davis et al. (1971) for use in concentrating uranyl nitrate solutions. The latter use has received attention in a water softening application by Smith (1970, 1971), and recently has been under study at the Savannah River Laboratories (SRL) of E.I. du Pont de Nemours and Company by several investigators (Wallace, 1965; Melsheimer et al., 1973) for use in removal of trace activity (Cs^{137}) and mercury from plant effluent streams.

The dialyzer configuration utilized at SRL is a parallel channel, countercurrent flow design with thin (13 to 40 mils) channels filled with screen for membrane support and channel definition. The membrane currently used is Nafion^{*} perfluorosulfonic acid cation exchange membrane. Single membrane units would not yield practical dialyzers for plant scale applications, so multiple membrane units with appropriate manifolding to route the feed (process) stream and strip stream to the flow channels are utilized.

An appreciable amount of laboratory study of the Donnan dialyzer has been conducted at SRL over the past several years, and recently pilot scale tests of multi-channel dialyzers have begun (Wallace, 1965). On the other hand, relatively little effort has been expended toward obtaining a quantitative understanding and characterization of the mass transfer processes involved in the parallel plate dialyzer. Wallace (1965, 1972) began analysis of the system, and Smith (1970, 1971) has also reported a simplified model for the counterion transport in a Donnan dialyzer. Recently, this investigator has renewed the attempt to model the dialyzer while at SRL as an Oak Ridge Associated Universities (O.R.A.U.) Faculty Research Participant in the summer of 1972. A mathematical model of the dialyzer was obtained, and has been subjected to limited tests for validity with moderately good results.

This model was based on a very simplified view of the membrane and of the electrolyte solution properties. The mass transfer was described in terms of overall coefficients, and ideal solutions are assumed in the fluid channels and in the membrane. The model was couched in the IBM CSMP/360 simulation language for computer solution, and parameter identification accomplished via nonlinear regression using the "Partan" optimization algorithm. Further details are given in Melsheimer, et al. (1973).

* Trademark of E.I. du Pont de Nemours & Company

The incentives for development of a fundamentally valid mathematical model of the Donnan dialyzer are twofold. First, from the practical point of view, a sound process simulation would provide a tool for use in the design of plant scale dialyzers. Experimental investigation of all dialyzer parameter combinations over the ranges of interest would require prohibitive amounts of time and equipment. A process simulation, verified by relatively small amounts of laboratory data, could be used to eliminate or greatly reduce the experimentation needed to obtain an optimal design.

The second reason for pursuing the mathematical modeling of the Donnan dialyzer is that it will lead to a better fundamental understanding of the scientific principles of ion exchange membrane processes. The mechanisms controlling mass transfer in such systems are not yet fully understood, though ion exchange systems have been the subject of investigation for many years. (Helfferich (1962), Tombalakian et al. (1967); Scattergood and Lightfoot (1968); Van Brocklin and David (1972); Dresner (1972)). These studies all incorporate many idealizations, and in general are directed to processes quite different from Donnan dialysis (reverse osmosis, or simple batch self-diffusion, for example). While of appreciable value in providing insight into various aspects of ionic transport, they do not address themselves to many of the problems central to achieving a viable model of Donnan dialysis.

For these reasons, this research project was undertaken with the objective of developing a useful, quantitative, mathematical model of the Donnan dialysis process. The research tasks for the first year of the research project were grouped into three categories, and are listed below:

Theoretical Analysis of Donnan Dialyzer

1. Complete testing, with modification as needed, of the single resistance model.

2. Correlation of the mass transfer coefficients of this model with systems parameters (velocity, channel height, and temperature).
3. Resolution of mass the transfer resistance into flow channel and membrane components. It is anticipated that this will allow improved correlations of the mass transfer parameters, and thus more accurate prediction of counterion, osmotic, and coion leakage fluxes.
4. Incorporation of activity coefficient data or correlations to account for nonideality of the solutions in the channels and in the membrane.

Plans also included initial work in two additional areas:

5. Development of counterion flux equations allowing for imperfect membrane exclusion of coions in counterion flux equation derivation, and corresponding coion and osmotic flux equations.
6. Incorporation of convective flux of ions due to osmotic flow through membrane in ionic flux expressions, with appropriate frictional drag coefficients.

Experimental Studies of Donnan Dialysis

Using sodium nitrate - nitric acid as the base system study the effect of:

1. Feed counterion (sodium) concentration in feed and strip streams
2. Acid concentration in strip stream and in feed stream
3. Feed and strip channel heights
4. Feed and strip stream velocities
5. Temperature level
6. Study the transport of alternate univalent feed counterions (for example, potassium and ammonium ions) and of bivalent counterions (calcium, uranyl for example)

Computational Aspects of Donnan Dialyzer Simulation

1. Conversion of dialyzer simulation program from relatively inefficient IBM CSMP/360 simulation language to a more efficient and flexible program in Fortran. This program to be modular in structure so as to allow independent variation of the parameter identification techniques, and of the numerical methods used in solving the dialyzer differential equations.
2. Search for more efficient schemes for identifying the dialyzer mass transfer parameters from laboratory data.
3. Investigate alternative solution techniques for the dialyzer differential equations.

The following additional task was to receive initial study as required

4. For more advanced models in which the membrane flux equations cannot be solved analytically, develop numerical solution technique for the membrane flux differential equations. These are coupled to the dialyzer differential equations arising from the mass balances in the flow channels.

SCOPE OF INVESTIGATION

The research actually conducted during the contract period was in substantial agreement with the goals set. There were some differences, primarily an unanticipated addition to the experimental program. This caused some reduction in effort on the last theoretical and computational research tasks outlined in the previous section. However, all primary goals for the contract period were met by the end of the period.

The major addition to the experimental program which was cited above was the separate determination of the membrane mass transfer coefficient for use in the multiple resistance model by means of stirred cell experiments. This was necessitated by the realization early in the contract period that the close coupling of the mass transfer coefficients for the fluid film and the membrane would make determination of both from the same set of dialyzer data rather difficult and imprecise. The additional data allows independent determination of these parameters.

The expenditures for the contract period generally followed the budget outline fairly closely, with the total expenditure matching the planned amount. One significant departure was the purchase of an equipment item not listed in the budget (a Balsbaugh Electrical Conductivity Meter for monitoring the deionized water supply) at a cost of \$338. This expenditure was balanced by a reduction in the level of travel expenditures (a curtailment of the level of study of Donnan dialysis at the Savannah River Laboratories reduced the need for travel to that location), and by use of some of the funds budgeted for expendible supplies.

The time and effort expended on the research project followed that planned in the proposal. During the academic year the principle investigator allocated

approximately one-sixth time and the research assistant one-half time to the project. During the summer period the principle investigator devoted two full months to the project, while the research assistant continued on a half-time basis. It should be noted that since the research assistant was pursuing his Ph.D. research in this area, he effectively contributed a full time effort to furthering the goals of this research project.

As well as can be determined all additional provisions of the contract were satisfied.

A detailed exposition of the theoretical and experimental investigation of this research project is available in the Ph.D. Dissertation of Michael Alan Lake, research assistant on this project (Lake, 1975). Additional presentations of the project results are the preprints of Lake and Melsheimer (1975a) of which copies are included with this report, and Lake and Melsheimer (1975b) to be presented later this year. The latter will also be submitted for journal publication, and is a comprehensive presentation of the project results. Copies will be forwarded upon completion. For completeness, a summary presentation of the major results of this project are included in the remainder of this report.

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 primary thrust of the theoretical portion of this research project was the development of mass transfer rate equations to adequately describe the counterion, coion, and osmotic fluxes in the dialysis process. To put the discussion of these flux equations in context the differential mass balances are listed below.

$$\frac{du_1}{dx} = \frac{\sum J_i (MW_i) + J_o (MW_s)}{\rho_1 D_1} \quad (1)$$

$$\frac{du_2}{dx} = \frac{\sum J_i (MW_i) + J_o (MW_s)}{\rho_2 D_2} \quad (2)$$

$$\frac{d(C_{i1} u_1)}{dx} = - J_i / D_1 \quad (3)$$

$$\frac{d(C_{i2} u_2)}{dx} = - J_i / D_2 \quad (4)$$

- where: u_1 and u_2 = feed and strip stream velocities, cm/sec
 J_i = molar flux of ion i , moles/cm²-sec
 J_o = molar osmotic flux, moles/cm²-sec
 ρ_1 and ρ_2 = densities of feed and strip streams, g/cc
 MW_i and MW_s = molecular masses of ionic species and solvent
 D_1 and D_2 = feed and strip channel thicknesses, cm
 x = axial distance from feed stream inlet, cm
 C_i = concentration of ion i , moles/cc

Assumptions made in formulating these equations were:

1. Steady state operation.
2. Plug flow in the channels

3. Countercurrent flow of feed stream (subscript 1 and strip stream (subscript 2).
4. Constant density and temperature in each stream.
5. Counterion, coion and osmotic fluxes may be decoupled and written independently.

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

$$\sum Z_i C_{i_1} = 0 \quad (5)$$

$$\sum Z_i C_{i_2} = 0 \quad (6)$$

$$\sum Z_i J_i = 0 \quad (7)$$

where: Z_i is the valence of ion i

In the development that follows the additional assumption is made that only two counterions (the feed counterion (A) which is being concentrated, and the strip counterion (B) which is the stripping agent) and one coion (N) are present in the system. Equations (5) and (6) may then be used to eliminate the component mass balances for the coions, and Equation (7) to eliminate the flux of counterion B from the component mass balance equations for ions A and B.

The resulting model thus consists of overall mass balance equations (1) and (2), component mass balance equations (3) and (4) each written for the two counterions, A and B, and flux equations, yet to be defined, for ion A, the coion (N), and osmosis along with the thermodynamic relations.

In addition, six boundary conditions are required. The input concentrations of ions A and B in each stream, plus the input velocities of the strip and feed streams provide the necessary 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 Donnan equilibrium relation 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 as

$$\left(\frac{\bar{a}_i}{a_i} \right)^{1/z_i} = \left(\frac{\bar{a}_j}{a_j} \right)^{1/z_j} = \dots \quad (8)$$

where: a_i = ionic activity, moles/cc

superscript bar denotes a membrane phase property.

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

$$\sum_i z_i \bar{C}_i = \bar{X} \quad (9)$$

where: X = the membrane fixed charge concentration, equiv/cc.

The model as presently constituted recognizes mass transfer resistances in the feed channel boundary layer and in the membrane itself. Strip channel boundary layer resistance was neglected due to earlier indications that it was relatively inconsequential, and to improve the model tractability. Figure 1 illustrates the concentration profiles of the dialysis system with these assumptions. The two resistance model thus consists of mass balance Equations (1) to (4) and the electroneutrality constraints presented earlier, plus the following flux equations:

$$J_A = K_{mA} (\bar{C}_{A_1} - \bar{C}_{A_2}) \quad (10)$$

$$J_A = K_{fA} (C_{A_1} - C'_{A_1}) \quad (11)$$

$$J_B = K_{fB} (C_{B_1} - C'_{B_1}) \quad (12)$$

Figure 1. Qualitative Concentration Profiles of Counterion "A" at a Point in the Dialyzer

$$J_N = K_N (C'_{N_1} - C_{N_2}) \quad (13)$$

$$J_O = K_O (\Delta P - \Delta \phi) \quad (14)$$

where: K_m = membrane phase counterion transport coefficient

K_{fA} and K_{fB} = feed channel fluid phase counterion transport coefficients for ions A and B, respectively

K_N and K_O = coion leakage and osmotic flux coefficients

ΔP and $\Delta \pi$ = hydrostatic and osmotic pressure gradients

primed quantities are located in the fluid phase at the membrane-fluid interface.

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

$$\left(\frac{\bar{a}_i}{a'_i} \right)^{1/z_i} = \left(\frac{\bar{a}_j}{a'_j} \right)^{1/z_j} = \dots \quad (15)$$

Note that the membrane resistance equation, Equation (10), is the same as that written for the earlier single resistance model. However, the computed feed channel side membrane concentration is different because of the feed channel film resistance and the change in the Donnan equilibrium equation. The solvent flux equation and coion flux equation are also similar to those used in the earlier model. The chief difference is the incorporation of the information at the feed channel interface. The film transport equations are completely new, of course. The two film transport coefficients are assumed to be related by

$$\frac{K_{fA}}{K_{fB}} = \frac{D_A}{D_B} \quad (16)$$

where:

D_A and D_B = individual ion diffusivities, cm^2/sec .

This essentially expresses the fact that the hydrodynamic environment of both counterions is identical and thus the difference in transport rates should be proportional to the diffusivities.

This set of equations is solved simultaneously to compute the counterion, coion, and solvent fluxes along the dialyzer. Data taken on a laboratory dialyzer then provides information for the determination of the system mass transfer parameters (K_{FA} , K_N , K_O). As discussed in the Experimental section, the membrane counterion transport coefficient (K_{mA}) was separately determined using a stirred cell apparatus. To evaluate the model, correlations, of the mass transfer parameters with the system operating variables (velocity, temperature, etc.) were sought. The final results of this effort are presented in the Experimental section.

Several versions of the basic model presented above were investigated before arriving at the final formulation. Initially, ideal solution behavior was assumed by substituting concentrations for activities in the Donnan equilibrium equation (15). This assumption was felt to be questionable, so the model was modified to incorporate the activity coefficient correlation of Bromley (1972). While significant non-idealities were observed, the ratio form of the Donnan equation caused the model predictions to be affected very little. Due to the appreciable increase in computer time consumption which resulted, the ideal solution assumption was retained for further work.

The initial model also assumed negligible coion absorption by the membrane. At the interface with the very concentrated strip solution this is suspect. The model was modified to incorporate this effect, but little improvement was observed in the transport coefficient correlations. There was some evidence of coion absorption, however, so this phenomenon may bear further study.

The results of the dialyzer studies with the bivalent feed ion, calcium, indicated its transport to be strongly membrane controlled. This was evidenced by using the single resistance model (membrane controlling) of Melsheimer et. al. (1973) to analyze the dialyzer data. The membrane coefficient (K_{mA}) values determined were nearly independent of the feed channel velocity. Further, when the two resistance model was applied the regression showed the feed channel coefficient (K_{fA}) values to have very little effect on the fit of the model predictions to the dialyzer data. However, the K_{mA} values for calcium as determined from dialyzer data were only one-third the magnitude of those determined with the stirred cell apparatus. 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 systems were reduced by comparable amounts, and the K_{fA} correlation redetermined. The resulting correlation, shown in Figure 5 in the Experimental section, possessed significantly less overall scatter than obtained previously. 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. The two resistance model, with reduced membrane coefficients accounting for the strip resistance, thus proved an adequate model for the dialyzer system over the range of interest.

To test this assertion, the two resistance model with the correlations for the various coefficients was used in the design model to predict the experiment

mental dialyzer effluent flows and concentrations. The poorest agreement observed was approximately ten percent in error. In most cases, the agreement was much better.

For design purposes, then, the two resistance model appears adequate where operating conditions are to be in the range of the experimental data from which it was derived. However, the hypothesized strip channel effect definitely requires further study and an improved fundamental treatment.

EXPERIMENTAL STUDIES

The experimental program of this research project was primarily intended to provide data with which to evaluate the mathematical model, and from which correlations of the system mass transfer parameters could be obtained. Initially, it was anticipated that only one experimental system, the parallel channel counterflow dialyzer, would be required. However, early in the research period it became apparent that an additional experimental system would be required to determine the membrane phase transport coefficient.

This system is the continuous flow stirred cell apparatus sketched in Figure 2. Constant flows of the feed solution and the strip solution were fed to the apparatus using Lapp Pulsafeeder diaphragm pumps and the flows and concentrations of the inlet and outlet streams were monitored. Flows were determined by time and volume measurements, and the hydrogen and metal ion concentrations found using titration and atomic absorption analysis, respectively. The transport coefficients were calculated for the membrane phase single resistance model given earlier. The stirring rates of the cells were varied, and the resulting set of transport coefficients plotted as shown in Figure 3. The data were extrapolated to infinite stirring rate to determine the apparent membrane mass transfer coefficient. Table I presents a summary of the stirred cell data. It will be observed from Figure 3 and Table I that the solution concentrations, both sodium and hydrogen, do affect the value of the membrane coefficient. As the sodium concentration is increased (with constant acid conditions) the apparent membrane coefficient tends to approach a limiting value. This is interpreted as indicating that the stirring rates of the cells being used are inadequate to completely eliminate the film resistances at low sodium concentration. As the supply of sodium on the feed side of the membrane

Figure 2. Experimental Constant Overflow Stirred Cells

Run Number	Average Concentrations		Extrapolated K_{mA}
	Sodium Ions in Feed Cell	Hydrogen Ions in Strip Cell	
	gmoles/liter	gmoles/liter	cm/sec $\times 10^4$
31-33	0.017	1.02	3.36
26-29	0.073	1.01	3.95
41-43	0.269	1.03	4.04

Figure 3. Modified Wilson Plot of Stirred Cell Data

Table 1. Membrane Counterion Coefficients from Stirred Cell Experiments Extrapolated to Infinite Stirring Rate

Counterion "A"	Temp.	Concentration of "A" in the Feed Cell	Concentration of Hydrogen Ions in the Strip	Extrapolated Membrane Counterion Coefficient
	°C	gmoles/liter	gmoles/liter	cm/sec x 10 ⁴
Sodium	25	0.073	1.01	3.95
	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
Potassium	25	0.071	0.95	4.88
	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
Calcium	25	0.012	0.99	2.37
	25	0.010	1.99	2.87
	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

increases at higher concentrations, the system more quickly approaches the point where the rate of transport through the membrane itself is limiting. Consequently, the extrapolated values of K_{mA} at the higher feed ion concentrations were taken as correct.

The acid concentration also affects the K_{mA} values significantly. This may be partly due to the change in membrane state, especially swelling, with this large change in the environment. It also may reflect to some extent an "overloading" of the membrane at the higher acid concentrations. In any case, this variation of K_{mA} with acid concentration was taken into account with a simple linear fit to the data.

The primary experimental system was the parallel channel dialyzer illustrated in Figure 4. Spacers of 28 mil stainless steel screen are indicated in the illustration, but 13.2 mil spacers were also used during the course of the research. The feed to this dialyzer was provided by a Milton Roy positive displacement pump. The feedstock was blended on line by mixing deionized water and a concentrated solution of the ion being studied, the latter being metered into the bleeding tank with a Lapp Pulsafeeder diaphragm pump. The deionized water was produced from the drinking water supply using cation and anion exchange beds in series. The quality of the water was monitored with a Balsbaugh electrical conductivity meter, and was kept below ten micromhos per centimeter during all runs.

The dialyzer data was analyzed using the mathematical model to determine the counterion feed channel mass transfer coefficient, the anion leakage mass transfer coefficient, and the membrane solvent permeability coefficient. Values of these parameters are given in Figures 5 and 6 and in Table II.

As discussed in the Theoretical section, the final model required a reduction of the stirred cell K_{mA} values by factors of about one-third for best

Figure 4. Experimental Countercurrent Dialyzer

Figure 5. Feed Boundary Layer Counterion Coefficient Correlation of Sodium and Potassium Data

Figure 6. Feed Boundary Layer Counterion Coefficient Correlation of Calcium Data

Table 2. Average Anion and Solvent Flux Coefficients for Sodium Data

Temperature	Approximate Strip H Concentration	Anion Flux Coefficient	Water Flux Coefficient
$^{\circ}\text{C}$	gmoles/liter	$\text{cm/sec} \times 10^{+6}$	$\frac{\text{gmoles water}}{\text{cm}^2\text{-sec-psia}} \times 10^{+9}$
25	1.0	4.17	1.71
25	3.0	6.60	1.26
50	1.0	6.54	2.42
50	3.0	7.79	1.95
70	1.0	9.30	2.85
70	3.0	13.40	2.47

correlation of the feed channel coefficient (K_{fA}) values. The exact adjustment factors for each ionic system are shown on Figures 6 and 7. The equation

$$N_{sh} = 0.201 N_{Re}^{0.62} N_{sc}^{0.40} \quad (17)$$

where:

N_{sh} = Sherwood Number, $K_{fA} D_1 / D_{AB}$

N_{Re} = Reynolds Number, $D_1 u_1 \rho_1 / \mu_1$

N_{sc} = Schmidt Number, $\mu_1 / \rho_1 D_{AB}$

D_{AB} = ionic diffusivity, cm^2/sec

μ_1 = fluid viscosity, gms/cm-sec

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

The K_o and K_n values were found to vary only with temperature and total ionic strength, as measured by the strip acid concentration. Values for the range of conditions studied are given in Table II. These values, along with equation (17), the K_{mA} values of Table I, and the K_{mA} adjustment factors, complete the model for design applications. As discussed in the theoretical section this design model has been tested against the laboratory data and found to be given adequate over the range of the experimental conditions.

COMPUTATIONAL ASPECTS

Significant advances were made in the efficiency of the computer program used to solve the dialyzer equations. The earlier single resistance model utilized a program written in the CSMP/360 simulation language with Runge-Kutta integration. It used a Partan optimization technique for parameter identification by nonlinear least squares regression. While the CSMP language is quite handy for use in model development, the user can pay a substantial penalty in computer time for the conveniences provided. For this reason the two resistance model was programmed in Fortran.

At the same time a study of several solution algorithms for the differential equations of the dialyzer model was undertaken. The Runge-Kutta technique was compared to simpler Euler and Modified Euler methods, with the somewhat surprising result that all required approximately the same integration step size for comparable levels of accuracy. Of course, the Euler method showed an appreciable advantage in computer time requirements under these conditions. In fact, the Euler solution requires less than one second per solution of the univalent two resistance model, and further improvement was not deemed necessary at the present stage of model complexity.

A search for an improved optimization method led to the Hooke-Jeeves Pattern Search technique. This method proved to be far superior to Partan in two respects. First, it has less tendency to get "hung up" in narrow valleys or sub-optimal minima of the least squares objective function. Thus, it requires less intervention by the user in proceeding from an initial set of parameter guesses to the final "best" set of mass transfer coefficients. Second, it reduced the total number of function evaluations (each of which is one solution of the dialyzer differential equations) required for identification appreciably.

The overall effect of these changes is an order of magnitude reduction in the computer time required to identify the mass transfer parameters of the two resistance model as compared to the earlier single resistance model program.

CONCLUSIONS

1. The counterion transport within the countercurrent dialyzer was successfully modeled using a model incorporating series transport resistance in the feed boundary layer and the membrane. However, the membrane counterion coefficients required in the model for the countercurrent dialyzer were approximately one third the values calculated from stirred cell experiments. A dimensionless correlation for the feed boundary layer coefficient, which fit the data over the entire experimental range, was determined. The four transport coefficients, determined from the model applied to experimental data, were used successfully in a prediction (design) program.
2. The transport of bivalent calcium was limited by the resistance in the membrane phase, whereas the transport of univalent sodium and potassium depended on both the feed boundary layer and membrane resistances, with the feed boundary layer generally dominant.
3. The overall study indicated strong evidence of a strip boundary layer resistance or other phenomena at the strip solution-membrane interface.

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DONNAN DIALYSIS:

A CONTINUOUS ION EXCHANGE MEMBRANE PROCESS FOR
REMOVING AND CONCENTRATING IONS FROM WASTE STREAMS

by

Michael A. Lake^{*}

and

Stephen S. Melsheimer

Chemical Engineering Department
Clemson University
Clemson, South Carolina

* Current Address:
Westvaco Corporation
Charleston, South Carolina

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Michael A. Lake^{*} and Stephen S. Melsheimer
Department of Chemical Engineering
Clemson University
Clemson, South Carolina

ABSTRACT

Donnan dialysis is a relatively new ion exchange process using ion exchange membranes to permit truly continuous operation. Potential applications exist in many areas where traditional columnar ion exchange is currently used, including removal of ionic species from waste water. This paper describes a mathematical model of the Donnan dialysis process which is being developed to facilitate evaluation of possible applications, and to provide a tool for the design of plant scale dialyzers. Mass transfer parameters for the model have been determined from laboratory data, and correlated with the system operating variables. The correlations are presented, along with typical laboratory results obtained with a small scale dialyzer.

* Current Address:
Westvaco Corporation
Charleston, South Carolina

INTRODUCTION

Ion exchange using particulate resins in packed or fluidized columns is used as a basic unit operation for removing dilute to moderate concentrations of ions from solution. The process is inherently intermittent since regeneration of the resin is required, though some continuous ion exchange schemes have been devised. Recently, a truly continuous ion exchange process using membranes, Donnan dialysis, has been developed (Wallace, 1969). This process has emerged as an attractive alternative to traditional columnar ion exchange for many applications, including renovation of wastewater.

In this application of Donnan dialysis, the waste stream containing ionic constituents to be removed is contacted countercurrently with a strip regenerant stream. The ion exchange membrane separates the two streams as diagrammed in Figure 1. The physical arrangement of the dialyzer may be a stacked parallel channel system similar to those used in electrodialysis, or a shell and tube arrangement using tubular membranes.

Figure 1. Countercurrent Donnan Dialyzer

A cationic membrane was used in this study, with cations being removed from the waste stream and concentrated into a strong acid strip stream. However, the system can just as easily be adapted to removing anions from a waste

stream by using an anionic membrane and a strong base as the stripping agent. In fact, a waste stream could be completely deionized by replacing the cations with H^+ ions and the anions with OH^- ions using two Donnan dialyzers in series.

Donnan dialysis is very effective for removing ions of very low concentrations. The reason for its effectiveness may be seen by examining the statement of equilibrium between streams 1 and 2 of Figure 1:

$$\left(\frac{C_{A1}}{C_{A2}}\right)^{1/z_A} = \left(\frac{C_{B1}}{C_{B2}}\right)^{1/z_B} \quad (1)$$

where: C_{A1}, C_{A2} = concentration of "A", the ion to be removed in streams 1, 2 respectively.

C_{B1}, C_{B2} = concentration of "B", the strip ion in streams 1, 2 respectively.

z_A, z_B = valence of ions A, B.

Note this Donnan equilibrium (Donnan, 1924) is quite different from the normal statement of equilibrium that concentrations in the two phases (streams 1 and 2) be equal. The ratios arise because the semipermeable membrane allows only the passage of cations. If a waste stream (stream 1 in Figure 1) containing ion "A" of less than 0.01 molarity, for example, were contacted with a strong strip (stream 2 of Figure 1) containing ion "B" of approximately 3 molar, the ratio on the right of equation (1) would be very small at any point in the dialyzer. In order to reach equilibria, the ratio on the left of equation (1) must also become very small, and ions "A" would be "pumped" across the membrane to achieve this, often against their overall gradient.

Using the nomenclature convention of ion exchange, ions which are

transported across the membrane are called counterions, and the ions of opposite charge which are prohibited from passing through the membrane are coions. Ions which are fixed in the polymer of the membrane, and which gives the membrane capacity to repel the coions, are appropriately referred to as fixed ions.

Donnan dialysis thus has obvious potential for use in concentrating valuable materials in ionic form from dilute solutions, and also in stripping undesired ionic species from process or waste streams. The latter application has been studied by Wallace (1967, 1969) and by Davis et al. (1971) for use in concentrating uranyl nitrate solutions. The former use has recieved attention in a water softening application by Smith (1970, 1971), and has been studied at the Savannah River Laboratories of E. I. duPont de Nemours and Company by several investigators (Wallace, 1965; Melsheimer et al., 1973) for use in removal of trace activity (Cs^{137}) and mercury from plant effluent streams.

MATHEMATICAL MODEL

To enable the prediction of the performance of Donnan dialyzers a mathematical model of the transport of ions in the dialysis process is required. Smith presented a simple reaction-kinetic equation which described the system in terms of the equilibrium equation (1). Melsheimer et al. presented a more traditional mass transfer model which assumed that the resistance to counterion transport in the membrane phase is dominant. The Donnan equilibrium equation was applied to each membrane-solution interface. The resulting model yielded satisfactory results for uranyl-hydrogen exchange but poor results for sodium systems.

The purpose of the current study was to develop an improved model that would be more generally applicable and more accurate. A two-resistance model was proposed as a result of the observation by Melsheimer et al. that the resistance to counterion transport varied with the waste stream velocity. In this model, series resistances were allowed in both the waste stream and in the membrane itself, with interfacial equilibrium following the Donnan relationship. The strip stream resistance was assumed negligible since prior evidence (Melsheimer et al, 1973) indicated variations in strip velocity had little effect.

The two mass transfer flux equations for the counterion are then

$$J_A = K_{mA} (\bar{C}_{A1} - \bar{C}_{A2})/1000 \quad (2)$$

in series with

$$J_A = K_{fA} (C_{A1} - C_{Ai})/1000 \quad (3)$$

where: J_A = flux of counterion A, gmoles/cm²-sec

- K_{mA} = counterion membrane coefficient, cm/sec
 K_{fA} = counterion boundary layer coefficient, cm/sec
 $\bar{C}_{A1}, \bar{C}_{A2}$ = concentration of A in the membrane at the waste and strip interfaces, respectively, gmoles/liter
 C_{Ai} = concentration of A in the waste stream at the waste-membrane interface, gmoles/liter.

Similar equations can be written for counterion "B". The concentration profile assumed by the two-resistance model is similar to that shown in Figure 2.

An ideal membrane would prohibit the passage of coions, but in practice, coion leakage occurs from the high concentration strip to the dilute waste stream. In this model the coion flux is expressed by

$$J_N = K_N(C_{Ni} - C_{N2})/1000 \quad (4)$$

- where:
- J_N = flux of coion N, gmoles/cm²-sec
 - K_N = coion leakage coefficient, cm/sec
 - C_{Ni} = concentration of coions at the waste stream-membrane interface, gmoles/liter
 - C_{N2} = concentration of coions in the strip stream, gmoles/liter.

Water also passes through the membrane under osmotic and pressure forces, the flux being given by

$$J_O = K_O (\Delta p - \Delta \phi) \quad (5)$$

- where:
- J_O = water flux, gmoles/sec
 - K_O = water flux coefficient, gmoles/sec-psia
 - Δp = pressure difference between streams 1 and 2, psia
 - $\Delta \phi$ = osmotic difference between streams 1 (at interface) and 2, psia.

Figure 2. Concentration Profiles Across Membrane

Note that the water and coion fluxes are written in terms of the solution properties of the streams on either side of the membrane, whereas the counterion flux contains the terms $\bar{C}_{A1}$ and $\bar{C}_{A2}$ which may not be experimentally determined. The membrane concentrations $\bar{C}_{A1}$ and $\bar{C}_{A2}$ may be algebraically eliminated using the electroneutrality constraint

$$z_A \bar{C}_{A1} + z_B \bar{C}_{B1} - \bar{X} = 0 \quad (6)$$

and the Donnan equilibrium at the interface

$$\left(\frac{C_{Ai}}{\bar{C}_{A1}} \right)^{1/z_A} = \left(\frac{C_{Bi}}{\bar{C}_{B1}} \right)^{1/z_B} \quad (7)$$

to yield for $z_A = 1$ and $z_B = 1$:

$$\bar{C}_{A1} = \bar{X} \left(\frac{C_{Ai}}{C_{Ai} + C_{Bi}} \right) \quad (8)$$

and for $z_A = 2$ and $z_B = 1$:

$$\bar{C}_{A1} = \frac{\bar{X}}{2} + \frac{1}{4} \left(\frac{C_{Bi}}{2C_{Ai}} \right)^2 \left\{ 1 - \sqrt{1 + 4\bar{X} \left(\frac{2C_{Ai}}{C_{Bi}^2} \right)} \right\} \quad (9)$$

where: C_{Bi} = concentration of B in the membrane at the waste solution interface, gmoles/liter

$\bar{X}$ = concentration of fixed ions, gmoles/liter.

Equation similar to (8) and (9) may be derived for $\bar{C}_{A2}$. The complexity of the equations increases as the valence increases. The interfacial concentration, C_{Ai} , disappears when the flux equations are combined with the restriction of zero current flux. The flux equations (2, 3, 4, and 5) are used in differential mass balances (Melsheimer et al., 1973) which are to be integrated over the length of the Donnan dialyzer. These equations define the system and

may be used to extract the flux coefficients K_{mA} , K_{fA} , K_N and K_O from experimental data. The set of mass balances and the flux equations are integrated numerically on a digital computer. A detailed exposition of the mathematics will be presented in a later paper, or may be found in Lake (1975).

The resulting set of flux coefficients depends on many of the system operating parameters (temperature, velocity, ions used, etc.). Correlation of these coefficients with the operating parameters is then sought in order that the experimental information can be used in predicting the performance of Donnan dialyzers in proposed applications. Here, the same system equations are solved with the known flux coefficients (using the developed correlations) to predict the resulting effluent concentrations for a given waste composition, stripping agent, and dialyzer configuration.

EXPERIMENTAL

Two experimental systems were used to gather the data for determination of the flux coefficients. The counterion membrane coefficient, K_{mA} , was calculated from continuous overflow, stirred cell experiments in the equipment illustrated in Figure 3, while the remaining coefficients (K_{fA} , K_N and K_O) were determined from countercurrent, single membrane dialyzer data. The stirred cell experiments circumvented the difficulties inherent in determining both K_{mA} and K_{fA} from dialyzer data.

E. I. duPont Nafion[®] perfluorosulfonic acid membrane of 10 mils thickness was used throughout. The waste species studied were sodium, potassium and calcium nitrates, with nitric acid as the stripping agent. Only binary exchange systems were studied, with the waste stream generally about 0.01 molar and the strip stream either one or three molar. The flow rate ratio of waste to strip ranged from 25-250, while the temperature was varied from 25 to 70°C.

The procedure for the determination of K_{mA} with the stirred cell apparatus was to measure apparent K_{mA} values at a series of stirring rates, increasing the rate until the K_{mA} value approached a constant. At this point, having eliminated the fluid boundary layer resistance, only the membrane resistance remains.

The single channel dialyzer is illustrated in Figure 4. The flow channels for the waste and strip streams were created by a stainless steel wire screen spacer with integral silicone rubber gasket. Two channel heights, using different screen thicknesses, were investigated. Detailed information on the experimental apparatus of both the stirred cell and single channel dialyzer systems is given by Lake (1975).

Figure 3. Stirred Cell Apparatus

Figure 4. Single Membrane Dialyzer

RESULTS

While the planned procedure of the stirred cell experiments was to increase the stirring rate on the cells until the solution boundary layer resistance was negligible, the practical upper limit of stirring, 4750 rpm, was reached prior to this rate. Consequently, a modified Wilson technique was used to extrapolate the data to an infinite stirring condition. The results of the stirred cell studies are summarized in Table I.

The characteristics of the ion-exchange membrane change with the concentration of electrolyte in contact with the membrane, and this is clearly indicated by the dependency of K_{mA} on the acid concentration in the strip cell, which was varied between one and three molar. An important trend to note is that the K_{mA} for the systems studied are in the order: potassium > sodium > calcium. In common terms, this means that under similar conditions potassium ions may be removed faster than sodium ions, which in turn may be removed faster than calcium ions. This descending order is in the same sequence as the diffusivity of these ions, which supports the validity of the experimental findings.

The data of Table I were applied to the flux and mass balance equations discussed earlier, and the three remaining coefficients (K_O , K_N , and K_{fA}) were determined by nonlinear regression for each dialyzer run. An optimization technique was used to find the set of coefficients that caused the mathematical model to best fit the experimental data. The counterion boundary layer coefficient was then correlated to the system operating parameters in terms in the standard dimensionless parameters for mass transfer, the Sherwood, Schmidt, and Reynolds numbers:

TABLE I. Membrane Counterion Coefficients from Stirred Cell Experiments

Extrapolated to Infinite Stirring Rate				
Counterion "A"	Temp. °C	Concentration		Membrane Coefficient K_{mA} cm/sec
		"A" in Feed Cell gmoles/liter	H ⁺ in Strip Cell gmoles/liter	
Sodium	25	0.073	1.01	3.95
	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
Potassium	25	0.071	0.95	4.88
	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
Calcium	25	0.012	0.99	2.37
	25	0.010	1.99	2.87
	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

$$N_{sh} = \frac{K_{fA} D}{h_f} \quad (10)$$

$$N_{sc} = \frac{\mu_f}{\rho_f D} \quad (11)$$

$$N_{re} = \frac{\rho_f h_f v_f}{\mu_f} \quad (12)$$

where: N_{sh} = Sherwood number
 N_{sc} = Schmidt number
 N_{re} = Reynolds number
 D = diffusivity, cm^2/sec
 h_f = channel height of feed (waste) stream, cm
 μ_f = viscosity of feed stream, gm/cm-sec
 ρ_f = density of feed, gm/cm^3
 v_f = velocity of feed stream, cm/sec .

The data for sodium and potassium over a wide span of concentrations and flow rates at 25°C are shown in Figure 5. Data at 50° and 70° were also found to fit this correlation if 0.400 was used as the exponent of the Schmidt number. A least squares fit resulted in the equation

$$N_{sh} = 0.201 N_{re}^{0.62} N_{sc}^{0.40} \quad (13)$$

Calcium data were not included in determining the above equation since the calcium system was found to be almost entirely membrane controlled. Consequently, the boundary layer coefficient, K_{fA} , had little effect on the computed results and the values determined were quite erratic. However, the calcium data were generally distributed around the correlation of equation

Figure 5. Counterion Film Coefficient Correlation

(13), and it can be used in the two resistance model when applied to calcium.

The anion and osmotic flux coefficients were very stable in the majority of the experimental runs, and were found to exhibit only slight trends with most variables (channel height, flow rate, concentrations) with the exception of temperature. Thus, it was sufficient to simply average the data at each temperature. It should be noted that the anion leakage coefficient, K_N , is very likely dependent on the specific anion being considered, but in this study only nitrate was used so no evidence on the extent of this variation is available. In addition, both K_N and K_O will almost certainly depend on the overall concentration level to some degree since the membrane properties change, but little difference was observed over the range considered in this work. The mean values of K_N and K_O are presented in Table II.

Table II. Anion and Osmotic Coefficients

Temperature	Anion Flux Coefficient	Osmotic Flux Coefficient
<u>°C</u>	<u>K_N cm/sec</u>	<u>K_{O_2} gmoles/cm²-sec-psia</u>
25	6.60×10^{-6}	1.27×10^{-9}
50	9.37	1.89
70	11.59	2.45

Using the K_N and K_O in Table II, the K_{mA} in Table I, and the K_{fA} in equation (13), the performance of a Donnan dialyzer may be predicted. These coefficients are based on approximately 120 experimental runs made with the stirred cells, and 150 runs with the dialyzer. Close agreement of replicate runs support the reliability of the data. Simulations of the experimental runs using the K_{mA} values, the averaged K_O and K_N data, and K_{fA} correlation verified the suitability of these results for prediction of dialyzer performance.

The correlations are applicable to parallel channel dialyzer systems using the duPont Nafion[®] membrane, and are applicable at this early stage of development only to binary systems in which only one cation (sodium, potassium, or calcium) is extracted from a waste stream and replaced with hydrogen. The use of the correlations on other chemical systems has not been tested to date. Continuing experimental work at Clemson will study the applicability of the model to other chemical systems, other membranes, and to multicomponent systems. Extension of the model to include explicit treatment of the strip stream film resistance has also been proposed.

The effectiveness of Donnan dialysis in removing dilute concentrations of ions from waste streams may be illustrated by a few examples of data from the experimental dialyzer given in Table III. The data of run A of Table III shows that 68% of the sodium was removed from the waste stream even though the waste stream contact time was only 14 seconds. Also, the sodium was concentrated from 0.0081 molar in the waste to 0.1583 molar in the concentrate stream, a factor of 20. The amount of removal is governed primarily by the residence time in the dialyzer, the percentage removal decreasing as the

Table III. Examples of Data from the Countercurrent Donnan Dialyzer

Single 2 x 35 inch membrane, 28 mil channel height

Counterion "A"	Run	Stream	Temp. °C	Concentration		Flow cc/min
				"A" gmoles/l	"H" gmoles/l	
Sodium	A	Waste (Feed)	25°	0.0081	0.0	104
		Recyc. Waste		0.0028	0.011	103
		Strip		0.0	3.06	3.1
		Concentrate		0.1583	2.03	4.0
Sodium	B	Waste	25°	0.0095	0.0	301
		Recyc. Waste		0.0050	0.0060	300
		Strip		0.0	3.06	3.0
		Concentrate		0.3333	1.84	3.9
Sodium	C	Waste	25°	0.0088	0.0	495
		Recyc. Waste		0.0054	0.0046	493
		Strip		0.0	3.14	9.0
		Concentrate		0.1746	2.54	9.9
Potassium	D	Waste	25°	0.0095	0.0	99
		Recyc. Waste		0.0021	0.0118	98
		Strip		0.0	2.97	2.8
		Concentrate		0.2043	1.95	3.8
Calcium	E	Waste	25°	0.0085	0.0	202
		Recyc. Waste		0.0045	0.0115	201
		Strip		0.0	3.02	2.8
		Concentrate		0.255	1.78	3.6
Sodium	F	Waste	25°	0.0019	0.0	292
		Recyc. Waste		0.00077	0.0027	291
		Strip		0.0	3.05	3.0
		Concentrate		0.0804	2.10	4.1
Sodium	G	Waste	50°	0.0084	0.0	318
		Recyc. Waste		0.0029	0.0077	316
		Strip		0.0	3.04	8.5
		Concentration		0.1732	2.27	10.5
Sodium	H	Waste	70°	0.0084	0.0	295
		Recyc. Waste		0.0023	0.0096	293
		Strip		0.0	3.01	8.5
		Concentrate		0.1757	2.11	11.0

contact time of the waste stream decreases. This may be seen from the first two data sets for sodium where the residence times are 14.0 seconds and 3.0 seconds, respectively. The ability of the dialyzer to concentrate the extracted ions is limited mainly by the flow of the strip stream: increasing the strip flow decreased the concentrating ability as may be seen by comparing the data of runs B and C of Table III. There is a practical lower limit for the strip flow (thus an upper limit for the concentrating ability) since the increased contact time of the strip allows added osmosis and anion leakage which decreases the transport of counterions (see equation 1).

Potassium was found to be removed even more easily than sodium under similar conditions, with 78% removal for potassium in data set D compared to the 68% removal for sodium in data set A. Calcium removal is less efficient than either sodium or potassium, with 47% removal for calcium achieved for run E compared to 55% for sodium at comparable flow conditions. These observations agree qualitatively with the stirred cell studies demonstrating that the "ease" of removal (transport and exchange with H^+) follows the order: potassium > sodium > calcium, the same as the order of the diffusivities of these respective ions.

One of the strengths of Donnan dialysis is that as the waste stream becomes more dilute, the efficiency of removal increases. The efficiency of the dialyzer in data set F for sodium at 0.019 molar is 59%, compared to 47% for sodium at 0.095 molar in data set B, other conditions being similar. This behavior is also observed with potassium and calcium.

Temperature has a marked effect on the transport, again paralleling the stirred cell observations. Comparing the data of run B for sodium in Table III

to the results of runs G and H the efficiency of removal is 47%, 65%, and 73% for 25°, 50° and 70°, respectively, other conditions being similar. The same trends are found in potassium and calcium results.

It should be noted that the results cited above are data collected primarily for the purpose of determining the system mass transfer coefficients, and are not representative of the best performance attainable with a Donnan dialyzer in removal of waste constituents. Removal of over 99% of sodium has been observed where the waste stream concentration was about .001 molar and the flows were set to achieve high removal efficiency (Melsheimer et al., 1973). Studies of the optimum conditions for waste constituent removal, and for maximizing the concentration in the strip effluent, can now be conducted using the model described herein.

CONCLUSIONS

A relatively simple mathematical model of the Donnan dialysis process has been developed which successfully correlates laboratory data. Where applicable, it will allow quantitative evaluation and design of Donnan dialyzer applications to be conducted with a minimum of laboratory experimentation.

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