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

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MASTER

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MASTER

SUMMARY

During the first 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. 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. The feed channel counterion mass transfer coefficient, along with the coion leakage coefficient and the solvent permeability constant, were determined from operating data on a parallel channel counterflow dialyzer.

Insufficient data have been analyzed to permit correlation of these parameters or evaluation of the adequacy of the two resistance model. Preliminary results do indicate that the model is tractible, yielding reasonably consistent parameter values with moderate computation time.

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 Pattern regression algorithm.

The research project is proceeding at a rate closely matching that outlined in the initial research proposal, and with expenditures generally following those outlined in the cost estimate budget. All primary goals are expected to be met by the end of the first research period.

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, the current 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 the system 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 coions in counterion flux equation derivation, and then empirically allows for coion "leakage" with a simple linear driving force expression.
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 first contract period will be in substantial agreement with the goals set for the first year. There are some differences, primarily an unanticipated addition to the experimental program. This has caused some degree of slippage in the timetable for completion of the other research tasks outlined in the previous section. However, all primary goals for the first contract period will be met by the end of the period three months hence.

The major addition to the experimental program which was cited above is the separate determination of the membrane mass transfer coefficient for use in the multiple resistance model by means of stirred cell experiment. 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 setbacks in the rate of progress on other research tasks should be confined to Items 5 and 6 under Theoretical Analysis, Item 6 under Experimental Studies, and Item 4 under Computational Aspects in the list given in the previous section. Only the sixth experimental task was expected to be substantially completed in the first contract period, and a significant amount of work will still be accomplished in this area during the current year. The other items cited above will simply receive somewhat less time than was originally planned.

The expenditures for the first contract period generally follow the budget outline fairly closely, with the total expenditure expected to match 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 will be 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 has followed that planned in the proposal to date. 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 will devote two full months to the project, while the research assistant continues on a half-time basis. It should be noted since the research assistant is pursuing his Ph.D. research in this area, he is effectively contributing a full time effort to furthering the goals of this research project.

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

THEORETICAL DEVELOPMENT

The mathematical model consists of overall and component mass balances, mass transfer rate equations, equilibrium relations and electromentality constraints, and thermodynamic equations for the system state properties. The primary thrust of the theoretical portion of this research project is 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 are:

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:

$$\sum Z_i C_{i1} = 0 \quad (5)$$

$$\sum Z_i C_{i2} = 0 \quad (6)$$

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

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:

$$\sum Z_i \bar{C}_i = \bar{X} \quad (9)$$

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

In the single resistance model first developed to represent the ionic and solvent fluxes these equations were written as

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

$$J_N = K_N (C_{N_1} - C_{N_2}) \quad (11)$$

$$J_O = K_O (\Delta P - \Delta \phi) \quad (12)$$

where: K_A = counterion flux coefficient, cm/sec

K_N = coion flux coefficient, cm/sec

K_O = membrane permeability coefficient, cm/atm-sec

ΔP = feed to strip pressure differential, atm

$\Delta \phi$ = feed to strip osmotic pressure differential, atm

Equation (11) is a simple empirical expression to express the coion "Leakage" of the membrane, and Equation (12) is a standard empirical form for solvent transport. Equation (10) can be shown to be a simplification of the Nernst-Planck Equation (Melsheimer et al., 1973).

The osmotic pressures of the feed and strip solutions may be represented by the van't Hoff relation, or may be obtained from data. A simple van't Hoff equation without activity corrections is presently used.

Observe that the counterion flux equation is based on membrane phase concentrations which are not measurable. These concentrations are computed by using Equations (8) and (9). With the activity coefficients in Equation (8) assumed to be unity the resulting equations for univalent strip ion and for univalent and bivalent feed ions respectively are

$$\bar{C}_{A_1} = \frac{C_{A_1}}{C_{A_1} + C_{B_1}} \quad (13)$$

$$\bar{C}_{A_1} = \frac{\bar{X}}{2} + \frac{C_{B_1}^2}{16C_{A_1}} \left[1 - \sqrt{1 + \frac{8C_{A_1} \bar{X}}{C_{B_1}^2}} \right] \quad (14)$$

As cited earlier, this single resistance model achieved only a limited degree of success, and indicated that multiple resistance models would be required.

Currently, the model being tested includes both feed channel boundary layer and membrane resistances, but neglects any strip channel mass transfer resistance. This is justified by the results of experimental tests in which variation in strip channel velocity with constant feed channel conditions produced no significant changes in the overall coefficient obtaining using the single resistance model. Future efforts will address this question.

At this writing activity corrections for non-ideal solution behavior have not been incorporated into the model. Reilly and Wood (1971) have correlated activity coefficients for electrolyte solutions, and their results will be added to the model by the end of the current contract period.

The two resistance model as presently constituted thus consists of mass balance Equations (1) to (4) and the electroneutrality constraints presented earlier, plus the following flux equations:

$$J_A = K_{mA} (\bar{C}_{A_1} - \bar{C}_{A_2}) \quad (15)$$

$$J_A = K_{fA} (C_{A_1} - C'_{A_1}) \quad (16)$$

$$J_B = K_{fB} (C_{B_1} - C'_{B_1}) \quad (17)$$

$$J_N = K_N (C'_{N_1} - C_{N_2}) \quad (18)$$

$$J_o = K_o (\Delta P - \Delta \phi) \quad (19)$$

$$\sum z_i C'_i = 0$$

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

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 re-written to express equilibrium between the film and membrane concentrations;

$$\frac{a_i}{(\frac{a_i}{a'_i})^{1/z_i}} = \frac{a_j}{(\frac{a_j}{a'_j})^{1/z_j}} = \dots \quad (21)$$

Notice that the membrane resistance equation, Equation (15), is the same as that written for the single resistance model. However, the computed feed channel side membrane concentration will be different because of the feed channel film resistance and the change in the Donnan equilibrium equation. The solvent flux equation also appears to be identical, but the osmotic pressure on the feed side is that at the fluid-membrane interface rather

than the bulk feed stream. The coion flux equation is also modified to use the fluid-membrane interface coion concentration, and the film transport equations are completely new. The two film transport coefficients are assumed to be related by

$$\frac{K_{fA}}{K_{fB}} = \frac{D_A}{D_B} \quad (22)$$

where:

$$D_A \text{ and } D_B = \text{individual ion diffusivities, cm}^2/\text{sec}$$

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 at any position along the dialyzer as the differential mass balances are integrated. For the univalent feed ion case the equations can be combined to give an explicit (but rather complex) expression for C'_{N1} as a function of bulk fluid properties, and the flux equations can then be rewritten explicitly in terms of C'_{N1} and the bulk fluid properties. For the bivalent case the set of equations is implicit and is solved iteratively.

This model will be adapted to include the effects of solution nonideality by use of activity coefficient correlations from the literature as mentioned earlier. These additional relations will cause the system of equations to be implicit for both univalent and bivalent systems, thus requiring iterative solution.

Correlations of the mass transfer parameters with the primary system operating variables (velocity, temperature, channel height) will be sought. Mass transfer coefficients for experimental data with similar operating conditions except for feed and strip compositions will be compared to determine the range of applicability of the model. This testing and correlation of the

present model will be completed within the present research period for at least two univalent and one bivalent feed ions.

Some values for the transport parameters of the two resistance model have been obtained, and are listed in the Experimental Studies section. Insufficient data are available at the present time to draw any conclusions regarding the adequacy of this model.

EXPERIMENTAL STUDIES

The experimental program of this research project is primarily intended to provide data with which to evaluate the mathematical models, and from which correlations of the system mass transfer parameters can 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 1. 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 2. The data were extrapolated to infinite stirring rate to determine the apparent membrane mass transfer coefficient. Table I presents the data currently available for the sodium nitrate-nitric acid system. It will be observed 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

Figure 1. Stirred Cell Apparatus

Figure 2. Effect of Stirring Rate

TABLE I

Membrane Coefficient K_{mA} , cm/sec	Temperature $^{\circ}\text{C}$	Feed Concentration $[\text{Na}^+]$, M	Strip Concentration $[\text{H}^+]$, M
3.36×10^{-3}	25°C	0.017	1.03
3.94×10^{-3}	25°C	0.073	1.01
4.01×10^{-3}	25°C	0.269	1.03
4.54×10^{-3}	25°C	0.016	3.02
5.12×10^{-3}	25°C	0.078	3.04
6.45×10^{-3}	50°C	0.070	0.96
6.46×10^{-3}	50°C	0.253	0.94
6.62×10^{-3}	70°C	0.0257	0.97

the supply of sodium on the feed side of the membrane 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 are 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, it appears that some accounting for this variation of K_{mA} with acid concentration will need to be included in the model.

The primary experimental system is the parallel channel dialyzer illustrated in Figure 3. Spacers of 28 mil stainless steel screen are indicated in the illustration, but several thicknesses will be used during the course of the research. The feed to this dialyzer is provided by a Milton Roy positive displacement pump. The feedstock is blended on line by mixing deionized water and a concentrated solution of the ion being studied, the latter being metered into the blending tank with a Lapp Pulsafeeder diaphragm pump. The deionized water is produced from the drinking water supply using cation and anion exchange beds in series. The quality of the water is monitored with a Balbaugh electrical conductivity meter, and is kept below ten micromhos per centimeter during all runs.

The dialyzer data is 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 for several experimental runs which have been analyzed are given in Table II. The value of the counterion membrane mass

DIALYZER COMPONENTS

STRIP PRESSURE ASSURES UNIFORM DIFFUSION DISTANCE

FIGURE 3. SINGLE MEMBRANE DIALYZER

TABLE II

Dialyzer Transport Coefficients

Feed - Sodium Nitrate Strip - 3.0 M Nitric Acid
 Temperature - 25°C Spacers - 13.3 mil

Hydrogen/Sodium Diffusivity Ratio - 2.015

Membrane Coefficient (K_{mA}) - 5.12×10^{-3} cm/sec

Run	Feed Concentration $M \times 10^3$	Velocity		Transport Coefficients		
		Feed cm/sec	Strip cm/sec	$K_{fA} \times 10^2$ cm/sec	$K_N \times 10^6$ cm/sec	$K_O \times 10^7$ cm/atm - sec
1	9.24	21.2	0.233	1.05	9.35	3.84
2	9.33	21.4	0.058	1.02	7.39	3.94
3	6.29	5.36	0.167	1.10	1.09	3.71
4	9.60	10.6	0.167	0.763	9.88	3.44
5	10.1	21.5	0.167	1.00	9.77	3.18
6	9.71	24.5	0.165	1.02	8.88	3.11
7	8.96	21.9	0.216	0.990	7.09	3.33
8	9.69	22.1	0.163	0.969	8.88	3.30
9	9.54	22.0	0.105	0.984	7.68	3.53

transfer coefficient (determined separately in the stirred cell apparatus) for the conditions of this set of runs is also listed.

It will be observed that the values of the mass transfer parameters are quite consistent throughout the set of runs shown in Table II. The only significant variation in K_{fA} occurs for Run 4, where the feed channel velocity is reduced to a value of 10.6 cm/sec compared to approximately 22 cm/sec for most of the other runs. This decrease is expected since this coefficient should be roughly proportional to the square root of the velocity (Smith, 1970). Actually, the single anomalous value of K_{fA} occurs in Run 3, where an abnormally high value was obtained for an even lower velocity.

It is particularly important to note that the transport coefficients show no significant variation with strip channel velocity. This tends to substantiate the assumption that in the operating ranges of this study the strip channel fluid phase resistance is negligible (or at least constant). For different operating conditions, of course, this may not be true.

The membrane permeability, K_o , shows no systematic variation with either velocity, though there is an appreciable amount of scatter. This is as it should be since this parameter is essentially a membrane phase property. The anion leakage coefficient, K_N , is also a membrane phase property and it also shows no correlation with velocity changes, although it is subject to even more scatter than K_o . This scatter indicates that it may be fruitful to give closer attention to the formulation of the coion leakage driving force. The present expression for this term is purely empirical with no rigorous foundation.

The range of operating conditions for the data given in Table II is not, of course sufficient to allow evaluation of the two resistance model. These results, though promising, are preliminary. Data to complete this evaluation is rapidly being gathered, and very shortly will be adequate for this purpose.

COMPUTATIONAL ASPECTS

Significant advances have been made in the efficiency of the computer program used to solve the dialyzer equations. The 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. Other, more sophisticated, numerical methods will be studied in the future, but the present Euler solution requires less than one second per solution of the univalent two resistance model, and further improvement is not urgent until the model complexity is increased substantially.

The Partan optimization scheme was used initially to identify the two resistance model parameters, but proved to be rather intractable in several cases. A search for an improved method led to the Hooke-Jeeves Pattern Search technique. This method proved to be far superior 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. This will become even more significant as the model complexity is increased by incorporation of activity coefficients and other terms presently neglected.

CONCLUSIONS

At this point in the research project it is premature to draw broad conclusions as to the accuracy of the two resistance model currently being studied, the feasibility of achieving the overall goal of a quantitative, rigorous mathematical model for design purposes. However, the following specific conclusions can be drawn from the results of the first nine months of study:

1. The analysis of a limited amount of sodium nitrate-nitric acid data indicates that the two resistance model yields reasonable and consistent results for the mass transfer parameters.
2. The use of both parallel channel and stirred cell experiments permits independent determination of fluid film and membrane mass transfer coefficients.
3. The efficiency of the computer simulation has been improved by an order of magnitude by changing parameter identification schemes and the program language.

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