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William E. Rush[a]; B. L. Baker[b]
[a] Chemical Technology Hoeschst Fibers, Spartanburg, S. C. [b] Emeritus University of South Carolina,

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QUANTITATIVE DESCRIPTION OF ION TRANSPORT IN DONNAN ION EXCHANGE MEMBRANE SYSTEMS

William E. Rush, Chemical Technology
Hoeschst Fibers, Spartanburg, S. C.

and

B. L. Baker, Professor Emeritus
University of South Carolina

ABSTRACT

Presented are simplified mass transfer techniques describing the transfer of ions in continuous ion selective membrane systems in which the resistance to ion transport through the membrane is small in relation to the resistance to ion transport in the solution phase. Methods are developed through the application of the transfer unit concept to the Donnan equilibrium. This equilibrium describes the equilibrium ion concentration on either side of an ion selective membrane. Data from one cation selection system is presented as evidence of the validity of these methods. Further techniques are shown that will allow the determination of ion transport given only equipment parameters and solution diffusivities. Supporting data are shown.

INTRODUCTION

The Donnan dialyzers discussed herein are continuous ion exchange membrane units that rely upon the Donnan equilibrium rather than external electrical energy to effect ion transport. Such systems have been of limited interest in the past, but due to present energy costs the low energy requirements of Donnan units should spur an increase in popularity for these systems.

A number of investigators have presented methods of describing the ion transport in Donnan Systems (1) (2) (3); however, use of these techniques to design a dialysis unit would be difficult without first obtaining data from a similar unit. The techniques that are presented in this paper, though not accurate for all dialyzers, do provide in many cases a relatively easy means of estimating the configuration of a Donnan system needed to perform a given ion extraction. These techniques are primarily applicable to systems containing dilute solutions where the membrane resistance is negligible. The small membrane resistance in such systems is because the ion concentration in the membrane is essentially constant no matter what the concentrations of the solutions are. The apparent diffusivities across the membrane therefore increase with decreasing solution concentration.

DONNAN EQUILIBRIUM

The transport of ions across an ion exchange membrane can be best understood by considering a dilute electrolyte solution in contact with one side of a cation selective membrane containing the same cation as the electrolyte (cation selective membranes are those having fixed negative sites to which cations can be attached). Under these conditions, the cation concentration in the membrane is higher than in the solution while the anion concentration is higher in the solution. As the solution first contacts the membrane, these concentration differences lead to the diffusion of cations into the solution and anions into the membrane. After diffusion of very few ions, a negative charge is built up in the membrane and a positive charge in the solution.

The resulting potential difference has been denoted as the Donnan potential in recognition of work by F. G. Donnan (4). Due to this potential, anions are repelled from the membrane while cations are pulled into the membrane. Donnan considered a cell in which a cation selective membrane divides two solution-filled chambers, one containing sodium ions and the other potassium ions with a common anion. The requirement of electroneutrality and the requirement that the change in free energy (F) equal zero at equilibrium lead to the following equations.

$$\Delta F = RT\left(\Delta n \log \frac{[Na]_{right}}{[Na]_{left}} + \Delta n \log \frac{[K]_{right}}{[K]_{left}}\right) = 0 \qquad (1)$$

where [ ] = concentration

R = gas constant

T = temperature

n = numbers of moles of each cation crossing the membrane.

right and left refer to opposite sides of the membrane.

Simplifying the above equation, since both sodium and potassium form monovalent ions, results in

$$\frac{[Na]_{right}}{[K]_{right}} = \frac{[Na]_{left}}{[K]_{left}} \qquad (2)$$

Similar reasoning leads to the following gneralized Donnan equation in terms of concentrations rather than activities:

$$\left(\frac{C_{iz_{right}}}{C_{iz_{left}}}\right)^{1/z} = k \qquad (3)$$

where C_{iz} is the concentration of the ith cation of charge z; right and left refer to opposite sides of the membrane, and k is a constant.

To illustrate this equilibrium relation, consider a nonflowing Donnan contactor in which a cation exchange membrane divides two solution filled chambers of equal volume. The initial and equilibrium values are as shown below. A and B represent monovalent ions while D and E represent divalent ions. Concentrations are in molar concentration units.

Initial		Equilibrium	
Left	Right	Left	Right
A 110	B 11	A 90.16	A 19.84
D 110	E 11	B 9.016	B 1.984
		D 104.92	D 5.08

Initial		Equilibrium	
Left	Right	Left	Right
		E 10.492	E .508
Total Equiv. 330	Total Equiv. 33	Total Equiv. 330	Total Equiv. 33

MASS TRANSFER RELATIONS

The transfer unit concept is the primary means used to quantitatively describe the mass transport in most types of continuous separation equipment. If the assumption is made that the membrane contributes only a small portion of the total resistance to ion transport, the subsequent concepts are valid.

For dilute solutions, a transfer unit is defined as follows for counter-current systems (5):

$$NTU_{OR} = \int_{x_2}^{x_1} \frac{dx}{x - x^*} \tag{4}$$

$$NTU_{OE} = \int_{y_2}^{y_1} \frac{dy}{y^* - y} \tag{5}$$

The elements of these equations are illustrated in Figure 1. NTU_{OE} and NTU_{OR} are related by the following expression:

$$NTU_{OE} = \frac{R}{mE} \times NTU_{OR} \tag{6}$$

where R/E is the ratio of flow rates of raffinate and extract phases and m is defined by the equation

$$m = \frac{y^* - y}{x - x^*} \tag{7}$$

If we limit the discussion to dialysis systems containing only monovalent ions, m will remain constant and equal to the ratio of ion equivalents between the extract and raffinate phases. *With m constant* Eq. (4) and (5) can be easily integrated. The

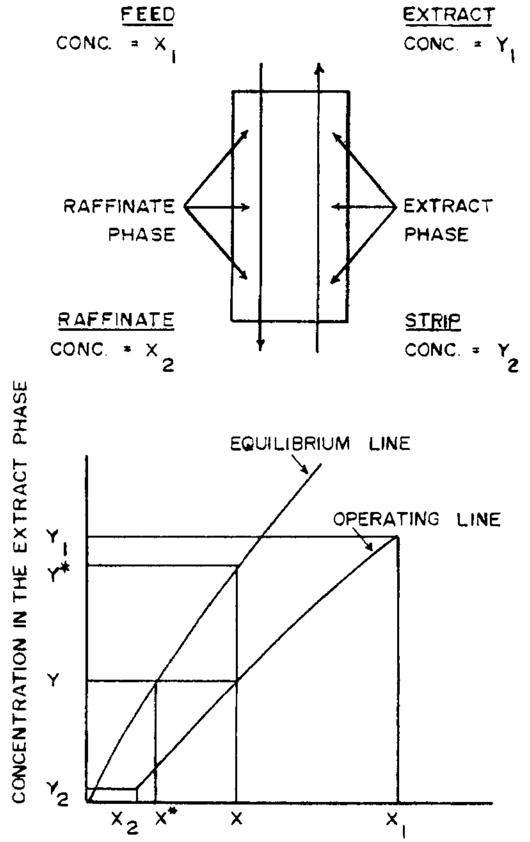

FIGURE 1. ILLUSTRATION OF TERMS USED IN TRANSFER UNIT CALCULATION

integrated expressions for countercurrent systems are:

$$NTU_{OR} = \frac{\ln\left[\left(\frac{x_1 - y_2/m}{x_2 - y_2/m}\right)\left(1 - \frac{R}{mE}\right) + \frac{R}{mE}\right]}{1 - \frac{R}{mE}} \qquad (8)$$

$$NTU_{OE} = \frac{\ln\left[\left(\frac{y_2 - mx_1}{y_1 - mx_1}\right)\left(1 - \frac{mE}{R}\right) + \frac{mE}{R}\right]}{1 - \frac{mE}{R}} \qquad (9)$$

EXPERIMENTAL

Several dialysis runs were made in an effort to test the mass transfer correlations advanced thus far. All runs were made using the same dialyzer. The construction of the dialyzer used in this work was essentially the same as previous devices used by Wallace (6) and by Davis, et. al. (7). A schematic representation of the dialyzer is depicted in Figure 2. A more

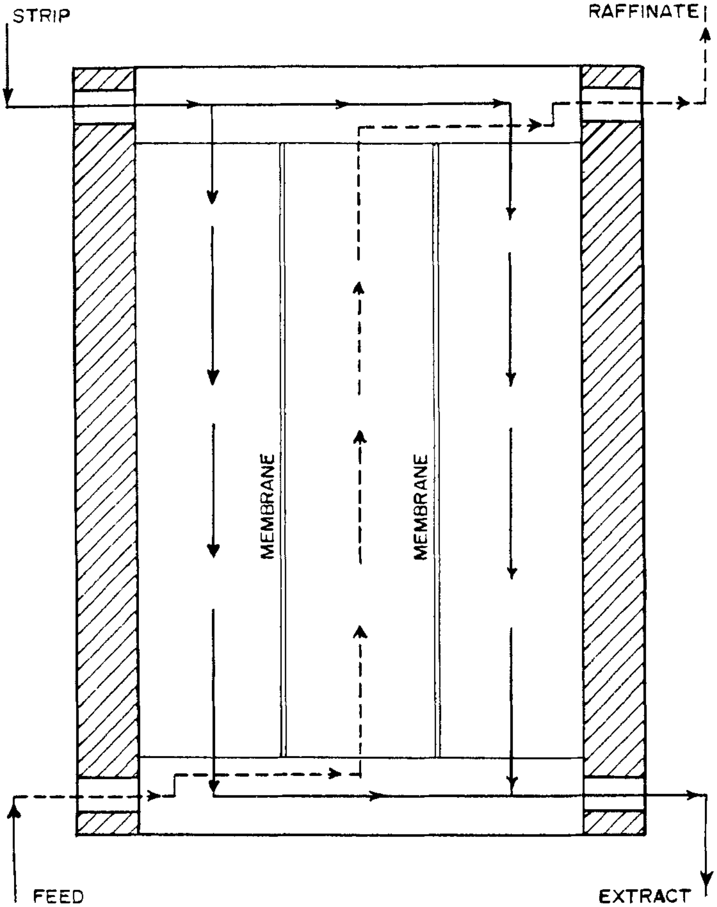

FIGURE 2. SCHEMATIC REPRESENTATION OF THE EXPERIMENTAL MEMBRANE SYSTEM

detailed drawing showing the elements comprising the dialyzer are shown in Figure 3. The dialyzer was a single pass-counter-current unit using two Nafion* perfluorosulfonic acid membranes. The thickness of the flow channels was .061 cm. The membrane area within the dialyzer was 50 x 10 centimeters for each membrane.

The usuable membrane area was undoubtedly somewhat less than the 1000 cm^2 because of collapsing membrane channels and because of the presence of air pockets within the channels.

For each of the runs a solution of sodium nitrate was introduced into the feed stream and a potassium nitrate solution into the strip stream. The concentrations of these solutions were varied but the feed and strip rates remained constant at 1050 ml/hr and 240 ml/hr respectively throughout all the runs. The stream compositions and the number of transfer units calculated from these compositions are shown in Table 1 for each of the runs. (Because of various non-idealities in the dialyzer system and analytical errors a slightly different value for the number of transfer units is obtained depending on whether the raffinate or extract concentrations are used for the calculations. In order to give some indication of the errors involved both values are given.)

The following equations relate overall NTU values to individual phase NTU's (8).

$$\frac{1}{NTU_{OE}} = \frac{1}{NTU_E} + \frac{mE}{R}\,\frac{1}{NTU_R} \qquad (10)$$

$$\frac{1}{NTU_{OR}} = \frac{1}{NTU_R} \quad \frac{R}{mE}\,\frac{1}{NTU_E} \qquad (11)$$

where NTU_E = number of extract phase transfer units.

NTU_R = number of raffinate phase transfer units.

If the mass transfer concepts are valid for Donnan dialyzers,

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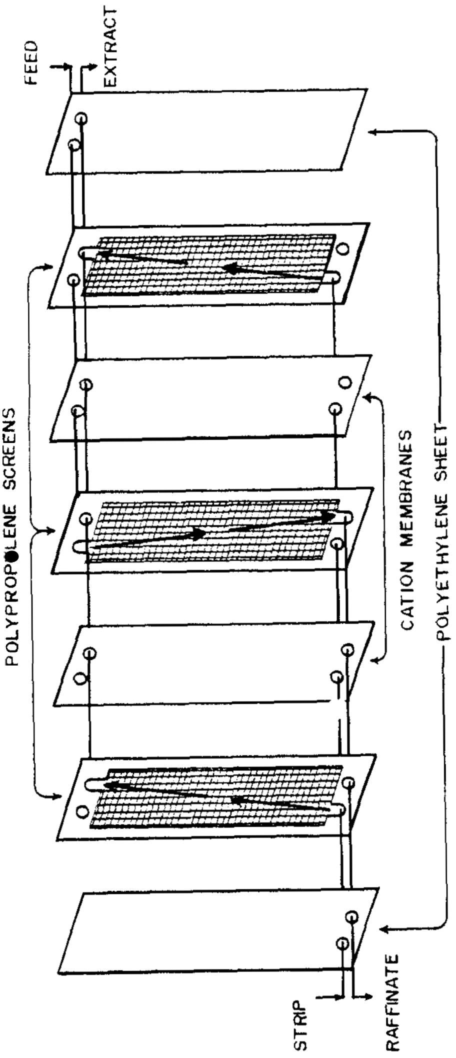

FIGURE 3. EXPLODED VIEW OF THE MEMBRANE SYSTEM

TABLE 1
OVERALL TRANSFER UNITS CALCULATED FROM EXPERIMENTAL DATA

Concentrations in (moles/liter) x 10^4

Run	Cation	(x_1) Feed Conc.	(y_2) Strip Conc.	(x_2) Raf. Conc.	(y_1) Ext. Conc.	$\frac{R}{mE}$	NTU_{OR}	NTU_{OE}
1	Na	274.0	0.0	-	-	47.3	.037	1.75
	K	0.0	25.1	-	4.45			
2	Na	264.0	0.0	237.0	96.8	8.72	.152-.180	1.33-1.56
	K	0.0	128.0	23.1	38.1			
3	Na	129.0	0.0	101.3	139.4	2.27	.400-.411	.907-.934
	K	0.0	253.0	32.2	113.6			
4	Na	62.0	0.0	41.2	108.0	1.06	.558-.642	.591-.680
	K	0.0	254.0	22.6	156.0			
5	Na	26.1	0.0	13.3	62.8	.407	.619-.823	.252-.335
	K	0.0	287.0	14.1	226.0			
6	Na	24.1	0.0	10.9	-	.118	.823	.097
	K	0.0	890.0	-				

the NTU_{OE} and NTU_{OR} values for the runs in Table 1 will be related by the above expressions. Sustituting data from any two of the runs defines the value of NTU_E and NTU_R. Using data from runs 1 and 6, the values of NTU_E and NTU_R are calculated to be:

$$NTU_E = 1.83$$

$$NTU_R = .87$$

With these values and the $\frac{R}{mE}$ values, NTU_{OR} and NTU_{OE} can be predicted for the other four runs by using eq. (10) and (11). Predicted and actual values are compared numerically in Table 2. The values are also compared graphically in Figure 4.

Use of the transfer unit equations when multivalent ions are present is somewhat more involved than when only monovalent ions are present because of the difficulties in integrating the transfer unit equations when the equilibrium relationship is not linear. With such systems an exact solution is obtained only if the transfer-unit equations are integrated graphically over the length of the dialyzer. However, an adequate technique in many cases is to assume an average value for (m), the distribution coefficient, and use the integrated equations shown above.

The transfer unit techniques are of significant value only if values of NTU_E and NTU_R can be predicted from system para-

Table 2

Comparison of Predicted and Experimental Values of NTU_{OE} and NTU_{OR}

	Experimental		Calculated	
Run	N_{OR}	N_{OE}	N_{OR}	N_{OE}
1	.037	1.75	.037	1.75
2	.152-.180	1.33-1.56	.166	1.45
3	.400-.411	.907-.934	.414	.939
4	.558-.642	.591-.690	.574	.609
5	.619-.823	.252-.335	.726	.296
6	.823	.097	.823	.097

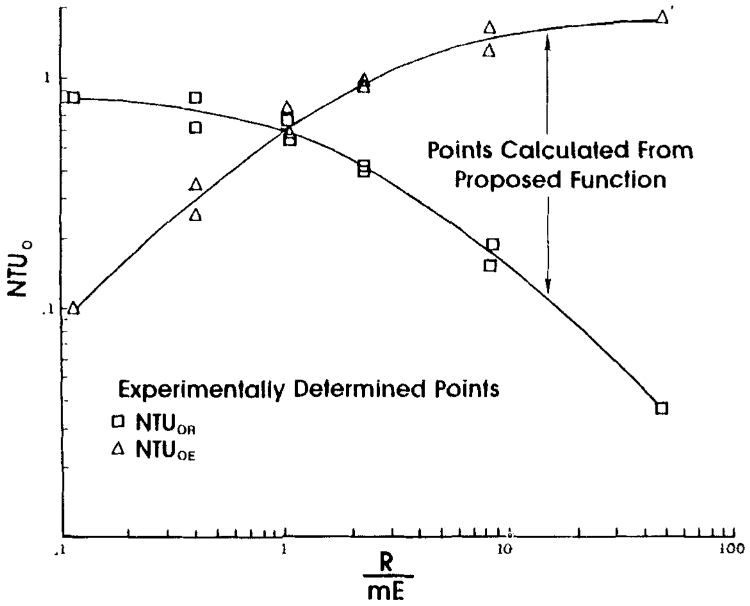

Figure 4
Comparison Between Experimental and Predicted NTU's

meters. NTU_E and NTU_R values are equal to the overall NTU values when the ion concentration at the membrane surface equals zero. If laminar flow is assumed an analogy can be made between ion flow from a dialysis solution and the flow of heat from a slab to its surroudings when the resistance to heat flow at the edge of the slab is negligible. Solutions to the equations describing a cooling slab under these conditions are presented in many texts. A graphical representation of the solution is shown in Figure 5 (9). Values for ion removal are given in terms of the fraction of initial ion concentration remaining in the exit stream and also in terms of NTU's. NTU values are calculated using Eq. (8) and (9) which become under these conditions:

$$NTU_R = \ln\left(\frac{x_1}{x_2}\right) \qquad (12)$$

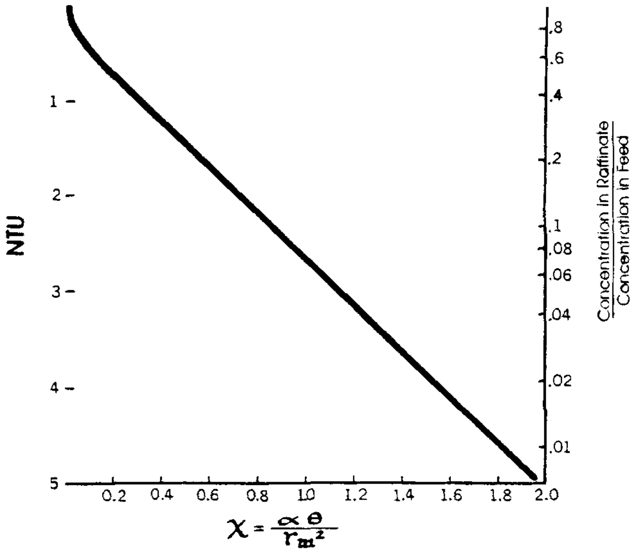

FIGURE 5
CALCULATION OF NTU VALUES FROM SYSTEMS PARAMETERS

$$NTU_R = \ln\left(\frac{y_2}{y_1}\right) \qquad (13)$$

Definition of the terms necessary to use Figure 5 for diffusion are as follows:

α = interdiffusion coefficient of ions in solution, cm^2/sec.

θ = residence time in dialyzer = membrane area x channel thickness/volume flow rate, sec.

r_m = channel thickness, cm

Due to the inexact construction of the dialyzer previously described, the channel thickness and membrane area could not be precisely determined. For this reason, prediction of individual-phase NTU values from equipment parameters is not possible in this case. However, data gathered by Wallace (10) using a carefully constructed dialyzer is suitable for applying the proposed correlation. A similar heat transfer analogy had been proposed by this investigator to describe his dialysis systems. The dialyzer used by Wallace consisted of five one membrane units in series, each having a membrane area of 232 cm^2. The channel thickness of each unit was 0.03 cm. The membranes were "Amfion"* C-103 cation selective membranes. Solutions of .01M uranyl nitrate and 3M nitric acid were run countercurrently through the dialyzer. Flow rates of the nitric acid stream were sufficiently high so that most of the resistance to transport can be assumed to be in the phase containing the uranyl solution.

The interdiffusion coefficient is determined using the following equation for coupled diffusion (11):

$$\alpha = \frac{D_A D_B \left(z_A + z_B\right)}{z_A D_A + z_B D_B} \tag{14}$$

where D_A and D_B are individual ion diffusion coefficients. The diffusion coefficient "D" for the hydrogen ion is found by applying the following equation (15) (13) to ionic conductance data (14):

$$D = \frac{RT\lambda}{zF^2} \tag{15}$$

where R is the gas constant, 8.314 joules/°k mole; F is Faraday's constant, 96500 coul/gm equiv; T is temperature, °K, Z is valence; and λ is the ionic conductance, cm^2/ohm gm equiv. The resulting diffusion coefficient is 9.3×10^{-5} cm^2/sec. The diffusion coefficient for the uranyl ion is approximately $.5 \times 10^{-5}$ cm^2/sec (15).

The fraction of uranium remaining in the raffinate phase was experimentally determined at three flow rates. The data is shown in Table 3. Also, in this table are the predicted values from the proposed correlation. The experimental and predicted values are compared again in Figure 6.

A meaningful evaluation of the accuracy of the analogy as

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Table 3

Data for Acid-Uranyl System

Flow ml/min		Uranium in Raffinate % of Feed		NTU	
Feed	Strip	Experimental	Predicted	Experimental	Predicted
10	.20	.07	.02	7.26	8.57
12	.28	.23	.07	6.07	7.31
16	.32	1.04	.33	4.57	5.71

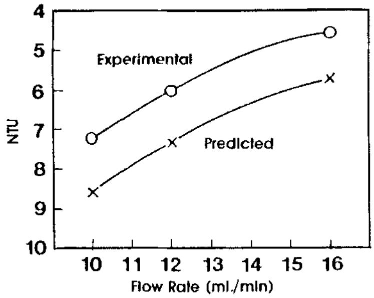

Figure 6
Comparison of Experimental and Predicted Values for Acid-Uranyl System

a design tool can be made only by comparing NTU values since NTU values and predicted membrane areas are directly related. In terms of transfer units and membrane area, the error is approximately 20%.

CONCLUSIONS

The transfer unit concept was shown to be useful in describing the ion transport in Donnan dialyzers in which the membrane's resistance to ion transport is relatively small and where anion leakage and osmosis are negligible. Most dialysis systems fit these criteria if dilute solutions are used.

Use of a heat transfer analogy was suggested as a means of estimating ion transport in dialyzers for which no data from previous runs or membrane diffusivities are available.

The analogy was shown to yield acceptible results even when one phase contained a concentrated electrolyte solution. For many situations, these techniques provide a simple means of estimating the size and configuration of a Donnan dialyzer required to accomplish a given extraction.

NOTATION

C_i = concentration of the ith cation
D = individual ion diffusion coefficient

E = flow rate of the extract phase
K = constant
m = distribution coefficient
NTU = number of individual phase transfer units
NTU_O = number of overall transfer units
R = flow rate of the raffinate phase
r_m = channel thickness
x = concentration of a component in the raffinate phase
x^* = concentration of a component in the raffinate phase that would be in equilibrium with with the extract phase
y = concentration of a component in the extract phase
y^* = concentration of a component in the extract phase would be in equilibrium with the raffinate phase
z = valence
α = interdiffusion coefficient
θ = residence time

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