Analysis of Data in Reverse Osmosis with Porous Cellulose Acetate Membranes Used

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Reverse osmosis experimental data for some inorganic salts with the porous cellulose acetate membrane used were analyzed to obtain their diffusivity in the membrane. A parameter including the diffusivity was found constant for each film in the concentration range investigated for a particular solute at a particular pressure. This parameter was also independent of feed flow rate. The effect of operating pressure on the parameter was found to depend on the film shrinkage. Mass transfer coefficient between the membrane and the feed solution was also obtained by the analysis, and this value was independently checked by the diffusion current method. Coincidence of these coefficients shows that the ordinary mass transfer coefficient can be used in reverse osmosis with the appropriate driving force. These facts facilitate the prediction of solute separation and membrane throughput rate in reverse osmosis.

The quantitative predictability of solute separation and throughput rate is a fundamental aspect of the reverse osmosis membrane separation process. Sourirajan showed (*12, 13*) that under identical experimental conditions of constant feed solution molality, feed flow rate, and operating pressure and temperature, the separation and throughput rate characteristics of a membrane are uniquely related for all solution systems containing cations and anions of the same respective valency. No method of predicting these relative separation characteristics of a membrane was given, but it was shown possible to predict the relative throughput rates of a membrane for the above solution systems (*14*). A method of predicting the separation characteristics of a membrane for different electrolyte solution systems was proposed by Glueckauf (*2*). This method is based on calculating the energy difference between the ion in solution and the ion in an aqueous hole, assumed to be in equilibrium with the bulk solution, and the probability of finding an ion at this energy level in the interior of the pore. While the results predicted by Glueckauf's theory seemed to be in good agreement with the experimental data obtained with the Schleicher and Schuell types of membranes, the agreement was not satisfactory with those obtained with the laboratory-made, high-flow cellulose acetate membranes (*3*). Recently Govindan and Sourirajan (*3*) postulated some empirical equations which predict the effect of pressure on solute separation and throughput rate, and the effect of concentration on throughput rate, but not on separation.

This paper presents a different analysis of the experimental separation and throughput rate data for some inorganic salts in aqueous solutions with the use of the laboratory-made, high-flow porous cellulose acetate membranes. This analysis is based on a generalized diffusion model applicable to the entire range of solute separation. It gives rise to the concept of an effective diffusivity parameter for the solute for the particular membrane-solution system. This diffusivity parameter remains essentially constant for a wide range of feed concentrations for the several systems tested and it is also independent of feed flow rate. Consequently this analysis makes it possible to predict the effect of feed concentration on solute separation and membrane throughput rate for a wide range of feed concentrations from a single set of experimental data. There also exist other interesting relationships between the effective diffusivity parameter of the solute and each one of the variables, operating pressure, and the diffusivity of pure water.

Furthermore, mass transfer coefficients between the membrane and the bulk of the solution obtained by the present analysis of data are found to agree with those experimentally determined by the diffusion current method (*6, 10*), indicating thereby that the mass transfer data available in literature can be used in the analysis presented in this paper.

The above relationships and the close agreement between the predicted and experimental separation and throughput data offer a new and useful approach to the study of the reverse osmosis membrane separation process.

ANALYSIS

The situation to be analyzed is shown in Figure 1. By the action of mechanical pressure applied, both the solute and the water tend to permeate the membrane. But because of the low value of the solute diffusivity in the

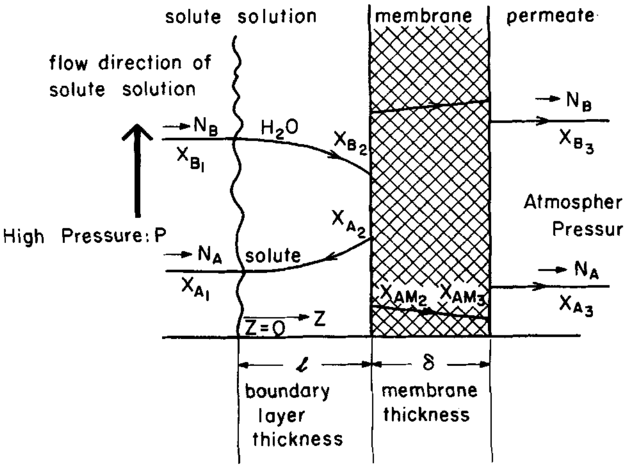

Fig. 1. Concentration distribution in the boundary layer and the membrane.

membrane, a large part of solute must diffuse back to the bulk solution through the boundary layer. Concerning the rate at which the pure water permeates the membrane N_B, the following relation has been used (8) and is also assumed here:

$$N_B = A[P - \{\pi(X_{A2}) - \pi(X_{A3})\}] \tag{1}$$

where $\pi(X_A)$ is an osmotic pressure corresponding to a mole fraction of solute X_A. A is defined here as a pure water permeability constant which is obtained independently from the pure water permeation data with the use of the following relation:

$$A = N_{BP}/P \tag{2}$$

where N_{BP} is the pure water permeation rate with pure water as the feed.

Concerning the solute permeation rate N_A, a simple diffusion equation is assumed as

$$N_A = \frac{c_M \cdot D_{AM}}{\delta} (X_{AM2} - X_{AM3}) \tag{3}$$

where D_{AM} and X_{AM} are the diffusivity and mole fraction of solute in the membrane, respectively, and δ is the effective thickness of the membrane.

If the distribution ratio of solute between the aqueous solution and the membrane is assumed constant, then

$$c \cdot X_A = K \cdot c_M X_{AM} \tag{4}$$

and Equation (3) becomes

$$N_A = \frac{c \cdot D_{AM}}{K \quad \delta} (X_{A2} - X_{A3}) \tag{5}$$

Concerning the mass transfer in the boundary layer of the solution, the film theory is adopted; that is, solute molecule transfers through the effective film thickness l by molecular diffusion. The Maxwell-Stefan equation in this case is given as follows:

$$N_A = X_A (N_A + N_B) - D_{AB}\, c \frac{dX_A}{dZ} \tag{6}$$

With the following stoichiometric equation used

$$X_{A3} = \frac{N_A}{N_A + N_B} \tag{7}$$

Equation (6) is integrated with a boundary condition $Z = 0, X_A = X_{A1}$ to give

$$\ln\left(\frac{X_A - X_{A3}}{X_{A1} - X_{A3}}\right) = \frac{Z}{c\, D_{AB}} (N_A + N_B) \tag{8}$$

The value of X_{A2} is determined from Equation (8) as

$$\ln\left(\frac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}}\right) = \frac{1}{c \; k} (N_A + N_B) \tag{9}$$

where k is defined as

$$k = \frac{D_{AB}}{l} \tag{10}$$

Equations (1), (5), (7), and (9) are combined to give the following relations:

$$N_B = A[P - \pi(X_{A2}) + \pi(X_{A3})] \tag{1}$$

$$= \frac{c \cdot D_{AM}}{K \quad \delta} \cdot \frac{1 - X_{A3}}{X_{A3}} \cdot (X_{A2} - X_{A3}) \tag{11}$$

$$= k \; c \; X_{B3} \frac{(X_{B1} - X_{B2})}{(X_A)_{l \cdot m.}} \tag{12}$$

where

$$(X_A)_{l \cdot m.} = \frac{X_{A2} - X_{A1}}{\ln\left(\dfrac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}}\right)} \tag{13}$$

In the reverse osmosis experiment the degree of separation R and the throughput rate Q are usually measured. These values may be expressed as

$$R = \frac{m_1 - m_3}{m_1} = 1 - \frac{(1 - X_{A1})}{X_{A1}} \cdot \frac{X_{A3}}{(1 - X_{A3})} \tag{14}$$

$$Q = \frac{N_B \cdot S \cdot M_B \cdot 3600}{\left[1 - \dfrac{1}{1 + \dfrac{1000}{m_1 M_A (1 - R)}}\right]} \tag{15}$$

EXPERIMENTAL DETAILS

Porous cellulose acetate membranes (designated earlier as CA-NRC-18 type films) made in the laboratory were used in these experiments. The film details, the apparatus, and the experimental procedure have been reported (*7, 12, 14*). By shrinking the film in hot water for about 10 min. at different temperatures, films capable of giving different degrees of solute separation were obtained; this film shrinkage procedure has been described (*7, 12*). Thus the films are distinguished by the different temperatures used for film shrinkage. The films used in this work were so chosen as to cover a wide range of solute separations as indicated by the data given in Table 1. The following solution systems were studied: 0.0625 to 4.0 M [$NaCl-H_2O$] and [$NaNO_3-H_2O$], and 0.25 M to 1.5 M [$Na_2SO_4-H_2O$], [$MgCl_2-H_2O$], and [$MgSO_4-H_2O$]. The operating pressure was in the range 8.7 to 102 atm. and the feed rate was in the range 20 to 250 cc./min. The feed solution was pumped under pressure past the surface of the membrane held in a stainless steel pressure chamber provided with two separate outlets, one for the flow of the membrane permeated solution and the other for the concentrated effluent. All the experiments were carried out at the laboratory temperature, which was in the range 23° to 26°C. The effective area of the film in the cell was 7.6 sq. cm. In each experiment the degree of separation and the throughput rate through the membrane were determined. The relative concentrations of

Table 1. Characteristics of the Porous Cellulose Acetate Membranes at Different Temperatures of Film Shrinkage

Membrane No.	Temp, of shrinkage, °C.	Pure water permeability constant, $A \times 10^6$	% Solute separation				
			NaCl	$NaNo_3$	Na_2SO_4	$MgCl_2$	$MgSO_4$
1	90	0.97	98.6	95.4			
2	88	1.46	93.4	85.0			
3	86	1.87	83.0	71.4			
4	84	2.37	60.3	44.8			
5	82	2.48	49.9	32.6			
6	80	2.93	26.8	14.3			
7	90	1.29	96.2	94.0	99.5	98.0	98.6
8	87	2.07	81.9	71.4	97.6	88.3	97.1
9	85	2.54	66.4	51.2	95.1	73.7	96.1
10	83.5	3.30	49.4	28.6	90.7	57.1	93.2
11	81	4.21	36.4	18.5	84.9	43.4	89.9
12	79	4.42	16.7	6.5	70.7	20.5	79.7
13	79.5	4.00	36.7		82.3	45.5	91.3
18	No shrinkage	5.68	4.8		55.9	7.5	72.3

Operating pressure, 102 atm.; feed molality, 0.5 M; feed rate, 250 cc./min.

the solute in the feed and the membrane permeated product solutions were determined either gravimetrically or by refractive index measurements with a precision Bausch and Lomb refractometer. The separation data are good to an accuracy of ± 1% and the throughput data are good within 3%.

To confirm the relation of mass transfer coefficient between the membrane and the flow of solutions, this value was measured independently by the diffusion current method (*6*, *10*). In this case the membrane was replaced by a platinum plate electrode and used as a cathode. A platinum anode, which had an area twice as large as the cathode, was held to the wall of a plastic cell, which had the same size of a stainless steel cell. The diffusion current of cathodic reduction of ferricyanide ion was measured by a similar method written in the literature (*6*, *10*). As a supporting electrolyte 1 *N* KNO_3 was used. To determine the effect of the Schmidt number solution temperature was changed from 10° ~ 40°C. Diffusivity of ferricyanide ion in an infinite dilute solution at 25°C. is given by the Nernst equation (*4*). This value was corrected with the assumption that the diffusivity is inversely proportional to the viscosity of solution. Relative diffusivities at the other temperatures to 25°C. were determined by measuring the diffusion current in a dropping mercury electrode and correcting by the Ilkovic equation (*4*). The range of the Schmidt number thus obtained was from 460 to 1,900.

RESULTS

Values of A for each membrane at a particular pressure were determined from the pure water permeation data with Equation (2). Values of X_{A2} were calculated from the experimentally observed values of Q and R (or X_{A3}) with Equation (1). Then values of $D_{AM}/K\delta$ and mass transfer coefficients were calculated with Equations (5) and (9), respectively. All data were processed by an IBM 360 computer in the computing center in the National Research Council. The osmotic pressure of these electrolyte solutions at 25°C. for various concentrations were calculated from the following relation (*5*, *11*):

$$\pi = \frac{RT\,\nu\,M_B}{\bar{V}_B\,1000}\,m\,\phi \qquad (16)$$

where R is the gas constant, T is the absolute temperature, ν is the number of ions produced by dissociation of one molecule of electrolyte, m is the solution molality, and ϕ is the osmotic coefficient at 25°C.

Effect of Concentration

Values of $D_{AM}/K\delta$ for membranes of different degree of shrinkage were plotted vs. concentration in Figure 2,

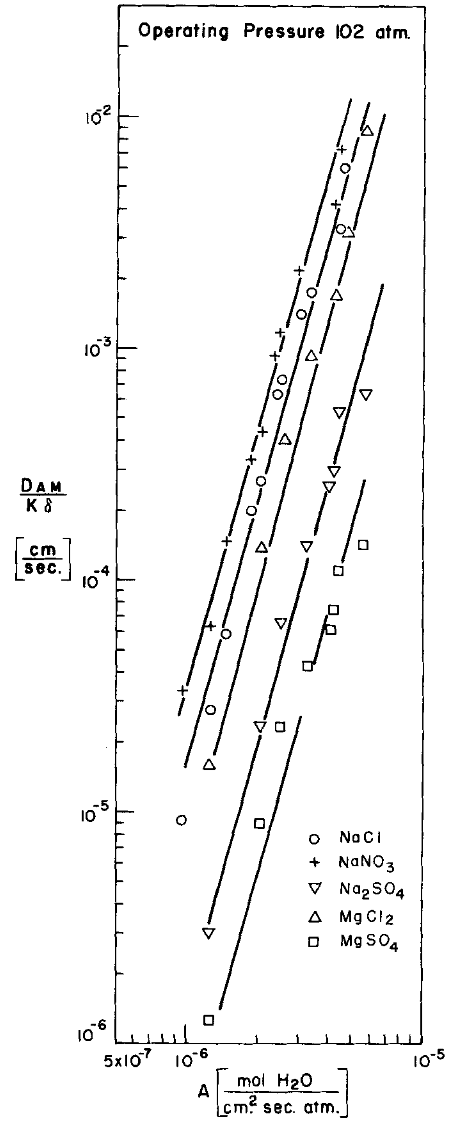

Fig. 3. $D_{AM}/K\delta$ vs. pure water permeability constant.

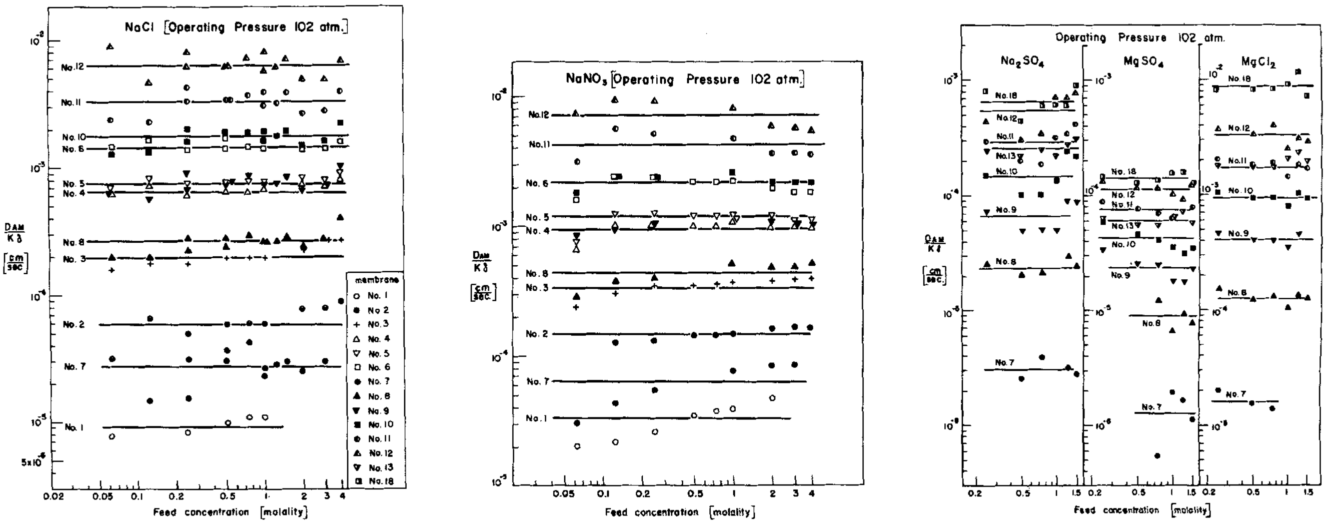

Fig. 2. Values of $D_{AM}/K\delta$ for different membranes for different solutes.

where the solid lines show the average value through the entire concentration range. It is seen from these figures that values of $D_{AM}/K\delta$ can be considered to have constant values in these concentration ranges. For high shrunk films, like No. 1 and 7, it seems that increasing tendency exists with increase of concentration, but in these cases the solute concentrations in the throughput are so low that the accurate determination of concentration and thus of $D_{AM}/K\delta$ is difficult. As scattering of data is rather large to determine the tendency, here it is regarded that $D_{AM}/K\delta$ is constant for these high shrunk film. It is shown later, however, that the prediction of R and Q is fairly well performed assuming the value of $D_{AM}/K\delta$ is constant throughout the entire concentration range.

An interesting relation between A and $D_{AM}/K\delta$ also exists and is shown in Figure 3. $D_{AM}/K\delta$ is proportional to 3.5 power of A at the particular operating pressure of 102 atm. and is parallel for different solutes. As it is already shown (8) that A may also be given as

$$A = D_{BM} \cdot C_{BM} \cdot \overline{V}_B \qquad (17)$$

it is apparent that some relation exists between the diffusivity of solute and that of water in the membrane. This fact also shows that once such a relation is fixed, $D_{AM}/K\delta$ can be predicted by simply measuring the pure water permeability constant.

Effect of Operating Pressure

Pure water permeability constant A of a membrane decreases when the operating pressure is increased. This may be due to the mechanical compression of the membrane. This change can be expressed as follows:

$$A = \theta_0 \, e^{-\alpha P} \qquad (18)$$

where θ_0 is a pure water permeability at zero pressure difference and is a characteristic value that corresponds to a particular degree of membrane shrinkage. Correlation of A by Equation (18) for different films shows that α is constant and is not dependent on the degree of shrinkage as shown in Figure 4.

The effect of pressure on $D_{AM}/K\delta$ is different from that of A. Values of $D_{AM}/K\delta$ of the high shrunk film are affected little, whereas those of the low shrunk film are much affected. This change can be expressed as

$$(D_{AM}/K\delta)/(D_{AM}/K\delta)_r = \left(\frac{P}{P_r}\right)^{-\beta} \qquad (19)$$

where suffix r represents a reference pressure, 102 atm. in this case. The value of β in Equation (19) is proportional to θ_0 up to a certain value of θ_0, and above that it becomes constant as shown in Figure 5. This pattern of the change is the same for different solutes. But for Na_2SO_4 β is nearly twice that of others. The reason for it is not clear at this stage.

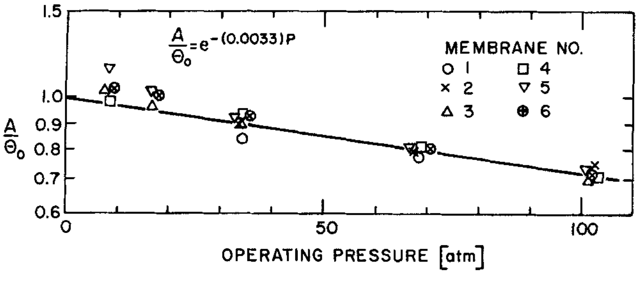

Fig. 4. Effect of operating pressure on pure water permeability constant.

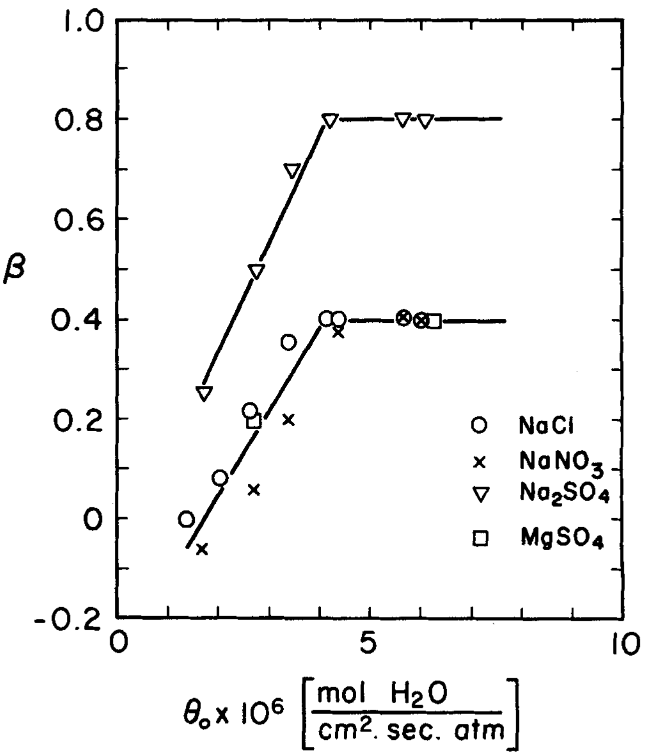

Fig. 5. β vs. θ_0.

Effect of Feed Flow Rate

The parameter $D_{AM}/K\delta$ does not depend on the feed flow rate. When the feed rate is increased, however, the throughput rate and the degree of separation increase. This is due to the increase of mass transfer coefficient between the membrane and the feed flow and the decrease of concentration polarization at the membrane-solution interface. Therefore the effect of feed flow rate is entirely explained by the mass transfer coefficient.

Mass Transfer Coefficients

Mass transfer coefficients defined by Equations (9) and (10) were calculated from the reverse osmosis experiment data with Equation (10) used. It was, however, not cer-

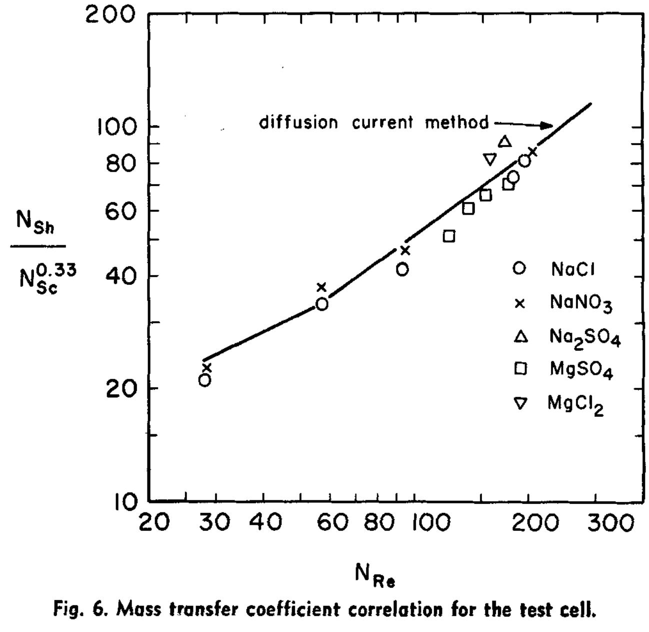

Fig. 6. Mass transfer coefficient correlation for the test cell.

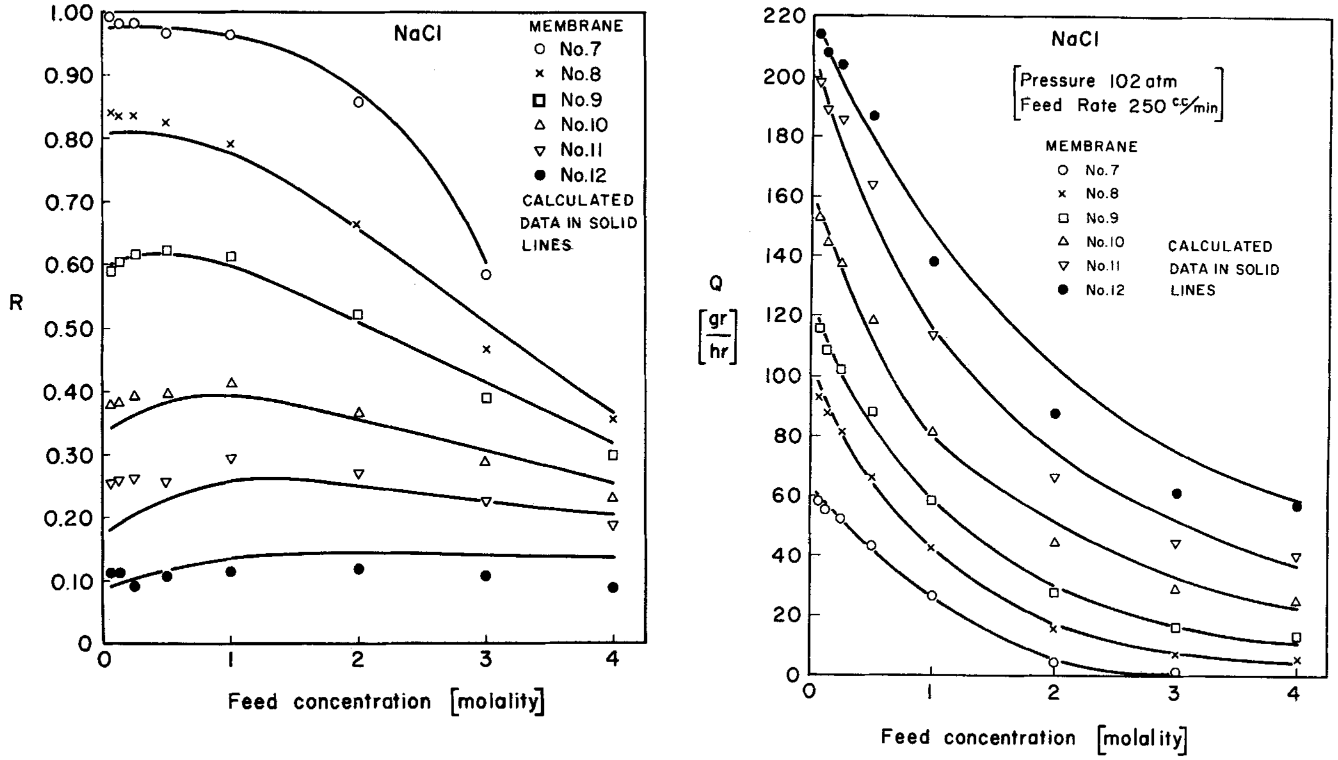

Fig. 7a and 7b. Comparison of experimental and calculated data for the system NaCl–H_2O for different membranes.

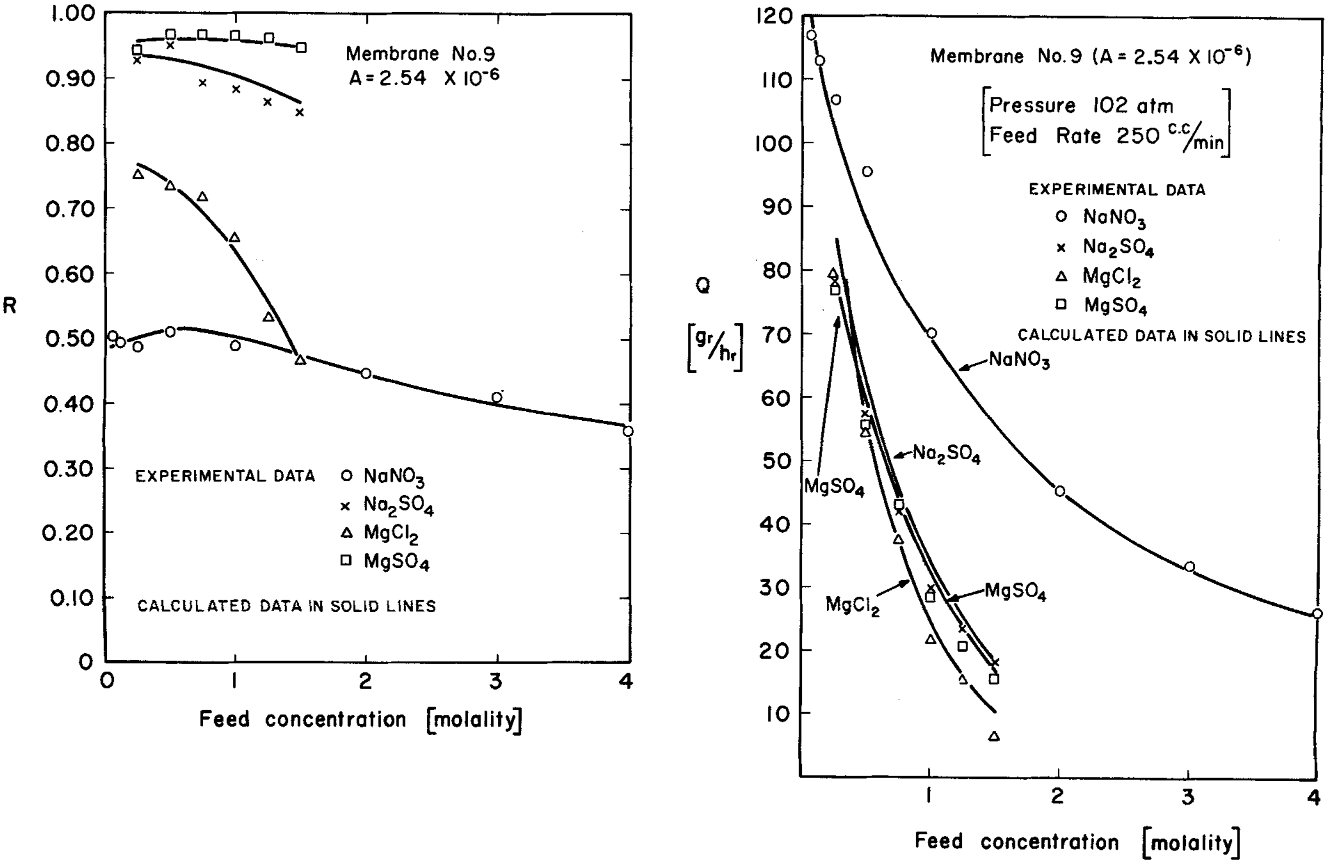

Fig. 8a and 8b. Comparison of experimental and calculated data for different systems for membrane No. 9.

tain whether the mass transfer coefficient thus defined had the same value compared to that which is usually defined as a proportionality constant between a driving force and a flux.

It is also interesting that Equation (12) expresses the more general definition of mass transfer coefficient in the unidirectional diffusion case; that is, when the solute does not leak through the membrane, X_{A_3} becomes zero and Equation (12) becomes the usual definition of a unidirectional mass transfer coefficient.

For these reasons the mass transfer coefficient was measured independently by the diffusion current method. The results are shown in Figure 6, where the solid line expresses the result of the diffusion current method and the points are those from reverse osmosis data. In the calculation of the latter value diffusivities of solutes in water were gathered from the literature (*1*, *9*).

As the agreement between these values is fairly good, it is considered reasonable to use the ordinarily measured mass transfer coefficient in the other types of apparatus in the reverse osmosis case.

Prediction

The effect of feed concentration and the feed flow rate on R and Q at a given operating pressure may be predicted from a single set of experimental N_{BP}, Q, and R (and hence X_{A_1} and X_{A_3}) data as follows. The values of A, X_{A_2}, $D_{AM}/K\delta$, and k are first calculated, as before, using Equations (2), (1), and (11) and (12) and (13) respectively. For the prediction calculations k should be known as a function of the feed flow rate and the properties of the solution as shown in Figure 6. For any feed concentration and the feed rate, the value of k is obtained from Figure 6, the values of A and $D_{AM}/K\delta$ are assumed constant, and those of X_{A_2}, X_{A_3}, and N_B are calculated by a trial and error procedure with Equations (1) and (11) through (13) used. Finally, R and Q are obtained from Equations (14) and (15).

Such calculations have been performed for NaCl with membranes No. 7 to 12, and for the other solutes with membrane No. 9. Results are shown in Figures 7 and 8, where the solid lines express the calculated results. In these calculations the constant value of $D_{AM}/K\delta$ was used for a particular solute regardless of the solute concentration. As data of diffusivities of solute in water were limited, and thus it was not always possible to calculate the mass transfer coefficient from data of the diffusion current method, average mass transfer coefficients from reverse osmosis data were used in the calculations. Results shown in these figures not only show the predictability of R and Q, but also show that it is reasonable to assume that the value of $D_{AM}/K\delta$ is constant for any particular membrane-solution system at least for the systems and concentration range tested.

To perform the prediction calculation for the other types of cell, a relation of N_{Sh} to N_{Sc} and N_{Re} must be known from the literature or from experiment to predict the effect of the feed rate and concentration on R and Q.

CONCLUSION

Reverse osmosis experimental data for some electrolytes have been analyzed by a simple model, in which the permeation of the solute molecule through the cellulose acetate membrane is assumed to follow the usual diffusion equation. A parameter thus obtained $D_{AM}/K\delta$, which includes the effective diffusivity of a solute in the membrane, is shown to be a constant for the particular membrane and the solute system in the entire concentration range investigated.

The effect of operating pressure on this parameter is small for high shrunk film and is large for low shrunk film. Also it is shown that this parameter has a simple relation with the pure water permeability constant A.

At the same time the mass transfer coefficient between the membrane and the flow of solution were analyzed and checked by the diffusion current method. As these two kinds of independently obtained coefficients coincide fairly well with each other, it can be considered that the usually measured mass transfer coefficient can be used in the mass transfer calculation in the reverse osmosis case with the appropriate values for the driving force in Equation (12).

The facts stated above facilitate the prediction of the throughput rate and solute separation in the particular cell used here; the analysis is also applicable to other types of cells, where the mass transfer coefficient is known, so long as the cellulose acetate membrane investigated here is used.

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NOTATION

A = pure water permeability constant, g.-mole H_2O/(sq.cm.) (sec.) (atm.)
C = solute concentration, g.-mole/cc.
c = molar density of solution, g.-mole/cc.
D = diffusivity, sq.cm./sec.
D_{AB} = diffusivity of solute in water, sq.cm./sec.
d = diameter of circular membrane, cm.
h = depth of cell, cm.
K = distribution ratio of solute between solution and membrane
k = mass transfer coefficient, cm./sec.
l = effective boundary-layer thickness, cm.
M = molecular weight, g./mole
m = molality, g.-mole/1,000 g. H_2O
N = flux through membrane, g.-mole/(sq.cm.) (sec.)
N_{Re} = ud/ν
N_{Sc} = ν/D_{AB}
N_{Sh} = kd/D_{AB}
P = operating pressure, atm.
Q = throughput rate, g./hr.
R = degree of separation as defined by Equation (14)
S = effective membrane area, sq.cm.
u = velocity of solution parallel to membrane, $Q/d.h$, cm./sec.
$\overline{V}_B$ = partial molar volume of water, cc./mole
X = mole fraction
Z = distance, cm.

Greek Letters

δ = membrane thickness, cm
ν = kinematic viscosity, sq.cm./sec.
π = osmotic pressure, atm.
θ_0 = pure water permeability at zero pressure difference, g.-mole H_2O/(sq.cm.) (sec.) (atm.)

Subscripts

A = solute
B = water
BP = pure water permeation
M = membrane phase
1 = bulk solution
2 = membrane-solution interface
3 = throughput

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An Investigation of Solids Distribution, Mixing, and Contacting Characteristics of Gas-Solid Fluidized Beds

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This two-part series describes an integrated experimental investigation. The first part is concerned with the determination of axial and radial solids concentration profiles at different superficial gas velocities for three columns having I.D. of 2.5, 6.5, and 9.5 in. respectively. The second part is concerned with steady state point source gas tracer experiments carried out in the 9.5-in. column and in which the tracer concentration was measured at different radial positions above and below the injection source at various gas velocities Both parts are complimentary to each other for describing the internal flow behavior of the gas-solid fluidized system.

PART I. STUDY OF SOLID CONCENTRATION PROFILES IN A GAS-SOLID FLUIDIZED BED

Despite the widespread use of gas-solid fluidized beds, many of their fundamentals are still poorly understood. In recent years, it has been realized that in order to achieve the desired understanding of the phenomenon of gas-solid contact in fluidized systems, the approach of determining the overall characteristics of the system has to be replaced by a more fundamental approach based on the measurement of the variation of the properties from point to point within the system. Such an approach was followed throughout this work.

The first part of this investigation was concerned with the study of time-averaged solids distribution of different diameter fluidized beds with the gamma ray attenuation

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