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Simple Graphical Method to Estimate Membrane Transport Parameters and Mass Transfer Coefficient in a Membrane Cell

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ABSTRACT

Reverse osmosis (RO) experiments are conducted in the laboratory using a cellulose acetate membrane in a flat disk cell. The data are used to estimate membrane parameters and mass transfer coefficient using Kimura–Sourirajan analysis (KSA) and by a new graphical method (GM). Even though the origin of the two methods is similar, the membrane parameters and coefficients are calculated using different procedures. The parameters estimated from the KSA method, in which every parameter is estimated at each data point, are prone to experimental errors and show marked variation with operating conditions. In contrast, the graphical method, in which data at different pressures but constant feed flow rate and constant feed concentration are used in a simple graphical procedure, show that the estimated membrane parameters are reasonably constant. It is therefore shown that the estimation of parameters using the KSA method may lead to the conclusion that the membrane parameters are functions of operating conditions such as pressure whereas in reality the parameters may not be functions of operating conditions at all.

INTRODUCTION

A reverse osmosis test cell is usually used to estimate membrane parameters and to study the concentration polarization phenomenon in reverse osmosis. The mass transfer coefficient (k) is required for these calculations. Mass transfer coefficient measurements related to reverse osmosis

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can be divided into three main groups: (a) direct measurements using optical or microelectrode measurements (1–4), (b) indirect measurements in which the true rejection of the membrane is calculated by extrapolation to infinite feed circulation (5, 6), and (c) indirect measurements in which a concentration polarization model with a membrane transport model is used for the required calculations (7–10). All these methods have their own merits and demerits. When a two-parameter model, such as the preferential sorption-capillary flow model or the solution-diffusion model, is used for describing the mass transfer phenomena inside the membrane, the estimation of membrane parameters and the mass transfer coefficient is usually carried out by Kimura–Sourirajan analysis (KSA) (9–11). In the KSA method the solute transport parameter, $D_{AM}/K\delta$, the pure water permeability coefficient, A, and the mass transfer coefficient, k, are estimated for each and every data point, making the method laborious and time-consuming. In the present work a simple graphical method is proposed to estimate $D_{AM}/K\delta$ and k, while A can be obtained from the slope of a plot of pure water permeability [PWP] vs applied pressure.

THEORY

Film Theory

To estimate the mass transfer coefficient in a reverse osmosis (RO) test cell, film theory is widely used in the literature (9–11). When a solute is rejected by the membrane, the solute concentration near the membrane surface increases. The build up in concentration at the membrane–liquid interface is termed "concentration polarization." At steady state the solute flux is constant throughout the film and equal to solute through the membrane, N_A. A material balance for the solute in a differential element gives

$$N_A = C_A J_v - D_{AB}(dC_A/dx) \tag{1}$$

which is to be solved using the following boundary conditions:

$$C = C_{A1} \quad \text{at} \quad x = 0$$

$$C = C_{A2} \quad \text{at} \quad x = l$$

where C_{A1} is the solute concentration in the feed, C_{A2} is the solute concentration in the boundary layer, and l is the boundary layer thickness. Integration of Eq. (1) and using the above boundary conditions results in the following equation:

$$(C_{A2} - C_{A3})/(C_{A1} - C_{A3}) = \exp(J_v/k) \tag{2}$$

where C_{A3} is the solute concentration in the product and k is the mass transfer coefficient, defined as D_{AB}/l. Equation (2) can be rearranged to give a relation between the observed rejection,

$$R_o \equiv (C_{A1} - C_{A3})/C_{A1} \tag{3}$$

and the true rejection,

$$R \equiv (C_{A2} - C_{A3})/C_{A2} \tag{4}$$

as

$$\ln[(1 - R_o)/R_o] = \ln[(1 - R)/R] + J_v/k \tag{5}$$

Kimura–Sourirajan Analysis (KSA) Method

The KSA method (9–11) is based on a generalized capillary diffusion model for the transport of solute through the membrane. The mathematical forms of the equations are similar to those of the solution-diffusion model though premises in their derivation are different. The working equations of the KSA method are:

$$A = [\mathrm{PWP}]/(M_B \times S \times 3600 \times P) \tag{6}$$

$$N_B = A(\Delta P - \Delta\pi) \tag{7}$$

$$= C(D_{AM}/K\delta)[(1 - X_{A3})/X_{A3})](X_{A2} - X_{A3}) \tag{8}$$

$$= Ck(1 - X_{A3})\ln[(X_{A2} - X_{A3})/(X_{A1} - X_{A3})] \tag{9}$$

where A is the [PWP] coefficient, M_B is the molecular weight of Component B, S is the active surface area of the membrane, N_B is the solvent flux, C is the molar density of the solution, $D_{AM}/K\delta$ is the solute transport parameter, and X_A is the mole fraction of Component A. Sourirajan and coworkers used the above equations to estimate A, $D_{AM}/K\delta$, and k in most of their work on reverse osmosis (9–11). The value of A is first estimated from Eq. (6) from the pure water permeability data. Once A is known, then Eq. (7) is used to calculate X_{A2}, which is the mole fraction of solute at the feed–membrane interface. Using this value of X_{A2}, $D_{AM}/K\delta$ and k are determined from Eqs. (8) and (9).

Graphical Method

The working equations of the solution-diffusion model (12, 13) are

$$J_v = A(\Delta P - \Delta\pi) \tag{10}$$

$$N_A = (D_{AM}/K\delta)(C_{A2} - C_{A3}) \tag{11}$$

where the parameter A is the same as the [PWP] constant and can be estimated from a plot of [PWP] vs applied pressure, and $D_{AM}/K\delta$ is considered as a single parameter, namely, the solute transport parameter. Equations (10) and (11) may be combined with Eq. (4), as illustrated by Pusch (14), to give

$$1/R = 1 + (D_{AM}/K\delta)(1/J_v) \tag{12}$$

Now, Eq. (12) can be substituted in Eq. (5) and after rearrangement it can be rewritten as

$$\ln[(1 - R_o) \times J_v/R_o] = \ln[D_{AM}/K\delta] + J_v/k \tag{13}$$

Equation (13) is the new working equation of combined solution-diffusion and film theory models. By using R_o and J_v data, taken at different pressures but at constant feed rate and constant feed concentration for each set, a plot of $\ln[(1 - R_o) \times J_v/R_o)]$ vs J_v will yield a straight line with a slope equal to $1/k$ and an intercept equal to $D_{AM}/K\delta$.

THE EXPERIMENTAL PROCEDURE

Reverse osmosis (RO) experiments were performed using membranes prepared in our laboratory, in an air-conditioned room, by the phase inversion method of Manjikian (15). The composition and conditions of the membranes are shown in Table 1. The reverse osmosis experimental setup

TABLE 1
Composition and Conditions of Membrane[a]

Composition, wt%	
Cellulose acetate (E-398-3)	15.0
Dioxane	40.0
Acetone	10.0
Maleic anhydride	5.0
Methanol	25.0
Acetic acid	5.0
Conditions:	
Wet membrane thickness, mm	0.25
Evaporation time, minutes	1.0
Gelation time in 0–3°C water, hours	>1
Annealing temperature, °C	90
Annealing time, minutes	10

[a] Pressure pretreatment given at 50 atm overnight and at 110 atm for about 3 hours. LR grade chemicals (Merck).

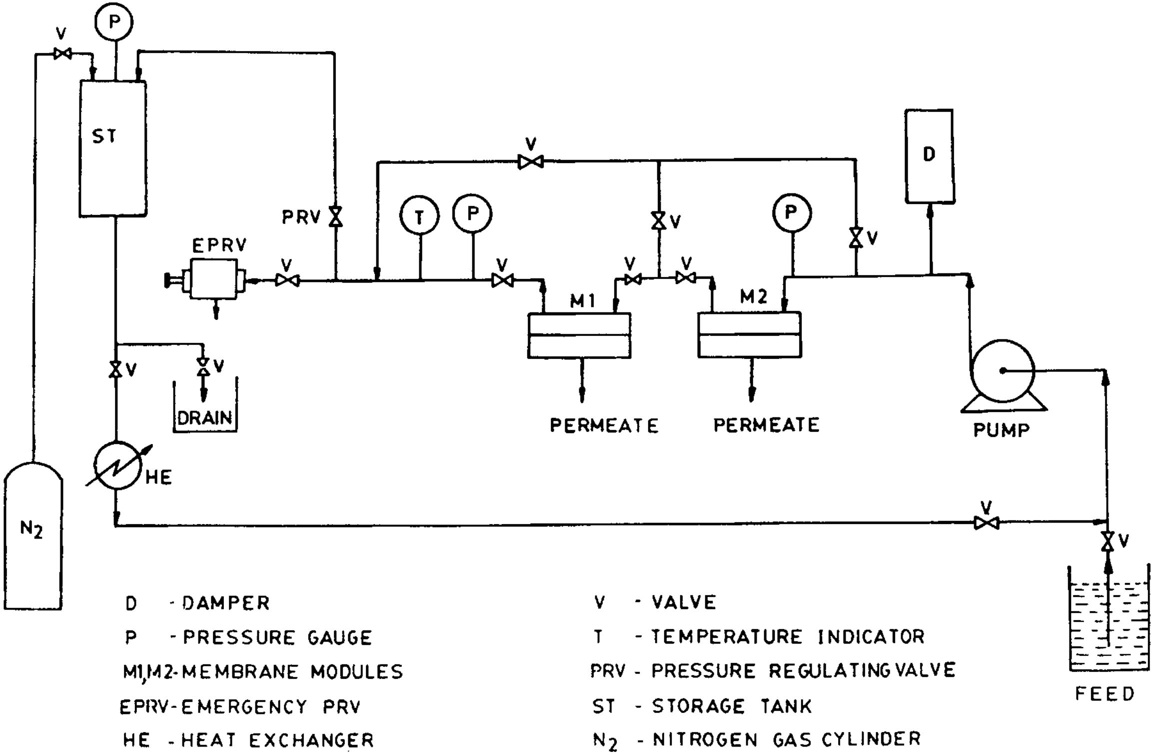

FIG. 1 Reverse osmosis experimental setup.

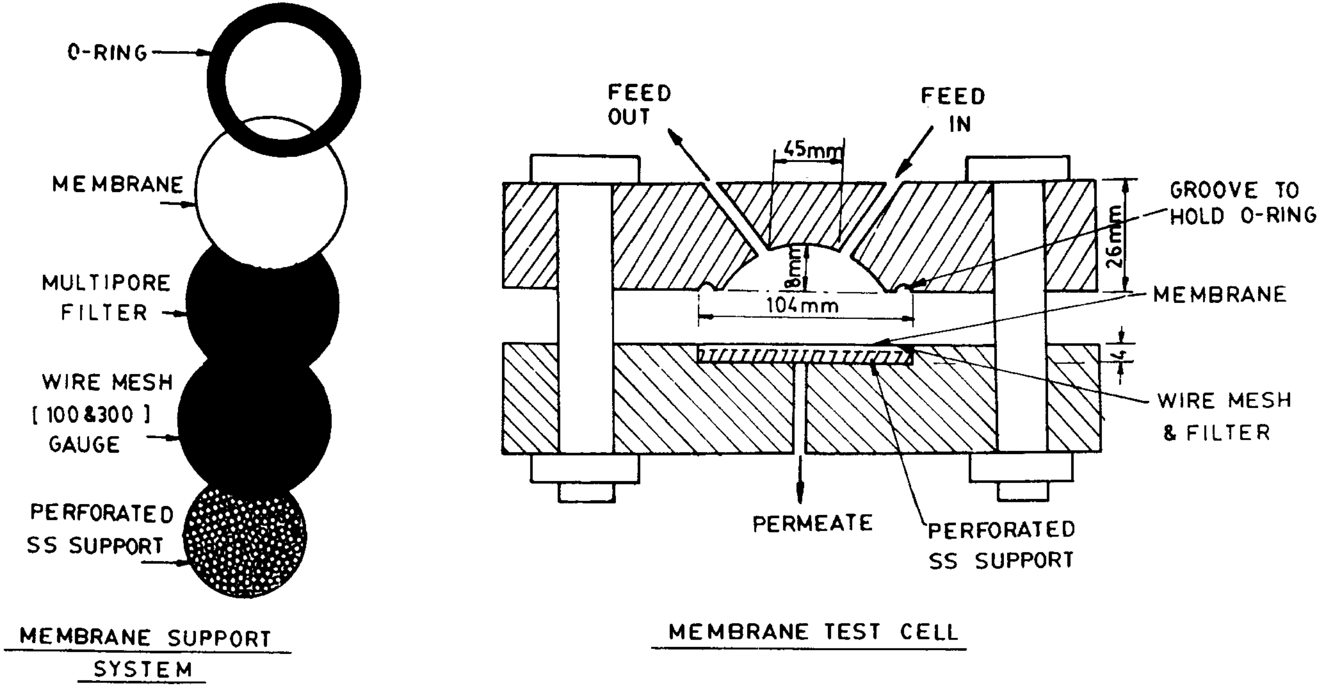

FIG. 2 Reverse osmosis test cell.

is shown in Fig. 1. The RO test cell and membrane support system are shown in Fig. 2. The test cell, which is in two halves, is made of stainless steel and is fastened together with high tensile bolts. The top section of the cell is the high pressure side flow distribution chamber and the bottom section, which is the lower pressure side, is used as the membrane support system. The support arrangement provides sufficient mechanical support for test membrane pressures up to 110 atm or more. The active membrane surface area is 60 cm^2.

To avoid membrane compaction during the separation process, the membrane is first pretreated overnight at 50 atm and then for about 3 hours at 110 atm with distilled water. The pure water permeability [PWP] is measured at different operating pressures. A sodium chloride–water system is used to get separation data in the concentration range from 6000 to 12,000 ppm. The brine feed solutions (about 12 L) are prepared by taking a calculated quantity of NaCl and dissolving it in distilled water. After pumping the feed solution to the storage tank, nitrogen gas is used for the initial pressure buildup and then the system is initially operated for about 2 hours to reach steady-state. The operating pressure is controlled with a pressure regulating valve. To measure the flux rate and concentration, two samples of permeate solution are collected over 45 minutes for every set of readings at a certain pressure. The feed and product samples are analyzed by the conductivity method (Global Electronics, Hyderabad) at 25°C. The feed rate is varied between 300 and 1500 mL/m, and the operating pressure is varied from 20 to 100 atm.

RESULTS AND DISCUSSION

The pure water permeability [PWP] data are shown in Fig. 3. The slope of the straight line, which is the [PWP] constant A, is 1.4904×10^{-5} cm/s. It is seen from Fig. 3 that A of the membrane used in the present work shows no dependence on the applied pressure, as was also shown for some membranes by Pusch and Mossa (16). The separation data for a feed concentration of 6000 ppm are shown in Figs. 4 and 5 where the observed rejection, R_o, and the product flux, J_v, are plotted against the applied pressure for different feed flow rates. Other data for a feed concentration of 12,000 ppm are given in Table 2b. The membrane parameters and k are now estimated from the KSA method as shown in Tables 2a and 2b. The osmotic pressures are taken from the literature (17) for the concentration range used in the experiments, and expressed by the virial expansion as mentioned by Jonsson (18):

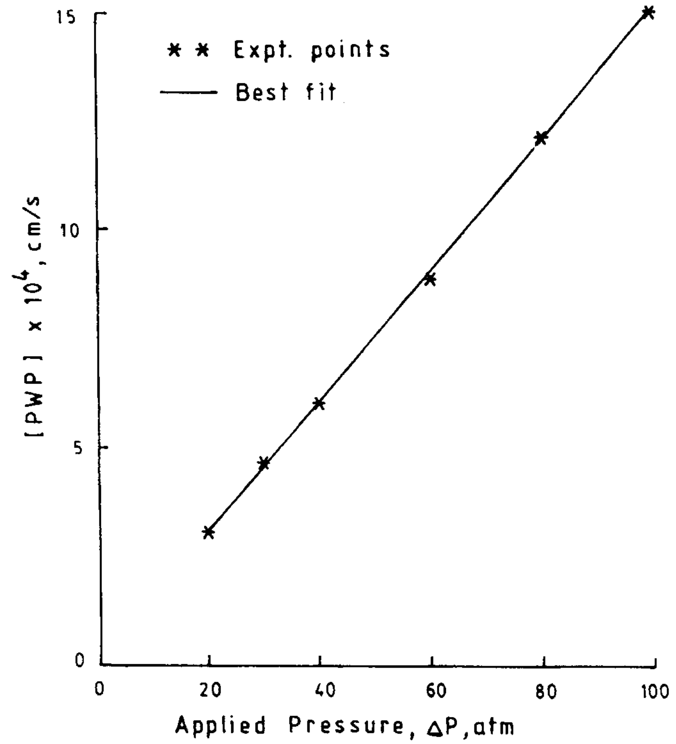

FIG. 3 The effect of applied pressure on [PWP].

$$\pi(X_A) = a_1X_A - a_2X_A^2 + a_3X_A^3 \tag{14}$$

or

$$X_A(\pi) = b_1[\pi(X_A)] + b_2[\pi(X_A^2)] - b_3[\pi(X_A^3)] \tag{15}$$

The results in Tables 2a and 2b show that the parameters $D_{AM}/K\delta$ and k vary with the operating conditions. Although k is expected to vary with respect to the feed flow rate as well as the feed concentration, the wide variation in the values of $D_{AM}/K\delta$ is unexpected. Estimation of each parameter for every pressure may not be required, and k, which is a function of feed flow rate, cell geometry, and solute system, varies with pressure in this analysis.

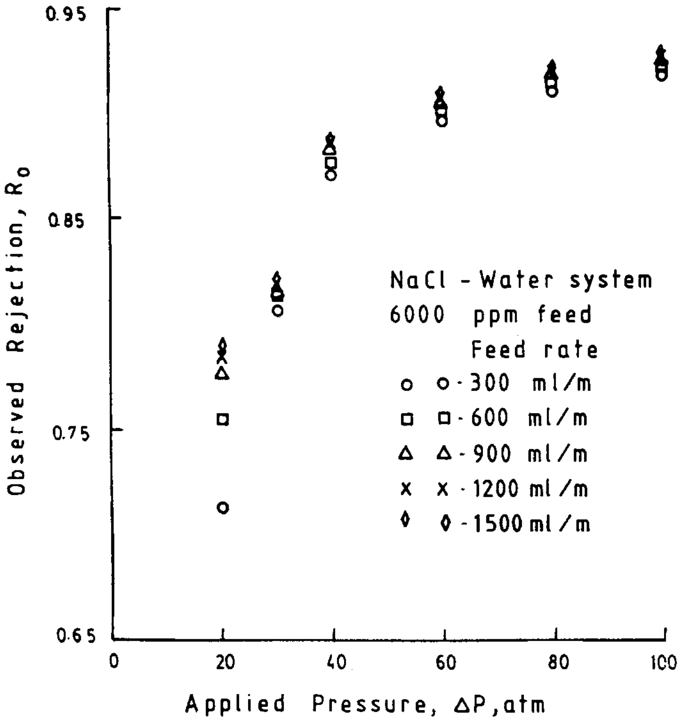

FIG. 4 The effect of applied pressure on observed rejection with different feed rates (6000 ppm NaCl–water feed).

The same data are now used to calculate parameters for the graphical method (GM) proposed earlier. In the GM method, data taken at different pressures while keeping the other operating variables constant, such as the feed concentration and the feed rate, form a single set used to estimate the parameters $D_{AM}/K\delta$ and k. Plots of $\ln[(1 - R_o) \times J_v/R_o]$ vs J_v were prepared as shown in Figs. 6 and 7. The excellent straight line fit of the experimental data clearly shows that the membrane parameters and mass transfer coefficient are independent of applied pressure. The parameters estimated from the GM method are given in Table 3. It can be observed

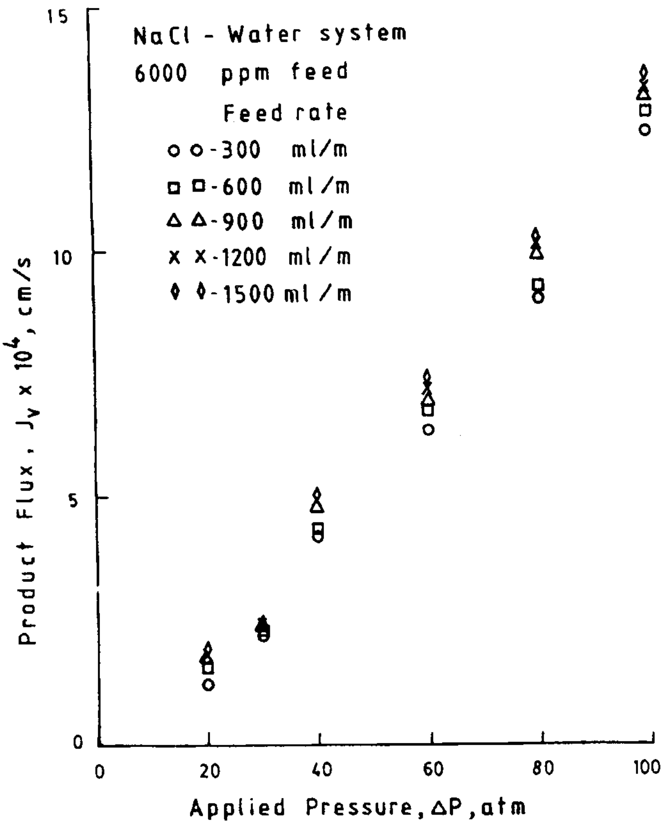

FIG. 5 The effect of applied pressure on product flux with different feed rates (6000 ppm NaCl–water feed).

that the parameter $D_{AM}/K\delta$ is nearly constant for the range of experimental data studied and that k varies with the feed rate.

Apart from our data, published data (Table 4) of Rosenbaum and Skiens (19) was used to verify the KSA and graphical methods. Parameters for these data calculated from the KSA method are shown in Table 4, and the same data were analyzed by the graphical method as shown in Fig. 8; the calculated parameters are given in Table 5.

TABLE 2a
Parameters Estimated Using the KSA Method with a Feed Concentration of $X_{A1} = 18.56 \times 10^{-4}$ (6000 ppm)

Set	Q (mL/m)	ΔP (atm)	$J_v \times 10^4$ (cm/s)	R_o	$k \times 10^4$ (cm/s)	$(D_{AM}/K\delta) \times 10^5$ (cm/s)
1	300	20	1.22	0.7127	0.955	1.371
	300	30	2.22	0.8061	1.560	1.288
	300	40	4.19	0.8703	3.903	2.135
	300	60	6.36	0.8962	4.565	1.829
	300	80	9.01	0.9101	5.738	1.851
	300	100	12.38	0.9173	8.943	2.796
2	600	20	1.54	0.7546	1.504	1.800
	600	30	2.31	0.8130	1.679	1.342
	600	40	4.38	0.8762	4.599	2.388
	600	60	6.74	0.9022	5.524	2.157
	600	80	9.23	0.9147	6.186	1.936
	600	100	12.77	0.9227	10.530	3.183
3	900	20	1.75	0.7761	2.080	2.178
	900	30	2.31	0.8140	1.680	1.335
	900	40	4.79	0.8835	7.470	3.327
	900	60	6.98	0.9050	6.373	2.451
	900	80	9.89	0.9182	8.056	2.582
	900	100	13.11	0.9248	12.630	3.777
4	1200	20	1.85	0.7839	2.471	2.413
	1200	30	2.38	0.8179	1.777	1.389
	1200	40	4.92	0.8859	9.466	3.769
	1200	60	7.18	0.9070	7.338	2.768
	1200	80	10.11	0.9197	9.021	2.878
	1200	100	13.21	0.9261	13.490	3.959
5	1500	20	1.92	0.7895	2.827	2.597
	1500	30	2.44	0.8210	1.865	1.438
	1500	40	5.02	0.8875	12.070	4.199
	1500	60	7.41	0.9088	8.969	3.256
	1500	80	10.24	0.9206	9.736	3.085
	1500	100	13.55	0.9272	17.920	4.995

If we compare the values in Tables 2a, 2b, 3, 4, and 5, we not only find substantial differences in the values of $D_{AM}/K\delta$ but also marked differences in the values of k, even for the same feed flow rate.

The main problem of the KSA method is that the value of the mole fraction at the feed–membrane interface, X_{A2}, needs to be indirectly calcu-

TABLE 2b

Parameters Estimated Using the KSA Method with a Feed Concentration of $X_{A2} = 37.27 \times 10^{-4}$ (12,000 ppm)

Set	Q (mL/m)	ΔP (atm)	$J_v \times 10^4$ (cm/s)	R_o	$k \times 10^4$ (cm/s)	$(D_{AM}/K\delta) \times 10^5$ (cm/s)
6	300	20	1.03	0.6802	1.412	2.337
	300	30	1.94	0.7880	2.259	2.213
	300	40	3.89	0.8644	7.186	3.553
	300	60	6.11	0.8942	7.693	3.268
	300	80	8.86	0.9094	9.624	3.517
	300	100	12.11	0.9168	15.370	4.999
7	600	20	1.23	0.7140	2.139	2.775
	600	30	2.11	0.8009	2.714	2.412
	600	40	4.14	0.8718	10.260	4.068
	600	60	6.55	0.9008	10.700	3.913
	600	80	9.11	0.9141	10.890	3.711
	600	100	12.43	0.9222	19.770	5.409
8	900	20	1.54	0.7551	4.696	3.601
	900	30	2.24	0.8100	3.141	2.577
	900	40	4.62	0.8810	54.330	5.734
	900	60	6.82	0.9039	14.130	4.476
	900	80	9.60	0.9171	14.650	4.507
	900	100	12.87	0.9244	27.600	6.605
9	1200	20	1.78	0.7781	14.860	4.507
	1200	30	2.42	0.8198	3.887	2.856
	1200	40	4.60	0.8854	49.680	5.433
	1200	60	7.04	0.9061	19.310	5.068
	1200	80	9.98	0.9193	20.450	5.379
	1200	100	13.14	0.9260	40.640	7.602
10	1500	20	1.89	0.7872	130.300	5.040
	1500	30	2.51	0.8245	4.364	3.008
	1500	40	4.60	0.8870	51.110	5.362
	1500	60	7.32	0.9083	38.120	6.101
	1500	80	10.12	0.9202	24.180	5.776
	1500	100	13.42	0.9270	88.940	9.090

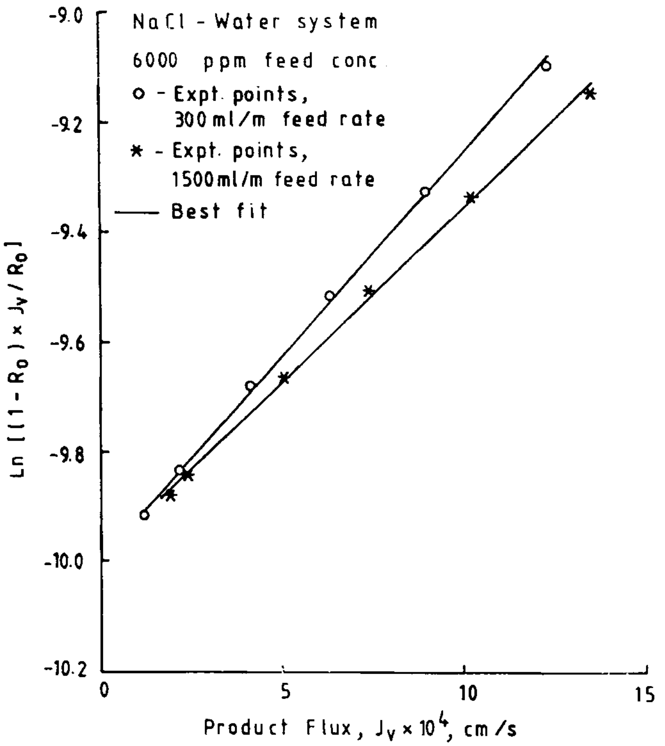

FIG. 6 Plot of ln[(1 − R_o) × J_v/R_o] vs J_v for 6000 ppm NaCl–water feed and 300 mL/m and 1500 mL/m feed rates.

TABLE 3
Parameters Estimated Using the Graphical Method (Eq. 13)

Set	Q (mL/m)	$k \times 10^4$ (cm/s)	$(D_{AM}/K\delta) \times 10^5$ (cm/s)
1	300	13.597	4.552
2	600	14.749	4.564
3	900	15.164	4.556
4	1200	15.564	4.576
5	1500	15.824	4.587
6	300	13.487	4.538
7	600	14.731	4.570
8	900	15.116	4.557
9	1200	15.565	4.579
10	1500	15.787	4.584

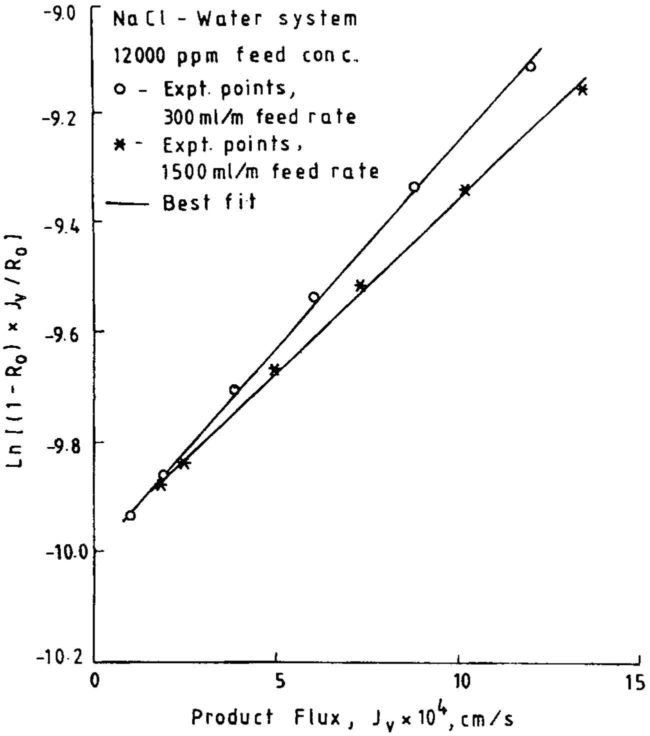

FIG. 7 Plot of $\ln[(1 - R_o) \times J_v/R_o]$ vs J_v for 12,000 ppm NaCl–water feed and 300 mL/m and 1500 mL/m feed rates.

lated from Eq. (7), i.e.,

$$\pi(X_{A2}) = \Delta P + \pi(X_{A3}) - N_B/A \qquad (16)$$

Once $\pi(X_{A2})$ is known, Eq. (15) is used to determine X_{A2}. Or, the calculation of X_{A2} requires the following experimentally measured quantities: ΔP, X_{A3}, N_B, and [PWP] data. Any errors in the measurement of these quantities adds up to give a large error in the values of X_{A2}, and then these errors are further propagated in the calculation of $D_{AM}/K\delta$ and k.

TABLE 4
Parameters Calculated Using Rosenbaum and Skiens Data [19] by the KSA Method

Set	ΔP (atm)	$A \times 10^8$ (g·mol/cm^2·s·atm)	R_o	$N_B \times 10^7$ (g·mol/cm^2·s)	$k \times 10^6$ (cm/s)	$(D_{AM}/K\delta) \times 10^8$ (cm/s)
			Feed 0.1 M NaCl–Water Solution			
1	6.8	2.32	0.961	1.46	3.417	4.943
	13.6	2.55	0.977	3.32	6.733	5.791
	27.2	2.56	0.986	6.81	13.490	7.013
	40.8	2.61	0.988	10.50	22.010	9.727
	54.4	2.64	0.989	14.20	27.530	11.230
	68.1	2.64	0.990	17.80	31.220	11.600
			Feed 0.1 M NaCl–Water Solution			
2	6.8	1.60	0.940	0.40	1.181	2.498
	13.6	2.15	0.977	1.89	4.989	4.050
	27.2	2.33	0.990	5.26	15.020	5.091
	40.8	2.51	0.992	9.07	25.630	6.964
	54.4	2.54	0.992	12.60	34.170	9.418
	68.1	2.59	0.993	16.30	39.860	9.908

CONCLUSION

The KSA method used in the literature is time-consuming and laborious, and the calculated parameters may show variation with operating conditions. In the present work the equations of the solution-diffusion model

TABLE 5
Parameters Calculated Using Rosenbaum and Skiens Data [19] by the Graphical Method

Set	$k \times 10^6$ (cm/s)	$(D_{AM}/K\delta) \times 10^8$ (cm/s)
1	27.18	10.681
2	20.75	5.686

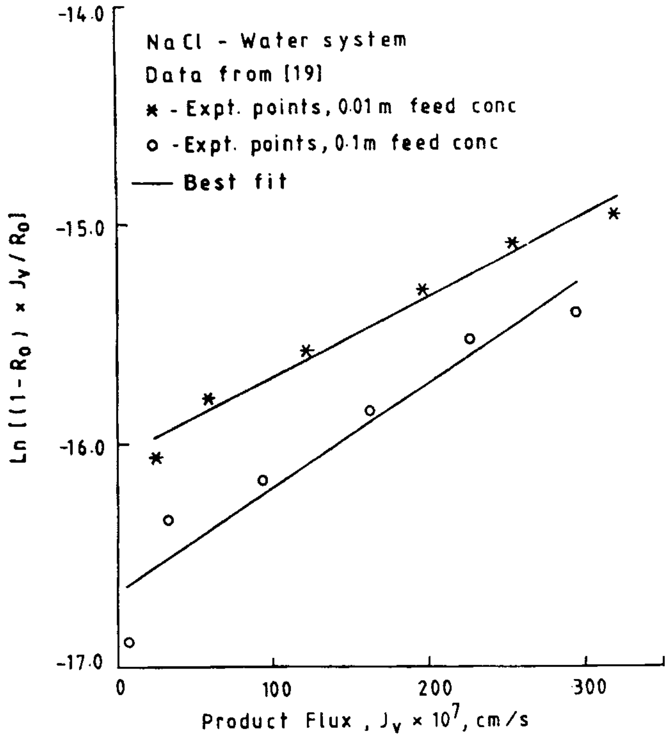

FIG. 8 Plot of $\ln[(1 - R_o) \times J_v/R_o]$ vs J_v for 0.01 M and 0.1 M NaCl–water feed solution [data of Rosenbaum and Skiens (19)].

and the film theory model are rearranged so that they can be used to estimate the membrane parameters $D_{AM}/K\delta$ and k simultaneously by a simple graphical method. The data obtained in our laboratory show that the membrane parameters found by using the GM method are essentially constant in the range of experimental data collected while the same data when analyzed by using the KSA method show marked variation in membrane parameters under different operating conditions.

NOTATIONS

a_i	virial coefficients in Eq. (14)
b_i	virial coefficients in Eq. (15)
A	PWP constant ($\mathrm{kmol/m^2 \cdot kPa}$ or m/s/kPa)
C	molar density of the solution ($\mathrm{kmol/m^3}$)
C_{ij}	molar concentration of component i in phase j ($\mathrm{kmol/m^3}$)
$D_{\mathrm{AM}}/K\delta$	solute transport parameter (m/s)
D_{ij}	diffusivity of component i in component j ($\mathrm{m^2/s}$)
J_{v}	solvent volume flux ($\mathrm{m^3/m^2 \cdot s}$)
k	mass transfer coefficient (m/s)
l	thickness of the concentration boundary layer (m)
N_i	molar flux of component i ($\mathrm{kmol/m^2 \cdot s}$)
ΔP	pressure difference across the membrane (kPa)
R	true rejection
R_{o}	observed rejection
x	coordinate direction perpendicular to the membrane (m)
Δx	membrane thickness (m)

Greek Symbols

δ	effective thickness of a membrane (m)
$\Delta \pi_i$	osmotic pressure difference across the membrane (kPa)

Subscripts

A	solute
B	solvent
M	membrane
1	feed solution
2	boundary layer solution
3	permeate solution

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