

Measurement of Diffusion Coefficient and Partition Coefficient of Sodium in Nonionic Polymer Membranes

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Synopsis

The difficulties involved in the measurement of the partition coefficient and diffusion coefficient of NaCl in hydrophilic polymer membranes are examined by the initial rate and late-time analysis of desorption data for three nonionic polymer systems. The late-time analysis, based on the plot of the logarithmic relative desorption versus time, was found to be useful when the diffusion is Fickian and the magnitude of D_2/l^2 is small. Depending on the magnitude of D_2/l^2 , an accurate measurement of k_2 and determination of D_2 cannot be achieved without correction for the effect of surface salt solution, impossible with late-time analysis. The initial rate measurement was found more versatile for general non-Fickian diffusion and it gave a means of correction of the errors involved in estimating the partition coefficient. In general, the diffusion of NaCl in hydrophilic polymers is not ideal Fickian and the discrepancy between the two analyses is appreciable.

INTRODUCTION

The diffusive permeability coefficient, P_2 , of sodium chloride can be obtained by the measurement of transport flux rate, such as dialysis rate. In order to gain more insight into the correlation between transport properties and membrane polymer characteristics, however, it is desirable to obtain further information on the diffusion constant, D_2 , and the partition coefficient k_2 which constitute the permeability coefficient P_2 , i.e., $P_2 = k_2D_2$. Since the transport data alone does not yield any information on these coefficients, it is necessary to carry out another set of experiments to obtain D or k individually, or D and k simultaneously.

The measurement of sorption or desorption has the advantage of obtaining these two coefficients simultaneously, and this method has been widely used to measure the solubility coefficient and diffusion coefficient of various vapors in polymers. The same treatment should be applicable for measurement of sorption and desorption by a polymer of NaCl by measuring the conductivity changes of the surrounding solution. However, measurement of the rate of solute transfer from one phase to another involves much more complicated experimental difficulties than does that of rate of vapor transfer from the polymer phase to vacuum.

The partition coefficient of sodium chloride has been considered one of the important parameters in characterizing the desalting property of a polymer membrane, and the sorption or desorption technique has been used to obtain this coefficient. It has been found, however, that an accurate measurement of k_2 also depends upon the diffusivity of the solute and cannot be achieved without correction of error introduced by the removal of the surface salt, except in some ideal case where D is very small.

NaCl is a solute that changes the chemical potential of water and, consequently, it changes the degree of swelling of polymers. Therefore, during the process of sorption or desorption of NaCl by a polymer membrane, the sample will undergo a process of deswelling or swelling. This may lead to apparent concentration- and/or time-dependent diffusion coefficients, depending upon the magnitude of the relaxation times of polymer deswelling (or swelling) and of the diffusion process. For polymers whose changes in degree of swelling are negligibly small or whose changes are very much slower than the time scale involved in the diffusion process, the diffusion would appear as ideal Fickian. However, in general, concentration- and/or time-independent diffusion constants cannot be expected, for the reason mentioned above, though NaCl itself does not interact with most nonionic polymers.

A sorption or desorption study by conductivity measurement depends on the change of NaCl concentration in the solution phase rather than that of the membrane phase. Since the total amount of salt sorbed in most polymers is small and since it is also rather difficult to read small changes of conductivity at high conductivity ranges, a desorption method was selected for this study.

The difficulties involved in the measurement of D_2 and k_2 by a desorption technique are explained by using three typical samples which showed (a) an ideal constancy of D during the measurement but slight concentration dependence; (b) nonideal D during the measurement but its value nearly independent of the concentration; (c) an apparent two-stage desorption during the measurement and highly concentration-dependent D .

Two methods of analysis available for the desorption data are differently affected by possible errors in the various phases of the desorption experiment. The applicability of each to the various types of polymer behavior can be determined by considering the requirements for each analysis that must be met if the equations used are to be valid.

ANALYTICAL PROCEDURE

Late-Time Analysis

When the diffusion coefficient is independent of concentration, Fick's second law of diffusion can be solved for diffusion into or out of a semi-infinite slab of thickness l with boundary conditions of instantaneous equilibration of sorbent entities at the surfaces. The solution is given as¹

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left\{ - \frac{(2n+1)^2 \pi^2 D t}{l^2} \right\} \quad (1)$$

where M_t is the amount of sorbate (sorbed or desorbed) at time t , M_∞ is the equilibrium amount sorbed after infinite time, D is the diffusion coefficient, and l is the film thickness.

Equation (1) can be used to calculate the diffusion constant from sorption or desorption rate measurement by the following analysis. Since the series in eq. (1) converges rapidly, it reduces for late-time of sorption or desorption to

$$\frac{M_\infty - M_t}{M_\infty} = \frac{8}{\pi^2} \exp\left(-\frac{\pi^2 Dt}{l^2}\right). \quad (2)$$

Therefore, a plot of $\log [(M_\infty - M_t)/M_\infty]$ versus time should be a straight line with a slope of $-\pi^2 D/2.3l^2$ and an intercept of $\log 8/\pi^2$, i.e., 0.81.

This relationship has been used as an experimental test of the constancy of D and as a method to evaluate D when it is independent of concentration for various vapors in polymers. This late-time analysis has been used to calculate diffusion constants of NaCl in cellulose acetate and some other membranes used for desalination by reverse osmosis.^{2,3}

The application of eq. (1) is based on the following assumptions: (1) D is concentration independent. (2) The concentration of sorbate in the membrane phase at each surface attains a value corresponding to the equilibrium concentration immediately after the membrane is placed in the solution and remains constant. (3) The thickness of the membrane does not change during sorption or desorption measurements. (4) The membrane is initially free of sorbate molecules (for sorption).

As shown in the results, these assumptions are not always satisfied in cases of NaCl sorption or desorption in polymers and many polymers do not give straight lines for the late-time analysis plot.

Initial Rate Analysis

Even if D is a function of the concentration of sorbate in the membrane, it has been shown from the Boltzmann solution of Fick's law for an infinite solid that, for the initial stage of sorption or desorption,⁴

$$\frac{M_t}{M_\infty} = K (\sqrt{t}/l). \quad (3)$$

If the initial slope, $K = [d(M_t/M_\infty)]/[d(t/l^2)^{1/2}]$, is observed in a sorption or desorption experiment, the average diffusion coefficient is given by

$$\bar{D} = \frac{\pi}{16} K^2 \quad (4)$$

where \bar{D} is the average diffusion coefficient defined by

$$\bar{D} = \frac{1}{C_0} \int_0^{C_0} D dc. \quad (5)$$

When sorption or desorption data yield no initial linearity of M versus \sqrt{t} ,

diffusion has been experimentally defined as anomalous or non-Fickian diffusion in studies of various vapors in many polymers.

Partition Coefficient

When a polymer membrane is equilibrated in a salt solution of concentration C_s , the concentration of the salt in the membrane phase, C_m , can be related by a partition coefficient, k , as

$$C_m = kC_s$$

$$\text{or } k = \frac{C_m}{C_s}. \quad (6)$$

This partition coefficient can be obtained from the desorption measurement by the following procedure. First a membrane (volume V_m) is equilibrated with a salt solution of concentration C_I . Then the equilibrated membrane is transferred into salt-free water of volume V_{II} . After the desorption equilibrium is reached, the concentration of extract water is measured as C_{II} . Then the total amount of salt going into the solution from the desorption process is $C_{II}V_{II}$.

If it can be assumed that k and V_m do not change, the amount of salt remaining in the membrane phase after the desorption is given by $kC_{II}V_m$.

Thus, the total amount of salt sorbed at the initial equilibrium is given by $C_{II}V_{II} + kC_{II}V_m$, and

$$C_m = \frac{C_{II}V_{II} + kC_{II}V_m}{V_m}. \quad (7)$$

Therefore k can be given as

$$k = \frac{C_{II}V_{II} + kC_{II}V_m}{C_I V_m}$$

$$= \frac{C_{II}V_{II}}{V_m(C_I - C_{II})}. \quad (8)$$

If k and V_m in the initial equilibration change to k' and V_m' after the desorption equilibrium is established and the changes can be expressed by

$$k' = k(1 + \Delta k), \quad (9)$$

$$V_m' = V_m(1 + \Delta V_m), \quad (10)$$

eq. (8) can be written as

$$k = \frac{C_{II}V_{II}}{V_m[C_I - C_{II}(1 + \Delta k)(1 + \Delta V_m)]}. \quad (11)$$

Since the total amount of salt sorbed in the membrane phase at the initial equilibrium is a certain fixed number, C_{II} can be controlled at any magnitude of concentration by changing V_{II} . In most cases, Δk and ΔV_m are small.

Therefore, when an experimental condition is set so that $C_I \gg C_{II}$, k can be obtained by

$$k = \frac{C_{II}V_{II}}{C_I V_m}. \quad (12)$$

EXPERIMENTAL

Materials

Cellulose acetate I, homogeneous film obtained from Gulf General Atomic, Inc., San Diego, California, was prepared from a 20% polymer solution of E-398-3 in acetone and was found to have a weight-fraction water content of 0.113.

The two other species of polymer films used in this study were prepared in this laboratory by casting the polymer solutions on glass plates by means of a Boston-Bradley adjustable blade, then allowing the cast films to air dry slowly under cover to prevent development of asymmetry. The dry films were then equilibrated in water and remained clear.

Cellulose acetate II was prepared by casting a standard Loeb solution⁵ of E-398-10 and allowing it to air dry very slowly to assure homogeneity of the final dry film. This cellulose acetate was found to have a weight-fraction water content of 0.210.

Both cellulose acetate polymers, E-398-3 and E-398-10, are Eastman products of 39.8% acetyl content and have a falling-ball viscosity of 3 sec and 10 sec, respectively, the higher time indicating a higher molecular weight.

The hydroxypropyl methacrylate (HPMA) homopolymer was obtained by polymerization, at room temperature, of a solution 90 wt-% dioxane, 10 wt-% HPMA, and 0.2 mole-% 2,2-azo-bis(2-methyl proprionitrile) (initiator) in a reaction tube sealed off after degassing. The polymer was precipitated in water, washed, dried, redissolved in dioxane to make a 15 wt-% polymer solution, and cast as described previously. The HPMA sample was found to have a weight-fraction water content of 0.271.

Desorption Rate Measurement

For each desorption experiment the polymer sample was equilibrated in a relatively large volume (e.g., 200 ml) of NaCl solution and then cut to convenient size (e.g., 4 × 8 cm). Due to the various degrees of film compaction in NaCl solutions of different concentration, measurement of sample dimensions was carried out after equilibration for each desorption experiment, allowing calculation of sample volume at equilibrium.

NaCl solution remaining on the surface of the sample when it is removed from the equilibration solution is crudely removed by blotting the sample between sheets of filter paper. Correction for the salt that may still be transferred with the sample must be made. The method for correction as

well as the advantages of the blotting method over rinsing techniques are discussed in a subsequent section.

After blotting, the sample is transferred to a vial containing a relatively small, exact volume (e.g., 25.0 ml) of deionized water at room temperature and previously equilibrated with the ambient CO_2 concentration. This eliminates sorption of CO_2 by, and subsequent increase in conductivity of, the extraction water during the desorption experiment. Change in the temperature of the extraction water during handling of the vial is avoided by wrapping the vial with asbestos tape. Contamination of the solution during the run is avoided by using rubber gloves while handling the vial.

When the sample is placed in the extraction water, the vial is quickly capped and shaken a short time, and the first measurement is taken by sucking up a portion of the extracting solution into a flow-through-type conductivity cell. The time of measurement and the conductivity of the solution are automatically noted on the chart of a recorder connected to the conductivity meter. The solution is then forced back into the vial, the cap is replaced, and the process is repeated to obtain further measurements. The increase in conductivity of the solution is followed as a function of time.

When a sufficient number of conductivity measurements have been taken, the vial is capped and set aside for a time long compared to the diffusion time. A final reading, M_f , can then be obtained.

RESULT AND DISCUSSION

The difficulties involved in an accurate measurement of D_2 and k_2 essentially consist of the following two major factors: (a) effect of the surface salt solution and (b) accurate measurement of change of conductivity and proper analysis of the transient sorption data. The former will, in principle, affect the accuracy of the k_2 value and the latter will determine the value of D ; however, in practical experiments both are closely related and the error in (a) will also influence the result of (b) to a great extent.

The error due to the transfer of surface salt solution is one of the most uncertain factors involved in the desorption measurement. It is nearly impossible to eliminate surface salt without affecting the sorbed salt in the membrane, except in an ideal case when D is very small and the membrane is thick enough so that rinsing of the surface can be achieved. Blotting of the surface has been widely used to eliminate the gross effect of surface salt; however, it is found in preliminary study that excess blotting can remove some of the sorbed salt when D is large. This also implies that an accurate estimate of k_2 cannot be made without knowledge of D_2 of a sample membrane. Since the concentration of the extracting solution during the desorption measurement is set to be much less than the original concentration of salt solution, the small amount of surface salt solution (of high concentration) would yield a great error in the final value of k_2 . Consequently, an accurate measurement of k_2 depends on the method of cor-

recting the error due to the surface salt solution, and the proper correction depends upon the proper analysis of the nonsteady-state sorption data. The error introduced in conductivity reading of extracting solution due to the surface salt solution also influences the analysis of sorption rate data.

In conductivity measurement, the rate of mixing the solution is very important in minimizing the concentration polarization effect at the boundary of membrane and solution. Without appropriate stirring, the rate of desorption observed could be considerably lower in some cases due to the transport resistance exerted by the boundary layer. For instance, D_2 observed without stirring of the solution showed decreasing values for membranes of increasing water content, although increasing D_2 's were expected. With proper stirring, D_2 was found to increase with increasing water content of the membranes. Therefore, the desorption rate measurement must be carried out with sufficient stirring of the solution on both sides of the membrane, which in itself is a rather difficult experimental procedure. Stirring rate of solution implies the relative velocity of solution movement to the membrane surface. If the membrane sample floats freely in the solution, the stirring speed does not indicate the effectiveness of eliminating concentration polarization. When D , more specifically D/l^2 , is very small, a gentle stirring of solution in which the sample membranes float freely would be sufficient. However, when D increases (generally with higher water content and softer texture of membranes), mechanical stirring caused many difficulties such as (a) wrapping of the membrane around the stirrer and/or conductivity cell, and (b) fluctuating conductivity reading. In principle, a membrane should be clamped and both sides of the membrane should be stirred efficiently for accurate measurement without effect of concentration polarization; however, such a setup would cause great difficulties in eliminating surface salt solution and the simplicity of the desorption measurement technique would be lost. An elaborate stirring technique does not assure elimination of concentration polarization and often results in defeating the purpose.

It was found that the intermittent reading of conductivity with shaking of the vial containing a membrane was most practical and versatile in measuring D_2 and k_2 for membranes of various water content and texture with minimized effect of concentration polarization.⁶

Correction of Initial Conductivity Due to Surface Salt

Since the extract water has a certain initial conductivity, $M_{\text{H}_2\text{O}}$, the value of M_∞ in eq. (2) is obtained as

$$M_\infty = M_f - M_{\text{H}_2\text{O}}. \quad (13)$$

However, this situation will only exist when D is sufficiently small and sufficient rinsing of the surfaces can be achieved without affecting the salt sorbed in the membrane phase. In the late-time analysis, there is no way of estimating the deviation from this ideal situation. On the other hand, in the initial rate measurement, it can be reasonably assumed that the

linear dependence found on the concentration versus \sqrt{t} can be extrapolated back to time zero. This extrapolated value, M_0 , is used to calculate M_∞ in the initial rate measurement; thus

$$M_\infty = M_f - M_0. \quad (14)$$

In order to investigate the validity of the assumption that the linear slope of the initial rate can be extrapolated back to time zero to estimate the contribution of extra salt on the surface or possible loss of salt in the membrane phase by excess effort to eliminate the surface salt, the following experiments were carried out.

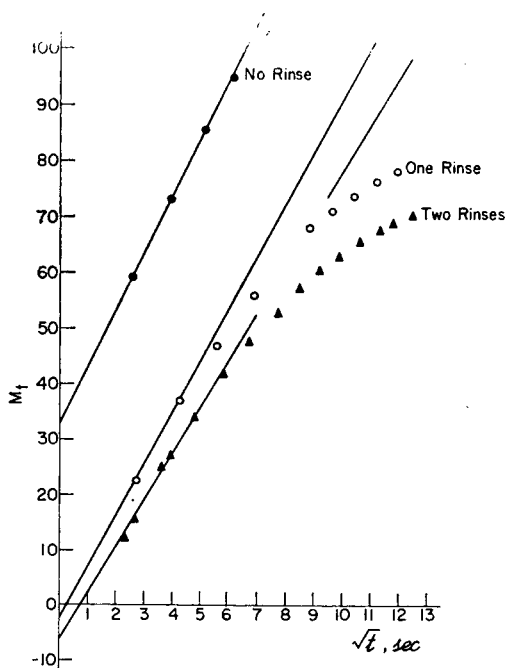


Fig. 1. Effect of rinsing on the initial rate measurement plot (M_t vs. \sqrt{t} sec) of NaCl desorption from cellulose acetate II ($C_1 = 8\%$ NaCl; $l = 4.65 \times 10^{-3}$ cm).

A single membrane sample of cellulose acetate II was used throughout these experiments. The procedure of the measurement was exactly the same as discussed previously except in the treatment of the surface salt. In one run, the sample was removed from the salt solution and shaken briefly in the air to eliminate big droplets of solution on the surfaces, but no blotting or rinsing was made. In another run, the membrane was quickly rinsed in deionized water once; in an additional run, a similar rinsing was repeated twice.

The results obtained with these various rinsings are summarized in Figure 1 and Table I. As is seen, M_0 obtained by extrapolation was much

TABLE I
Effect of Rinsing on D_2 and k_2 of Cellulose Acetate II
($C_I = 8\% \text{ NaCl}$; $l = 4.65 \times 10^{-3} \text{ cm}$)

	$D_2, (\text{cm}^2/\text{sec}) \times 10^8$	k_2	
		Without M_0 correction	With M_0 correction
No rinse	4.13	.274	.206
One rinse	4.02	.181	.197
Two rinses	4.31	.168	.170
Blotted	4.01	.187	.206

higher than $M_{\text{H}_2\text{O}}$ for the no-rinse run but negative for the one-rinse and two-rinse runs.

When these M_0 values were taken into account, the resulting values of D and k became reasonably constant, as is shown in Table I. The diffusion coefficients were not calculated from the late-time analysis, because any value could be obtained depending on how the straight line is drawn on the continuously bending curve.

The effect of rinsing on the k value is quite evident. Without M_0 correction, the variance in k values between no rinse and two rinses is as high as 63%, but with correction of M_0 by the extrapolation, this difference is reduced to 21%. The similar difference between no rinse and one rinse is reduced from 51% to 4.6% by the M_0 correction.

This result indicates that moderate rinsing or blotting will yield satisfactory results if M_0 correction is made. Excess rinsing causes loss of salt in the membrane phase and M_0 correction alone cannot compensate for the loss.

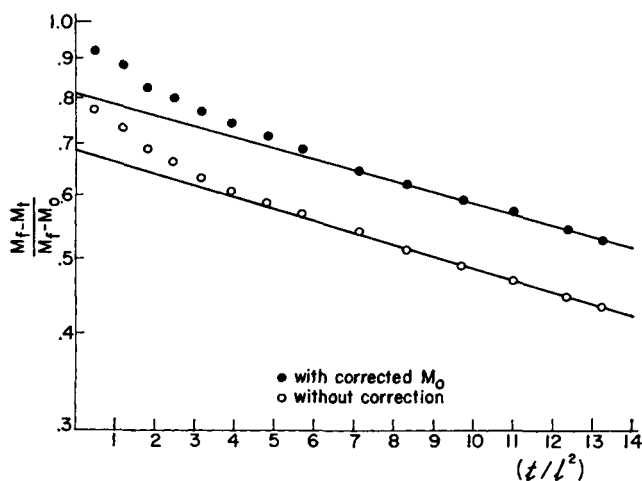


Fig. 2. Effect of M_0 correction on the late-time analysis plot ($M_f - M_t / M_f - M_0$) vs. t/l^2 of NaCl desorption from cellulose acetate I ($C_I = 8\% \text{ NaCl}$; $l = 3.60 \times 10^{-3} \text{ cm}$).

In the case of cellulose acetate I, the diffusion seems to be ideal and the value of D is very small. In this case, rinsing will be a very useful way to eliminate the surface salt. When insufficient blotting was used for this membrane, the late-time analysis plot often did not intercept at 0.81. Even in these cases, however, when M_0 obtained by the initial rate plot was used instead of M_{H_2O} , the plots became ideal. An example of M_0 correction on the late-time analysis (ideal Fickian case) is shown in Figure 2. This also seems to support the validity of M_0 correction by the initial slope measurement.

Choice of Two Analytical Procedures

Results obtained with three membranes when they were blotted twice by filter paper before the desorption measurements are shown in Figures 3 and 4. This blotting procedure may leave a certain amount of salt on the surfaces of the samples or it may take a part of the salt sorbed in the membrane phase, depending on the nature of the membranes.

Figure 3 indicates a linear slope on the conductivity reading versus \sqrt{t} plot for each membrane. This linear slope does not necessarily start from

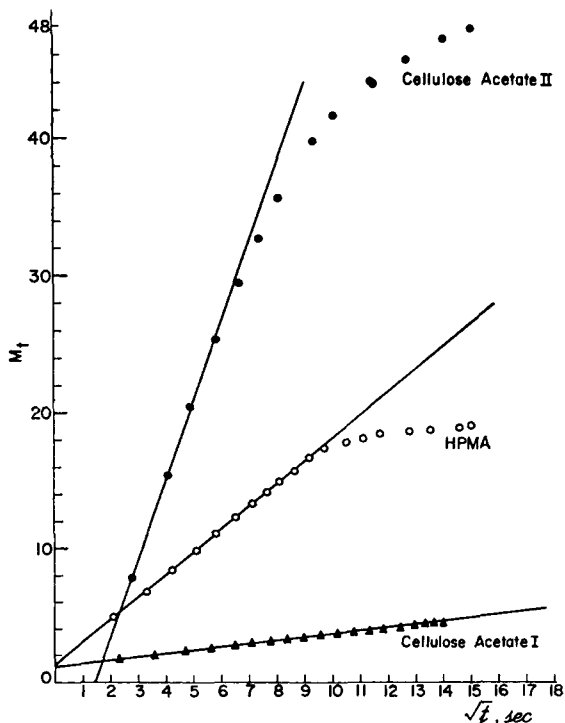


Fig. 3. Initial rate measurement plots (M_t vs. \sqrt{t} sec) of NaCl desorption from cellulose acetate I, cellulose acetate II, and HPMA ($C_1 = 5\%$ NaCl; $l = 3.80 \times 10^{-3}$, 4.70×10^{-3} , and 6.28×10^{-3} cm, respectively).

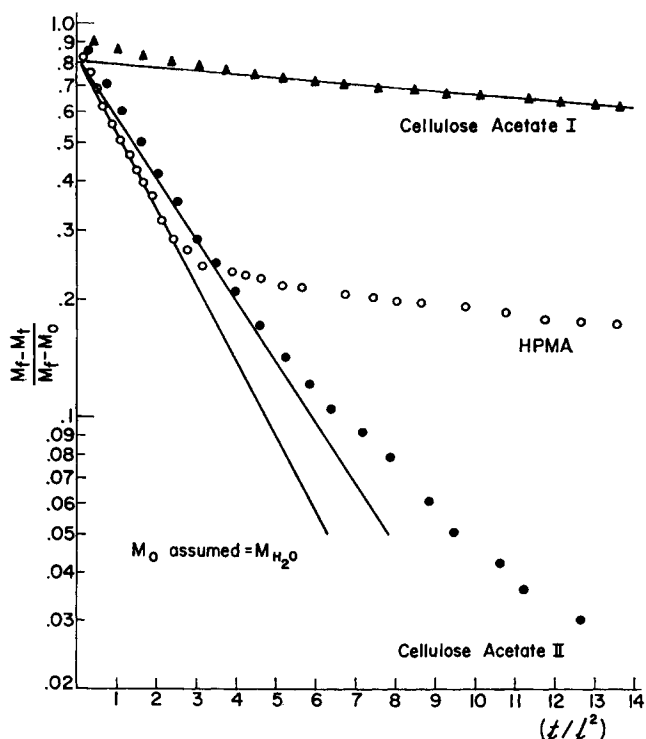


Fig. 4. Late-time analysis plots ($M_f - M_t/M_f - M_0$ vs. t/l^2) of data shown in Figure 3.

the conductivity of the extract water, and this is probably due to the effect of surface salt or excess elimination of salt from the membrane phase, as mentioned in the previous section.

Figure 4 shows the plots of the identical data based on the late-time analysis. If eq. (2) is valid, each plot should yield a straight line that intercepts 0.81 at $t = 0$. As is seen, the three membranes show three different cases. Cellulose acetate I shows the ideal case. The late-time data is perfectly linear and the intercept is 0.81. HPMA and cellulose acetate II deviate from the ideal case, indicating that the constancy of the diffusion coefficient is not maintained during the measurement. In the case of HPMA, a linear dependence that intercepts at 0.81 is found in the relatively early part of the data, but it then bends sharply from the straight line. Another straight line can be drawn in the later time data. In the case of cellulose acetate II, the plot is a continuously bending curve. One has the choice, then, to take a straight line for the initial part that does not intercept at 0.81, or to draw an asymptotic line starting from 0.81.

In general, the desorption of NaCl may not be ideal and, if this is the case, the late-time analysis cannot be used to calculate the diffusion coefficient. As is expected from the equation for the initial rate, a linear dependence was found for these nonideal desorptions.

During the process of desorption measurement, most polymers undergo swelling due to the vast difference between chemical potential of water in the initial salt solution in which the membrane is equilibrated and that of the extracting water. This swelling proceeds from the surface toward the inner portion of the membrane because the decrease of salt concentration inside the membrane occurs from the surface inward as the diffusion of salt proceeds.

Although the diffusivity of NaCl in polymer membranes has been found to be a direct function of the equilibrium swelling of the polymer,⁶ the rates of change of these two processes (i.e., transport of NaCl and deswelling) are not necessarily related in a simple manner and, in general, may be considered as two independent processes. Therefore, as time passes, the difference in these two processes may change the apparent mode of diffusion observed during a measurement if the relaxation times of these two processes are of comparable magnitude. Thus, the concentration dependence of D observed as a function of the concentration of NaCl may not be just due to the dependence of D on the concentration, but it may be an overall result of more complicated interactions in water-salt-polymer systems. By the same reason, concentration-dependent D 's could be found for a membrane which shows an ideal diffusion constant during a measurement. In Table II some examples of the apparent concentration dependence of D

TABLE II
Concentration Dependence of D_2 and k_2 ^a

NaCl concentration	Cellulose acetate I			Cellulose acetate II		HPMA	
	Late-time analysis	Initial rate analysis		Initial rate analysis		Initial rate analysis	
	D_2	D_2	k_2	D_2	k_2	D_2	k_2
1%	0.380	0.306	0.032	1.40	0.149	6.90	0.115
5%	0.284	0.250	0.036	2.65	0.158	4.87	0.097
8%	0.331	0.310	0.044	2.57	0.170	4.23	0.092

^a D_2 in (cm²/sec) $\times 10^8$.

and k are shown for the three membranes investigated. The initial rate measurements with correction of M_0 are used to calculate D 's and k 's, and the values are the average of three-run sample membranes.

The effect of the osmotic compaction is evident with HPMA; i.e., k values decrease with the concentration of the salt solution. In the case of cellulose acetate, of which dimensional change in water and in salt solution is very small, changes in k and D are found to be relatively small.

As concluding remarks, the following points might be mentioned: (a) When the diffusion is ideal, the two analyses show reasonably good agreement. However, even with an ideal diffusion, the late-time analysis tends to yield erroneous results due to errors involved in both M_0 and M_f values in conductivity measurement. Therefore, the late-time analysis is limited

to the case where the diffusion is Fickian and the value of D/l^2 is small and rinsing can be achieved. (b) The initial rate measurement seems to be more versatile for all kinds of cases if a linear portion is found in the M_t versus \sqrt{t} plot. (c) An extrapolation of the initial slope measurement decreases the error in finding the partition coefficient, k . This procedure is particularly important when D is high and the washing of the surfaces causes serious errors. (d) The late-time analysis can be conveniently used to check the constancy of D during the measurement.

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