

# Distribution and Diffusion Coefficients of NaCl in Polyamide (Nylon-6,6 and Polyxylyleneadipamide) Membranes

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**ABSTRACT:** Thin membranes of an aliphatic polyamide (nylon-6,6) and an aromatic polyamide (polyxylyleneadipamide) (PXAP) were prepared, and their distribution ( $K$ ) and overall diffusion ( $D$ ) coefficients of sodium chloride were measured with the unsteady-state and steady-state dialysis method. The overall diffusion coefficients at a zero concentration [ $D^{(0)}$ ] of sodium chloride for nylon-6,6 and PXAP were 1.3–0.8  $\mu\text{m}^2/\text{s}$  (from 2 min of interfacial polymerization to 4 min) and 0.078, respectively.  $D^{(0)}$  for PXAP was about 3 times greater than that of a cellulose acetate (CA) membrane (0.024  $\mu\text{m}^2/\text{s}$ ). The  $K$  values for nylon-6,6 and PXAP were 0.7–0.5 from 2 to 4 min and 0.05, respectively.  $K$  for PXAP was almost the same as  $K$  for CA (0.06). A two-part (dense and porous) model of the membrane structure was applied to obtain  $D_d$  (the diffusion coefficient in the dense part of the membrane) and  $D_p$  (the diffusion coefficient in the porous part of the membrane) for CA, PXAP, and nylon-6,6 thin membranes. The values of  $D_d$  were almost the same for both nylon-6,6 and PXAP (0.05–0.061  $\mu\text{m}^2/\text{s}$ ) and about 10 times greater than the value for the CA membrane ( $5.6 \times 10^{-3}$   $\mu\text{m}^2/\text{s}$ ).  $D_p$  for PXAP was almost the same as  $D_p$  for CA. However,  $D_p$  for the nylon-6,6 membrane was 10–16 times greater than  $D_p$  for the PXAP membrane. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2605–2612, 2002

**Key words:** polyamides; reverse-osmosis membranes; sodium chloride; distribution coefficient; diffusion coefficient

## INTRODUCTION

After Reid and Breton<sup>1</sup> discovered that a cellulose acetate (CA) film rejected sodium chloride

(NaCl) from its aqueous solution, many types of polymers were tested for their rejection capability toward NaCl. Among the tested polymers, membranes based on polyamide and its derivatives, particularly thin-film composite membranes, have shown superior abilities for separating salts from aqueous solutions<sup>2–12</sup> and have become mainstream materials for reverse-osmosis (RO) membranes.

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RO membranes are usually characterized by water flux and salt rejection; only in relatively few publications<sup>13–21</sup> have they been characterized by water and salt permeabilities and permeances (for asymmetric membranes). It is not very difficult to obtain the diffusivity of water through a membrane, with the water content, if the water permeability is known. However, it is a time-consuming and tedious process to measure the salt coefficients of distribution and diffusion in RO membranes by the desorption–diffusion method because the membranes should be equilibrated with a solution over night. This is the main reason there are very few publications<sup>13–21</sup> reporting the salt coefficients of distribution and diffusion in RO membranes in comparison with the huge number of publications on gas separation membranes.

Therefore, the effect of functional groups in a polymer on (or the relationship between the structure of the polymer and) the salt coefficients of diffusion and distribution in its RO membrane is not yet established. If these effects or the relationship were known, it might be easier to design the best polymer structure for an RO membrane.

With only one small piece of a membrane (ca. 2 cm in diameter), both coefficients can be determined at once with a new method of unsteady-state and steady-state dialysis we have been developing.<sup>22–25</sup> This new method is similar to that for gas separation but requires additional measurements of highly time-dependent osmosis flux. In a previous study,<sup>25</sup> distribution coefficients ( $K$ ) and overall diffusion coefficients ( $D$ ) of alkali, alkali-earth, and aluminum chlorides (LiCl, NaCl, KCl, RbCl, CsCl, MgCl<sub>2</sub>, CaCl<sub>2</sub>, and AlCl<sub>3</sub>) in symmetric Loeb–Sourirajan-type CA (40% acetyl) membranes were obtained.

In this article, we report on the diffusional characteristics of NaCl in two types of polyamide membranes, a symmetrical polyamide membrane and an interfacially polycondensed nylon-6,6 thin membrane.

## EXPERIMENTAL

### Membranes

#### CA Membranes<sup>26,27</sup>

The CA used (E-398-3) was an Eastman product with a 39.8% acetyl content and a falling-ball viscosity of 3 s. The composition of the dope solution is shown in Table I.

**Table I** Composition of the Dope Solution (Weight Fraction)

Type		
CA	Formamide	Acetone
0.208	0.083	0.709


The apparatus for membrane preparation was the same as that reported earlier.<sup>26,27</sup> The preparation procedure for the symmetric membrane was as follows. First, a clean and dry glass plate was immersed in the dope solution for about 15 min. Then, the glass plate was drawn up by a motor at a speed of about 13 mm/s and kept in the air for 2 nights for complete evaporation of the solvent. The glass plate was immersed in water for about 1 day, and a membrane 12–23 mm thick was obtained. The membrane was heat-treated in water at 75°C for 10 min before use. The symmetry of the membrane was verified in terms of salt rejection and pure water permeability on both surfaces as reported earlier.<sup>26,27</sup>

#### Nylon-6,6 Thin Membranes

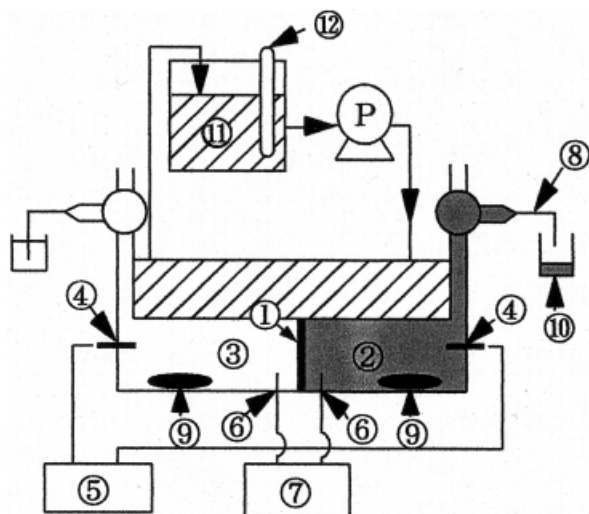
Nylon-6,6 thin membranes were prepared by interfacial polymerization between an aqueous solution (0.4N NaOH) of 1,6-hexanediamine and a carbon tetrachloride solution of adipoyl dichloride in a 50-mL beaker for 2 or 4 min. The polymerized membranes were placed on filter paper (Advantec no. 2, average pore diameter = 5 μm, porosity = 70.3%, thickness = 0.3 mm), removed from the beaker, heat-treated in water at 80°C for 10 min, and stored in pure water. The thickness of the thin membranes was measured with a micrometer and weighing method to be 5.4 ± 0.6 μm.

#### Aromatic Polyamide Membranes

Polyxylyleneadipamide (PXAP; m/p = 70/30) was dissolved in a solution of formic acid and *m*-cresol (F/C = 11/3), the composition of which follows:

$-\text{CO}(\text{CH}_2)_4\text{CO}-\text{NHCH}_2-$  $-\text{CH}_2-$	16.5wt%
(MW≈10 000 Daltons)	
Formic Acid	65.9wt%
<i>m</i> -Cresol	17.6wt%

The dope solution was dropped on the surface of pure water, and a thin layer of polymer was al-



**Figure 1** Schematic diagram of the dialysis experiment apparatus: (1) membrane, (2) dialysate chamber, (3) diffusate chamber, (4) electrode, (5) recorder, (6) thermocouple, (7) temperature controller, (8) capillary for permeate water, (9) magnetic stirring bar, (10) sampling bottle, (11) constant-temperature bath, and (12) heater.

lowed to develop. The thin layer was removed from the surface of the water and heat-treated in water at 80°C for 10 min. The thickness of the thin film was 3  $\mu\text{m}$ .

## Measurements

### Water Contents

The water contents were determined by membranes being weighed before and after drying at 70°C for 1 day.

### Unsteady-State and Steady-State Dialysis Experiments

For the purpose of obtaining diffusion and distribution coefficients of the solute, unsteady-state and steady-state dialysis experiments were carried out with the same experimental apparatus and the same methods reported earlier.<sup>24</sup>

**Apparatus.** The experimental apparatus is shown schematically in Figure 1. The effective membrane area was 2 cm<sup>2</sup>. More details on the apparatus are reported elsewhere.<sup>24</sup>

**Unsteady-State Dialysis Experiments.** At first, the two chambers (the dialysate chamber and the diffusate) were filled with pure water. After the temperature of water in the chambers reached a

constant value of 25°C, a certain volume of water was pulled out from the dialysate chamber, and then the same volume of an aqueous NaCl solution of a known concentration was injected into it with a syringe. This injected moment was defined as  $t = 0$ , and the concentration in the dialysate chamber was defined as the initial concentration ( $c_0$ ). The concentration of NaCl in the diffusate chamber was measured continuously by a conductive bridge equipped with a recorder (model LR 4210 from Yokogawa Co., Japan). With the concentration in the diffusate chamber and chamber volume, the amount of the permeated solute (NaCl) through the membrane could be calculated. The osmosis flux [ $j_w(c)$ ] was determined by the weighing method. The experiments were continued until the solute flux became constant.

## RESULTS

### Water Contents

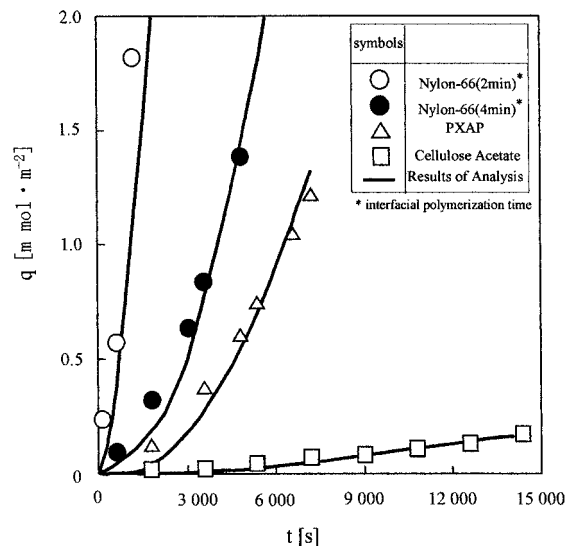
Table II shows the water contents of the CA membrane (heat-treated at 75°C), PXAP membranes, and nylon-6,6 thin membranes (heat-treated at 80°C).

### Unsteady-State and Steady-State Dialysis Experiments

Figure 2 shows a typical example of the results of the unsteady-state and steady-state dialysis experiments with the CA, PXAP, and nylon-6,6 membranes (polymerized for 2 and 4 min with interfacial polymerization) for aqueous NaCl solutions. The sequence of the dialysis rates were in the order nylon-6,6 thin membranes (interfacially polymerized for 2 and 4 min), PXAP membranes, and CA membranes, and the flux rates with steady-state dialysis ( $J_s^\infty$ ) were 5.9, 0.92, 0.26, and 0.031  $\mu\text{mol}/(\text{m}^2 \text{s})$ , respectively. For the measurement of the slower  $J_s^\infty$  for PXAP and CA with greater accuracy, the NaCl concentrations in the dialysate compartment were increased about 10 times with respect to that for nylon-6,6.

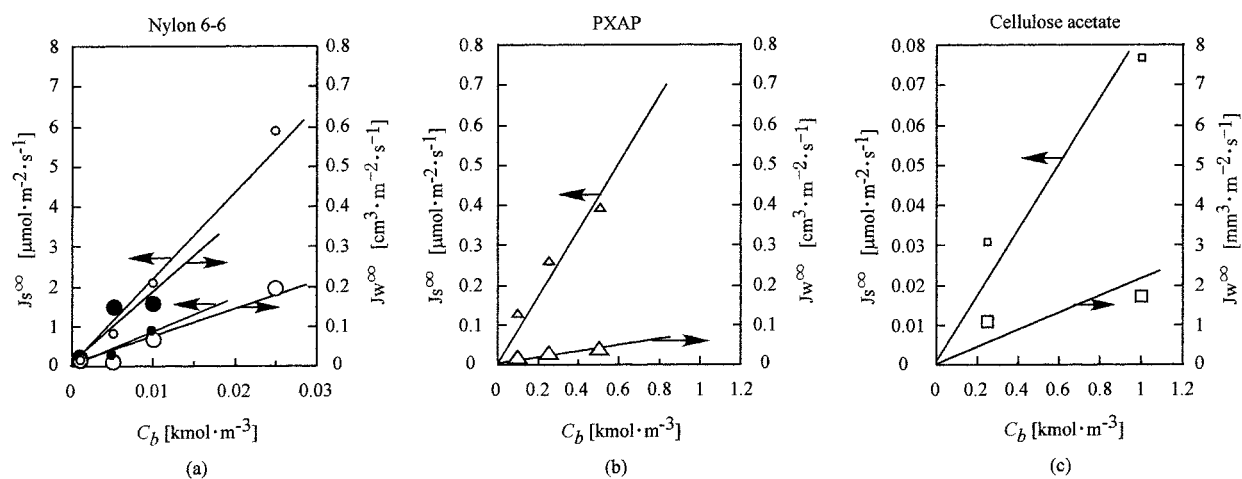
**Table II** Water Content in the Membrane (wt %)

CA Membrane	PXAP Membrane	Nylon-6,6 Thin Membranes
0.164	0.63 $\pm$ 0.08	0.83 $\pm$ 0.03



**Figure 2** Unsteady-state and steady-state dialysis curves for nylon-6,6 thin membranes for 2 and 4 min of interfacial polymerization: PXAP and CA. Nylon-6,6 and PXAP were heat-treated at 80°C, and CA was heat-treated at 75°C. The concentrations of NaCl in the dialysate chamber were 0.025M for nylon-6,6 (2 min), 0.01M for nylon-6,6 (4 min), and 0.25M for PXAP and CA.

Figure 3 shows the dependence of the solute fluxes ( $J_s^\infty$ ) and the water flux ( $J_w^\infty$ ) on the solute concentration in the dialysate compartment. Both fluxes increased almost linearly with the increase in the solute concentration. This linear relationship was already confirmed with CA membranes.<sup>24</sup> Therefore, for CA membranes, only two levels of solute concentration were adopted.



**Figure 3** Dependence of  $J_s^\infty$  and  $J_w^\infty$  on  $C_b$  for (a) a nylon-6,6 membrane heat-treated at 80°C, (b) a PXAP membrane heat-treated at 80°C, and (c) a CA membrane heat-treated at 75°C. The symbols are defined in Figure 2

## ANALYSIS OF THE DATA FROM THE UNSTEADY-STATE DIALYSIS EXPERIMENTS

### Analytical Procedure

The same analytical procedure reported in a previous article<sup>23</sup> was applied to obtain  $K$  and  $D$  of NaCl for CA, PXAP, and nylon-6,6 membranes from their unsteady-state and steady-state dialysis data.

### Results of the Analysis

A typical example of the analysis for the data shown in Figure 2 is given in Table III. Figure 4 shows the relationship between the concentration of the bulk ( $C_b$ ) and  $D$  of NaCl for CA, PXAP, and nylon-6,6 membranes.  $D$  increased almost linearly with the increase in the solute concentrations in the dialysate compartment. The extrapolated values of  $D$  to zero concentration [ $D^{(0)}$ ] were obtained: 1.3, 0.77, 0.024, and 0.078  $\mu\text{m}^2/\text{s}$  for nylon-6,6 thin membranes polymerized for 2 and 4 min, CA membranes, and PXAP membranes, respectively.

The obtained values of the distribution coefficients for NaCl are plotted in Figure 5 against the solute concentration. The values of the distribution coefficients of the PXAP membrane and CA membrane were 0.04–0.06 and decreased with the increase in the solute concentration, and those for nylon-6,6 thin membranes were 0.4–0.8 and increased with the increase in the solute concentration.

**Table III** Results of Analysis for Data Shown in Figure 2

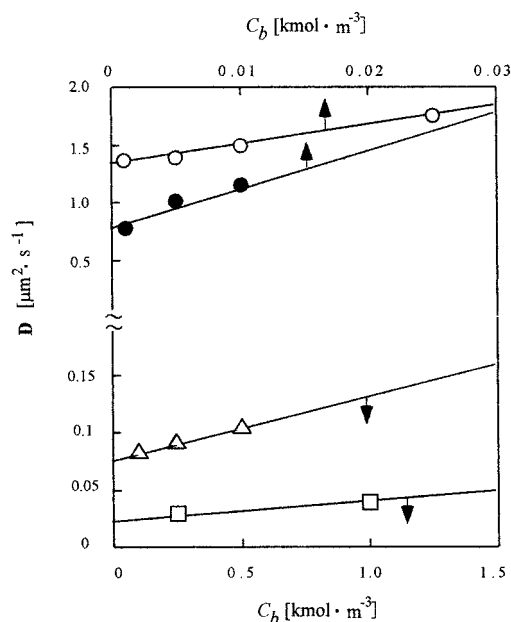
	Nylon-6,6 (2 min) <sup>a</sup>	Nylon-6,6 (4 min) <sup>a</sup>	PXAP	CA
Heat-treated temperature [°C]	80	80	80	75
$C_b$ [M]	0.025	0.01	0.25	0.25
$J_s^\infty$ ( $\mu\text{mol}/\text{m}^2 \text{ s}$ )	5.9	0.81	0.39	0.031
$J_w^\infty$ ( $\text{cm}^3/\text{ms}$ )	0.02	0.16	0.025	$1.1 \times 10^{-3}$
$D^{(0)}$ ( $\mu\text{m}^2/\text{s}$ )	1.3	0.77	0.078	0.024
$K$ (-)	0.8	0.56	0.05	0.064
$\tau$ (s)	3000	2200	350	400

<sup>a</sup> Interfacial polymerization time.

## DISCUSSION

### Two-Part Model

In earlier studies,<sup>24,25,28</sup> the concentration dependency of  $D$  was well explained by the assumption of the two-part model of the membrane proposed by Lonsdale et al.<sup>14</sup> [dense (or perfect) and porous (or imperfect)], and the concentration-independent diffusion coefficients of NaCl,  $D_d$  for the dense part and  $D_p$  for the porous part, were obtained. The same calculation procedure was applied to obtain  $D_d$  and  $D_p$  for CA, PXAP, and nylon-6,6 membranes. The calculated results are shown in Table IV.



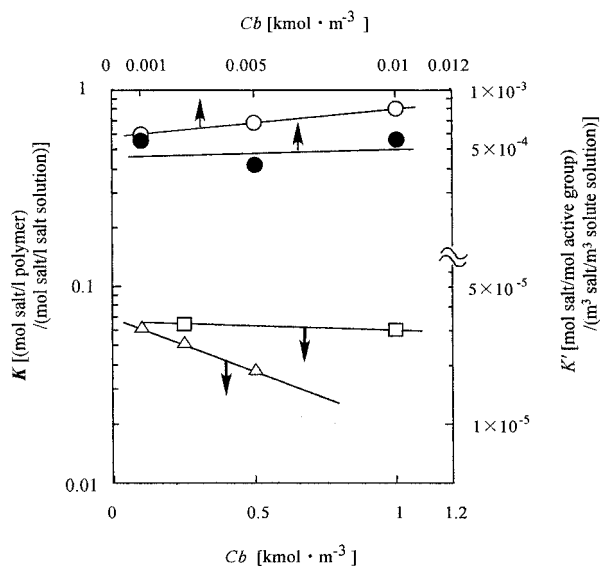
**Figure 4** Dependence of  $D$  on  $C_b$  for a PXAP membrane heat-treated at 80°C, a nylon-6,6 membrane heat-treated at 80°C, and a CA membrane heat-treated at 75°C. The symbols are defined in Figure 2

### Structure of the Polyamide

The values of  $D_d$  were almost the same for both nylon-6,6 and PXAP ( $0.05$ – $0.061 \mu\text{m}^2/\text{s}$ ) and about 10 times greater than that for CA membrane ( $5.6 \times 10^{-3}$ ). CA seemed to have a much denser structure.

$D_p$  for PXAP was almost the same as that for CA. Also,  $D_p$  for nylon-6,6 membranes were 10–16 times greater than  $D_p$  for PXAP membranes and 1/1000 of that in the bulk solution ( $1500 \mu\text{m}^2/\text{s}$ ).

$K$  was drastically reduced (ca. 10 times) with changes in the polyamide structure from aliphatic to aromatic. It was possible to compare the sorptive capacities of active groups for the investigated polymers: the amide groups in the aliphatic polyamide were more active than the acetate groups in CA, and the latter were more active than the amide groups in PXAP.



**Figure 5** Effect of  $C_b$  on  $K$  and  $K'$  for PXAP, nylon-6,6 and CA membranes. The symbols are defined in Figure 2

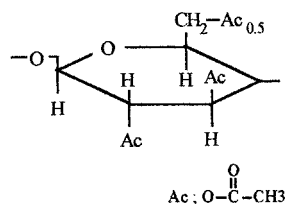
**Table IV** Diffusion Coefficients  $D^{(0)}$ ,  $D_d$ ,  $D_p$ , and  $K'$  for Nylon-6,6 Thin Membranes, PXAP Membrane, and CA Membrane

Membrane	$D^{(0)}$ ( $\mu\text{m}^2/\text{s}$ )	$D_d$ ( $\mu\text{m}^2/\text{s}$ )	$D_p$ ( $\mu\text{m}^2/\text{s}$ )	$W_w$ (wt %)	$K \times 10^5$ av [(mol of salt/mol of active group)/ (mol of salt/ $\text{m}^3$ of solution)]
Nylon-6,6 (2 min)	13	0.05	1.6	83	69
Nylon-6,6 (4 min)	0.77	0.061	0.91	83	51
PXAP	0.078	0.05	0.095	63	25
CA	0.024	$5.6 \times 10^{-3}$	0.11	16	3.1

$K'$  values [(mol of salt/mol of active group of polymer)/(mol of salt/ $\text{m}^3$  of solution)] were calculated from the ordinary defined distribution coefficient  $K$  [(mol of salt/ $\text{m}^3$  of membrane)/(mol of

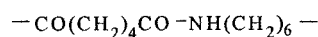
salt/ $\text{m}^3$  of solution)] for CA, nylon-6,6, and PXAP and are shown in Figure 5 together with values of  $K$ . The active groups for the polymer are chosen as follows:

CA

Molecular weight  
of active group

315

Nylon 6-6



211

PXAP



231

The values of  $K$  and  $K'$  for nylon-6,6 membranes were obtained at very low values of  $C_b$  (0.001–0.1M), but for CA and PXAP membranes,  $C_b$  was 0.1–1.0M.

The values of salt sorbed per unit active group were between 0.3 and  $7 \times 10^{-3}$  mol/mol for all membranes investigated. The values of  $K$  and  $K'$  for nylon-6,6 were high compared with those for PXAP; even the water contents for the membranes were almost the same, about 0.83. The large difference between the membranes might be due to the structure of the diamine, aliphatic or aromatic.

This suggests that the aromatic structure of the diamine and dicarboxylic acid groups might offer very low distribution coefficients in membranes.

### Effect of the Support Filter

Nylon-6,6 membranes were prepared on filter paper with an average pore diameter of  $5 \mu\text{m}$ , a thickness ( $l_p$ ) of 0.3 mm, and a porosity ( $\epsilon$ ) of 70%. For the analysis of the unsteady-state and steady-state dialysis data, the diffusional resistivity of the filter was ignored. To ensure that this was a reasonable assumption, we developed the following.

Because of the average pore size in the filter (pore), the effective diffusivity of NaCl in the pore may equal the product of the porosity times the diffusivity of NaCl in free water. The diffusional resistance in the filter ( $R_p$ ) can be calculated as follows:

$$R_f = 1_f/(\varepsilon \times D_{\text{NaCl}}(\text{in free water})) = 3 \times 10^5 \text{ s/m}$$

The diffusional resistance in the nylon-6,6 membrane ( $R_m$ ) can be calculated as follows:

$$\begin{aligned} R_m &= 1_m/D^{(0)} = 5.6 \times 10^{-6}/((0.77 - 1.3) \times 10^{-12}) \\ &= 4 - 7 \times 10^6 \text{ s/m} \end{aligned}$$

$R_m$  is larger than  $R_f$  by a factor of 10.

The diffusional time constant in the filter was estimated to be less than 90 s, far smaller than the time constant  $\tau$  shown in Figure 2. Therefore, it might be reasonable to ignore  $R_f$ .

## CONCLUSIONS

1. From the unsteady-state and steady-state dialysis data of the initial response experiment for nylon-6,6 thin membranes and PXAP membranes (m/p = 70/30), the best fit combination of  $K$  and  $D$  of NaCl was calculated by numerical analysis with a partial differential diffusion equation including the effect of osmotic flux, which depended heavily on time.
2.  $D^{(0)}$  values for nylon-6,6 (interfacially polymerized for 2 and 4 min) and PXAP were 1.3, 0.8, and  $0.078 \mu\text{m}^2/\text{s}$ , respectively.  $D^{(0)}$  for PXAP ( $0.078 \mu\text{m}^2/\text{s}$ ) was about 3 times greater than that for CA heat-treated at  $75^\circ\text{C}$  ( $0.024 \mu\text{m}^2/\text{s}$ ).
3.  $K$  values for nylon-6,6 (interfacially polymerized for 2 and 4 min) and PXAP were 0.7, 0.5, and 0.05, respectively.  $K$  for PXAP (0.05) was almost the same as that for CA (0.06).  $K'$  allowed us to compare the sorptive capacities of active polymer groups; amide groups in the aliphatic polyamide were more active than acetate groups in CA, and the latter were more active than the amide groups in PXAP.
4. With the polyamide structure changed from being aliphatic to being aromatic, both distribution and diffusion coefficients were reduced by about 1/10.
5. A two-part model (dense and porous) was applied to obtain  $D_d$  and  $D_p$  for PXAP and nylon-6,6. The values of  $D_d$  were almost the same for both nylon-6,6 and PXAP ( $0.05\text{--}0.061 \mu\text{m}^2/\text{s}$ ) and about 10 times greater than that for CA membranes ( $5.6 \times 10^{-3} \mu\text{m}^2/\text{s}$ ).  $D_p$  for PXAP was almost the

same as that for CA. Also, the  $D_p$  values for nylon-6,6 membranes were 10–16 times greater than the values for PXAP membranes and 1/1000 of that in the bulk solution ( $1500 \mu\text{m}^2/\text{s}$ ).

6. Our approach seems very promising for investigating the influence of the polymer chemical structure on the RO properties of polymer membranes.

## REFERENCES

1. Reid, C. E.; Breton, E. J. *J Appl Polym Sci* 1959, 1, 133.
2. Orofino, T. A. Development of Hollow Filament Technology for Reverse Osmosis Desalination Systems; OSW R&D Report No. 549; Washington, DC, 1970.
3. Mckinney, R., Jr.; Rhodes, J. H. *Macromolecules* 1971, 4, 633.
4. Mckinney, R. In *Reverse Osmosis Membrane Research*; Lonsdale, H. K.; Podall, H. E., Eds.; Plenum: New York, 1972; p 253.
5. Scala, L. C.; Frost, L. W.; Lee, P. K.; Giliberti, D. F.; Dixon, C. D.; Bower, C. M. OSW R&D Report No. 860; Washington, DC, 1973.
6. Credali, L.; Chiolle, A.; Parrini, P. *Proc Int Symp Fresh Water Sea* 1973, 4, 95.
7. Matsuura, T.; Blais, P.; Dickson, J. M.; Sourirajan, S. *J Appl Polym Sci* 1974, 18, 3671.
8. Dickson, J. M.; Matsuura, T.; Blais, P.; Sourirajan, S. *J Appl Polym Sci* 1976, 20, 1491.
9. Ohya, H.; Negishi, Y.; Yamamoto, T. *Membrane* 1978, 3(2), 143.
10. Sundet, S. A.; Arthur, S. D.; Campos, D.; Eckman, T. J.; Brown, R. G. *Desalination* 1987, 64, 259.
11. Arthur, S. D. *J Membr Sci* 1989, 46, 243.
12. Chan, W.-H.; Lam-Leung, S. Y.; Ng, C.-F.; Xi, S.; Ding, J.; He, X. *Polymer* 1997, 38, 99.
13. Sourirajan, S. *Reverse Osmosis and Synthetic Membranes*; National Council Canada: Ottawa, Canada, 1977.
14. Lonsdale, H. K.; Merten, U.; Riley, R. L. *J Appl Polym Sci* 1965, 9, 1341.
15. Yasuda, H.; Lamaze, C. E. *J Appl Polym Sci* 1969, 13, 2209.
16. Glueckauf, E.; Sammon, D. C. *Proc Int Symp Fresh Water Sea* 1970, 2, 397.
17. Kimura, S.; Nomura, T.; Shiomi, K.; Miyauchi, T. *Maku* 1975, 1, 197.
18. Kimura, S.; Irie, J.; Miyauchi, T. *Maku* 1976, 1, 231.
19. Kimura, S. *Proc Int Symp Fresh Water Sea* 1973, 4, 197.
20. Kimura, S. In *Membranes and Membrane Processes*; Drioli, E.; Nakagaki, M., Eds.; Plenum: New York, 1986; p 223.

21. Lee, K. L.; Baker, R. W.; Lonsdale, H. K. *J Membr Sci* 1981, 8, 141.
22. Huang, J.; Ohya, H.; Yamashida, S.; Negishi, Y. *Membrane* 1994, 19(2), 99.
23. Mori, K.; Ohya, H.; Semenova, S., I; Fujimoto, T.; Aihara, M.; Negishi, Y. *Membrane* 1998, 23(3), 132.
24. Mori, K.; Ohya, H.; Semenova, S., I; Kawahara, T.; Aihara, M.; Negishi, Y.; Fujimoto, T. *Desalination* 2000, 127, 225.
25. Ohya, H.; Semenova, S.; Fujimoto, T.; Ogihara, J.; Fukaya, S.; Mori, K.; Aihara, M.; Negishi, Y. *Desalination*, to appear.
26. Ohya, H.; Imura, Y.; Moriyama, T.; Kitaoka, M. *J Appl Polym Sci* 1974, 18, 1855.
27. Ohya, H.; Konuma, H.; Negishi, Y. *J Appl Polym Sci* 1977, 21, 2515.
28. Ohya, H.; Semenova, S.; Sawada, A.; Fukaya, S.; Suzuki, Y.; Aihara, M.; Negishi, Y. *Desalination*, to appear.