

## Permeabilities to Salts and Water of Macrocyclic Polyether-Polyamide Membranes

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### Synopsis

The polyether-polyamide (PC-6) strongly absorbs sodium salts from their aqueous solutions. Membranes based on PC-6 and on its polymeric alloys with poly(vinylpyrrolidone) (PVP) are, however, much more permeable to water than to salts. The membrane permselectivity is due to the low mobility of the absorbed salts. Desorption experiments were conducted to determine the values of the diffusion coefficients of the sodium ions in the investigated membranes. They were found to vary from  $5 \times 10^{-12}$  cm<sup>2</sup>/sec in loose PC-6 membranes to  $1.7 \times 10^{-9}$  cm<sup>2</sup>/sec in the polymeric alloy containing 30% PVP. Water permeation experiments with the alloy membranes yielded values of the diffusion coefficients in the range of  $2-5 \times 10^{-7}$  cm<sup>2</sup>/sec. The apparent "energy of activation of the diffusion" of sodium ions in such membranes was found to be essentially identical ( $\sim 12$  kcal) with the energy of activation of the decomplexation of the sodium-crown complex. The ramifications of the proposed "site to site jump" diffusion mechanism were discussed. The permeability characteristics of PC-6 membranes were found to be strongly affected by their "history." The observed phenomenon was explained in terms of reversible changes in the structure of the polymeric network, in the presence and in the absence of the absorbed salts. It has been found that PVP has a stabilizing effect on the permeability characteristics of the membranes. Reverse osmosis experiments indicated that their intrinsic osmotic characteristics seem to be superior to those of the commercially used materials. Their salt rejections are in the range of 95-99.5%, and their permeabilities to water are at least one order of magnitude higher than those of the unmodified aromatic polyamides.

### INTRODUCTION

Macrocyclic polyethers are capable to bind alkali metal ions.<sup>1</sup> Polymers with macrocyclic polyetheral rings attached to the polymeric backbone have also been synthesized,<sup>2-5</sup> and it was shown that the complexing ability of the polyetheral cavity is preserved in such systems. The solubility of a given salt in the polymer phase may probably be also affected by the nature of the polymeric segments around the complexing sites. For a given cation, it depends strongly on the nature of the counterion, which must be absorbed together with the complexed ion in order to preserve the electroneutrality of the system. Although some information on the solubility of various salts in such complexing polymeric systems has already been published,<sup>3,4</sup> no data are yet available about the mobility of thus dissolved salts in the polymeric network. In this respect, it seems to be of great interest to find out to what extent the respective diffusion coefficients may be correlated with the rates of the complexation reactions in solution. The kinetics of complexation of sodium ions with several 18-crown-6 ethers was extensively investigated in various sol-

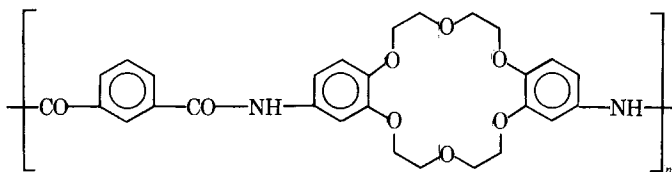
vents by the  $^{23}\text{Na}$ -NMR technique.<sup>6</sup> A high molecular weight aromatic polyamide PC-6 containing 18-crown-6 rings in the polymeric backbone was recently synthesized in this laboratory and was found to form mechanically strong thin membranes. It was also noted that PC-6 can be modified by blending it in various proportions with poly(vinylpyrrolidone) (PVP). The two polymers mix well and seem to form polymeric alloys.<sup>5</sup>

We decided, therefore, to investigate sorption and diffusion of sodium salts in membranes based on PC-6 and on its polymeric alloys with PVP. The results of this investigation were described in the present paper. The investigated membranes were also tested under osmotic and hyperfiltration conditions.

## EXPERIMENTAL

### Materials and Membrane Preparation

High molecular weight polyamide (PC-6), with the 18-crown-6 rings incorporated into the polymeric backbone and of the general formula



was synthesized as described elsewhere.<sup>5</sup> PC-6 used in the experiments had  $[\eta]_{\text{HMPA}}^{30} = 7.5$  dl/g and  $T_g = 216^\circ\text{C}$ . Poly(vinylpyrrolidone) (PVP) (Aldrich, MW  $\approx 360,000$ ) was dried at  $10^{-6}$  torr.

Thin films (25–50  $\mu$ ) were cast from 3–7% solutions. DMF, containing an equivalent amount of NaSCN (4.7–11.4 g/l) was used as a solvent. It was removed from the membrane by a slow evaporation under vacuum (up to  $10^{-6}$  torr at  $90^\circ\text{C}$  for 72 hr).

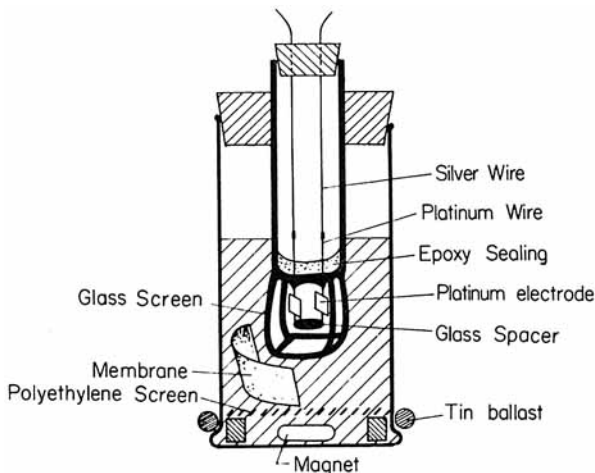


Fig. 1. Conductometric elution cell.

Membranes were also cast from hexafluoroisopropanol (HFP) (PCR Inc.). They were left in a hood for 8 hr and then dried overnight at room temperature under vacuum (20 torr).

### Determination of Solubility and Diffusivity of Sodium Salts in the Membranes

Strips of membranes were equilibrated at  $25^\circ \pm 0.1^\circ\text{C}$  in appropriate salt solutions. The membranes were then dipped into distilled water for 1 sec, blotted with filter paper, and placed in the elution cells shown schematically in Figure 1. The cells were filled with 100 ml  $\text{H}_2\text{O}$  and immersed into a constant-temperature bath.

Rate of desorption of salt from the membrane was determined from changes in the conductivity of the aqueous solution in the elution cell.

Values of the diffusion coefficients ( $D_s$ ) were calculated from the initial slopes of  $(\kappa_\infty - \kappa_t)/(\kappa_\infty - \kappa_0)$  versus  $\sqrt{t}/l$  from the equation<sup>7</sup>

$$\frac{\kappa_\infty - \kappa_t}{\kappa_\infty - \kappa_0} = C_t/C_0 = 1 - \left( \frac{16D_s t}{\pi l^2} \right)^{1/2} \quad (1)$$

where  $C_0$  and  $C_t$  are salt concentrations in the membranes at time zero and time  $t$ , respectively;  $l$  is membrane thickness;  $\kappa_t$  and  $\kappa_0$  are the conductivity of the aqueous solution at time  $t$  and time zero; and  $\kappa_\infty$  is the conductivity after total elution. Solubilities of the salts in the membranes were calculated from the values of  $\kappa_\infty$ .

### Determination of Water Fraction in the Membrane

Membrane strips equilibrated with water were placed on a Mettler semimicro balance. It took 10–15 sec to blot excess water from the membrane surface and to put it on the scale. The first reading was taken after 30 sec and was followed by two to three additional readings at 30-sec intervals. Small corrections, which have to be introduced to calculate the initial weight from the first reading, were computed by extrapolation. The membranes were dried for three days in a vacuum oven ( $10^{-4}$  torr) at  $90^\circ\text{C}$ , and the weight of absorbed water was calculated from the difference.

In order to calculate the volume fraction ( $f_w$ ) of water in the membrane, its density was determined in a density gradient column.<sup>8</sup>  $\text{CCl}_4$ -heptane mixtures kept at  $22^\circ \pm 0.1^\circ\text{C}$  in a double-walled cylinder were used for these measurements. The column was calibrated with droplets of 24–45% KI solutions.

Since  $d_w \approx 1$ , it was assumed that the water partition coefficient  $\alpha_w \approx f_w$ .

### Self-Diffusion of Water

Two compartments of a permeation cell were separated by the tested membrane. Absence of leaks was checked by filling one half-cell with 2.5M  $\text{MgSO}_4$  and the other with distilled water. (The conductance of water after 5 hr should not exceed  $1 \times 10^{-5}$  ohm $^{-1}$ .cm). The two compartments were then thoroughly rinsed, one half-cell was filled with  $\text{H}_2\text{O}$  (13 ml) and the other with 13 ml of the tritiated water (340,000 counts $\cdot$ min $^{-1}$ .ml $^{-1}$ ).

The permeation cell was placed in a constant-temperature bath and magnetic stirring was started. Samples (0.1 ml) were taken at 5–20 min intervals during 3 hr and their activity was determined in a Packard Liquid Scintillation Spectrometer. Slopes of the plots of  $\log \{R_0'/(R_t' - R_t'')\}$  versus  $(1/V' + 1/V'')$   $A \cdot t$  yielded water diffusion coefficients ( $D_w$ ) which were calculated from the relationship

$$D_w = \frac{1}{\alpha_w \beta t} \ln \{R_0'/(R_t' - R_t'')\} \quad (2)$$

where  $R_0'$ ,  $R_t'$ , and  $R_t''$  are radioactivities of water in compartments 1 and 2, respectively, at time zero and time  $t$ ;  $V'$  and  $V''$  are volumes of water in the two compartments;  $\beta \equiv (1/V' + 1/V'')A$ ; and  $A$  is the effective area of the membrane.

### Osmotic Permeation Experiments and $g^*$ -Value Determination

Experiments analogous to those described in the previous section were performed in order to determine the  $g^*$  porosity factor. In these experiments, water was replaced by 3M NaCl. The total volume flow and salt flow were calculated from the conductivity changes in the two compartments. The following relationships were used to calculate membrane permeability to salts and water from the measured fluxes:

$$J_v = P_w \bar{V}_w \Delta \pi / RTl \quad (3)$$

$$J_s = P_s \Delta C / l$$

where  $J_v$ ,  $P_w$  and  $J_s, P_s$  are water and salt fluxes and permeabilities, respectively;  $\bar{V}_w$  is the molar volume of water;  $\Delta \pi$  and  $\Delta C$  are the osmotic and concentration gradients across the membrane; and  $l$  is membrane thickness.

Hyperfiltration experiments were carried out in a hyperfiltration testing "loop" described elsewhere.<sup>9</sup> 0.1N NaCl solutions were used in these determinations. Salt rejections [ $R = 1 - (C_p/C_f)$ ] were calculated from the concentrations of chloride ions in the product ( $C_p$ ) and feed solutions ( $C_f$ ), which were determined with an automatic chloride titrator (American Instr. Co.).

## RESULTS AND DISCUSSION

### PC-6 Membranes

The strong complexing interaction between the 18-crown-6 rings of PC-6 and certain alkali metal ions is reflected by the solubility properties of the polymer. Thus, the addition of NaSCN, KSCN, AgClO<sub>4</sub>, or Ba(SCN)<sub>2</sub> to DMF makes possible its dissolution in this solvent. On the other hand, the addition of the poorly complexed lithium salt is ineffective in this respect. It could, therefore, be expected that the complexing ability of 18-crown-6 rings will also enhance the solubility of the salts in the polymeric network. Indeed, experimental results supporting such expectations were already reported by Feingenbaum et al.<sup>3</sup> and by Blessius et al.<sup>4</sup> The solubility of salts in the polymer depends not only on the nature of the cation but also on its counter-

TABLE I  
The Solubility of Sodium and Lithium Salts in PC-6 Membranes Equilibrated with Aqueous Solutions

Equilibrating solution	Membrane cast from DMF + NaSCN ( $f_w = 0.20$ )		Membrane cast from HFP ( $f_w = 0.19$ )	
	$\bar{C}_s$ , mmole/cc	$\alpha_s$ , mmole/cc	$\bar{C}_s$ , mmole/cc	$\alpha_s$ , mmole/cc
NaCl, 0.1M	0.43	4.27		
NaSCN, 0.02M	0.48	24.0		
NaSCN, 0.1M	1.15	11.5	0.91	9.1
NaSCN, 0.5M	1.35	2.7		
NaSCN, 1.0M	1.92 <sup>a</sup>	1.92		
LiSCN, 0.1M	0.095	0.95	0.10	1.0

<sup>a</sup> A value of  $\bar{C}_s = 1.97$  is calculated for the 1:1 molar ratio between the absorbed salt and the macrocyclic rings.

ion. In the present study, values of partition coefficients were determined for NaCl, NaSCN, LiSCN, and water. As can be seen from the results, summarized in Table I, sodium thiocyanate is indeed strongly absorbed by PC-6. Replacement of  $\text{SCN}^-$  by  $\text{Cl}^-$  causes about threefold decrease in solubility.  $\text{Li}^+$  is about ten times less soluble than  $\text{Na}^+$ . The considerable solubility of water in PC-6 is apparently due to the combined hydrophilicities of the amide and etheral groups.

The mobility of the absorbed sodium ions in the polymeric network is, however, very low. Thus, it is not surprising that preliminary osmotic experiments indicated that PC-6 membranes which were cast from HFP or from thiocyanate solutions in DMF were permselective while highly permeable to water. A pronounced decline in permeability was, however, noted when membranes which were cast from HFP were stored in distilled water. The changes in permeability were not accompanied by comparable changes in selectivity. It appears, therefore, that the observed phenomenon should not be attributed to closing of pores or defects, but rather to structural changes within the polymeric network. The essentially "pore free" nature of the investigated membranes was also confirmed by scanning electron microscope evidence.

In order to gain a more detailed information on the dependence of membrane characteristics on its "history," the investigated membranes were submitted to a controlled conditioning in distilled water or in salt solutions at various temperatures. The preconditioned membranes were tested in subsequent osmotic and desorption experiments.

In the case of highly selective membranes, the coupling between the diffusional fluxes of salt and water is very small and, in the first approximation, can be neglected. The membrane permeability to salt ( $P_s$ ) and to water ( $P_w$ ) may be thus calculated from the respective fluxes by means of relationships derived from Fick's first law for steady-state diffusion, see experimental section, eqs. (3) and (4). By definition,  $P_s = D_s \alpha_s$  and  $P_w = D_w \alpha_w$ . Values of  $P_s$  and  $P_w$  calculated from the experimentally determined osmotic fluxes are summarized in Table II.

TABLE II  
Permeability to Salt and Water of PC-6 Membranes in Osmotic Experiments at 25°C with 3M Sodium Chloride Against Water<sup>b</sup>

Membrane no.	Casting solution <sup>c</sup>	Conditioning <sup>d</sup>			$P_w \times 10^7$ , cm <sup>2</sup> /sec	$P_s \times 10^{11}$ , cm <sup>2</sup> /sec	$\frac{J_s}{J_w \Delta C} \times 100^e$
		Medium	Temp., °C	Time, days			
9	B	air	R.T.	3	0.51 ± 0.03	1.8 ± 0.3	0.3
10	B	air	R.T.	3	0.44 ± 0.03	1.6 ± 0.2	0.3
112	B	air	R.T.	700	0.07	0.02	0.02
106	A	airf	—	—	1.63 ± 0.07	12.0 ± 0.3	1.4
107	A	airf	—	—	1.9 ± 0.2	12.5 ± 0.6	0.6
105	A	airf	—	—	1.0 ± 0.1	5.8 ± 1.3	0.5
1	A	60% NaSCN	123	3	0.75 ± 0.01	3.0 ± 0.1	0.4
		H <sub>2</sub> O	25	2	0.55 ± 0.01	1.3 ± 0.05	0.2
		H <sub>2</sub> O	100	1	0.011	0.011	0.09
7	A	H <sub>2</sub> O	25	2	0.52 ± 0.05	1.0 ± 0.2	0.2
		60% NaSCN	123	3	0.82 ± 0.05	4.6 ± 0.3	0.5
8	A	0.1N NaSCN	R.T.	550	0.28	0.93	0.3
3	A	H <sub>2</sub> O	25	4	0.44 ± 0.1	0.9 ± 0.5	0.2
		60% NaSCN	123	3	0.93 ± 0.02	6.5 ± 0.4	0.6
		airg	R.T.	700	<0.1	<0.1	—
		60% NaSCN	123	3	0.75 ± 0.01	4.2 ± 0.1	0.5
		H <sub>2</sub> O	100	1	<0.1	<0.1	—

4	A	H <sub>2</sub> O	25	2	0.96 ± 0.03	3.8 ± 0.2	0.4
		H <sub>2</sub> O	25	200	0.012	—	—
		25% NaSCN	100	3	0.43 ± 0.01	2.3 ± 0.2	0.5
		air <sup>g</sup>	25	100	<0.1	<0.1	—
23, 24	A'	60% NaSCN	123	3	0.9 ± 0.1	5.3 ± 0.3	0.6
23		air	R.T.	3	6.0 ± 0.5	170 ± 20	2.5
25	A'	H <sub>2</sub> O	100	1	<0.01	—	—
		50% Ba(SCN) <sub>2</sub>	107	3	4.0 ± 1	60 ± 10	1.4
		(h)		60	3.4 ± 0.1	41 ± 2	1.05

<sup>a</sup> The tabulated values are averages of three consecutive experiments. The first osmotic experiment was considered to be equivalent to preconditioning and was always rejected.

<sup>b</sup> Average concentration gradients during experiments  $\bar{\Delta}C = 2.9M$ .

<sup>c</sup> A = 0.1M NaSCN in DMF; A' = 0.1M Ba(SCN)<sub>2</sub> in DMF; B = HFP.

<sup>d</sup> When various treatments are listed for the same membrane, they refer to consecutive conditionings in air and in various aqueous solutions.

<sup>e</sup>  $J_s/J_w \approx P_s/2P_w \cdot V$ .  $100(1 - J_s/J_w \Delta C)$  corresponds, in a first approximation, to the salt rejection ( $R$ ) to be expected under hyperfiltration conditions.

<sup>f</sup> Membranes containing NaSCN obtained after casting from solution A were stored in air for 18–20 months.

<sup>g</sup> The membrane was stored in air after the absorbed salt was washed out in distilled water.

<sup>h</sup> Results obtained after 60 days under osmotic concentration gradients at 25°C.

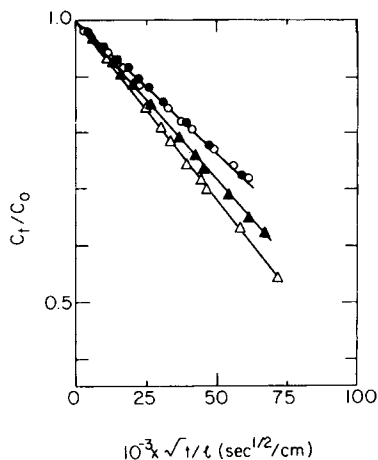


Fig. 2. Desorption of sodium thiocyanate from PC-6 membranes equilibrated at 25°C in 0.1N NaSCN: ( $\Delta$ ) membrane cast from DMF + NaSCN, dried, and left in water for 3 days; ( $O$ ) membrane  $\Delta$  after reflux in 60% NaSCN and a six-month storage in 0.1N NaSCN; ( $\bullet$ ) membrane cast from HFP; ( $\blacktriangle$ ) membrane cast from HFP after a six-month storage in 0.1N NaSCN.

As may be seen from the tabulated data, the initial high permeability of the freshly cast membrane decreases by nearly two orders of magnitude as result of its treatment in boiling water (#1), after a prolonged storage in distilled water at room temperature (#4), or when a salt-free membrane is stored in air (#3, 112). At the same time, the increase in selectivity is marginal. Most interesting is the reversibility of the observed changes. Thus, when the conditioning in distilled water is followed by treatment with concentrated NaSCN solution (cf. #3 and #4), the initial high permeability is restored, while subsequent treatment in distilled water reduces it again. The reversibility of the process seems to imply thermodynamically controlled transitions in the structure of the polymeric network. Such changes do not seem to occur even if the membranes are stored in even fairly diluted salt solutions (cf. #8 in Table II).

Results of absorption and desorption experiments lead to similar conclusions. Thus, for membranes stored in distilled water, the absorption of NaCl was extremely slow; and from subsequent desorption, one could estimate  $D_s < 5 \times 10^{-13}$  cm<sup>2</sup>/sec. On the other hand, values of  $D_s$  were very little affected by a six-month storage of the membranes in 0.1M NaSCN at room temperature. From the slopes of plots of  $C_t/C_0$  versus  $\sqrt{t}/l$  shown in Figure 2, one calculates  $D_s \approx 0.5 \times 10^{-11}$  cm<sup>2</sup>/sec. A faster desorption ( $D_s \approx 10^{-11}$  cm<sup>2</sup>/sec) observed in membrane freshly cast from DMF + NaSCN (after three days of conditioning in 0.1M NaSCN) may be partially attributed to traces of DMF still remaining in the film. (It was noted that even when the membrane was dried for four days at 90° at  $10^{-6}$  mm Hg, as much as 3% of DMF was still retained, and it could be completely removed only by extraction with water. DMF acts as an effective plasticizer of PC-6, and obviously its presence affects very strongly the value of the diffusion coefficient.)

It appears that two hypotheses may be considered to explain the experimental results. (A) An amorphous polymeric network is initially formed,



hence the high permeability of the freshly cast membranes. During storage in water crystallization occurs, and the formation of crystalline regions is responsible for the observed changes in permeability. The dependence of permeability on the degree of crystallinity was indeed reported for various polymeric membranes.<sup>10</sup> However, in our system, such explanation was not supported by the results of x-ray diffraction measurements which failed to detect any crystallinity in the low-permeability membranes. Moreover, it is not really clear why crystalline regions should be so easily destroyed by treatment in concentrated NaSCN solutions.

(B) An alternative explanation of the observed phenomenon can be based on the assumption that the initial high permeability is due to a loose but ordered structure of the polymeric network. The decrease in permeability may be attributed to the collapse of such structure, which takes place after the complexed salt is removed from the polymer. The latter hypothesis seems to be strongly supported by evidence provided by x-ray diffraction measurements.<sup>11</sup> It also seems to be consistent with the very high permeability of membranes cast from Ba(SCN)<sub>2</sub> solutions in DMF (cf. membranes #23-25 in Table II). Obviously, more open structure may be expected when NaSCN is replaced by the bulky barium thiocyanate.

#### Polymeric Alloys of PC-6 and PVP

Whatever the reason of the time-dependent changes in the permeability characteristics of PC-6 membranes, such changes are certainly undesirable if practical applications of membranes of this type are to be considered. We reported recently<sup>5</sup> that PC-6 can be blended with PVP. Though PVP is soluble in water, it is not extracted by water from its blends with PC-6. Such behavior indicates an intimate mixing of the two polymers which form a polymeric alloy.<sup>12</sup> It appears that the introduction of PVP also prevents structural changes in the PC-6 matrix. Indeed, the permeabilities of the polymeric-alloy membranes were essentially unaffected by a six-month storage in distilled water.

Incorporation of PVP enhances the solubility of water, but not of sodium salts in the membrane. The upper limit for their solubility seems to be determined by the concentration of the macrocyclic rings in the polymer. Saturation concentrations are reached when membranes are equilibrated with concentrated salt solutions. Hence, under such conditions (equilibration with 1M NaSCN), values of  $\bar{C}_s$  decrease with the increase in the fraction of PVP in the polymeric alloy (see Table III).

In membranes equilibrated in less concentrated solutions, only a fraction of the macrocyclic sites is occupied by the salt molecules. Under such conditions, the degree of complexation must depend strongly on the concentration of free uncomplexed salt in the polymeric medium. The latter apparently increases in the presence of PVP. Thus, dilution of PC-6 with PVP may be compensated by the increase in the fraction of the complexed sites. Indeed, it may be seen from data in Table III that when membranes are equilibrated with 0.1M NaSCN, the concentration of the salt in the membrane is little affected by the composition of the alloy.

Water fraction in the polymeric alloy membranes represent nearly one third of their total volume. It may be asked, therefore, if they behave as

TABLE III  
Solubility of Salts and Water in PC-6/PVP Polymeric  
Alloys Cast from 0.1M NaSCN in DMF

A. Membrane Characteristics				
Membrane designation <sup>a</sup>	A(0)	A(20)	A(25)	A(30)
Miliequivalents of "crown" rings per 1 ml salt-saturated polymers	1.97	1.47	1.33	1.16
Specific gravity, g/ml				
a) water-saturated polymer	1.32	1.27	1.26	1.23
b) water- and salt-saturated polymer	1.33	1.31	1.29	1.25
Water solubility, % v/v				
a) in the polymer	20	28	32	32.5
b) in the salt saturated polymer	15	21	23	26
B. Solubilities of Salts ( $\bar{C}_s$ in mmole/ml)				
Equilibrating solution	A(0)	A(20)	A(25)	A(30)
NaCl, 0.1M	0.36	0.30	—	0.34
NaSCN, 0.02M	0.48	0.38	—	0.34
NaSCN, 0.1M	0.9	0.77	0.74	0.72
LiSCN, 0.1M	0.095	0.14	0.15	0.14
NaSCN, 1.0M	1.92	1.50	—	1.16

<sup>a</sup> Numbers in brackets designate the weight per cent PVP in the dry polymeric alloy.

dense films or rather as water-filled porous gels. Membrane porosity can be determined by comparing total osmotic volume flow with tracer flow of tritiated water. Plots showing changes in the radioactivity with time for A(20) and A(30) membranes exposed to 3M NaCl on one side and tritiated water on the other side of the membrane are shown in Figure 3. The respective slopes yield values of  $J_T/C_T$  ( $C_T$  and  $J_T$  are tracer concentration and flux, respectively). The  $g^*$ -value, which describes membrane porosity, is calculated from the expression<sup>13,14</sup>

$$g^* = \ln \left( \frac{J_T}{C_T} / \left( \frac{J_T}{C_T} - J_v \right) \right) / 2\sigma\phi\Delta C\bar{V}_w$$

where  $J_v$  (cm/sec) is total volume flux;  $\sigma$  is membrane reflection coefficient;  $\phi$  is salt osmotic coefficient;  $\Delta C$  is salt concentration gradient across membrane; and  $\bar{V}_w$  is molar volume of water.

Apparent pore diameter  $d$  is related to  $g^*$ -value by the expression

$$d = \left| \frac{32\eta\bar{V}_w D_w^0}{RT} (g^* - 1) \right|^{1/2}$$

where  $D_w^0$  is self-diffusion coefficient of water and all other symbols have their usual meaning. Thus, at 25°C,  $d = 7.3 (g^* - 1)^{1/2} \text{ \AA}$ .

Values of membrane parameters computed from this experiment are summarized in Table IV. The value of  $g^* = 2.36$  is obtained for A(20). This value is similar to those observed for acetyl cellulose membranes.<sup>15</sup> It seems to be indicative of a relatively loose structure of the polymeric network with water molecules aligned along the hydrophylic sites. For A(30), the apparent

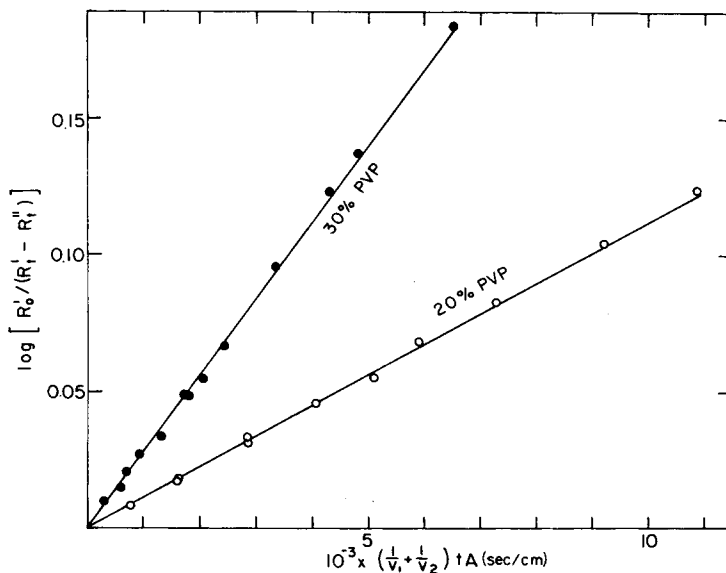


Fig. 3. Fluxes of tritiated water, across polymeric alloy membranes, induced by concentration gradients of NaCl and THO ( $\Delta C_0 = 3M$  NaCl): (O) 40- $\mu$ -thick A(20) membrane; (●) 29- $\mu$ -thick A(30) membrane.

pore diameter is as high as 12.4 Å. It does not necessarily mean that "true" capillaries are actually present in the membrane but certainly indicates a considerable "clustering" of the absorbed water molecules.

The diffusion coefficients at 25°C were calculated from experiments in which THO and H<sub>2</sub>O were separated by the investigated membranes (see experimental section). From slopes shown in Figure 4, one calculates for A(20) and A(30) values of  $D_w \alpha_w = 0.675 \times 10^{-7}$  cm<sup>2</sup>/sec and  $1.52 \times 10^{-7}$  cm<sup>2</sup>/sec, respectively. In conjunction with the previously determined  $\alpha_w$ 's, these values yield  $D_w = 2.5 \times 10^{-7}$  cm<sup>2</sup>/sec and  $4.83 \times 10^{-7}$  cm<sup>2</sup>/sec, respectively. The diffusion coefficient of water in the A(30) membrane is therefore only 50 times smaller than in pure water.

The diffusion of sodium salts in the investigated membranes was followed by desorption experiments. The initial slopes of  $C_t/C_0$  versus  $\sqrt{t}/l$ , shown in Figures 5 and 6, yield values of the diffusion coefficients summarized in Table V.

Values of  $D_s$  increase strongly with the increase in the fraction of PVP in the membranes. The apparent effect of the counter ion seems, in fact, to be due to the concentration dependence of  $D_s$  (sodium concentration in membranes equilibrated with 0.1N NaSCN is two to three times higher than in

TABLE IV  
 $g^*$ -Values and Apparent Pore Size of the Polymeric Alloy Membranes

Membrane designation	$(J_T/C_T) \times 10^5$ , cm/sec	$J_v \times 10^5$ , cm/sec	$\sigma$	$g^*$	$d$ , Å
A(20)	2.59	0.595	0.98	2.36	8.5
A(30)	6.45	2.15	0.95	3.88	12.4

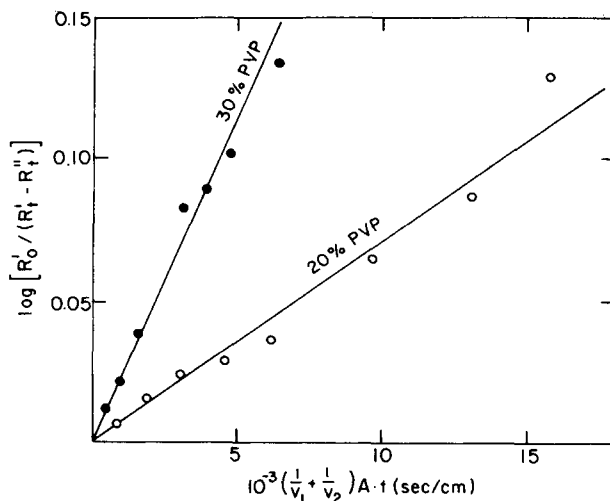


Fig. 4. Self-diffusion of tritiated water across polymeric alloy membranes: (O) 40- $\mu$ -thick A(20) membrane; (●) 29- $\mu$ -thick A(30) membrane.

those equilibrated with 0.1N NaCl). Nearly identical values of  $D_s$  were, indeed, obtained for membranes equilibrated with 0.02N NaSCN or 0.1N NaCl in which concentrations of sodium ions are similar.

Qualitatively, the concentration dependence of the diffusion coefficients is consistent with a site to site jump diffusion mechanism proposed by Eigen<sup>16</sup> which predicts

$$D_s = k\lambda^2 \quad (5)$$

where  $k$  is the rate constant of the decomplexation reaction at the bonding sites and  $\lambda$  is the average "jump" distance. Obviously, the average distance between the occupied and unoccupied sites increases with the increase in sodium concentration in the membrane. However, the experimentally ob-

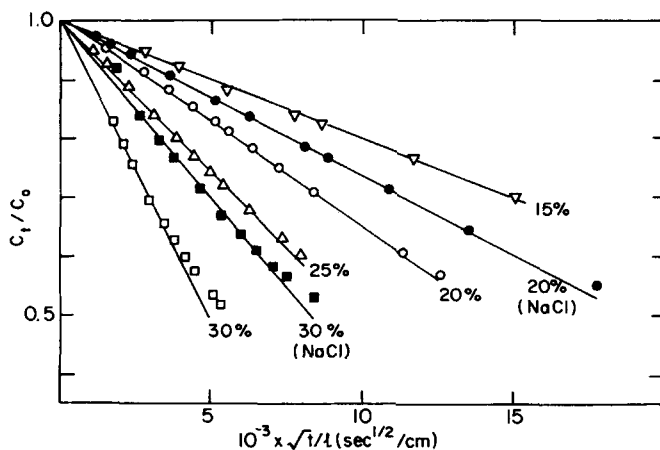


Fig. 5. Desorption of sodium salts at 25°C from the polymeric alloy membranes: ( $\nabla$ ) A(15); (O, ●) A(20); ( $\Delta$ ) A(25); ( $\square$ ,  $\blacksquare$ ) A(30). Open and full signs denote experiments in which membranes were equilibrated in 0.1M NaSCN and in 0.1M NaCl, respectively.

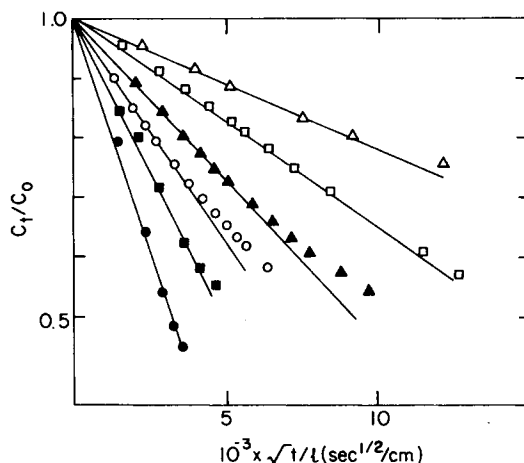


Fig. 6. Desorption of sodium thiocyanate at 25°C, A(20) and A(30) membranes equilibrated in: (Δ,▲) 0.02M NaSCN; (□,■) 0.1M NaSCN; (○,●) 1M NaSCN. Open and full signs denote A(20) and A(30) membranes, respectively.

served increase of  $D_s$  is larger than predicted by a simple model, e.g., the concentration of free sites,  $S'$ , is 1.09 in A(20) membranes which have been equilibrated with 0.02M NaSCN. On the other hand,  $S''$  is 0.70M in membranes which have been equilibrated with 0.1M NaSCN (cf. Table III). Thus, the ratio  $(\lambda''/\lambda')^2 = (S'/S'')^{2/3} = 1.34$ . Values listed in Table V yield, however,  $D_s''/D_s' \sim 2.2$ . Apparently, some structural changes, due to the presence of the absorbed salt in the alloy membranes, should also be considered to explain the observed concentration dependence of the diffusion coefficients.

Estimates based on application of eq. (5) yield  $D_s$  in the range of  $10^{-9}$ – $10^{-10}$  cm<sup>2</sup>/sec, hence of the same order of magnitude as the actually observed values of  $D_s$  in the alloy membranes. (The average distance between macrocyclic rings in the water-swollen alloy membranes is in the range of 8–12 Å, and the rate constants of decomplexation of the sodium complexes in various solvents at 25°C were found<sup>6</sup> to be in the range of  $(1.5-10) \times 10^4$  sec<sup>-1</sup>.) Such agreement may be coincidental. Nevertheless, it seems to provide some support for the assumption that values of  $D_s$  in these membranes are determined by the rate constants of the decomplexation reaction. An even stronger evidence supporting such an assumption is provided by the study of the

TABLE V  
Diffusion Coefficients of Sodium Salts in the Membranes

Equilibrating Solution	$D_s \times 10^{11}$ , cm <sup>2</sup> /sec				
	A(0) <sup>a</sup>	A(15)	A(20)	A(25)	A(30)
0.1M NaCl	—	—	13 ± 1	—	80 ± 10
0.02M NaSCN	—	—	9	—	60
0.1M NaSCN	0.44 ± 0.1 <sup>b</sup>	8.0	20 ± 6	70 ± 20	170 ± 30
1.0M NaSCN	—	—	116	—	470

<sup>a</sup> Membrane designation.

<sup>b</sup> After six months of conditioning in 0.1M NaSCN.

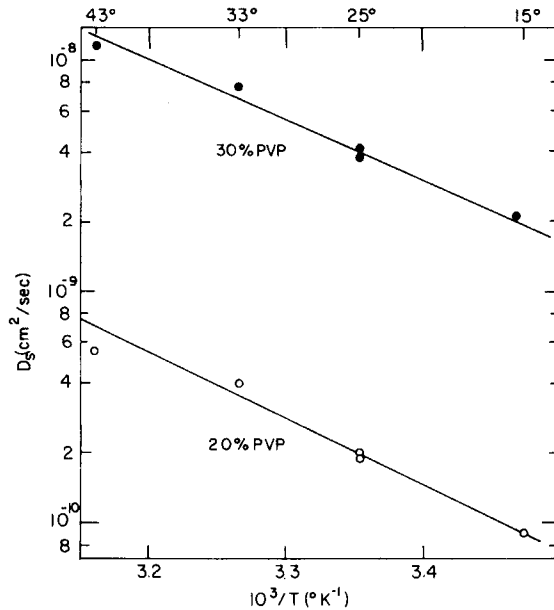


Fig. 7. Temperature dependence of the diffusion coefficients. Membranes equilibrated in 0.1M NaSCN: (O) A(20) membranes; (●) A(30) membranes.

temperature dependence of the diffusion coefficients. The semilogarithmic plots of  $D_s$  versus reciprocals of absolute temperatures, shown in Figure 7, yield value of  $\sim 12$  kcal/mole as the "energy of activation" of diffusion in A(20) and A(30) polymeric alloys. This value is essentially identical with the energy of activation of the decomplexation reaction in solution, which was previously determined<sup>6</sup> for the sodium ion complexes of the dibenzo-18-crown-6 derivatives.

In pure CP-6 membranes, the diffusion mechanism may be more complicated. In this system, the observed values of  $D_s$  are at least one order of magnitude lower than the estimated ones. Equation (5) is based on the explicit assumption that the time required for the transfer of the diffusing molecule from one site to another is much shorter than the time it stays at the bonding site, hence the term "jump" mechanism. In systems in which inert polymeric segments may act as barriers separating active sites, such an assumption may not always be justified. Apparently, this is the case in pure CP-6.

### Results of Reverse Osmosis (RO) Experiments

It is evident from the results discussed in the preceding sections that both PC-6 and its alloys with PVP are much more permeable to water than to salts and, therefore, may act as highly selective hyperfiltration membranes. Aromatic polyamides are used commercially in reverse osmosis water desalination units.<sup>17</sup> It seems, therefore, of great interest to compare the performance of the polymeric alloys of PC-6 with that of unmodified polyamides.

Accordingly, A(20) and A(30) membranes were tested under hyperfiltration conditions as well as under osmotic gradients. Pure PC-6 membranes

TABLE VI  
 Osmotic Characteristics of the Membranes<sup>a</sup>

		A(20) <sup>b</sup>	A(30)	A'(0) <sup>c</sup>	CA	I
RO	$P_w \times 10^7$ , cm <sup>2</sup> /sec	3.6	6.3 6.1 <sup>d</sup>	6.0	2.6	0.1-0.8
	Salt rejection, %	98.0 <sup>e</sup>	95 99.7 <sup>d</sup>	99.4	99.8	99.8
Direct osmosis	$\left(1 - \frac{J_s}{J_w \Delta C}\right) \times 100$	97.8	88.3	97.5	99.7 <sup>f</sup>	—
	$P_w \times 10^7$ , cm <sup>2</sup> /sec	3.6	7.3	6.0	2.5 <sup>f</sup>	—

RO experiments were conducted at 95-98 atm; 0.1N NaCl feed solutions were used in all, but one experiment (d). Tabulated results for direct osmosis are an average of three consecutive experiments on at least two different membranes, for  $\Delta C = 2.9N$  NaCl.

<sup>a</sup> Values quoted by Lonsdale<sup>17</sup> for the 2.5-cellulose acetate (CA) and Chemstrand aromatic polyamides (I) are listed for the sake of comparison.

<sup>b</sup> Membrane designation, the number in brackets indicates weight percent of PVP in the dry alloy. 20-30  $\mu$  thick membranes were used in these experiments.

<sup>c</sup> Membrane cast from 0.1M Ba(SCN)<sub>2</sub> in DMF.

<sup>d</sup> 0.1M MgCl<sub>2</sub> was used as feed solution.

<sup>e</sup> Tests with rhodamine B indicated presence of some imperfections in the membranes. We estimate that the limiting salt rejection is higher than 99%.

<sup>f</sup> Results from this laboratory.

cast from Ba(CNS)<sub>2</sub> in DMF solutions were also sufficiently stable (cf. Table II) to enable reliable determination of their hyperfiltration characteristics. Results of such experiments are summarized in Table VI. Inspection of the tabulated data reveals that the water permeabilities of the macrocyclic polyether-polyamides and of their blends with PVP are at least one order of magnitude higher than those of the Chemstrand aromatic polyamides, while their salt rejections are comparable. The osmotic characteristics of the A(20) and A'(0) seem also to be superior to those of cellulose acetate membranes.

The information about the x-ray diffraction pattern of the investigated membranes is based on experiments conducted by Dr. Ada Yonath.

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