

## Polyacrylic Desalination Membranes. I. Synthesis and Characterization

ALLAN S. HOFFMAN, MICHAEL MODELL, and PETER PAN,  
*Department of Chemical Engineering, Massachusetts Institute of Technology,  
Cambridge, Massachusetts 02139*

### Synopsis

A new class of desalination membranes has been developed. The membranes were prepared by polymerizing mixtures of two hydrophilic monomers (N-methylolacrylamide and acrylic acid), a hydrophobic monomer (ethyl acrylate) and a hydrophobic crosslinking monomer (trimethylol propane trimethacrylate) followed by heat treatment. The membranes were homogeneous, averaging about 6 mils in thickness. They were characterized by measuring water contents and salt distribution coefficients using an immersion technique. The fractional water contents in the membranes varied between 0.16 and 0.44 as the molal salt distribution coefficients increased from ca. 0.22 to 0.43. Increasing contents of the hydrophobic monomer and/or crosslinking monomer led to decreased water and salt contents, as expected. A model is postulated in which the water is assumed to be distributed within the polymer in two forms: (1) as primary water, hydrogen-bonded with hydrophilic polymer groups, and (2) secondary water, imbibed with salt from the external solution into hydrophilic regions or defects within the polymer matrix. It was found that primary water content was approximately constant for all compositions and varied between ca. 2-3 moles of primary water/mole of hydrophilic monomer in the membrane.

### INTRODUCTION

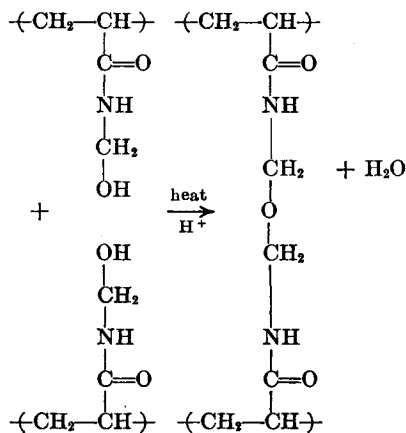
Within the last decade, it has been demonstrated that commercially available materials can be used in membrane form to desalinate water by reverse osmosis.<sup>1</sup> Of the materials studied previously, the most promising is cellulose acetate,<sup>2</sup> which rejects more than 98% salt from solutions as concentrated as sea water. For cellulose acetate and other uncharged membranes which are free of imperfections and pores, the solution-diffusion model has been found to describe adequately salt and water transport.<sup>3-7</sup> In this model, water and salt dissolve in the membrane at the interface with the feed solution and diffuse independently through the membrane under their respective chemical potential gradients. Thus, one of the essential requirements for desalination membranes is that they should preferentially absorb water over salt. In order to achieve this, the membrane should contain hydrophilic groups to imbibe water, along with hydrophobic groups and/or crystalline regions and/or crosslinks to prevent excessive swelling which would lead to sorption of too much salt along with the water.

In the work described here, desalination membranes were prepared by copolymerizing mixtures of hydrophilic, hydrophobic, and crosslinking monomers. The objective was to have sufficient flexibility in membrane composition so that desalination properties could be optimized. The synthesis of these membranes and characterization with respect to water and salt sorption are described here. Water and salt transport properties under conditions of reverse osmosis will be described in the following paper.

## PROCEDURE

### Selection of Monomer Systems

The first mixture polymerized consisted of acrylamide (AAM), N-methylolacrylamide (NMA), and acrylic acid (AAc). The AAM was chosen because the amide forms very strong hydrogen bonds. NMA was chosen because it is known to form crosslinks in the presence of heat and acid by the following condensation reaction:<sup>8,9</sup>



It was reasoned that ultrathin skins on a highly permeable support could be formed by a postpolymerization heat treatment of the surface of a relatively thick membrane. AAc was included in the monomer mixture so that the acid required for catalyzing the NMA crosslinking would be readily available within the membrane. Of course, carboxylic acid groups of AAc could subsequently also contribute to the transport of water through the membrane. Polymer films made from these mixtures exhibited excessive swelling in deionized water (>200 wt-% water based on dry gel weight) even after heat treatment of the entire membrane.

In an effort to reduce the swelling, AAM was replaced by ethyl acrylate (EA), which is a hydrophobic monomer. The results for the NMA-AAc-EA system are reported here as series E membranes. To reduce further the sorption of water by these membranes, a hexafunctional crosslinking monomer, trimethylol propane trimethacrylate (TPT), was incorporated in the

monomer mixture. The results for the NMA-AAc-EA-TPT systems are reported here as series TE and ET membranes.

### Materials

All monomers were used directly as received from the manufacturer without further purification. Acrylic acid and ethyl acrylate were obtained as pure monomers from Rohm and Haas Co.; trimethylolpropane trimethacrylate was obtained as a pure liquid from Sartomer Resins, Inc., and N-methylolacrylamide was obtained as a 60 wt-% aqueous solution from the American Cyanamid Company. Benzoyl peroxide (BP) and dimethyl aniline (DMA) were both reagent-grade chemicals.

### Membrane Preparation

The monomers to be polymerized were first mixed together in a beaker. Then 1 wt-% BP was dissolved in this mixture. Two drops of pure DMA were then added to 5 cc of the monomer solution and thoroughly mixed by shaking. After a few seconds, the color of the solution had turned light green and the solution was poured onto a Teflon-coated metal surface and covered by a clean, smooth glass plate. After 15 min, the monomers had polymerized and the glass plate was lifted off the substrate. The membrane remained attached to the glass plate. Some membranes were then heat treated for a prescribed period of time. Heat treatment consisted of either a 30-min exposure to a 250-watt infrared lamp at a distance of 3.5 in. from

TABLE I  
Composition of Membrane Synthesis Solutions<sup>a</sup>

Membrane no.	EA, mole-%	TPT, mole-%	Heat treatment	Hydrophilic compounds in membrane, <sup>b</sup> vol-%
E-1	10.2	0	IR lamp	77.0
E-2	18.7	0	" "	62.5
E-3	25.6	0	" "	52.7
E-4	31.4	0	" "	45.5
E-6	40.7	0	" "	35.7
ET-01	0	4.0	oven	56.3
ET-11	9.9	3.6	"	45.7
ET-21 (TE-12)	18.0	3.3	"	38.5
ET-21X	18.0	3.3	none	52.7
ET-31	24.8	3.0	oven	33.2
TE-02	18.7	0	oven	45.7
TE-12 (ET-21)	18.0	3.3	"	38.5
TE-22	17.6	6.5	"	33.2
TE-32	16.9	9.4	"	29.2

<sup>a</sup> All solutions contained H<sub>2</sub>O, AAc, and NMA in mole ratios of 19:12:5.

<sup>b</sup> Includes AAc + NMA + H<sub>2</sub>O if not oven treated, and just AAc + H<sub>2</sub>O if oven treated.

the membrane or a 20-min heating at 80°C in an oven. The membrane was then released from the glass plate by immersion in distilled water. Membranes prepared by this technique were between 6 and 8 mils thick and exhibited good mechanical properties; in addition, the thickness was quite uniform across any one membrane. Membrane compositions and their respective heat treatments are listed in the first four columns of Table I.

### Water Contents and Salt Distribution Coefficients

**Series Membranes.** Circular membrane samples of 1 in. diameter were first washed in deionized water and then immersed in fresh deionized water for five days at 25°C. They were then removed, gently blotted twice with dry Kimwipe tissue, and weighed in tared weighing bottles. The samples were dried in a vacuum desiccator (0.02 mm Hg) at room temperature for three days and then weighed in air after closing the weighing bottles. The fractional water content of the membranes,  $C_w^*$ , is reported as (weight loss in drying)/(weight of wet membrane). The samples were next immersed in a 1 wt-% NaCl solution at 25°C for four days. They were then removed, quickly dipped in deionized water, gently blotted twice with dry Kimwipe tissue, and immersed in 10 cm<sup>3</sup> of deionized water at 25°C for three days. An aliquot of this solution was then injected into a calibrated conductivity cell and the concentration was determined. The membrane salt content was calculated from this concentration. The procedure was then repeated using a 4 wt-% NaCl solution. Molal salt distribution coefficients were calculated and are reported as

$$K^* = \frac{(g_s/g_w)_m}{(g_s/g_w)_e} \quad (1)$$

where subscripts *s* and *w* are salt and water, respectively, and subscripts *m* and *e* are membrane and external solution phases, respectively. All time periods involved in these procedures and those described below were determined to be more than sufficient to reach equilibrium in the respective steps.

**Series ET and TE Membranes.** The procedure differed from that described above in that the water contents were determined in 1 and 4 wt-% NaCl solutions rather than in deionized water. Thus the samples were equilibrated in 1 wt-% salt, the wet weights were measured, and then the salt contents were determined by the conductivity procedure. The procedure was repeated for 4 wt-% NaCl solution. The dry membrane weights were then determined after drying for ten days in the vacuum desiccator. Water contents were calculated by difference between wet and dry weights; the weight of salt in the membrane was generally negligible compared to the weight of water. The molal salt distribution coefficients were again calculated from eq. (1).

In the determination of salt contents, all salt solutions were adjusted to pH 4.0 in order to suppress ionization of the carboxylic acid groups of acrylic acid.

## RESULTS AND DISCUSSION

### Reproducibility of Data

The average values and maximum deviations of the calculated water contents and salt distribution coefficients are reported in Table II. The maximum deviations for the series E membranes ranged from  $\pm 5\%$  to  $\pm 10\%$  for  $C_w^*$  and  $\pm 2\%$  to  $\pm 17\%$  for  $K^*$ , the largest deviations corresponding to the membrane with lowest water sorption. The reproducibility of values for the ET and TE membranes were significantly better; maximum deviations ranged from  $\pm 1\%$  to  $\pm 7\%$  for  $C_w^*$  and  $\pm 1\%$  to  $\pm 12\%$  (with most deviations around  $\pm 4\%$ ) for  $K^*$ .

The deviations probably resulted from the imprecision associated with the blotting procedure used to remove excess solution prior to weighing.

### Variation of $C_w^*$ and $K^*$ with External Salt Concentration

For series E membranes, calculated  $K^*$  values were significantly smaller for membranes equilibrated with 4 wt-% salt than for those with 1 wt-% salt. The shifts probably were the result of a decrease in water sorption with increasing external salt concentration. (Note that in calculating  $K^*$  for series E membranes, the water contents were assumed equal to those measured in deionized water.) A decrease in water activity in the external solution at higher salt contents should decrease water sorption within the membrane. In addition to this, increased salt concentration in the external solution should lead to increased salt sorption in the membrane. Since the solubility of organics in water generally decreases with increasing salt concentration, it is reasonable to expect that increasing the salt concentration in the membrane phase decreases the association of water with the organic hydrophilic groups, which in turn would also result in a decrease in membrane swelling (i.e., water sorption). Thus,  $K^*$  calculated at higher salt concentrations is lower than the true value since the  $(g_w)_m$  quantities used were higher than their true values. This discrepancy in  $K^*$  will be less pronounced at 1 wt-% salt than at 4 wt-% salt. Therefore, the comparisons of salt and water contents of series E membranes with series ET and TE described in later sections are based on the values for 1 wt-% salt solutions.

For series ET and TE membranes, the water contents and salt distribution coefficients did not vary significantly with external salt concentration. As discussed above, the salt distribution coefficients would not be expected to change because the water contents did not change. The insensitivity of the water contents of the ET and TE series membranes to external salt concentration is believed to be related to two factors: (1) the swelling tendency of these membranes is significantly less than that in the E series due to more effective crosslinking (as discussed below), and (2) the internal salt concentration is generally lower than that in the E series and, consequently, the effect of salt on the water-organic association is diminished.

TABLE II  
Water Contents and Salt Distribution Coefficients<sup>a</sup>

Membrane no.	$C_w^*$ deionized water	$C_w^*$		$K^*$	
		1 wt-% salt	4 wt-% salt	1 wt-% salt	4 wt-% salt
E-2	$0.44 \pm 0.02$			$0.43 \pm 0.03$	$0.36 \pm 0.03$
E-4	$0.28 \pm 0.02$			$0.41 \pm 0.01$	$0.33 \pm 0.01$
E-6	$0.21 \pm 0.02$			$0.37 \pm 0.04$	$0.24 \pm 0.04$
ET-01		$0.258 \pm 0.004$	$0.257 \pm 0.006$	$0.257 \pm 0.005$	$0.249 \pm 0.008$
ET-11		$0.239 \pm 0.002$	$0.232 \pm 0.002$	$0.242 \pm 0.007$	$0.231 \pm 0.012$
ET-21		$0.222 \pm 0.001$	$0.218 \pm 0.002$	$0.229 \pm 0.008$	$0.221 \pm 0.022$
ET-31		$0.198 \pm 0.004$	$0.197 \pm 0.004$	$0.213 \pm 0.004$	$0.201 \pm 0.024$
ET-21X		$0.244 \pm 0.016$	$0.243 \pm 0.012$	$0.240 \pm 0.007$	$0.233 \pm 0.003$
TE-02		$0.327 \pm 0.003$	$0.321 \pm 0.004$	$0.252 \pm 0.012$	$0.237 \pm 0.009$
TE-22		$0.190 \pm 0.006$	$0.185 \pm 0.001$	$0.230 \pm 0.006$	$0.227 \pm 0.002$
TE-32		$0.168 \pm 0.009$	$0.164 \pm 0.009$	$0.220 \pm 0.005$	$0.210 \pm 0.007$

<sup>a</sup> The reported values are averages of four determinations for series E membranes and three determinations for series ET and TE membranes. The limits reported are the maximum deviations from the average values.

### Effectiveness of Crosslinking

The water contents for membranes equilibrated with deionized water (series E) or 1 wt-% salt solution (series ET and TE) are presented as a function of EA concentration in the monomer mixture in Figure 1. The relative effectiveness of NMA and TPT crosslinking can be seen by comparing the water contents of swelled membranes with approximately equal EA concentration.

The effectiveness of NMA crosslinking in the absence of TPT can be evaluated by comparison of membranes E-2 and TE-02. The only difference here is that the former was infrared heat treated and the latter was oven heat treated. The decrease in  $C_w^*$  resulting from oven treatment is evidence that NMA (in the absence of TPT) is an effective crosslinking

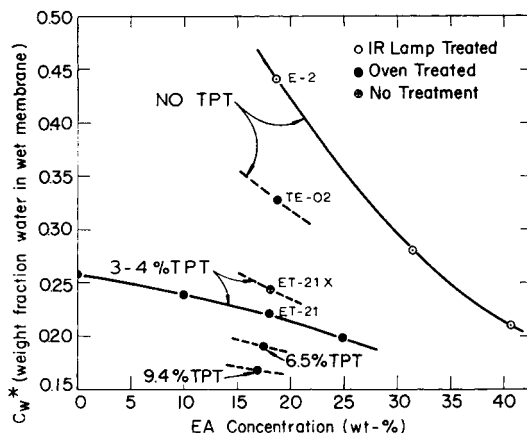


Fig. 1. Water contents of membranes as a function of ethyl acrylate (EA) content for varying trimethylol propane trimethacrylate (TPT) contents and heat treatments.

agent under proper heat treatment. The infrared heat treatment was insufficient to produce effective crosslinking in the TE-02 membrane, based on reverse osmosis performance (see part II, to follow this paper). It was for this reason that infrared heat treatment was discontinued after studying the series E membranes.

For membranes containing TPT, oven heat treatment also resulted in NMA crosslinking, as can be seen by comparing ET-21 and ET-21X. However, it can be seen by comparing E-2, TE-02, and ET-21X that TPT resulted in much more effective crosslinking than NMA. Effective crosslinking of membranes containing ca. 11 mole-% NMA in the absence of TPT decreased the fractional water content,  $C_w^*$ , from 0.44 to 0.33 (E-2 to TE-02), whereas a membrane containing 3.3 mole-% TPT (with about the same NMA concentration but not heat treated) showed a decrease in the water content from 0.44 to 0.24 (E-2 to ET-21X).

Mole for mole, TPT would be expected to be a more effective crosslinking agent than NMA. TPT is incorporated during polymerization whereas NMA is crosslinked after completion of polymerization. In the latter case, two NMA molecules on neighboring chains must be juxtaposed for a crosslink to be formed. Since NMA is presumably incorporated into the growing chains in a random manner, the rate of formation of an NMA crosslink should be roughly proportional to the second power of the NMA concentration. This rate would seem to be low for infrared lamp treatment of the membrane compositions studied here; the oven treatment appears to have been much more effective in causing NMA crosslinking.

### Variation of $C_w^*$ with Membrane Composition

Increased crosslinking (TPT) and/or increased hydrophobic monomer content (EA) resulted in decreased water contents, as discussed above. Under equilibrium swelling conditions, the water content is dependent upon a balance of two factors which affect water activity: (1) association of water with hydrophilic groups of the membrane, which tends to decrease water activity, and (2) the internal hydrostatic pressure created by the retractive force of the swollen crosslinked polymer network on the sorbed water, which tends to increase water activity. Thus, the equilibrium water content should depend upon the hydrophilic character of the membrane network and the effectiveness of crosslinking.

$C_w^*$  may be correlated with the hydrophilic content of the membrane. The hydrophilic content is defined in the following manner: the components in the synthesis mixture which would be expected to contribute to hydrophilic content are AAc, NMA, and  $H_2O$ . (It would seem reasonable to expect  $C_w^*$  to depend on the concentration of water present in the initial

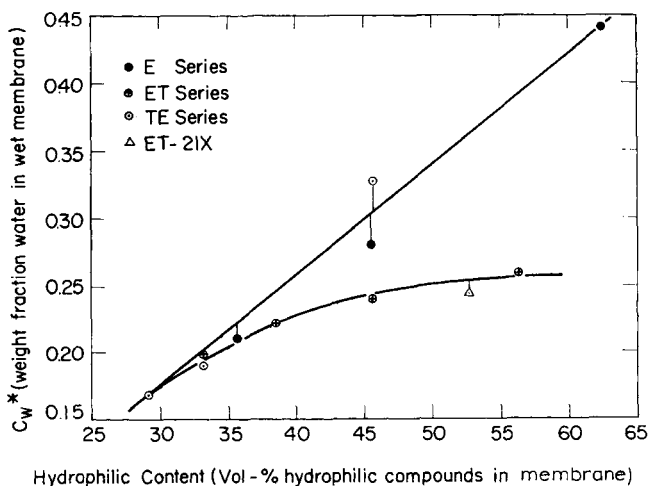


Fig. 2. Water contents of membranes as a function of hydrophilic content (see text for definition).



monomer mixture since the water is not expelled during the polymerization.) When the membrane is then oven treated at 80°C for 20 min, it may be assumed that the acid-catalyzed condensation of  $\text{>N-CH}_2\text{OH}$  groups goes essentially to completion, removing NMA as a significant contributor to the hydrophilic content of the membrane. It is likely that this condensation reaction did not occur to such a great extent throughout the membrane in the case of the infrared heating, and certainly it cannot be expected to proceed significantly in the absence of any postheat treatment. Based on these assumptions, the hydrophilic content of any membrane is defined as the sum of the volume fractions in the reaction mixture of AAc, H<sub>2</sub>O, and NMA (no oven treatment) or just AAc and H<sub>2</sub>O when the membrane was postoven treated. These values are listed in Table I.

The  $C_w^*$  values are plotted against hydrophilic content in Figure 2. Two general correlations are evident. For all membranes containing TPT, there is one curve showing a slow rise in water content with increase in hydrophilic content. For the four membranes not containing TPT, regardless of their heat treatment, the curve rises approximately linearly. These observations suggest that, in the absence of TPT, additional AAc, NMA, or H<sub>2</sub>O simply leads to imbibition of proportionate amounts of water, but that when TPT is added these groups or hydrophilic regions are no longer completely accessible to the water molecules and less than proportionate increases in swelling result.

#### Effect of Composition on Salt Content— Model of Swollen Membrane Structure

In a single-phase, three-component system of water, salt, and water-miscible organic (i.e., containing hydrophilic functional groups), the salt ions and hydrophilic groups are both solvated by the water. The competition for available water results in a mutual salting-out effect. In addition, it is known that the addition of water-compatible organics increases the activity of salt ions in water.<sup>2,10</sup> In such solutions, the salt activity coefficient is mainly dependent on the water concentration.<sup>10,11,12</sup>

These general observations for solutions may be applied qualitatively in interpreting the salt sorption data for the membranes studied here. For example, consider a polymer network swollen with salt solution. At equilibrium, the activities of salt and water are uniform throughout the matrix. The salt activity coefficient should be greatest in the vicinity of polymer chain to which hydrophilic groups are attached and should decrease continuously to a minimum value in the region farthest removed from the chains. Thus, the salt concentration should have a maximum value farthest from the chains. If the polymer is sufficiently swollen (i.e., if the distance between chains is large), the concentration of salt in the central region could approach that in the external solution (neglecting the small effect of hydrostatic pressure on salt activity). (Actually, in addition to the salting-out mechanism, one may postulate the existence of hydrophilic

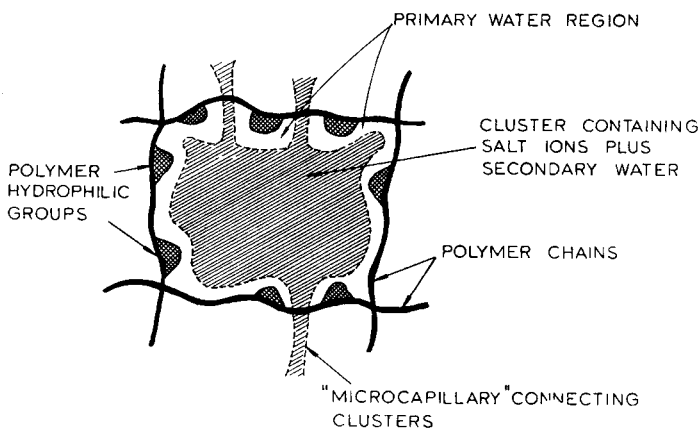


Fig. 3. Proposed model of hydrophilic clusters within the membrane microstructure.

clusters due to formation of microvoids or defects in the membrane structure based on the following other possible causes: (1) preassociation of hydrophilic monomers and/or water in the solution before polymerization; (2) presence of water and unreacted monomer molecules in the membrane after polymerization; (3) variations in monomer reactivity ratios leading to blocks of hydrophilic monomers along the polymerizing chains; and (4) microvoid formation due to polymerization shrinkage stresses.)

This model can be simplified somewhat by introducing an imaginary boundary in a manner analogous to the introduction of a Gibbs surface at an interface. In this case, the boundary separates the water-rich region into two regions: (1) secondary-bound water which is assumed to be relatively uninfluenced by the hydrophilic organic groups and therefore to contain the same concentration of salt as in the external solution, and (2) primary-bound water, which is closely associated with hydrophilic groups and is assumed to be free of salt. Figure 3 suggests the appearance of this model. (One is neglecting here the possible structuring of the water molecules into "icebergs," e.g.,<sup>13</sup> by the hydrophobic bonding along the polymer chains. This could have a significant effect on the distribution of salt and water within a swollen membrane, but it is difficult to estimate such an effect at this time.) These hydrophilic clusters are assumed to be interconnected by narrow hydrophilic passages (microcapillaries).

The concentrations of primary- and secondary-bound water can be calculated from the following equations:

$$K^* = \frac{(g_s/g_w)_m}{(g_s/g_w)_e} = \frac{x_{s_e}(C_{w2}^*/C_w^*)}{x_{s_e}} = \frac{C_{w2}^*}{C_w^*} \quad (2)$$

where  $C_w^* = C_{w1}^* + C_{w2}^*$  and  $C_{w1}^*$  and  $C_{w2}^*$  are, respectively, the weight fractions of primary- and secondary-bound water in the wet membrane (i.e.,  $g$  water/ $g$  wet membrane), and  $x_{s_e}$  is the weight fraction of salt in the external solution in equilibrium with the wet membrane. Values of these

TABLE III  
Primary and Secondary Water Contents

Membrane no.	$C_{w1}^*$ , wt fraction	$C_{w2}^*$ , wt fraction	Moles primary water per mole hydrophilic monomer
E-2	0.251	0.189	3.3
E-4	0.165	0.115	2.2
E-6	0.132	0.078	2.1
ET-01	0.192	0.066	2.3
ET-11	0.181	0.058	2.4
ET-21 (TE-12)	0.171	0.051	2.5
ET-31	0.156	0.042	2.8
ET-21X	0.185	0.059	
TE-02	0.245	0.082	2.8
TE-12 (ET-21)	0.171	0.051	2.5
TE-22	0.146	0.044	2.7
TE-32	0.131	0.037	2.9

parameters were calculated for membranes equilibrated in 1 wt-% salt and are presented in Table III. The moles of primary water per mole of hydrophilic monomer (NMA + AAc if no oven treatment; AAc only, if oven treated) are also presented in this table. It is interesting to note that these values vary roughly between 2 and 3 and, when TPT is present, the range narrows to between 2.3 and 2.9. It is easy to imagine two or three water molecules H-bonded to a  $-\text{CO}_2\text{H}$  group, with no hydrated salt ions in the vicinity.

In the absence of TPT, increasing EA concentration (E-2 to E-6) results in a 50% decrease in  $C_{w1}^*$  and a 60% decrease in  $C_{w2}^*$ . As EA concentration is increased, the membrane network becomes both more rubbery and more hydrophobic and salt is excluded as the region of secondary water shrinks. At the same time, the decreasing concentration of hydrophilic groups also results in a decrease of primary water.

Similar results are evident upon increasing EA concentration in the presence of TPT (ET series) although membranes ET-01 to ET-31 vary from brittle to rubbery behavior in this case. The changes in  $C_{w1}^*$  and  $C_{w2}^*$  are also less pronounced due to the presence of TPT.

In the TE series, increasing amounts of TPT cause a sharp reduction in both primary and secondary water, especially in the former. Furthermore, the levels of and decrease in primary water contents with increasing TPT in this series parallel those in the E series, while the secondary water contents in the TE series are about half those in the E series. The TE membranes go from rubbery to brittle behavior between TE-02 and TE-32.

It is concluded that when membrane composition is varied by selecting different types and amounts of hydrophilic, hydrophobic, and crosslinking monomers, one may control water and salt sorption in the membranes over

wide ranges. Such control of sorption characteristics should lead to control over flux and permselectivity in such membranes.

This research was sponsored by the U.S. Department of the Interior, Office of Saline Water, under Grant No. 14-01-0001-1256. The authors wish to thank Mr. T. A. Jadwin and Mr. Akif Azizoglu for their assistance in the laboratory.

### References

1. C. E. Reid and E. J. Breton, *J. Appl. Polym. Sci.*, **1**, 133 (1959).
2. J. S. Johnson, Jr., L. Dresner, and K. A. Kraus, in *Principles of Desalination*, K. S. Spiegler, Ed., Academic Press, New York, 1966.
3. H. K. Lonsdale, U. Merten, and R. L. Riley, *J. Appl. Polym. Sci.*, **9**, 1341 (1965).
4. A. S. Michaels, H. J. Bixler, and R. M. Hodges, *J. Colloid Sci.*, **20**, 1034 (1965).
5. U. Merten, H. K. Lonsdale, R. L. Riley, and D. K. Vos, *Reverse Osmosis for Water Desalination*, Office of Saline Water, Research and Development Progress Report No. 208, 1966. Govt. Printing Office, Washington, D. C.
6. W. Banks and A. Sharples, *The Mechanism of Desalination by Reverse Osmosis, and Its Relation to Membrane Structure*, Office of Saline Water, Research and Development Progress Report No. 143, 1965. Govt. Printing Office, Washington, D. C.
7. B. Keilin, *The Mechanism of Desalination by Reverse Osmosis*, Office of Saline Water, Research and Development Progress Report No. 117 (1964). Govt. Printing Office, Washington, D. C.
8. A. J. Hall, *Textile Finishing*, American Elsevier, New York, 1966, chapter 4.
9. D. H. Solomon, *The Chemistry of Organic Film Formers*, Wiley, New York, 1967, p. 265.
10. R. D. Lanier, *J. Phys. Chem.*, **69**, 2697 (1965).
11. C. F. Coleman, *J. Phys. Chem.*, **69**, 1377 (1965).
12. R. R. Davison, W. H. Smith, Jr., and D. W. Hood, *J. Chem. Eng. Data*, **11**, 304 (1966).
13. H. S. Frank and M. J. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

Received March 19, 1969

Revised June 11, 1969