

## Crosslinked Poly(hydroxyethyl Methacrylate) Membranes for Desalination by Reverse Osmosis

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### Synopsis

A series of crosslinked hydroxyethyl methacrylate (HEMA) membranes for reverse osmosis desalination has been prepared. The crosslinkers used were trimethylol propane trimethacrylate (TPT) or ethylene glycol dimethacrylate (EGD). Membranes were synthesized by polymerizing the monomers as a thin homogeneous film. In addition to reverse osmosis tests, the membranes were also characterized by osmosis experiments and sorption measurements. The reverse osmosis water flux (1500 psi applied pressure, 4% NaCl brine, pH = 5) for these membranes decreases from 0.6 gallon-mil/ft<sup>2</sup>-day (GMFD) to 0.055 GMFD and salt rejection increases from 78% to a maximum of 94% as the amount of TPT is increased from 0 to 11 mole-%. Water contents decrease from 42% to 15% over the same range of crosslinker, but the preferential sorption of water to salt does not vary. Thus, rises in reverse-osmosis semipermeability were found to result from changes in water-salt diffusivity ratios. The mechanism of permselectivity has been interpreted in terms of parallel diffusive fluxes across the membrane of primary H-bonded water and secondary water plus salt ions.

### INTRODUCTION

Reverse osmosis has been of interest as a method for desalinating brackish water or sea water since 1959 when Reid and Breton<sup>1</sup> at the University of Florida reported that membranes composed of cellulose acetate could provide up to 99% rejection from salt solutions, although with extremely low flow rates. Loeb and Sourirajan<sup>2</sup> increased the commercial potential of reverse osmosis as a competitive method of desalination by producing an asymmetric cellulose acetate membrane. They were able to achieve flow rates an order of magnitude higher than that observed by Reid and Breton with no loss of salt rejection. Although cellulose acetate is by no means the only material semipermeable to salt solutions, it has received most of the attention for reverse osmosis applications because its rejection characteristics are good and it can be made effectively as an ultrathin membrane on a porous sublayer. These asymmetric membranes provide 98%-99% rejection and flow rates of 10 gallons/ft<sup>2</sup>-day (GFD) from sea

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water brines at 1500 psi applied pressure.<sup>3</sup> However, better materials for reverse osmosis desalination are continually being sought. Not surprisingly, a rather fruitful area of research has been with other celluloses, e.g., disubstituted cellulose nitrate is capable of 99% salt rejection from 4% NaCl solutions at 1800 psi applied pressure.<sup>4</sup> Several noncellulosics have also shown promise, among them polyurethanes, poly(vinyl alcohol), poly(hydroxyethyl methacrylate), and poly(vinylene carbonate).<sup>5,6</sup> Membranes with ionogenic groups are also capable of rejecting salt in dilute solutions (e.g., 0.1*N*) by a Donnan-type exclusion.<sup>7</sup> The work reported here is on the preparation of membranes by polymerization of monomer mixtures in thin homogeneous films. In searching for new membrane materials, it is considered to be advisable initially to test homogeneous, thin membranes (e.g., 4–5 mils) thereby reducing the problem of pinholes. A pinhole not affecting the water flux to any great extent may still decrease the salt rejection. Once a membrane having superior permeability characteristics is found, one may then profitably expend some effort to develop a defect-free, ultrathin skin or asymmetric membrane.

### CRITERIA FOR SELECTION OF THE MONOMER SYSTEM

A survey of uncharged membranes, i.e., those not dependent on Donnan exclusion for semipermeability, reveals that hydrogen-bonding groups are desirable for good salt rejection. Reid and Breton<sup>1</sup> first proposed that water may be transported across a membrane by successive bonding to these groups, and salt is rejected because it is unable to form hydrogen bonds. If this mechanism is correct, the small salt flux found in semipermeable membranes may be either through pinholes (Poiseuille flow) or by diffusion under a concentration gradient where there is a small water flux associated with the diffusing salt ions which is not involved in H-bonding with the polymer hydrophilic sites.

It is convenient to divide the membrane water content, perhaps arbitrarily, into water bound to hydrophilic groups ("primary" water) and unbound water ("secondary" water).<sup>8</sup> High water contents are desirable in a membrane since they generally lead to high water fluxes. However, a membrane with a high total water content would be expected to contain a high secondary water content also and consequently to display high salt permeabilities. Distribution of water in the membrane is also important. Ideally water should be molecularly distributed in the membrane; clusters or pockets of water could lead to increased salt transport. Molecular dispersion of water is aided by a random distribution of hydrophilic groups in the membrane; however, there still must be a means to control membrane swelling in order to keep the secondary water content at a minimum.

Several methods may be utilized to accomplish this: the hydrophilic-hydrophobic ratio in the polymer may be varied, or the presence of crystallites and/or crosslinks may be employed. Changing the hydrophilic-hydrophobic ratio in a membrane as the sole means of regulating water

contents usually involves a reduction in the number of hydrogen bonding sites. The last method seems particularly desirable, because one may include a relatively large number of hydrophilic groups while still closely controlling the membrane water content. Thus, the approach taken in the study reported here was to polymerize various mixtures of a relatively hydrophilic monomer with a hydrophobic crosslinking monomer.

Other considerations in selecting the monomer systems to be studied include physical stability under reverse osmosis conditions, e.g., the membrane should not be subject to cold flow, and crosslinks should be helpful in this regard. Resistance of the membrane to bacterial or chemical attack is also necessary.

Graves<sup>9</sup> found that crosslinked poly(hydroxyethyl methacrylate) (HEMA) showed some promise as a reverse osmosis membrane<sup>5,10</sup>. Filter paper was impregnated with monomers of HEMA, varying amounts of ethylene glycol dimethacrylate (EGD) crosslinker, a peroxide initiator, and water or methanol. Heat was then applied to polymerize the monomers. The addition of water or methanol to the monomers served to increase openness of the membrane structure. Rejections of up to 87.6% at a flow rate of 0.17 gallon-mil/ft<sup>2</sup>-day (GMFD) were obtained with these membranes for 4% NaCl solutions and 1700 psi applied pressure. While the results of Graves were encouraging, the exact role of the reinforcing material remained in doubt. Membranes prepared without a reinforcing agent gave negligible rejection because bubble formation during polymerization resulted in pinholes. Furthermore, filter paper was found to be superior to other reinforcing agents for good rejection—flow rate properties. True permeabilities of HEMA membranes also could not be determined since this was a heterogeneous system.

The structure of HEMA suggests it might have semipermeable characteristics. Like cellulose acetate, it has both ester and hydroxyl groups. Unlike cellulose acetate, HEMA polymers are very resistant to hydrolysis; conditions which would completely hydrolyze cellulose acetate, or for that matter an acrylate polymer, have no effect on a methacrylate polymer.<sup>11</sup> The  $\alpha$ -methyl groups on the polymer chain evidently impart hydrolytic stability to these membranes. Water contents of HEMA polymers may also be readily controlled by the incorporation of crosslinking agents. Therefore, HEMA membranes with trimethylol propane trimethacrylate (TPT) or ethylene glycol dimethacrylate (EGD) as crosslinking agent were selected for study, and a new polymerization technique was developed so that thin, homogeneous, unreinforced membranes could be prepared.

## EXPERIMENTAL

### Membrane Preparation

The membranes were prepared by directly polymerizing the monomers as a thin film. Hydroxyethyl methacrylate (HEMA) and methacrylic acid (MAAc) monomers were supplied by Rohm and Haas Company.

Trimethylol propane trimethacrylate (TPT) or ethylene glycol dimethacrylate (EGD) monomers, supplied by Sartomer Resins, Inc., were used as crosslinking agents. The monomers were generally used without further purification.

The monomers were weighed to the nearest 0.0001 g, mixed with 0.5 mole-% benzoyl peroxide, and filtered to remove any dust particles. Immediately before forming a membrane, 1 vol-% of N,N-dimethylaniline was added to the solution; this acts as an accelerator for the decomposition of the benzoyl peroxide catalyst and allows room temperature polymerizations.<sup>12</sup> The membranes were generally 5–7 mils thick in order to reduce the danger of pinholes and were stored in distilled water prior to evaluation.

No reinforcing material was required for these membranes, unlike those prepared by Graves.<sup>10</sup> Apparently, this is because no hole-forming diluents were incorporated with the monomers in this study.

### Salt and Water Sorption

Salt and water sorptions were determined by equilibrating the membranes in a salt solution at 25°C for nearly a week. They were then taken out, their thickness and diameter were determined, and they were replaced in the solution for another day. Next, they were removed from the solution, quickly dipped in deionized water to remove excess surface salt solution, blotted, weighed, and equilibrated in a known volume of deionized water for at least three days to leach the salt out of the membrane. The volume of deionized water was always large compared to the water in the membrane. The concentration of salt in the leach water was determined conductimetrically. A conductivity meter (Radiometer, Type CDM 2) and cell (Radiometer, Type CDC 114) were calibrated with solutions prepared from reagent-grade salts. Finally, the membranes were dried in a vacuum desiccator and weighed. Knowing both the volume and weight of the wet membrane, weight of the polymer salt, and water in the membrane, water contents and salt distribution coefficients could be determined.

### Reverse Osmosis Experiments

Membranes to be tested for reverse osmosis properties were placed in a pressure cell shown in Figure 1. The cell was constructed of stainless steel to minimize corrosion. The membrane was supported by a sintered stainless steel disc. A magnetic, Teflon-coated stirrer bar placed above the membrane minimized concentration polarization; this is a concentration buildup occurring because most of the salt is unable to pass through the membrane.<sup>3</sup> The stirrer bar was driven by a magnetic stirrer motor beneath the pressure cell. A Sprague diaphragm pump pressurized the salt solutions.

Reverse osmosis tests were allowed to run at least for two weeks, and usually a month, assuring that the membranes were stable under these

conditions. Values for flow rates and rejections are therefore averages taken over several days after the membranes reached steady state. Generally close to a week was required to attain steady state; part of this was due to the need to flush out the downstream compartment.

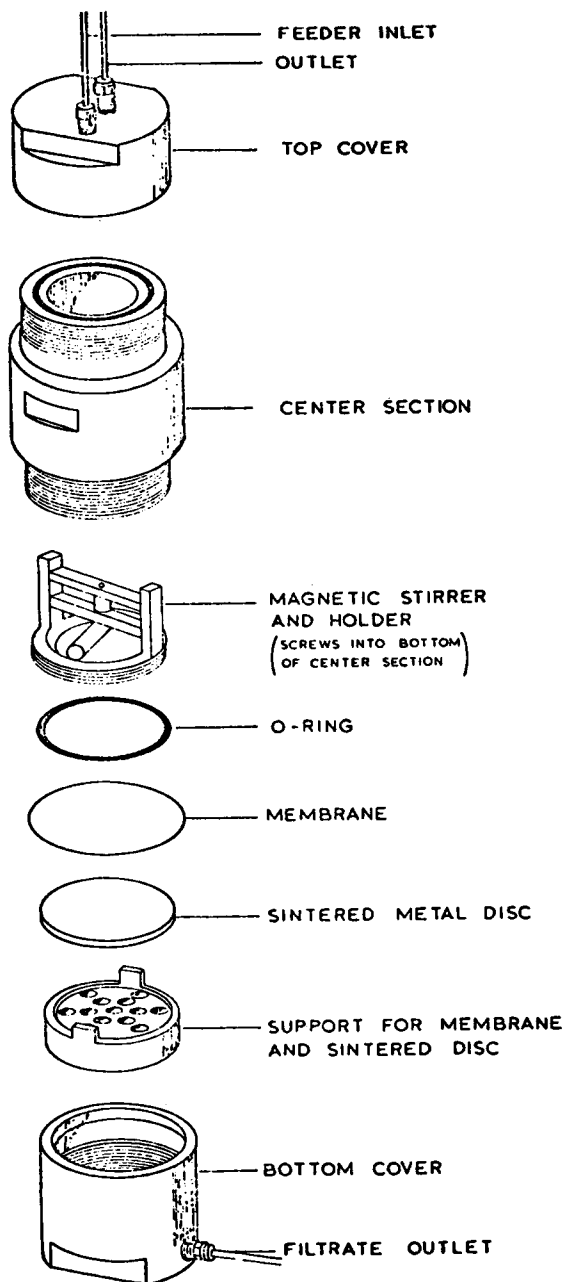


Fig. 1. Exploded view of pressure cell.

Flow rates for these membranes are normalized to 1 ml, since they are homogeneous and do not have an asymmetric structure. (This was confirmed by determining that membrane properties were not dependent on which side of the membrane the pressurized brine faced.)

Salt concentrations of the desalinated water were determined conductimetrically.

Corrosion products, harmful because they foul membrane surfaces, could be kept in solution by including 250 ppm of (ethylenedinitrilo)-tetraacetic acid disodium salt (EDTA) in the brine. With this concentration of EDTA, the brine had a pH of about 5.

### Salt Osmosis Experiments

A limited number of salt osmosis tests were performed in a cell made from two matched squares of Plexiglas, each with circular compartments and ports for filling with solutions. A membrane sealed with soft rubber gaskets separated the two compartments. The compartments were filled on one side with a concentrated salt solution and on the other side with deionized water. Agitation was provided by a shaker to which the osmosis cell was fastened. After predetermined lengths of time, a small amount of solution was removed from the dilute compartment, its concentration was measured conductimetrically, and was then immediately returned to the cell. This complete procedure took about 4 min. The overall salt osmosis experiment took about 4 hr, generally. Water permeabilities were not determined.

## RESULTS AND DISCUSSION

### Mass Transport Equations

The analysis of membrane transport in the most general terms would be through the use of irreversible thermodynamics.<sup>13</sup> However, as a good approximation, the solution-diffusion model developed by Lonsdale et al.<sup>14</sup> may be used for systems exhibiting high salt rejection, wherein the transport of solute and solvent is assumed to be uncoupled. That is, flow of one component has no effect on the flux of the other. The equation derived by Lonsdale et al. for water transport is

$$J_w = \frac{D_w C_{wm} \bar{V}_w}{RT} \left( \frac{\Delta P - \Delta \pi}{\Delta x} \right) \quad (1)$$

where  $J_w$  = water flux (g/cm<sup>2</sup>-sec),  $D_w$  = water diffusion coefficient (cm<sup>2</sup>/sec),  $C_{wm}$  = water content in the membrane (g/cm<sup>3</sup> wet membrane),  $R$  = gas constant,  $T$  = absolute temperature (°K),  $\bar{V}_w$  = partial molar volume of water (cm<sup>3</sup>/mole),  $\Delta P$  = applied pressure difference (psi),  $\Delta \pi$  = osmotic pressure difference (psi), and  $\Delta x$  = membrane thickness (cm).

Equation (1) was derived by starting with Fick's law and converting a concentration-driving force to a chemical potential-driving force by assuming that the membrane-water system follows dilute solution rules. The water permeability  $P_w$  is defined as

$$P_w = D_w C_{wm} \quad (2)$$

From Fick's law and converting to bulk solution concentrations through the molar distribution coefficient  $K$ , Lonsdale et al.<sup>14</sup> obtained the following equation for salt transport:

$$J_s = -D_s K \frac{\Delta C_{SB}}{\Delta x} \quad (3)$$

where  $J_s$  = salt flux (g/cm<sup>2</sup>-sec),  $\Delta C_{SB}$  = bulk solution concentration difference across the membrane (g/cm<sup>3</sup>),  $D_s$  = salt diffusion coefficient (cm<sup>2</sup>/sec), and  $K$  = molar distribution coefficient (g salt/cm<sup>3</sup> wet membrane/g salt/cm<sup>3</sup> solution).

The salt permeability ( $P_s$ ) is defined as

$$P_s = D_s K \quad (4)$$

Another quantity commonly used in describing reverse osmosis transport is the percent salt rejection ( $\%R_s$ ),

$$\%R_s = \frac{\Delta C_{SB}}{C_{SB}'} \times 100, \quad (5)$$

where  $C_{SB}'$  is the concentration of the feed brine.

Osmosis experiments are those where a membrane separates two compartments of unequal salt concentration at atmospheric pressure. After steady state is reached in such an experiment, a plot of total salt diffused versus time is a straight line given by<sup>15</sup>

$$Q_s = \frac{D_s K C_{SB}'}{\Delta x} \left( t - \frac{\Delta x^2}{6D_s} \right) \quad (6)$$

where  $Q_s$  = total amount of salt diffused per unit area in time  $t$  (g/cm<sup>2</sup>),  $C_{SB}'$  = concentrated bulk solution concentration (g/cm<sup>3</sup>) (the dilute compartment salt concentration is always negligible compared to the concentrated compartment), and  $t$  = time (sec).

Equation (6) is derived by integrating Fick's second law and retaining only the steady-state terms. Both  $D_s$  and  $K$  are assumed independent of salt concentration and constant with time. Although both the permeability ( $D_s K$ ) and the diffusivity are obtainable from a plot of  $Q_s$  versus  $t$ , the uncertainty in the intercept (and thus in  $D_s$ ), is greater than that in the slope (or  $D_s K$ ). Therefore, diffusivities were determined by performing a separate sorption experiment to determine the distribution coefficient  $K$  and then dividing  $D_s K$  (obtained from the slope) by this value.

Transport equations developed from irreversible thermodynamics take into account the possibility that water and salt fluxes may be independent or coupled.<sup>13</sup> In osmosis experiments, water and salt flux are in opposite directions. However, for reverse osmosis transport, both salt and water are transported in the same direction. Therefore, if salt and water transport are closely coupled, osmosis tests should give lower salt permeabilities than reverse osmosis experiments because the water flux in the former would oppose the salt flux. The solution-diffusion model, on the other hand, predicts that salt permeabilities will be the same for both experiments. For membranes investigated in this study, osmosis salt permeabilities were found to be essentially identical to reverse-osmosis salt permeabilities (extrapolated to atmospheric pressure, to avoid the complication due to membrane compaction) which supports use of the solution-diffusion model.

### Water Sorption

Figure 2 gives the water sorption for TPT- or EGD-crosslinked HEMA membranes as a function of added crosslinker. It should be pointed out that membranes which contain no added crosslinker are actually lightly crosslinked with EGD impurities present in HEMA monomer. (There is also a small amount of methacrylic acid present in the HEMA monomer.) It is evident that TPT is more effective in reducing water content than

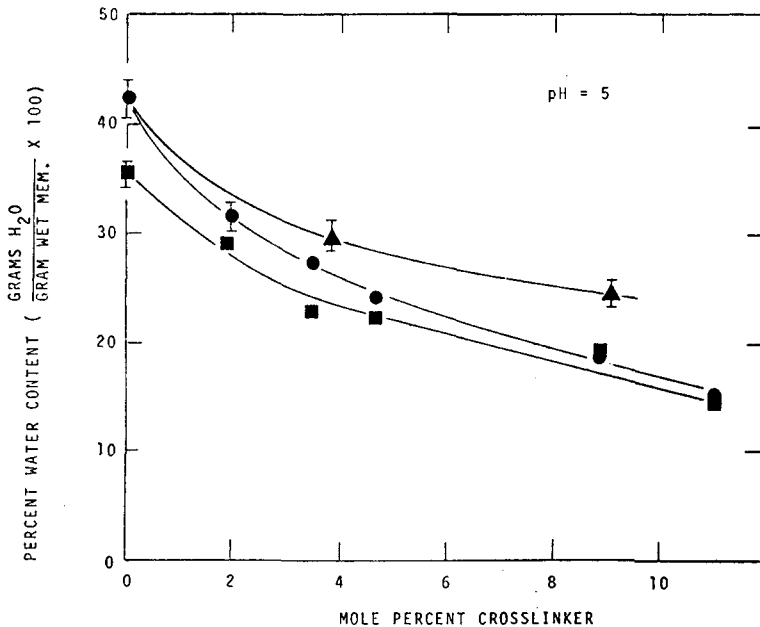


Fig. 2. Water content of HEMA membranes as a function of crosslinking monomer content; pH = 5: (▲) EGD, distilled water; (●) TPT, distilled water; (■) TPT, 4.0 wt-% NaCl.



EGD for a given amount of crosslinker, as expected of a trivinyl crosslinking agent compared to a divinyl one.

Increased crosslinking generally results in lower sorptions of liquids in polymers.<sup>16,17</sup> This is particularly true for polymers that sorb appreciable amounts of penetrant. The swelling of a crosslinked network involves opposing forces; tendency toward solution is resisted by the elastic retractive force of the network as the chains between crosslinks are elongated. This retractive force is caused by a decrease of entropy as the polymer chains are distorted from their most probable conformation.<sup>18</sup> At higher levels of crosslinking, equilibrium between these opposing forces occurs at lower degrees of swelling.

HEMA membranes with no added crosslinker are quite swollen in distilled water and have a water content of 42 wt-%. Refojo<sup>19</sup> reported a water content of 41.09 wt-% for similar HEMA polymer membranes equilibrated in distilled water. It may be noted in Figure 2 that these membranes deswell with increasing salt concentration; this may be simply due to the lower activity of the water. However, Refojo has found marked dependence of swelling behavior on salt species, indicating a more complex situation. He suggests that certain ions reduce the solvent power of water for HEMA polymers and therefore cause increased interaction between the hydrophobic portions of the polymer chain. This phenomenon is sometimes referred to as hydrophobic bonding, and these hydrophobic bonds act as additional "crosslinks" in the membrane. At high crosslink densities (11 mole-% TPT), water contents decrease to 15 wt-%, a value only slightly higher than cellulose acetate.<sup>14</sup> (Unless otherwise stated,

TABLE I  
Salt and Water Sorption Results for Various Salt Species<sup>a</sup>

TPT crosslinker, mole-%	Water content, wt-%	Molar dist. coeff. <i>K</i>	Molal dist. coeff <i>K</i> *	Water molecules per hydroxyl group
		LiCl		
0	32.8	0.228	0.612	3.52
4.63	21.8	0.137	0.527	2.28
8.85	17.5	0.0937	0.496	1.91
		NaCl		
0	33.1	0.130	0.320	3.57
4.63	22.3	0.087	0.330	2.35
8.85	19.2	0.073	0.315	2.15
		KCl		
0	32.8	0.131	0.345	3.53
4.63	21.2	0.0884	0.348	2.19
8.85	17.6	0.0703	0.325	1.93

<sup>a</sup> Salt concentration = 0.7*N*; pH = 4; temperature = 25°C. (Data are averages of at least three membranes.)

the term cellulose acetate will refer to a membrane of 39.8% acetyl content.) Also, as the amount of crosslinking is increased, it can be seen in Figure 2 that swelling differences between distilled water and salt solutions become negligible; this may possibly be due to increased restraint on the polymer chains preventing rearrangements to form hydrophobic bonds.

Water sorption for a limited number of TPT crosslinked membranes equilibrated with various salt species is shown in Table I. For the salts chosen (LiCl, NaCl, and KCl), the water content is apparently not a function of salt species, within experimental accuracy of the determination. Refojo<sup>19</sup> likewise found that swelling differences of HEMA membranes in these three salt solutions were small at equal molarities.

The number of water molecules per hydroxyl group is readily calculated, and these results are also shown in Table I. As may be seen in Table I, the net effect of crosslinking is to reduce the number of water molecules from about 3.5 at no added crosslinker to approximately 2 per hydroxyl group at 8.85 mole-% TPT. Three possibilities exist for hydroxyl groups in the membrane: (1) they may bond to water molecules, (2) they may bond to each other, or (3) they may be unbonded to water or to each other. At low levels of crosslinking, possibility (1) would predominate, but as the crosslinking was increased; (2) and (3) would become more important. Of course, if the water is either partially or wholly distributed as clusters of secondary water, then the effect of increasing crosslinking may be simply to decrease the number and/or size of these clusters, and the number of water molecules per hydroxyl group loses physical significance.

### Salt Sorption

The molar distribution coefficient  $K$  is shown in Figure 3 as a function of crosslinking monomer concentration for TPT-crosslinked membranes;  $K$  decreases from over 0.13 with no added crosslinker to slightly less than 0.06 at 11 mole-% TPT. This is in all cases higher than cellulose acetate, whose molar distribution coefficient is about 0.035 in 4% NaCl.<sup>14</sup>

However, the molar distribution coefficient does not reveal the selectivity of a membrane for water over salt. For example, polyethylene will have an extremely low molar distribution coefficient, i.e., based on the volume of wet membrane, because it sorbs little water. A *molal* distribution coefficient  $K^*$  defined as

$$K^* = \left( \frac{\text{grams salt}}{\text{gram water}} \right)_{\text{membrane}} / \left( \frac{\text{grams salt}}{\text{gram water}} \right)_{\text{solution}} \quad (7)$$

gives directly this selectivity of water to salt. Figure 4, a plot of  $K^*$  versus mole-% TPT crosslinker, shows that this molal distribution coefficient remains practically constant at 0.32 over the entire range of crosslinker. Therefore, a decreasing *molar* distribution coefficient  $K$  in Figure 3 merely reflects the decreased water content of the membrane, not any increase in preferential sorption of water.  $K^*$  for cellulose acetate was

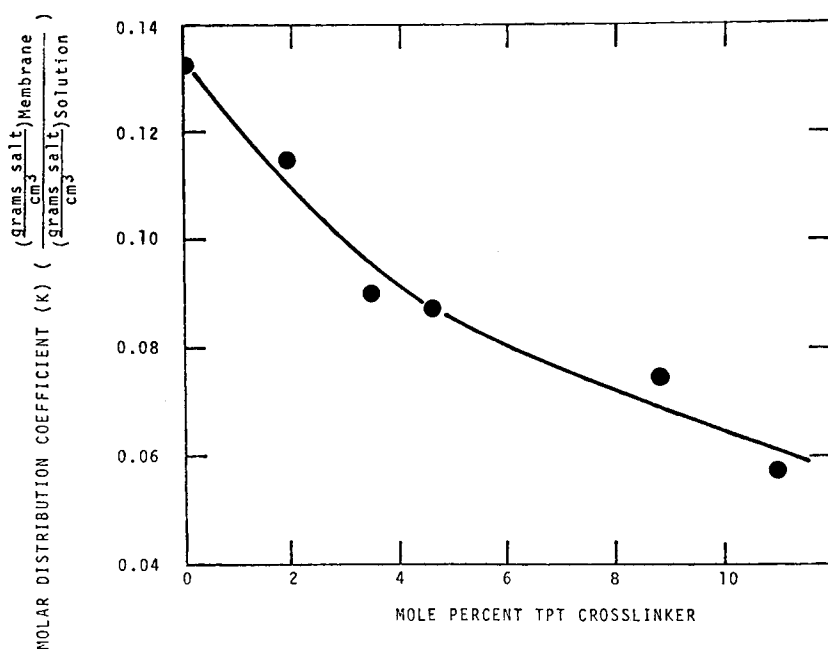


Fig. 3. Molar salt distribution ratio,  $K$ , of HEMA membranes as a function of TPT-crosslinking monomer content; pH = 5; external salt concentration = 4.0 wt-% NaCl.

found to be 0.24 (based on equilibration in 10% NaCl) which is not strikingly lower than values obtained for HEMA membranes.

The manner in which water is distributed in a membrane is possibly reflected by  $K^*$ , lower values signifying greater molecular dispersion of this water. A more specific interpretation of  $K^*$  may be made in terms of a primary-secondary water concept. If one assumes that the primary water does not sorb salt while the secondary water has a salt concentration equal to that in the bulk solution,<sup>20</sup> then

$$K^* = \frac{\text{grams of secondary water in the membrane}}{\text{grams of total water in the membrane}} \quad (8)$$

On this basis, the secondary water content in HEMA membranes is approximately one third of the total water content, at least for sodium chloride solutions. Increasing crosslink density decreases the total water content but does not appear to affect the ratio of secondary to total water, or, consequently, the ratio of primary to secondary water.

Both molar and molal distribution coefficients are given in Table I for HEMA membranes equilibrated in solutions of LiCl, NaCl, or KCl. Membranes equilibrated in NaCl and KCl solutions have similar distribution coefficients, but those equilibrated in LiCl solutions sorb appreciably more salt. This high sorption may be due to specific interactions between

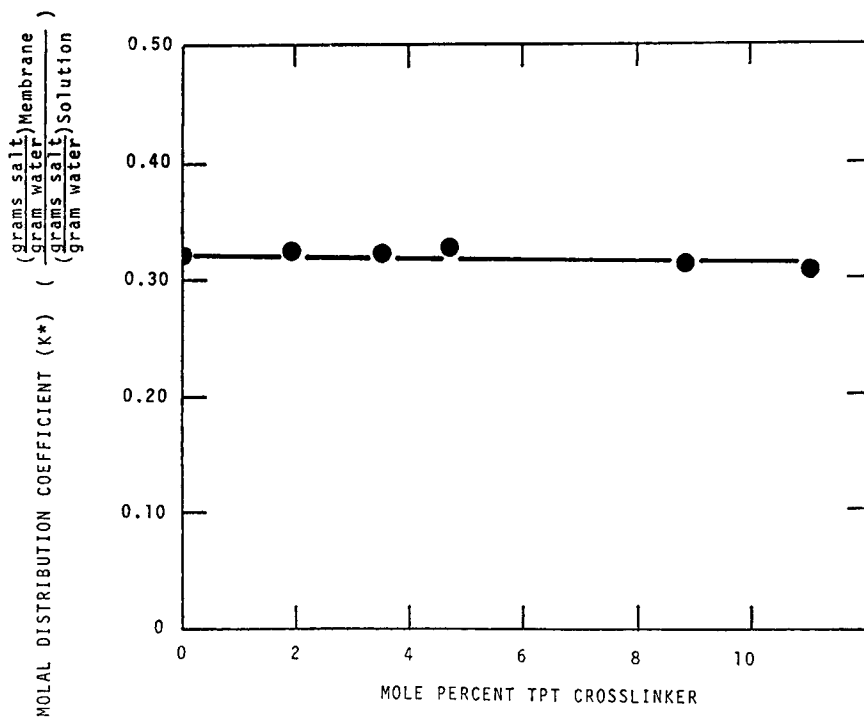


Fig. 4. Molal salt distribution ratio,  $K^*$ , of HEMA membranes as a function of TPT-crosslinking monomer content; pH = 5; external salt concentration = 4.0 wt-% NaCl.

the incompletely hydrated lithium ion and hydrophilic groups in the membrane (and thus  $K^*$  may overestimate the secondary water content in this system). The solubility of both NaCl and KCl in ethanol, which may be crudely thought of as an organic liquid analogue to HEMA membranes, is less than 0.1%; however, the solubility of LiCl in ethanol is about 20%.<sup>21</sup> It should be mentioned that the order of distribution coefficients found for HEMA membranes in this study,  $\text{LiCl} > \text{NaCl} \approx \text{KCl}$ , does not agree with that found by Thomas and Barker<sup>22</sup> for cellulose acetate membranes, namely,  $\text{NaCl} > \text{LiCl} > \text{KCl}$ . However, it has been pointed out<sup>3</sup> that the 48-hr immersion times allowed by Thomas and Barker may have been too short for attainment of equilibrium in cellulose acetate membranes, particularly for more slowly diffusing salts such as LiCl.

### Reverse Osmosis Properties

The water flux for TPT-crosslinked and a limited number of EGD-crosslinked membranes, expressed as gallon-mil/ft<sup>2</sup>-day (GMFD), is given in Figure 5. Each point is a separate membrane and is an average water flux obtained during at least two weeks of operation. Flow rates decrease most rapidly for small added amounts of crosslinker, dropping from 0.6

GMFD for no added crosslinker to 0.25 GMFD with 1.96 mole-% TPT. After this, the decrease in water flux with added crosslinker is less. Water fluxes are higher for a given amount of EGD compared to TPT crosslinker, but if water fluxes were correlated with the molecular weight between crosslinks (assuming 100% efficiency of the crosslinking reaction), the two curves would be identical.

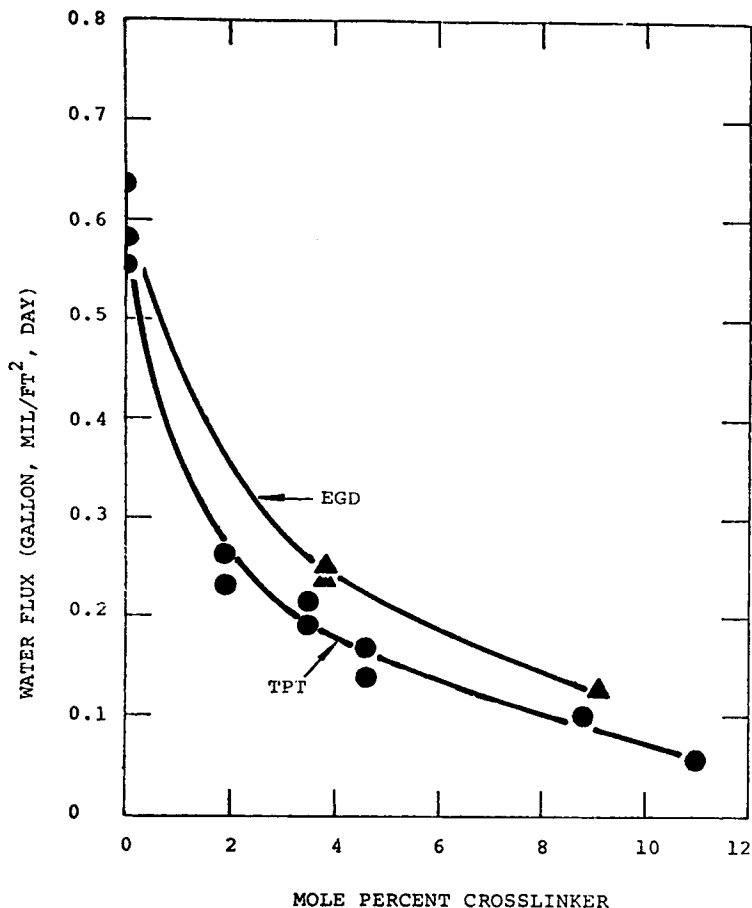


Fig. 5. Water flux through HEMA membranes as a function of crosslinking monomer content; applied pressure = 1500 psi; salt concentration = 4.0 wt-% NaCl; pH = 5.

Investigations with crosslinked membranes have shown decreasing permeabilities with increasing crosslink density.<sup>16,23</sup> From eq. (2), the water permeability is composed of both a diffusion and a solubility term; increased crosslinking can decrease values of both. The diffusion coefficient is decreased for two reasons: first, there is restricted segmental mobility due to shorter chain distances between crosslinks, and second, the lower

water contents result in a reduced plasticization effect. Water contents are reduced for reasons discussed previously.

Salt rejections for crosslinked HEMA membranes under reverse osmosis operation are given in Figure 6. Rejections increase with added crosslinker from 78% to a maximum of 94% at 8.85 mole-% TPT. There is a slight decrease in rejection at 11 mole-% TPT, but this trend is not firmly established since only one membrane was tested at this high crosslink density. In any event, the water permeabilities of membranes above 9 mole-%

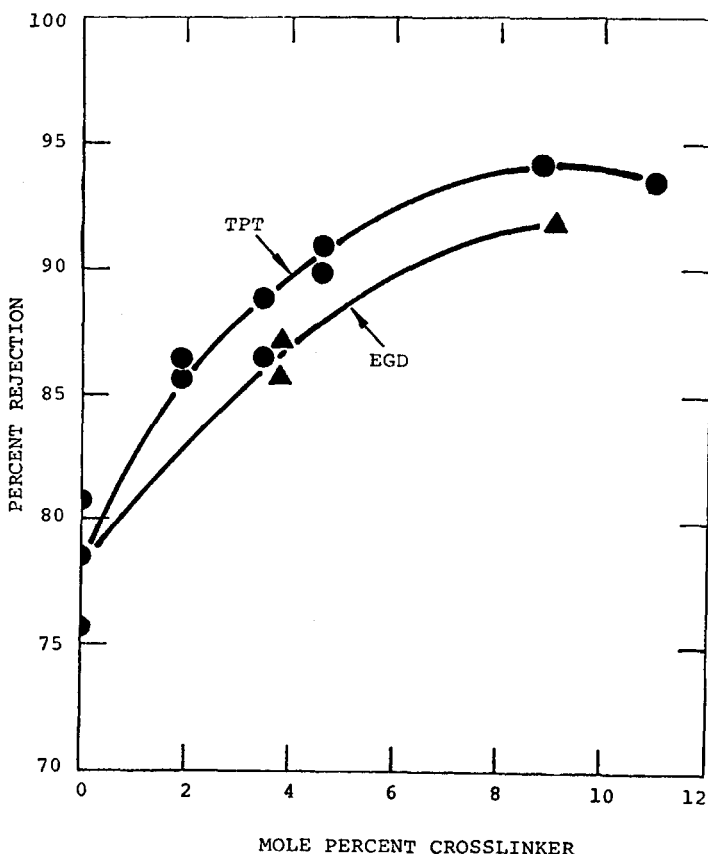


Fig. 6. Salt rejection by HEMA membranes as a function of crosslinking monomer content; applied pressure = 1500 psi; salt concentration = 4.0 wt-% NaCl; pH = 5.

TPT are too low to be of interest. For a given amount of crosslinker, EGD-crosslinked membranes give somewhat lower rejections.

Water and salt permeabilities calculated from one-point determinations, eqs. (1)–(6), are presented in Figure 7 as a function of the applied pressure for a HEMA membrane with no added crosslinker. Compaction of the membranes at higher  $\Delta P$  is evident as the water and salt permeabilities both decrease with the applied pressure.

While individual salt and water diffusivities cannot be separated owing to membrane compaction, their ratio may be determined with a fair degree of confidence. Taking the ratio of water permeability to salt permeability, which is a measure of the rejection capability of a membrane (semipermeability),

$$\frac{P_w}{P_s} = \frac{D_w C_{wm}}{D_s K}, \quad (9)$$

one may separate the right-hand side into kinetic (diffusivity) and exclusion (solubility) effects:

$$\frac{P_w}{P_s} = \left( \frac{D_w}{D_s} \right) \left( \frac{C_{wm}}{K} \right) \cong \left( \frac{D_w}{D_s} \right) \left( \frac{1}{K^*} \right). \quad (10)$$

(kinetic) (exclusion)

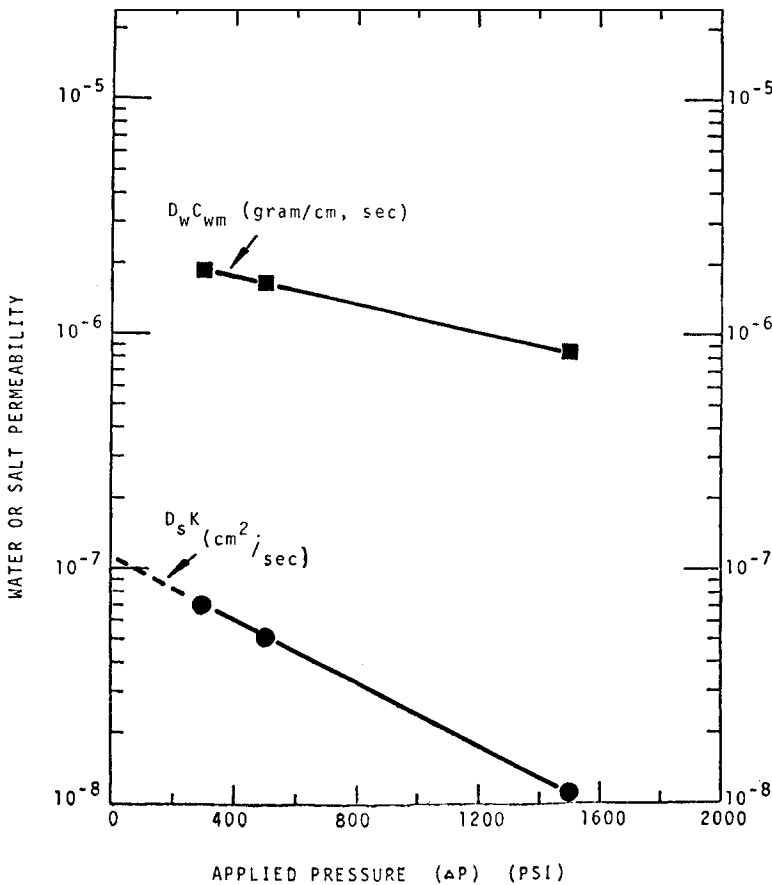


Fig. 7. Water and salt permeabilities as a function of applied pressure for a HEMA membrane with no added crosslinking monomer; salt concentration = 4.0 wt-% NaCl; pH  $\cong$  4.5.

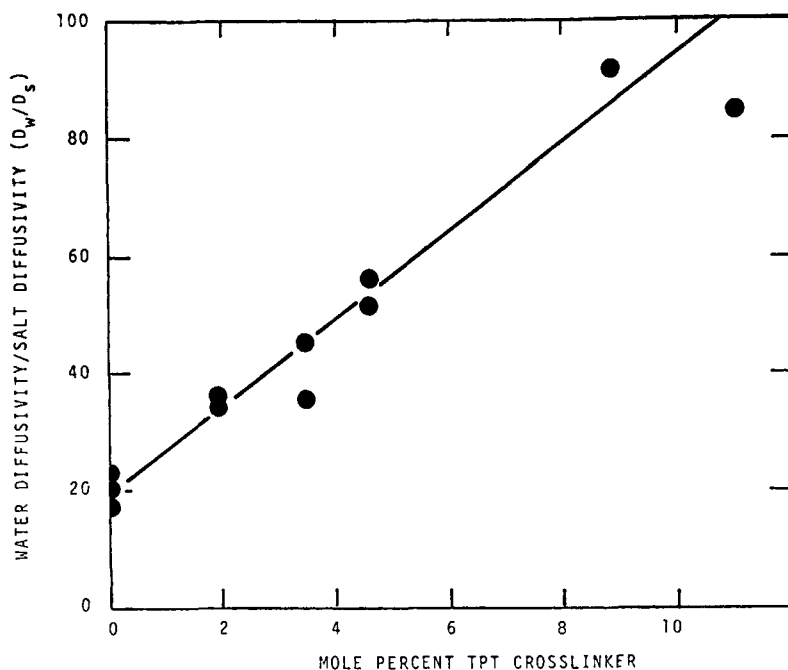


Fig. 8. Ratio of water diffusivity to salt diffusivity within HEMA membranes as a function of TPT-crosslinking monomer content. Reverse osmosis conditions: applied pressure = 1500 psi; salt concentration = 4.0 wt-% NaCl; pH = 5.

(The difference between  $C_{wm}/K$  and  $1/K^*$  is less than 2% for 4 wt-% NaCl solutions.) Since  $K^*$  is essentially constant at 0.32 over the entire range of crosslinker concentration, it is independent of  $C_{wm}$  over a twofold change in water content. Therefore, as a first approximation, one may assume that  $K^*$  is also constant with increasing pressure, since pressure probably also changes water contents. If  $P_w/P_s$  is multiplied by  $K^*$ , the change in diffusivity ratios as a function of added crosslinker may be obtained (Fig. 8). The ratio  $D_w/D_s$  rises from 20 to almost 100 as the crosslink density is increased. Therefore, while both  $D_w$  and  $D_s$  are decreasing, the latter is decreasing at a much faster rate than the former.

These results may be explained on the basis of the primary-secondary water model. Although as crosslinker content increases, the ratio of primary to secondary water does not change in HEMA membranes (constant  $K^*$ ), the total water content does decrease. Water may be transported across primary water regions by a hydrogen-bonding mechanism, but it also is free to diffuse into and out of secondary water pockets as it traverses the membrane. Salt ions, on the other hand, are restricted to secondary water regions in the membrane. These secondary water regions must be interconnected in order to transport salt. As the total water content is decreased, the cross-sectional areas of these interconnections, or "microcapillaries," between secondary water pockets become smaller and



diffusion of salt ions through them is increasingly hindered. At higher levels of crosslinking, it is probable that some of the secondary water pockets become totally isolated and no longer contribute to the salt flux. This would explain the sharper decrease in  $D_s$  relative to  $D_w$ .

### Osmosis Properties

Osmosis experiments are carried out at atmospheric pressure; this allows one to determine diffusivities as well as permeabilities since there is no membrane compaction. These experiments were carried out with three salt solutions, LiCl, NaCl, and KCl, on crosslinked HEMA membranes.

TABLE II  
Osmosis Results for Various Salt Species<sup>a</sup>

Membrane number	TPT crosslinker, mole-%	$D_s K$ , (cm <sup>2</sup> /sec) × 10 <sup>9</sup>	Molar dist. coeff. $K$	$D_w$ , (cm <sup>2</sup> /sec) × 10 <sup>9</sup>
LiCl				
Os-20	0	157	0.228	688
Os-21		157		688
Os-22	4.63	11.8	0.137	86.2
Os-23		11.4		83.2
Os-24	8.85	2.05	0.0937	21.9
Os-25		1.80		19.2
NaCl				
Os-20	0	125	0.130	962
Os-21		126		968
Os-22	4.63	9.25	0.087	106
Os-23		9.10		105
Os-24	8.85	1.70	0.073	23.3
Os-25		1.52		20.8
KCl				
Os-20	0	218	0.131	1660
Os-21		218		1660
Os-22	4.63	11.7	0.0884	132
Os-23		11.5		130
Os-24	8.85	1.90	0.0703	27.0
Os-25		1.73		24.6

<sup>a</sup>  $K$  obtained from sorption measurements; salt concentration = 0.7*N*; pH = 4.

Table II gives salt permeabilities, molar distribution coefficients determined from sorption measurements, and diffusivities for these membranes. Water contents of these membranes equilibrated with the different salts at 0.7*N* did not vary (at constant crosslink density) within experimental error (Table I). Generally, salt permeability is lowest for NaCl at any level of crosslinking. However, diffusivities are of most interest since they directly reflect kinetic factors involving transport across a membrane.

From Table II it may be seen that for a given membrane, diffusivities increase in the order

$$\text{LiCl} < \text{NaCl} < \text{KCl}. \quad (11)$$

This is in the same order as the decreasing hydrated radius of the cation; crystal radii<sup>24</sup> and hydrated radii<sup>25</sup> for these three ions are given in Table III.

TABLE III  
Crystal and Hydrated Radii for  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$

Ion	Crystal radius, <sup>24</sup> Å	Hydrated radius, <sup>25</sup> Å
$\text{Li}^+$	0.60	3.82
$\text{Na}^+$	0.95	3.58
$\text{K}^+$	1.33	3.31

The salt diffusivity differences in HEMA membranes evidently reflect the ease with which the hydrated ion traverses interconnections between secondary water pockets; a larger hydrated ion is hindered more than a smaller one. Interestingly, differences between ion diffusivities for a given membrane are largest at low crosslink density. At 8.85 mole-%, TPT diffusivity differences have almost disappeared. At low levels of added crosslinker, the polymer chains are more easily displaced, and it appears that the salt ions may be doing this without losing water of hydration. However, as the amount of added crosslinker is increased, polymer chain displacement becomes increasingly difficult and, in addition, interconnections between secondary water pockets become progressively smaller. It is conceivable that all three ions require some dehydration at higher levels of crosslinking in order to pass through these interconnections and, consequently, mobility differences between ions become smaller. The adsorption energy of water molecule around a monovalent ion has been estimated a 1.3 to 2.4 kcal/mole greater than the latent heat of vaporization of water,<sup>26</sup> a water molecule being considered bound to an ion when its adsorption energy exceeds the latent heat of vaporization. Helfferich<sup>27</sup> states that ion mobilities follow sequence (11) in lightly crosslinked ion exchange resins; however, for highly crosslinked resins, where there is less room for hydration water, this sequence may be reversed.

#### Osmosis and Reverse-Osmosis Salt Permeability Comparison

Osmosis and reverse-osmosis salt permeabilities are given in Table IV. The osmosis NaCl concentration was  $0.7\bar{N}$ , fairly close to the reverse-osmosis brine concentration of 4.0 wt-% (4.0 wt-% NaCl =  $0.704\bar{N}$ ). Applied pressure in the reverse osmosis experiments was 1500 psi. Repeated values represent different membranes.

There are significant differences between osmosis and reverse-osmosis  $D_s K$  values; this may be due to compaction of the membrane under pres-

TABLE IV  
Osmosis and Reverse-Osmosis NaCl Salt Permeability Comparisons

TPT crosslinker, mole-%	Osmosis $D_s K$ , ( $\text{cm}^2/\text{sec}$ ) $\times 10^9$	Reverse-osmosis $D_s K$ , ( $\text{cm}^2/\text{sec}$ ) $\times 10^9$
0	125	20.8
	126	15.9
		21.5
4.63	9.25	1.63
	9.10	2.21
8.85	1.70	0.76
	1.52	

sure. It may be noted that differences between the two experiments become smaller as the amount of added crosslinker is increased. Tensile tests performed on water-equilibrated membranes revealed that Young's modulus increases from  $5.56 \times 10^6$  dynes/cm<sup>2</sup> for no added crosslinker to  $2.33 \times 10^9$  dynes/cm<sup>2</sup> at 8.85 mole-% TPT. From these moduli it is probable that there will be considerable compaction for lightly crosslinked membranes, but only slight compaction at 8.85 mole-% TPT. Extrapolation of the salt permeability obtained from reverse osmosis experiments for a membrane with no added crosslinker in Figure 7 to atmospheric pressure gives a value of  $1.10 \times 10^{-7}$  cm<sup>2</sup>/sec. This may be compared to an average osmosis salt permeability of  $1.26 \times 10^{-7}$  cm<sup>2</sup>/sec in Table IV obtained under approximately the same pH and brine concentration conditions. Agreement of the two values is quite good. It should be pointed out that this compaction under pressure is reversible: membrane thickness was the same, within experimental error, before and after reverse osmosis testing.

Attempts to produce membranes with a skin-type structure from a linear, solvent soluble HEMA polymer will probably not be successful. The modulus of the porous support would likely be lower than that of a homogeneous HEMA membrane of low crosslink density, and one would expect a porous structure with such a low modulus to collapse under pressure. Therefore, if such asymmetric membranes are desired, the porous support must be composed of a material other than HEMA polymer. The ideal material would, of course, be totally incompressible at the pressures encountered in reverse osmosis operation. One avenue of approach may be vapor deposition of monomer on an incompressible porous support followed by a rapid polymerization. Among other methods, the polymerization could be initiated by ionizing radiation.

## CONCLUSIONS

The reverse-osmosis water flux for HEMA membranes decreases from 0.6 gallon-mil/ft<sup>2</sup>-day (GMFD) to 0.055 GMFD and salt rejection increases from 78% to a maximum of 94% as the amount of TPT crosslinker

is increased from 0 to 11 mole-%. The effect of crosslinking on transport properties is due to kinetic factors (changes in water-to-salt diffusivity ratios) rather than changes in preferential sorption of salt or water. That is, as crosslinker content increases, the diffusivity of salt decreases much faster than the diffusivity of water across the membrane. These results appear to be adequately interpreted by speculating that the water in the membrane is present in two forms: first, "primary" hydrogen-bonded water which is assumed to be molecularly distributed in the membranes at hydrophilic sites and to diffuse via an activated diffusion mechanism and, second, clusters of "secondary" water plus salt ions interconnected by hydrophilic molecular channels, or "microcapillaries." It is suggested that salt ions diffuse along with the secondary water from cluster to cluster through the interconnecting "microcapillaries," also via activated diffusion.

Osmosis results using the chloride salts of lithium, sodium, and potassium reveal that at low crosslinking, the larger the size of the hydrated cation the smaller its diffusivity. At higher crosslink levels, diffusivity differences between the three salts are small, suggesting that increasing hindrance in the microcapillaries interconnecting the secondary water pockets may promote some dehydration of the cation.

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