

## Performance of Solution-Cast Membranes of Poly(Hydroxyethyl Methacrylate) in Osmosis and Reverse Osmosis

R. BLOCH\* and W. R. VIETH,† *Chemical Engineering Department, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

### Synopsis

Noncrosslinked copolymers of hydroxyethyl methacrylate (HEMA) with ethyl methacrylate (EMA) were prepared and investigated as candidate materials for reverse osmosis membranes. Water and salt flux were calculated from the results of osmosis experiments, compared with cellulose acetate and found to be somewhat smaller. The mobility of water varies by several orders of magnitude between a high flux cellulose acetate membrane and a low flux HEMA-EMA membrane.

### INTRODUCTION

Although cellulose acetate membranes have thus far been uniquely successful in reverse osmosis desalination, the search for alternative materials is being continued. Some of the attention in this laboratory has been directed toward membranes based on hydroxyethyl methacrylate (HEMA). Baddour et al.<sup>1</sup> demonstrated that terpolymers of ethylene glycol monomethacrylate, ethyl methacrylate, and ethylene glycol dimethacrylate show appreciable water flux at 80% salt rejection. Subsequent work in this laboratory includes the doctoral research of T. A. Jadwin, wherein membranes were obtained which, when compared with cellulose acetate membranes of equal thickness, show more promising water flux and salt rejection.

A comparison with a homogeneous cellulose acetate membrane of equal thickness of course does not take into account the ingenious Loeb-Sourirajan modification of cellulose acetate<sup>2</sup> whereby carefully chosen casting conditions result in formation of a membrane with a composite structure; i.e., a thin, dense, salt-rejecting "skin" of about 0.2  $\mu$  supported by a coarsely porous sublayer without appreciable resistance to water flow, and without salt rejection. Therefore, in order to develop an alternative to cellulose acetate, not only does water flux have to be comparable to a homogeneous membrane of this material, but a technique has to be available to reduce the

\* Present address: Hydronautics-Israel, Rehovot, Israel.

† Present address: Department of Chemical Engineering, Rutgers University, The State University of New Jersey, New Brunswick, New Jersey 08903.

selective layer to a fraction of a micron. Loeb's technique inherently could not be applied to the HEMA membranes described above as they are cross-linked and therefore cannot be cast. Crosslinked systems were used in order to reduce the hydrophilicity of pure HEMA which was found too hydrophilic and consequently having too high a permeability for salt.

It was a first objective of the work reported here to demonstrate that the hydrophilicity of a noncrosslinked HEMA-polymer can be reduced by copolymerization with a more hydrophobic monomer; i.e., ethyl methacrylate (EMA). Variation of HEMA/EMA composition allowed optimization with respect to water flow and salt rejection.

Such copolymers were expected and found to be soluble in a number of solvents. It was therefore an ancillary objective to find casting conditions which might yield a stable, Loeb-type composite membrane of HEMA-EMA copolymers. Such conditions remain, however, undetermined.

Cellulose acetate and HEMA-EMA copolymers show considerable chemical similarity. In both polymers hydroxyl groups and ester groups are attached to a polymeric chain: a cellulosic chain in the former, an acrylic chain in the latter case. Comparison of the relevant parameters of these two systems, which determine their potential as reverse osmosis membranes, i.e., water content and water flux, salt content and salt flux, should indicate whether these parameters are functions of the chemical composition or rather of physical parameters of the membrane. Examples of the latter are the molecular packing of the polymer in the membrane and its crystallinity, both of which would be expected to influence the mobility of free water. The chemical composition may profoundly affect the state of water in the membrane in the sense of water aggregation and clustering or other such interactions with the polymer.

For the same reasons, a similar comparison is of interest between cross-linked and noncrosslinked membranes of pure HEMA. Results of this comparison may also contribute to an assessment of whether transport through water-selective membranes is by molecular diffusion through fluctuating chain-spacings or by flow through nonrigid pores of molecular dimensions.

## EXPERIMENTAL

### Preparation of Polymers

The problem to be mastered in the preparation of HEMA-based copolymers for the preparation of membranes is the elimination of all possibilities of crosslinking which would render the polymer insoluble. After a number of unsuccessful attempts to polymerize in emulsion, solution polymerization was chosen. The requirement to obtain noncrosslinked polymers of sufficiently high molecular weight (to cast membranes suitable for reverse osmosis experiments) thus posed considerable difficulties.

The polymerizations were carried out in a three-necked, round-bottomed glass flask equipped with reflux condenser, thermometer, stirrer, nitrogen

inlet, and dropping funnel. The total monomer: small solvent ratio was 2:1. The solvent chosen finally was methyl ethyl ketone which, with its boiling point of 79°C provided automatic temperature control. Azobisisobutyronitrile was used as catalyst in suitable quantities with respect to total monomer content. Reactions were carried out for 4–6 hr, after which time a highly viscous solution was obtained. The polymers were precipitated several times with water, redissolved, and air-dried.

### Membrane Preparation

Membranes were prepared by dissolving the polymers in a suitable solvent (acetone at low hydroxyl content; acetic acid or dimethylformamide for pure HEMA) and coating with a doctor blade on glass plates. The mechanical strength of the HEMA copolymer membranes was considerably inferior to that of cellulose acetate films, probably due to insufficiently controlled molecular weight. In order to remove the membranes undamaged from their coating support, they were soaked in distilled water for at least several hours. The avoiding of pinhole imperfections posed a particularly difficult problem of technique which was never entirely satisfactorily solved.

### Membrane Testing

The transport properties were determined by two types of measurements, osmosis and reverse osmosis. For osmotic transport determinations the membrane was clamped between two Lucite half cells. The membranes were self-sealing. A concentrated salt solution (2*M*) was placed on one side of the membrane, pure water on the second side. Both salt and water transport were determined conductometrically; salt transport by the increased conductivity of the water side, water transport by dilution of the solution side. As a rule, the osmosis cells were not shaken or stirred as control experiments showed that transport rates were slow enough that negligible concentration polarization resulted. The measurements were carried out at ambient temperature.

In evaluating these osmosis measurements we follow the method of Lonsdale et al.<sup>3</sup> which assumes both water and salt flux to be governed by Fick's law and Henry's law. The water permeability  $D_1c_1$  then is defined by

$$J_1 = D_1c_1 \bar{v}_1 (\Delta p - \Delta\pi)/RT \Delta x \quad (1)$$

where  $D_1$  and  $c_1$  signify diffusion coefficient and concentration of water in the membrane,  $\Delta x$  its thickness,  $\bar{v}_1$  the partial molar volume of water,  $\Delta p$  the hydrostatic head, and  $\Delta\pi$  the osmotic pressure difference between the two chambers of the osmosis cell.

As one side of the osmosis cell contains pure water, the equation reduces to

$$J_1 = -D_1c_1 \bar{v}_1 \Delta\pi/RT \Delta x \quad (2)$$

where  $\Delta\pi$  is the osmotic pressure of the salt solution used in the experiment.

The salt permeability  $D_2K$  according to Lonsdale is determined from the salt flux  $J_s$  (given in grams salt per square centimeter per second) by

$$J_s = D_2 K c_0 / \Delta x \quad (3)$$

where  $D_2$  is the diffusion coefficient of salt in the membrane and  $K$  its distribution coefficient between membrane phase and adjoining salt solution.

Reverse osmosis tests were carried out by the standard procedure used in this laboratory and described elsewhere.<sup>4</sup>

### Water Content

Water contents were determined both by immersion and by vapor sorption and gave generally equivalent results. For the immersion method the membranes were equilibrated for at least 24 hr with distilled water, removed, carefully wiped with wet filter paper, and vacuum-dried at 60°C. In most cases results differed from values obtained by sorption at 100% relative humidity by less than 5%.

## DISCUSSION

### Homogeneous Membranes of HEMA-EMA Copolymers

Jadwin's unpublished results on pure HEMA membranes prepared by bulk polymerization *in situ* without addition of crosslinker (referred to later in Table III) forced the conclusion that pure HEMA is too hydrophilic and, consequently, has too low a salt rejection to be considered a candidate material for reverse osmosis membranes. While his approach was to decrease the hydrophilicity of HEMA by crosslinking, we achieved the same by copolymerizing it with varying amounts of ethyl methacrylate, (Table I).

Table II gives a summary of the water and salt transport through membranes of various HEMA-EMA compositions as measured by osmosis experiments. Osmosis experiments were chosen for this comparison as the fabrication of pinhole free membranes posed difficulties and membrane

TABLE I  
Hydroxyl Content of Various HEMA/EMA Copolymers

No.	Monomer ratio (by weight) HEMA/EMA	Hydroxyl content, %	
		Theoretical	Found
1	5:2	9.3	9.3
2	2:1	8.6	8.9
3	1:2	4.3	5.0
4	1:0	13.0	13.0
5	1:1	6.5	6.7
6	Cellulose acetate, acetyl content 39.8%	3.35	3.43

TABLE II  
Water Flux and Salt Flux through Various HEMA-EMA Membranes: Comparison with Cellulose Acetate

No.	HEMA content, %	Thickness, mil	Water flux, g/cm <sup>2</sup> -sec	Permeability to water, D <sub>w</sub> , g/cm-sec	Salt flux, g/cm <sup>2</sup> -sec	Apparent permeability to salt, D <sub>s</sub> K, cm <sup>2</sup> /sec
1	94.5 (theoretically pure HEMA)	1.0	5.65 × 10 <sup>-6</sup>	1.23 × 10 <sup>-7</sup>	2.66 × 10 <sup>-8</sup>	5.76 × 10 <sup>-10</sup>
		1.0	4.8 × 10 <sup>-6</sup>	1.64 × 10 <sup>-7</sup>	2.45 × 10 <sup>-8</sup>	5.30 × 10 <sup>-10</sup>
		2.5	4.34 × 10 <sup>-6</sup>	2.40 × 10 <sup>-7</sup>	6.60 × 10 <sup>-8</sup>	3.63 × 10 <sup>-9</sup>
		1.1	4.2 × 10 <sup>-6</sup>	1.00 × 10 <sup>-7</sup>	7.05 × 10 <sup>-8</sup>	1.96 × 10 <sup>-9</sup>
		1.5	3.0 × 10 <sup>-7</sup>	0.99 × 10 <sup>-7</sup>	2.41 × 10 <sup>-8</sup>	7.85 × 10 <sup>-10</sup>
		1.5	2.5 × 10 <sup>-6</sup>	0.83 × 10 <sup>-7</sup>	2.00 × 10 <sup>-8</sup>	6.56 × 10 <sup>-10</sup>
2	78.6	2.0	2.94 × 10 <sup>-6</sup>	1.27 × 10 <sup>-7</sup>	0.77 × 10 <sup>-8</sup>	3.34 × 10 <sup>-10</sup>
		2.0	2.60 × 10 <sup>-6</sup>	1.12 × 10 <sup>-7</sup>	0.89 × 10 <sup>-8</sup>	3.86 × 10 <sup>-10</sup>
		1.2	4.40 × 10 <sup>-6</sup>	1.14 × 10 <sup>-7</sup>	1.47 × 10 <sup>-8</sup>	3.82 × 10 <sup>-10</sup>
		1.2	3.61 × 10 <sup>-6</sup>	0.94 × 10 <sup>-7</sup>	1.22 × 10 <sup>-8</sup>	3.17 × 10 <sup>-10</sup>
		1.2	2.49 × 10 <sup>-6</sup>	0.65 × 10 <sup>-7</sup>	1.0 × 10 <sup>-8</sup>	2.61 × 10 <sup>-10</sup>
		2.5	4.6 × 10 <sup>-7</sup>	2.5 × 10 <sup>-8</sup>	9.1 × 10 <sup>-13</sup>	7.8 × 10 <sup>-11</sup>
3	68.5	2.5	4.8 × 10 <sup>-7</sup>	2.1 × 10 <sup>-8</sup>	2.22 × 10 <sup>-12</sup>	1.9 × 10 <sup>-11</sup>
		3.5	8.7 × 10 <sup>-8</sup>	6.6 × 10 <sup>-9</sup>	1.85 × 10 <sup>-10</sup>	1.37 × 10 <sup>-11</sup>
4	54	2.4	6.4 × 10 <sup>-7</sup>	3.33 × 10 <sup>-9</sup>	1.73 × 10 <sup>-11</sup>	8.96 × 10 <sup>-13</sup>
		2.4	6.4 × 10 <sup>-7</sup>	3.33 × 10 <sup>-9</sup>	1.73 × 10 <sup>-11</sup>	6.55 × 10 <sup>-13</sup>
6	Cellulose acetate, acetyl content 39.8 wt-% This work	1.0	6.8 × 10 <sup>-6</sup>	1.46 × 10 <sup>-7</sup>	0.97 × 10 <sup>-8</sup>	2.1 × 10 <sup>-10</sup>
		1.0	8.7 × 10 <sup>-6</sup>	1.87 × 10 <sup>-7</sup>	3.3 × 10 <sup>-8</sup>	7.2 × 10 <sup>-10</sup>
		1.0	10.1 × 10 <sup>-6</sup>	2.17 × 10 <sup>-7</sup>	2.7 × 10 <sup>-8</sup>	5.9 × 10 <sup>-10</sup>
		1.4	6.2 × 10 <sup>-6</sup>	7.2 × 10 <sup>-7</sup>	4.3 × 10 <sup>-8</sup>	3.0 × 10 <sup>-9</sup>
		1.4	1.3 × 10 <sup>-6</sup>	1.7 × 10 <sup>-7</sup>	9.7 × 10 <sup>-10</sup>	6.8 × 10 <sup>-11</sup>
		1.2	2.6 × 10 <sup>-6</sup>	2.7 × 10 <sup>-7</sup>	3.9 × 10 <sup>-8</sup>	2.4 × 10 <sup>-10</sup>
6	Data of Lonsdale <sup>8</sup>	1.3	2.3 × 10 <sup>-6</sup>	2.5 × 10 <sup>-7</sup>	3.8 × 10 <sup>-9</sup>	2.4 × 10 <sup>-10</sup>

imperfections obscure interpretations of reverse osmosis results considerably more than those of osmosis experiments. Expectedly, water flux and salt flux decrease with increasing content of the more hydrophobic monomer EMA. Some results with membranes of 39.8% acetylated cellulose acetate are included in Table II for comparison with HEMA-EMA copolymers.

In Table III, the values of  $D_1c_1$  and  $D_2K$  were used to calculate water fluxes and salt rejections as used to characterize reverse osmosis performance. The purpose of giving these values is to show the optimum performance which can be expected if pinhole free membranes will become available for testing by reverse osmosis. Column 4 in Table III converts

TABLE III  
Water Fluxes and Equivalent Salt  
Rejection Calculated from Osmosis Experiments

Membrane HEMA content, %	$D_1c_1$ , g/cm-sec	$D_2K$ , cm <sup>2</sup> /sec	Water flux, gal-mil/ day-ft <sup>2a</sup>	Equivalent salt re- jection, %
94.5	$1.23 \times 10^{-7}$	$5.76 \times 10^{-10}$	0.120	96.0
	$1.04 \times 10^{-7}$	$5.30 \times 10^{-10}$	0.101	95.7
	$2.40 \times 10^{-7}$	$3.63 \times 10^{-10}$	0.232	95.7
	$0.83 \times 10^{-7}$	$6.56 \times 10^{-10}$	0.081	90.9
78.6	$1.12 \times 10^{-7}$	$3.86 \times 10^{-10}$	0.108	97.1
	$1.27 \times 10^{-7}$	$3.34 \times 10^{-10}$	0.124	97.7
	$1.14 \times 10^{-7}$	$3.82 \times 10^{-10}$	0.111	97.1
	$0.94 \times 10^{-7}$	$3.17 \times 10^{-10}$	0.092	97.0
68.5	$2.5 \times 10^{-8}$	$7.8 \times 10^{-11}$	$0.243 \times 10^{-1}$	97.3
	$2.1 \times 10^{-8}$	$1.9 \times 10^{-11}$	$0.204 \times 10^{-1}$	92.8
54	$6.9 \times 10^{-9}$	$8.4 \times 10^{-12}$	$0.67 \times 10^{-2}$	99.0
	$6.6 \times 10^{-9}$	$13.7 \times 10^{-12}$	$0.65 \times 10^{-2}$	98.9
38.4	$3.3 \times 10^{-9}$	$6.55 \times 10^{-13}$	$0.32 \times 10^{-2}$	99.84
	$3.3 \times 10^{-9}$	$8.96 \times 10^{-13}$	$0.32 \times 10^{-2}$	99.77
Pure HEMA (bulk- polymerized)	$2.64 \times 10^{-8}$	$1.53 \times 10^{-7}$	2.58	50.0
Cellulose acetate, acetyl content 39.8 wt-%				
Present work	$1.46 \times 10^{-7}$	$2.1 \times 10^{-10}$	0.142	98.85
	$1.87 \times 10^{-7}$	$7.2 \times 10^{-10}$	0.182	97.0
	$2.17 \times 10^{-7}$	$5.9 \times 10^{-10}$	0.211	98.25
Data of Lonsdale <sup>3</sup>	$2.6 \times 10^{-7}$	$3.0 \times 10^{-10}$	0.25	99.05

<sup>a</sup> Effective pressure 220 psi, converted from ml/cm<sup>2</sup> into gal/ft<sup>2</sup>.

the value of  $D_1c_1$  into a water flux expressed in gal-mil/day-ft<sup>2</sup>. Column 4 gives an apparent salt rejection, calculated under the assumption that salt and water flux are unchanged when flowing in the same direction as in reverse osmosis or in opposite directions as in an osmosis experiment. Column 5 gives an apparent salt rejection<sup>5</sup> defined in a manner analogous to the salt rejection in reverse osmosis as

$$\begin{aligned}
 R_{app} &= \frac{c_0 - (J_s/J_w)}{c_0} = 1 - \frac{J_s}{J_w c_0} \\
 &= 1 - \frac{D_2 K (RT/\Delta x)}{D_1 c_1 \bar{v}_1 (\Delta \pi/\Delta x)} \\
 &= 1 - \frac{D_2 K}{D_1 c_1} \left( \frac{1}{\bar{v}_1 2f_0 c_0} \right) \quad (4)
 \end{aligned}$$

where  $f_0$  is the activity coefficient of a 2M salt solution with the value 1.53<sup>6</sup> and, therefore, for an osmosis experiment with a 2M salt solution

$$R_{app} = 1 - (D_2 K/D_1 c_1) 8.6 \quad (5)$$

The use of "apparent salt rejections" to predict optimum performance in reverse osmosis by a perfect membrane is only valid under the assumption that compaction under hydrostatic pressure either does not influence the permeability or will influence all permeabilities to the same extent.

It is seen from results in Table III that optimum values for water permeability of HEMA copolymer membranes are somewhat, but not greatly, smaller than those of 39.8% acetylated cellulose acetate. Water permeability of the latter polymer found by us is somewhat smaller than the values given by Lonsdale, while the salt flux is comparable. We cannot immediately account for this difference, which may be caused by different experimental procedural details such as cell geometry, stirring or possibly inaccuracies in the determination of membrane thickness. For the present purpose we shall therefore correlate results on our HEMA membranes with our own measurements on cellulose acetate.

The most promising of the HEMA copolymers is the 5:2 HEMA-EMA system whose water permeability is about one-third smaller than cellulose acetate (measured by us) with comparable salt rejection. Increasing the EMA content leads to a marked decrease in salt permeability but to an even more pronounced decline in water flux. Despite the high value of the apparent salt rejection, the exceedingly low water flux eliminates these copolymers of high EMA content from the possible candidate materials of reverse osmosis membranes.

Comparing osmosis results on the solution-cast HEMA copolymers with the unpublished results of Jadwin obtained with HEMA membranes obtained from bulk polymerization without crosslinker, one sees that his membranes show appreciably higher water fluxes, combined, however, with a similar increase in salt flux. The mode of preparing HEMA-membranes obviously has a strong influence on their permeability characteristics.

Table IV summarizes the most successful reverse osmosis experiments. For cellulose acetate membranes, rejections were identical whether obtained from osmosis or reverse osmosis measurements. HEMA membranes, however, were obviously not prepared free of imperfections, as demonstrated by increased water and salt-fluxes and decreased rejection. We cannot say at this stage if HEMA copolymers inherently are inferior as film formers to

TABLE IV  
Results of Reverse Osmosis Experiments<sup>a</sup>

Membrane HEMA content, %	Flux, gal-mil/ ft <sup>2</sup> -day	Salt rejection, %	$D_1c_1$ , g/cm-sec	$D_2K$ , cm <sup>2</sup> /sec
94.5	0.074	85.2	$2.33 \times 10^{-7}$	$1.2 \times 10^{-9}$
	0.092	88.3	$2.95 \times 10^{-7}$	$1.2 \times 10^{-9}$
	0.196	87.5	$9.4 \times 10^{-7}$	$4.7 \times 10^{-9}$
78.6	0.065	87.5	$2.1 \times 10^{-7}$	$8.1 \times 10^{-10}$
	0.084	87.3	$2.4 \times 10^{-7}$	$10.5 \times 10^{-10}$
68.5	0.020	91.8	$6.4 \times 10^{-8}$	$1.8 \times 10^{-10}$
	0.029	87.2	$9.2 \times 10^{-8}$	$4.0 \times 10^{-10}$
Pure HEMA (bulk- polymerized) <sup>b</sup>	0.64	78.5	$1.3 \times 10^{-8}$	$2.1 \times 10^{-8}$
Cellulose acetate, 39.8 wt-% acetyl	0.061	98.6	$1.9 \times 10^{-7}$	$9.1 \times 10^{-11}$
	0.071	98.7	$2.2 \times 10^{-7}$	$9.8 \times 10^{-11}$

<sup>a</sup> Measured at 800 psi with a solution of 10000 ppm NaCl.

<sup>b</sup> At 40000 ppm and 1500 psi.

cellulose acetate or if improvements in polymerization and purification procedure would considerably improve film formation and therefore decrease the number of imperfections.

### Comparison of Water Transport through Membranes of Cellulose Acetate with Membranes of HEMA Copolymers

We have referred earlier to the chemical similarity between cellulose acetate and HEMA copolymers, both of which contain hydroxyl groups and ethyl ester groups bound to a chain backbone. The molecular architecture of these two classes of polymers is, of course, distinctly different. Cellulose acetate is a rigid, linear, extended-chain molecule while acrylics are randomly coiled polymers with high internal mobility of the polymeric chains. In addition, crystallinity of the polymer as well as water structuring may have significant influence on transport properties.

Figure 1 shows the amount of sorbed water as a function of the concentration of hydroxyl groups in the two polymers. Values of water content of cellulose acetate are quoted from Lonsdale.<sup>3</sup> It is clearly seen that, at equal hydroxyl content, cellulose acetate binds considerably more water than HEMA polymers; i.e., pure HEMA with a hydroxyl content of 13 g/100 g polymer absorbs the same amount of water as 33.6% acetylated cellulose acetate with a hydroxyl content of 7.8%. Better steric accessibility as well as the presence of an etheric oxygen in the cellulose chain may account for the increased hydrophilicity of cellulose.

As is apparent from Figure 1, the water content of "pure" HEMA (94.5%) is considerably higher than that of 5:2 HEMA-EMA copolymers. Results in Table II show that this is not reflected in an equivalent increase in water permeability  $D_1c_1$ . It cannot readily be explained why the additional water sorbed by pure HEMA does not contribute to water transport,



unless it is used up entirely in joining immobile clusters. From Figure 2, where the diffusion coefficient of water  $D_1$  is plotted as function of water content, it is evident that water in HEMA membranes is an order of magnitude less mobile than in cellulose acetate membranes. Figure 3 shows the

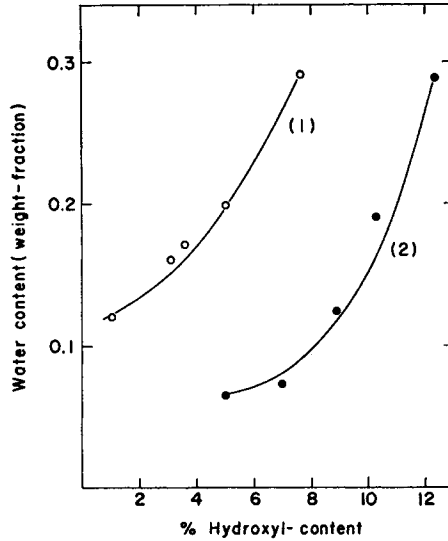


Fig. 1. Water contents of HEMA and cellulose acetate as functions of % Hydroxyl content.

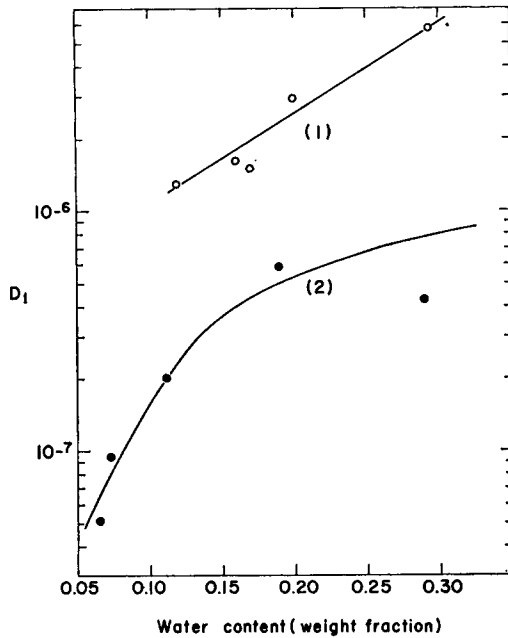


Fig. 2. Diffusion coefficient of water ( $D_1$ ) as a function of water content.

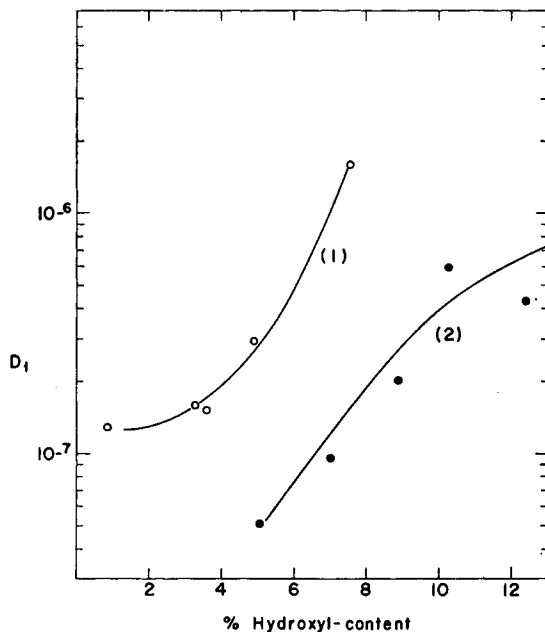


Fig. 3. Diffusion coefficients of water ( $D_1$ ) in HEMA and cellulose acetate as functions of % Hydroxyl content.

same phenomenon by a plot of  $D_1$  against hydroxyl concentration in the polymers. Thus, all data demonstrate that cellulose acetate not only sorbs water more strongly than HEMA but the sorbed water is also more freely mobile.

In summary, noncrosslinked membranes of copolymers of HEMA-EMA were prepared and investigated as candidate materials for reverse osmosis membranes. Water and salt flux were calculated from the results of osmosis experiments, compared with cellulose acetate and found to be somewhat smaller. The mobility of water varies by several orders of magnitude between a high-flux cellulose acetate membrane and low-flux HEMA-EMA membrane.

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