

# Hydrophilic Interpolymer Membranes from Crosslinked Blends of Poly(vinylalcohol), Poly(styrene sodium sulfonate) and Poly(vinyl methyl ether-*alt*-maleic anhydride)

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## Synopsis

Interpolymer ion exchange membranes were prepared from a compatible casting solution that contained poly(styrene sodium sulfonate), poly(vinyl methyl ether-*alt*-maleic anhydride), and poly(vinyl alcohol). Crosslinking of the films was accomplished through the formation of ester linkages that were stable in aqueous environments. Membrane properties (water content, capacity, concentration potential, equivalent conductivity) were measured over a wide range of membrane compositions. Ultrafiltration was carried out with a feed solution that was 0.01*N* in KCl and 15 ppm in erythrosin. Rejection and hydraulic permeability data were reported as a function of membrane composition.

## INTRODUCTION

Poly(vinyl alcohol) (PVA) can be crosslinked to yield hydrophilic, water-swollen films by esterification with diacids<sup>1</sup> or with polyacids,<sup>2</sup> acetal formation with polyfunctional aldehydes,<sup>3-8</sup> or radiation-induced chemical processes.<sup>9-11</sup> Reid and Breton<sup>2</sup> were among the first to propose the use of crosslinked PVA polymeric systems as a basis for reverse osmosis membranes. Nishimura and co-workers<sup>6,7</sup> considered the possibility of preparing interpolymer membranes from PVA and poly(styrene sulfonic acid), accomplishing crosslinking by heating the films and initiating an intermolecular etherification reaction.

Gryte and Gregor<sup>13,14</sup> have reported the preparation and characterization of interpolymer membranes based on poly(vinylidene fluoride) as the matrix polymer. Both anionic and cationic fixed charge groups were incorporated into the films by employing the appropriate polyelectrolytes. In earlier work, Gregor<sup>15</sup> has described membranes based on similar polymeric components.

Although most multicomponent polymer blends are incompatible, Bohn<sup>16</sup> and more recently Krause<sup>17</sup> have reviewed the instances in which compatibility has been observed. In blends of poly(vinyl methyl ether) and polystyrene, for example, Thies and co-workers<sup>18</sup> and more recently Nishi and Kwei<sup>19</sup> observed that though the blends were compatible, they did phase separate at elevated temperatures and their compatibility was dependent on the solvent from which the films were prepared. In such systems as in the present case, it is always necessary to question whether that apparent compatibility is a metastable dis-

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persion or a true thermodynamic solid solution. Polyblends have been used as membrane materials. Hopfenberg and Stannett<sup>20</sup> studied the permeability of the miscible system polystyrene-poly(phenylene oxide). In the research reported herein the three polymers are hydrophilic; all are water soluble. Thus, crosslinking of the chains into a three-dimensional network is essential to maintain the integrity of the membranes in an aqueous environment. In the present approach, an extended matrix structure was prepared into which were trapped extensive domains of a strongly ionic polyelectrolyte. In contrast to previously reported interpolymer membranes<sup>13,14</sup> that employed a hydrophobic matrix polymer, this research incorporates a crosslinked hydrophilic polymer as the matrix component.

The three components in this new membrane structure are hydrophilic polymers: the matrix PVA, the polyelectrolytes PSSNa and poly(vinyl methyl ether-*alt*-maleic anhydride) (PVM/MA), the crosslinking agent. This system differs from the polyelectrolyte complex membranes developed by Michaels<sup>21</sup> wherein the gel network resulted from an ionic coacervation of the two oppositely charged polymeric components. In the present instance the gel network is caused by the intermolecular esterification of the functional groups on the PVA and the PVM/MA. The charge character results from the presence of two different polyanions: the sulfonate groups of the PSSNa and the carboxylate groups of the hydrolyzed but unesterified PVM/MA.

Since the entire gel structure of the membrane is hydrophilic, the water permeability is expected to occur throughout the membrane. In multicomponent polymer systems, a microphase separation of the polymeric components is often observed on the molecular level. Thus, in a membrane containing three polymeric components, at least two or perhaps three different types of macromolecular domains are expected to exist. Such a phase separation is commonly observed in block and graft copolymers and in many polyblends.<sup>22</sup> In the PSSNa domains, a Donnan equilibrium determines electrolyte rejection and the carboxyl groups of PVM/MA exert their own fixed charge ion exclusion. Such is not the case if a neutral PVA crosslinking agent such as a dialdehyde is used. In this latter case the PVA domains would be nonionic, and thus a nonpermeable path would exist through which electrolyte could flow across the membrane. Thus, the application of a polyfunctional polycarboxylic acid in this work serves two purposes: to provide effective crosslinking and at the same time to impart a fixed charge character to the crosslinked PVA matrix component.

## EXPERIMENTAL

### Materials

Poly(vinyl alcohol) (PVA) (Gelvatol 1-90, Monsanto) was of medium molecular weight grade and 98% hydrolyzed; it was used as received. Poly(vinyl methyl ether-*alt*-maleic anhydride) (PVM/MA) (Gantrez AN-119, General Aniline and Film) was of molecular weight 250,000. The poly(styrene sodium sulfonate) (PSSNa) (Dow Chemical, Et-409) has a molecular weight as determined<sup>23</sup> from viscosity of 700,000.

### Compatibility

The temperature dependence of the compatibility of this multicomponent polymer mixture was characterized by the temperature at which phase separation was observed. This temperature, the cloud point, was determined by the method of Dayakonova.<sup>24</sup> A polymer solution (10% by weight polymer in water) was prepared in a sealed glass tube. The mixture was equilibrated at different temperatures. The temperature at which the turbidity sharply increased defined the cloud point. The turbidity was measured in a colorimeter at a wave length of 340 nm. This temperature was reproducible to within  $\pm 2^\circ\text{C}$ .

### Membrane Preparation

Separate solutions (10% by weight) of PSSNa, PVA, and PVM/MA were prepared by adding these polymers with rapid stirring to water at  $80^\circ\text{C}$  and subsequently filtering the solutions while hot. To retard biological activity 0.1% propionic acid was added to all solutions. Casting solutions were prepared by mixing appropriate amounts of the three solutions in 25-cc centrifuge tubes. The casting solution was deaerated under vacuum for 15 min and then centrifuged to remove all of the remaining air bubbles. Glass plates were prepared by subsequent washings in chromic acid, distilled water, acetone, methanol, and finally distilled water. The films were cast using a Gardner knife (Gardner Laboratories Inc., Bethesda, Md.) at the required blade opening to give the desired membrane thickness. The films were dried at  $60^\circ\text{C}$  in a natural-convection dust-free oven and subsequently cured at  $140^\circ\text{C}$  for a 3-hr period. The membranes were removed from the glass plate by soaking them in 1N KCl for periods upward of 48 hr.

### Membrane Characterization

Membrane thickness, water content, concentration potential (S.C.E. || 0.1N KCl | membrane | 0.2N KCl || S.C.E.), and ionic conductivity were determined by methods previously reported in detail.<sup>25</sup> Membrane capacity was determined by titration in two stages. A piece of membrane ( $4\text{ cm}^2$ ) was converted to the acid-form and the wet weight was determined. This membrane was put into 15 ml 1N KCl for 24 hr. The strong acid capacity (including the sulfonate fixed charge and a certain fraction of the carboxylate) exchanged at this point as the external solution pH dropped to between 3 and 4. The external solution was quantitatively separated from the membrane and titrated with 0.1N KOH to a pH 7 endpoint. The membrane was then put into 5 ml 0.1N KOH for 24 hr. Under these conditions the remaining weakly acidic carboxylate groups were exchanged, and their capacity was determined by back titration of the KOH. The membranes were reequilibrated in distilled water and their water content and dry weight were determined. The capacity is reported as meq/g dry film.

The ultrafiltration experiments were carried out with a test feed solution that was 0.1N in KCl and 15 ppm in erythrosin. The membranes (circles 44 mm in diameter) were supported on a modified Gelman filter assembly. The feed solution was circulated over the surface of the membrane at a rate of 7.5 l./min at a transmembrane pressure of about 6 atm. The circulation apparatus has been described elsewhere.<sup>25</sup>

## DISCUSSION OF RESULTS

There are few published reports on the behavior of three different polymeric components dissolved in a single solvent. The membranes reported in this work were prepared from a compatible aqueous casting solution of PVA, PSSNa, and PVM/MA.

Although these solutions were clear and compatible at room temperature, to varying degrees they all separated into two different phases as the temperature of the casting solution was increased. The temperature at which this phase separation first began to appear is called the cloud temperature. In Figure 1(a), cloud point data are given as a function of the polymeric composition of the casting solutions. It is well documented<sup>26</sup> that in aqueous solutions where hydrogen bonding and the accompanying "water structure" predominate, a decrease in entropy accompanies mixing. This results in the observation of a lower consolute temperature.

The data in Figure 1(a) clearly show that solutions in water of PVA and PVM/MA are highly compatible and this compatibility is temperature independent. Though mixtures of PSSNa and PVM/MA are compatible in aqueous solution at 25°C, they separate into two different phases at temperatures as low as 45°C. Binary mixtures of PVA and PSSNa behave in somewhat similar fashion. However, it was observed that 5% PVM/MA added to a mixture of PVA and PSSNa increased considerably the thermal stability of the casting solution. This is evident by the maximum in the isotherms that were observed for these mixtures. Further, an increase in the PVM/MA content into the region where the three components were present in nearly equal amounts yielded solutions with cloud points as low as 35°C. As homogeneity is a prime criterion for membrane strength and selectivity, casting conditions and membrane drying procedures were defined to minimize this phase separation. All of the films in this report were cast from solution at room temperature and dried in an air circulation oven at 60°C.

In Figure 1(b), a summary of the observed membrane properties is given as a function of the membrane composition. The PVA-PSSNa-PVM/MA system is divided into six regions. In the extreme of high PSSNa content (region VI, no membrane could be prepared. However, at the other limit (region I), strong, rigid, and optically clear membranes could be prepared over a wide range of PVA-PVM/MA compositions. Each of these two polymers acted as a cross-linking agent for the other. In region III, the membranes were strong but they appeared to be somewhat cloudy and translucent. This can be interpreted in terms of a premature separation that occurred as the films were dried at 60°C. These compositions lie in the area of minimum cloud temperatures as indicated in Figure 1(a). That there is a relationship between the temperature at which a phase separation occurs, and the physical properties of the membrane is evident in region II. This rather small composition domain corresponds to a region of high consolute temperature for the three membrane components. In comparison to the translucent membranes of region III, the films prepared under the same conditions in region II were perfectly transparent. As the polyelectrolyte content is increased the films become weak gels. The PSSNa in these formulations apparently acted as a swelling agent to expand the crosslinked matrix of PVA-PVM/MA. The films of region IV were opaque when swollen in water indicating considerable segregation of the polymeric components within the

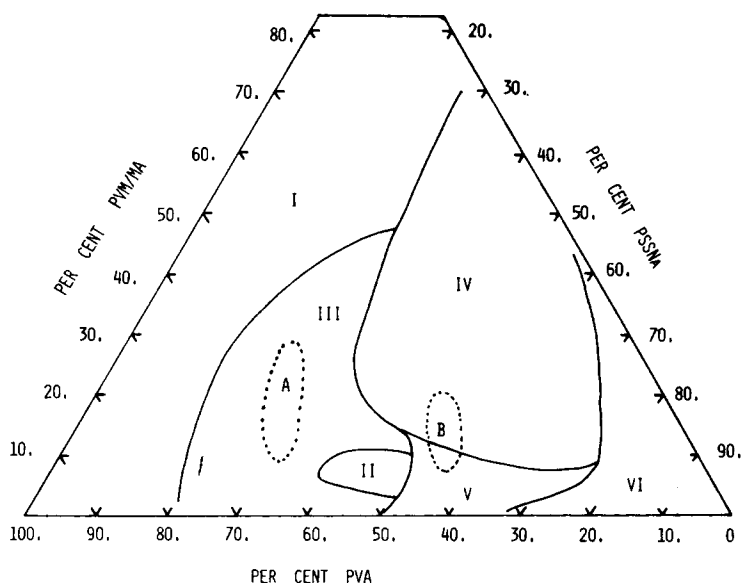
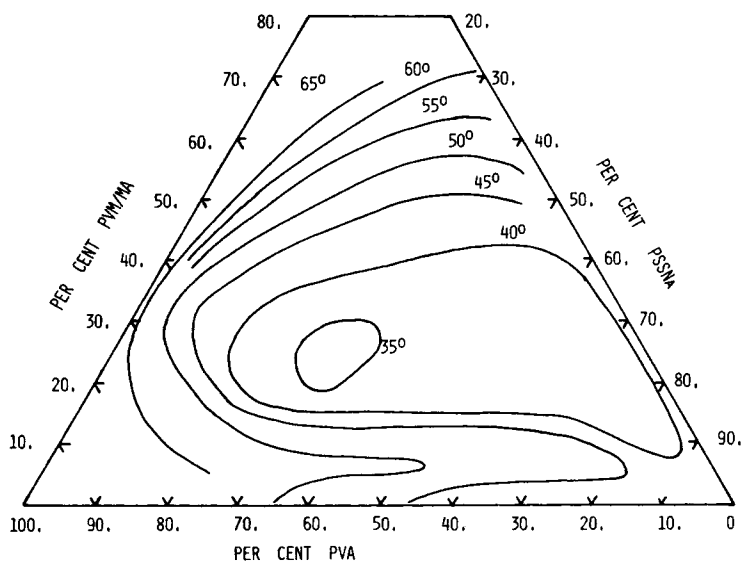


Fig. 1. (a) Casting solution cloud point temperatures for PVA-PSSNa-PVM/MA-water system as function of composition (all solutions 10% by weight of polymer). (b) Observed membrane properties as function of casting solution concentration for PVA-PSSNa-PVM/MA system.

membrane. However, in no case was the phase separation to such an extent that the film appeared optically to be heterogeneous. In Figure 1(b), areas are outlined which represent the composition ranges for two series of membranes (A and B) which were investigated in some detail as to their ultrafiltration properties.

The PVA-PVM/MA-PSSNa system formed a crosslinked network as a result

of the interchain ester linkages that occur during the curing stage. The polymer film, depending on composition, swelled in water to an equilibrium value that remained constant, indicating a considerable stability of the membrane network structure. Experiments were carried out to determine the optimum time for the crosslinking reaction at 140°C. The swelling of the films was observed to decrease during the first 2 hr of the cure at 140°C. Properties remained constant for films cured for times between 2 and 6 hr. It was concluded that 3 hr at 140°C was sufficient to develop fully the esterification reaction between the PVA and PVM/MA. Similar ester linkages involving low molecular weight polyacids and PVA have been reported in the literature.<sup>1,2</sup> The water content of the films was determined for the membranes in the hydrogen form. These data are plotted in Figure 2 as a function of the membrane composition.

Membranes with small amounts of PVM/MA have water contents, regardless of the PSSNa content, that are above 60%. This results from the fact that the crosslinked network at these compositions is not very effective. As the ratio of the PVA to PVM/MA approaches unity the water content drops to a minimum and seems, in some cases, to increase for membranes with large amounts of PVM/MA. This is consistent with the hypothesis that the most effective interchain ester links will occur with equimolar amounts of the two reacting polymers. In Figure 2, it is evident that the swelling of the polymer films depends

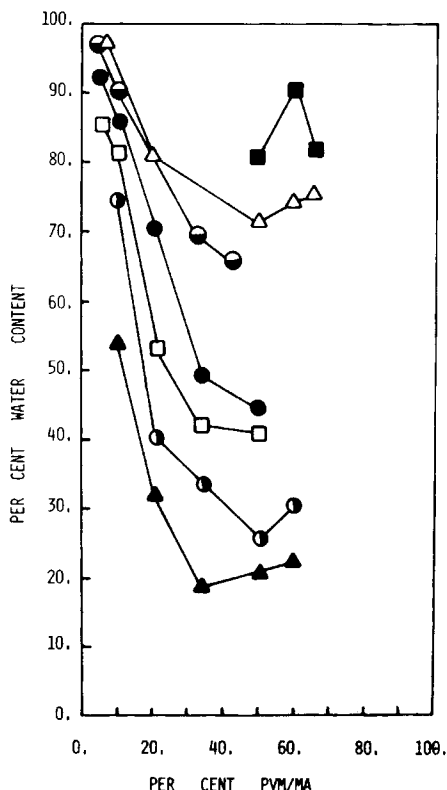


Fig. 2. Water content of PVA-PSSNa-PVM/MA membranes of different composition (films in the hydrogen ionic form). PSSNa/PVA weight ratio in casting solution: (▲) 0.11; (●) 0.44; (□) 0.67; (●) 1.00; (◐) 2.38; (△) 4.00; (■) 9.00.

directly on the PSSNa within the casting solution. At 40% PVM/MA, the water content for these membranes increases from 15% for a PSSNa/PVA ratio of 0.11 to over 80% water for a ratio of 4. Though not reported herein, water contents of these films were also measured for the same films in the potassium form. These water contents were, as expected, 10% higher than the film's swelling in the hydrogen form. This swelling for films in different ionic forms was totally reversible.

The films contained significant amounts of two polyelectrolytes and thus had substantial ion exchange capacity made up of two types of ionic groups: the fixed-charge sulfonate anions from the PSSNa and the fixed carboxylate anions from the PVM/MA. As is the case in all interpolymer membranes where highly water soluble polymers are being trapped in a crosslinked polymer network, a certain fraction of the polyelectrolytes were dissolved when the films were initially put into the water. It was observed that after an extraction period of about one week, the membrane properties remained stable. The capacity data and membrane properties reported herein refer to membranes in this quasi-equilibrium state.

PVM/MA alone, when dissolved in water, hydrolyzes to form maleic acid residues in the repeating unit. Unlike poly(acrylic acid), the first ionization of the maleic acid residue of hydrolyzed PVM/MA is rather strong. Mandel indicates that at pH 4 very little of the hydrogen is ionized in poly(acrylic acid), even in the presence of 0.4*N* KCl.<sup>28</sup> On the other hand, Strauss<sup>29,30</sup> has given titration data for PVM/MA that indicate that at similar pH and ionic strength about half of the first and none of the second maleic acid carboxyl is ionized. Thus, the interpretation of the capacity data measured for these membranes cannot be separated as to its sources, i.e., PSSNa or PVM/MA, but rather according to its behavior during titration. The strongly acidic capacity was measured by using excess electrolyte at a pH in the range of 3 to 4. This represents certainly all of the sulfonate fixed anions of the PSSNa and about half of the first ionization of the maleic acid residues of the PVM/MA. The remaining carboxylate capacity was determined by equilibration at pH 11. This represents the weakly acidic fixed charge capacity.

In Figure 3, the strongly acidic fixed charge capacity of the polymer films is given as a function of the PVM/MA content in the membrane casting solutions. This capacity is observed to remain approximately constant for a given ratio of PSSNa/PVA, increasing with this ratio. At low PSSNa contents, where the losses of this polyelectrolyte may be considered small, the rise in strong acid capacity with increasing PVM/MA reflects the contribution of the maleic acid residues on the PVM/MA. At very high PSSNa contents, the strongly acidic capacity does not reflect the PSSNa content of the membrane casting solution. Much of this polyelectrolyte is dissolved from the films during the initial swelling in water. In Table I, the weakly acidic capacity determined by titration is reported. These data are similar in magnitude to the PVM/MA content of the membrane casting solution. From the titrated capacity data, it is concluded that only a small fraction of the carboxylate groups is involved in the formation of the ester crosslinks with the PVA. The total membrane fixed-charge capacity found by summing the contributions of all functional groups is found to be very close to the theoretical value at low membrane PSSNa contents. However, as the PSSNa content of the membrane increases, particularly when the films are

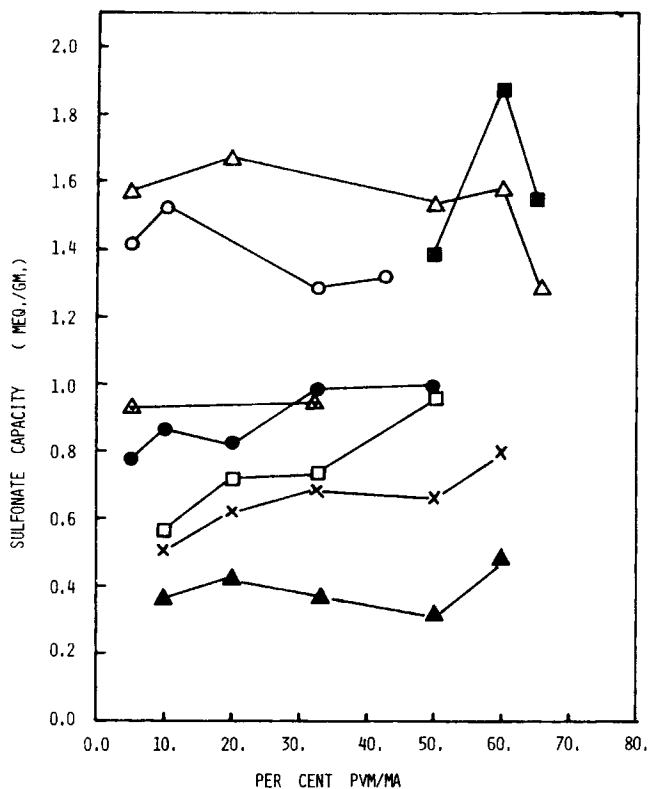


Fig. 3. Titrated strong acid capacity as it depends on membrane casting solution composition. PSSNa/PVA weight ratio: (▲) 0.11; (x) 0.44; (□) 0.67; (●) 1.00; (△) 1.50; (○) 2.38; (△) 4.00; (■) 9.00.

highly swollen at low PVM/MA contents, the total observed capacity is almost half the value predicted from the composition of the membrane casting solution.

That this fixed charge capacity was effective in excluding ions is evident from the membrane potential data given in Figure 4. The internal fixed charge capacity was calculated from the strong acid capacity and the membrane water content. The measurement of the concentration potential was made at an average ionic strength of  $0.15N$  and the pH was higher than 4. The ionized fraction of the carboxyl fixed charge would be significantly higher under these conditions. However, the strong acid capacity seemed more representative of this active membrane capacity than the total concentration of the fixed ionic groups. The data are consistent with the theory of Donnan and the theoretical equations for the membrane potential developed by Teorell, Seivers, and Meyers.<sup>27</sup> At low membrane internal molality, the ion exclusion is weak and the membrane potential is small. The potential increases as the pore fixed charge concentration increases.

The permeability of these films to ions and to neutral species (such as solvent) depends upon the swelling of the polymer network and the resulting porosity of the gel structure. Membranes prepared with a hydrophobic matrix polymer such as poly(styrene sulfonic acid)-poly(vinylidene fluoride)<sup>13,14</sup> permit the



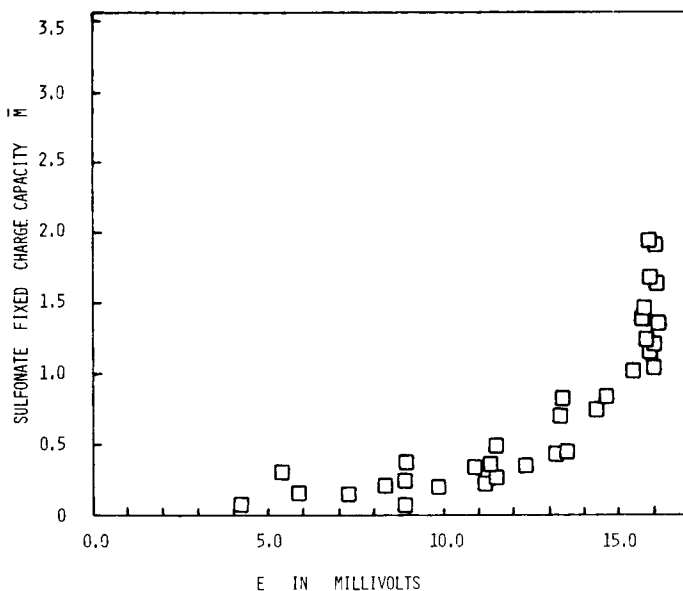


Fig. 4. Concentration potential as function of internal molality of strongly acid groups within the membranes.

passage of ions and solvent only through the polyelectrolyte domains of the membrane since the matrix component forms an impenetrable barrier. In the present case, however, the PVA-PVM/MA matrix, which is a water-swollen gel, is permeable to both ionic and solvent species. It has a significant fixed-charge capacity in itself. The function of the PSSNa is to expand the size of the open pore regions of the gel and to impart ion exchange capacity to those regions. The PSSNa does not, however, control the total matrix permeability as it does in the interpolymer systems that incorporate a hydrophobic matrix. The mobility of the ions within the membranes was determined from the measurement of conductance. The ionizable fraction of the fixed-charge groups was in the potassium form.

The data are plotted in Figure 5 as a function of membrane composition. The equivalent conductance was calculated from the observed membrane conductivity ( $\text{ohm}^{-1} \text{cm}^{-1}$ ), the titrated strong acid capacity, and the water content. For a given ratio of PSSNa to PVA in the casting solution, the mobility of ions within the films decreased as the PVM/MA content increased. Generally, the increase in the PSSNa content of a membrane (increasing its water content and thus its porosity) had a much greater effect on the mobility within the membrane than a corresponding increase of the crosslinking component in the membrane formulation. The conductance data were calculated assuming that only part of the capacity (the strongly ionized part) contributed to the mobile fixed charge concentration within the membrane. This is an oversimplification. Thus, the reported equivalent conductances should in fact be somewhat smaller in magnitude since in their calculation the number of mobile ions was underestimated. Membranes having the highest PSSNa contents and low amounts of PVM/MA were weak and fragile. Their conductivity was difficult to measure since their specific conductivity was very similar to that of the electrolyte in which the measurements were being made.

TABLE I  
Properties and Composition of Interpolymer Ion Exchange Membranes for the PVA-PSSNa-PVM/MA System

No.	Composition, wt-%		Observ. <sup>a</sup>	Cloud temp., °C	$\phi^b$	Capacity <sup>c</sup>		$E_m$ , mV	Conductivity, $\text{Ohm}^{-1} \text{cm}^{-1}$	
	PVA	PSSNa				PVMMA	$\text{SO}_3\text{H}$			COOH
4-1	80.9	9.1	10.0	TRs	75	54.5	0.36	1.16	12.4	$2.5 \times 10^{-3}$
4-2	72.0	8.0	20.0	TRs	58	32.3	0.42	2.38	16.0	$1.0 \times 10^{-3}$
4-3	60.0	6.7	33.3	TRs	45	19.7	0.35	1.56	15.7	$1.6 \times 10^{-5}$
4-4	45.0	5.0	50.0	TRs	60	21.7	0.31	3.55	16.0	$5.0 \times 10^{-5}$
4-5	36.0	4.0	60.0	TRs	66	22.5	0.49	4.43	15.7	$5.8 \times 10^{-5}$
5-1	63.0	27.3	10.0	LFS	49	75.1	0.51	1.03	9.9	$9.5 \times 10^{-3}$
5-2	56.0	24.0	20.0	ORS	40	41.0	0.63	2.28	15.4	$7.7 \times 10^{-3}$
5-3	46.7	20.0	33.3	LRS	40	34.1	0.69	3.34	16.1	$5.0 \times 10^{-3}$
5-4	35.0	15.0	50.0	TRs	51	26.7	0.66	3.86	15.9	$1.5 \times 10^{-3}$
5-5	28.0	12.0	60.0	TRs	60	30.2	0.80	5.00	16.1	$1.7 \times 10^{-3}$
6-1	57.2	38.1	5.0	LFS	49	85.4	0.46	0.90	7.3	$1.5 \times 10^{-2}$
6-2	54.5	36.4	10.0	LFS	47	82.8	0.55	1.16	8.4	$1.5 \times 10^{-2}$
6-3	48.1	32.0	20.0	OFS	32	53.0	0.71	3.02	14.6	$1.8 \times 10^{-2}$
6-4	40.0	26.7	33.3	OFS	34	42.8	0.73	4.04	15.8	$9.5 \times 10^{-3}$
6-5	30.0	20.0	50.0	TRs	45	41.7	0.95	6.09	16.0	$8.0 \times 10^{-3}$
7-1	47.7	47.7	4.8	TFS	52	92.3	0.77	—	5.9	$2.3 \times 10^{-2}$

7-2	45.5	45.5	9.1	TFS	48	86.0	0.86	2.05	8.7	$1.8 \times 10^{-2}$
7-3	40.0	40.0	20.0	LFW	40	70.1	0.80	2.86	11.5	$2.5 \times 10^{-2}$
7-4	33.3	33.3	33.3	LFW	42	49.1	0.99	3.56	15.9	$2.4 \times 10^{-2}$
7-5	25.0	25.0	50.0	TRS	47	44.9	0.95	5.22	16.1	$2.0 \times 10^{-2}$
8-1	38.1	57.2	4.8	LFG	45	88.1	0.93	1.66	8.9	$3.2 \times 10^{-2}$
8-4	26.7	40.0	33.3	LRW	42	54.7	0.95	1.41	14.3	$3.0 \times 10^{-2}$
9-1	28.5	66.7	4.8	TFG	45	97.3	1.40	1.55	5.4	$6.1 \times 10^{-2}$
9-2	27.2	63.7	9.1	OFW	42	90.7	1.54	—	9.0	$4.3 \times 10^{-2}$
9-4	20.0	46.7	33.3	ORW	39	69.0	1.29	1.41	13.3	$6.8 \times 10^{-2}$
9-5	17.1	40.0	43.0	LRS	39	66.5	1.32	4.74	13.4	$4.5 \times 10^{-2}$
10-1	19.1	76.2	4.7	TFG	46	97.9	1.57	—	4.3	—
10-3	16.0	64.0	20.0	OW	36	81.4	1.67	3.96	10.9	—
10-5	10.0	40.0	50.0	LW	49	72.8	1.53	7.23	13.3	—
10-6	8.0	32.0	60.0	W	55	74.6	1.57	7.88	11.3	—
10-7	6.6	26.7	66.7	W	49	75.2	1.27	6.69	13.4	—
11-5	5.0	45.0	50.0	W	44	80.5	1.38	5.84	11.5	—
11-6	4.0	36.0	60.0	W	56	90.1	1.86	6.04	11.4	—
11-7	3.3	30.0	66.7	W	58	82.0	1.55	7.75	11.3	—

<sup>a</sup> T = Transparent; R = rigid; S = strong; L = translucent; O = opaque; F = flexible; W = weak; G = gel-like.

<sup>b</sup> % water, film in H-form.

<sup>c</sup> meq/g dry film in H-form; SO<sub>3</sub>H = strong acid capacity; COOH = weak acid capacity.

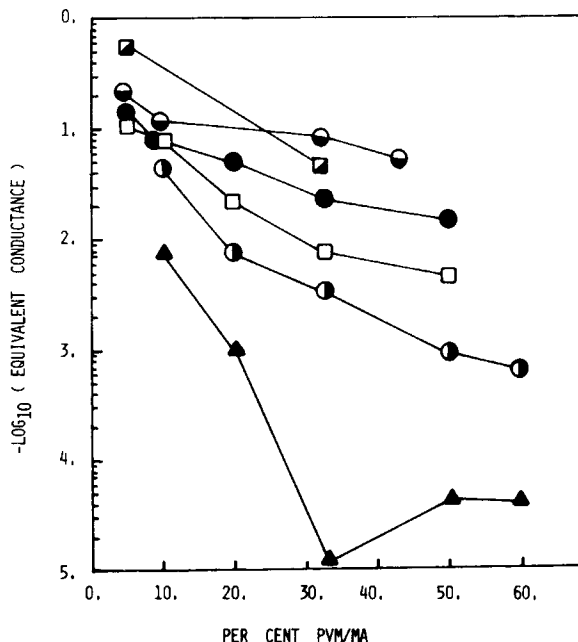


Fig. 5. Equivalent ionic conductance as function of membrane composition for PVA-PSSNa-PVA system. PSSNa/PVA weight ratio: (▲) 0.11; (●) 0.44; (◻) 0.67; (●) 1.00; (◼) 1.50; (◐) 2.38.

Two series of membranes were subjected to further characterization by ultrafiltration. Series B membranes had PSSNa/PVA = 2, with series A having PSSNa/PVA = 0.6. In each case membranes were prepared with increasing amounts of PVM/MA. Referring to Figure 1(b), it is evident that these two membrane series represent extremes in physical properties: series A membranes were strong and flexible, also quite clear and uniform; series B membranes were weak and gel-like, quite fragile, requiring support on filter paper for measurement. The membranes used for the characterizations reported in Table I had thicknesses in the range of 100 to 200 microns. For the ultrafiltration experiments, membranes with thicknesses in the range of 3 to 10 microns were prepared. Though weak, they did maintain their integrity and showed no tendency to degrade during the ultrafiltration experiments.

Ultrafiltration experiments were carried out by circulating a test solution (0.01*N* in KCl and 15 ppm in erythrosin) under pressure over the surface of the membrane. The hydraulic permeability was determined from the volumetric flow through the membrane. The rejection of dye was determined colorimetrically. In Figure 6, the hydraulic permeability for series A and series B membranes is plotted as a function of the PVM/MA content in the membrane-casting solution. The transmembrane pressure was 6.6 atm; no correction was made for any back osmotic pressure that would exist. The membrane thicknesses were between 3 and 10 microns in the water-swollen state, and no corrections were applied to account for this variation. The PVM/MA, acting as a crosslinking component, decreased the membrane hydraulic permeability as its proportion in the membrane formulation increased. This effect was more predominant when the PSSNa content of the films was relatively small (series A). In the series B films, the effect of the PVM/MA was much less dominant, reflecting the overwhelming effects of the sulfonate component.

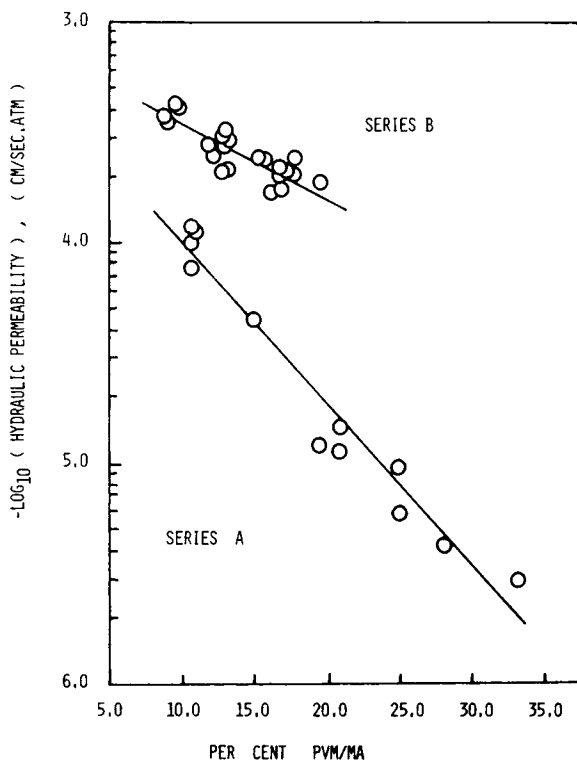


Fig. 6. Hydraulic permeability as function of membrane composition.

All of these membranes appeared homogeneous in cross section. In other experiments, the thickness of the films was varied over an order of magnitude, and it was observed that both the equivalent conductance and the membrane hydraulic permeability were inversely proportional to the membrane thickness. This evidence confirms the fact that rejection in these films depends upon bulk rather than surface properties of the membrane barrier.

The data of KCl and erythrosin rejection expressed as a function of membrane composition are scattered. The data do show the trend that as the PVM/MA content in the membrane casting solution increases, the rejection of both the KCl and the erythrosin increases. This holds regardless of the PSSNa content of the films. In Figure 7, these data have been plotted for the series A and the series B membranes not as a function of membrane composition, but as a function of the membrane hydraulic permeability. In previous reports, it has been shown<sup>14</sup> that for interpolymer membranes, the rejection characteristics are nearly a single-valued function of the water flux through the membranes. Membranes that are highly swollen have open pores that permit not only the solvent water but also the ionic solutes to pass through the polymer gel. Thus, in Figure 7 it is observed that the rejection for the salt at 0.01*N* concentration increases to a limiting value of 50% rejection as the membranes become more restrictive. At the same time the erythrosin rejection increases to about 95%. The data for the series A and the series B membranes are somewhat overlapping. However, it does seem clear that for a given membrane hydraulic permeability, the rejection of the ionic solutes is definitely higher when the PSSNa content of the casting

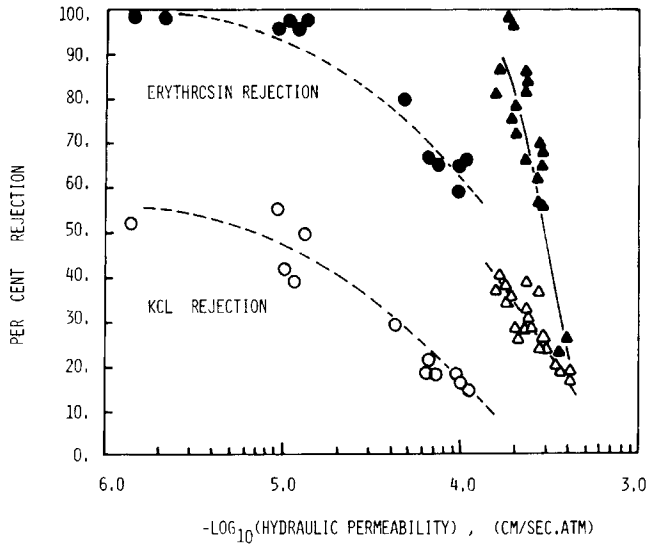


Fig. 7. Rejection as function of hydraulic permeability for feed solution 0.01*N* in KCl and 15 ppm in erythrosin: (●) series A membranes; (▲) series B membranes.

solution is higher. It is concluded that the rejection of the series B membranes is enhanced because of the significantly higher membrane fixed charge, which in turn causes a greater exclusion of the external electrolyte. In all cases, membranes having very high hydraulic permeabilities have virtually no solute rejection characteristics.

No attempt is made to interpret these data in terms of a theoretical description of the transport mechanism. Such a theory has been developed and experimentally verified elsewhere.<sup>14</sup> In the present case, not only must the transport through the polyelectrolyte domains of the membrane be considered, but also consideration of the flux through the water swollen PVA regions must be made. Within these domains, the ion exclusion is dependent on the effectiveness of the carboxylic fixed charge. The weak acid polyelectrolyte is expected to be less effective in the Donnan exclusion of the external electrolyte. This then may account for the lower rejection profile of the series B membranes.

The membranes described herein retained their mechanical integrity throughout the tests. The most permeable membranes were, as indicated in Figure 1(b), relatively weak. On the other hand, the stronger membranes, those containing less of the PSSNa in the casting solution, had lower hydraulic permeabilities and thus were less practical from an application point of view. The role of the matrix polymer is evident in these facts. The water-swollen PVA-PVM/MA matrix system reported in this work should be compared with a water-insoluble poly(vinylidene fluoride) matrix that has been described in earlier publications.<sup>14</sup> The PVA, being highly swollen, cannot maintain a strong framework in the series B membranes and thus cannot mechanically support the highly desirable PSSNa regions in these films. The poly(vinylidene fluoride) does not interact with the water and thus can more effectively hold the PSSNa regions together. In addition, the water-swollen PVA domains in the present series of membranes may in fact short circuit the excluding PSSNa pores and permit a significant ion flux to occur through the water-swollen PVA-PVM/MA

domains. In general, however, it is to be concluded that the PVA-PVM/MA-PSSNa system does exhibit characteristics similar to those observed in other interpolymer ultrafiltration membrane systems.

## CONCLUSIONS

The PVA-PVM/MA-PSSNa interpolymer ion exchange membrane system can be prepared in aqueous systems from an aqueous casting solution provided care is taken to avoid regions and conditions of polymer incompatibility. The membranes so produced can have a wide range of physical and transport properties. However, the system is limited by the fact that the exceedingly attractive and permeable membranes having a high polyelectrolyte content are physically rather fragile and weak. The system does, however, demonstrate a typical Donnan exclusion of ionic solutes.

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