

# Novel Polymer Alloy Membranes Composed of Poly(4-Vinyl Pyridine) and Cellulose Acetate. I. Asymmetric Membranes

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## Synopsis

The preparation of a novel asymmetric membrane cast from a homogeneous mixture of poly(4-vinyl pyridine) and cellulose acetate is described. The two polymers were found to be compatible in the presence of Lewis acids, yielding hydrophilic homogeneous alloys when properly prepared. Asymmetric membranes were cast from a six-component dope mixture containing chloroform, methanol, acetone, and formamide. The as-cast solution, when coagulated in water at ambient temperature, yields a highly plasticized anisotropic matrix which solidifies into a glassy state as the chloroform slowly diffuses into the water. The membranes, following this stage, exhibit a semi-permeable dense skin that produces high fluxes and salt rejections when tested in a high-pressure reverse osmosis mode (no annealing is required). The anisotropic morphology was confirmed by scanning electron microscopy studies which revealed a dense skin resting on a highly porous, open-celled foamlike structure. This structure does not collapse upon drying and retains its original wet dimensions. Brief attempts to quaternize the matrix are also reported.

## INTRODUCTION

The rapid progress in membrane separation technology has been very much a consequence of the development of the so-called asymmetric membranes first reported almost two decades ago by Loeb and Sourirajan.<sup>1</sup> The complexity involved in the development of these membranes is the subject of numerous publications,<sup>2</sup> and only a handful of such membranes have been discovered hitherto. One of the main impediments is the scarcity of polymeric materials that comply with the unique configuration required, i.e., having the polymer perform in two capacities, ultrathin, dense semipermeable layer extending out of rather thick, highly porous supporting matrix.

In recent years, several successful attempts have been reported<sup>3,4</sup> to compound different polymers into a homogeneous blend from which asymmetric alloy membranes can be produced. The discovery that asymmetric membranes can be developed from polymer blends is of much interest, especially since polymer blending provides simpler, more feasible technology than do other methods that compound different polymers and monomers to yield new polymeric material, e.g., copolymers.

The homogeneous polymer alloy consists of two (or more) polymers that are compatible at the molecular level, thus combining the properties of the polymeric components to yield a distinct new material. However, such polymer blends are scarce because of the thermodynamic incompatibility of most polymers;

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exceptions are known to exist in polymeric systems which display specific interaction. Nevertheless, even with the latter, the degree of miscibility of the components is not very well defined, and aggregation and clustering of the macromolecules are very much functions of method of preparation, temperature, physical properties, and other specific parameters. The differentiation between "true" compatibility and that which exhibits microphase separation is frequently obscure (from a practical point of view, compatibility is achieved when the alloys display homogeneity with regard to some desired properties, e.g., optical clarity, single glass-transition temperatures).

The discovery of new compatible polymer systems is based more on trial and error than on empirical methods, since the criteria by which one can predict polymer compatibility are quite tenuous. The conventional use of Hildebrand solubility parameters<sup>5</sup> or three-dimensional solubility diagrams<sup>6</sup> is helpful but far from conclusive. The application of equations of state theories for the prediction of polymer compatibility,<sup>7</sup> though promising, is laborious and again inconclusive when applied to polymers whose compatibility is characterized by their site-to-site interactions (e.g., Lewis bases and acids).

Compatible polymer blends consisting of phosphonate ester derivatives of polystyrene and polyphenylene oxide blended with cellulose esters have been reported by Cabasso et al.<sup>3,4</sup> Asymmetric alloy membranes prepared from such blends were shown to be very effective in azeotropic liquid separations<sup>3</sup> and for water desalination by reverse osmosis.<sup>4</sup>

The reason for the compatibility of polymers containing pendant phosphonate ester groups (PPN) with cellulose acetate is not yet well understood. These polymers are identified by the electron-rich oxygen of the phosphoryl group,  $P \rightarrow O$ , which readily interacts with proton donor species; hence, since it is a pendant group on the polymer chain, it is believed to have the degree of freedom required for interaction with the hydroxyl and acetyl groups, of cellulose acetate (CA). In search for other polymers compatible with cellulose acetate, we observed that poly(4-vinyl pyridine) ( $P_4VPy$ ) shares similar notable characteristics with the aromatic polyphosphonates, PPN, because of its electron-rich nitrogen in the para position to the polymer chain. Both polymers, PPN and  $PVPy$ , also share solubility characteristics, such as high solubility in organic solvents identified as proton donors (e.g., methanol). Therefore, compatibility of cellulose acetate with poly(vinyl pyridine), which resembles the PPN-cellulose acetate blend, was seen as a possibility and was subsequently investigated.

In respect to membrane fabrication, the polymer unit, which consists of 4-vinyl pyridine, has received attention in the past as a candidate for the construction of reverse osmosis and ion exchange<sup>8</sup> membranes. Canepa et al.<sup>9</sup> have reported the grafting of 4-vinyl pyridine onto poly(tetrafluoroethylene) films; Yasuda<sup>10</sup> has reported the plasma polymerization of the molecule onto various porous substrates to obtain composite membranes; and Oikawa and Ohsaki<sup>11</sup> have recently reported the properties of membranes prepared from a copolymer of poly(4-vinyl pyridine) and acrylonitrile.

In the present article, we wish to describe the preparation, morphology, and some transport properties of asymmetric membranes cast from a poly(4-vinyl pyridine)/cellulose acetate blend. The asymmetric membranes developed in this stage were characterized in reverse osmosis recirculating test cells for their water and salt (NaCl) diffusive permeability. While the potential use of these

membranes is not necessarily limited to water desalination, the reverse osmosis testing provides a broad outlook for hydrophilic asymmetric membranes such as these alloys.

Aside from the principal discovery that these polymers yield a homogeneous blend when properly prepared, the fabrication of dense and asymmetric membranes from such blends provides a new outlet for the membrane separation technology. The fact that the pyridine unit is a hydrophilic Lewis base, which can be further quaternized in various ways to yield an ion exchange surface or matrix, presents some attractive possibilities which will be discussed in subsequent articles.

## EXPERIMENTAL

### Materials

Poly(4-vinyl pyridine): (Polysciences, Inc.) Lot No. 1693.  $[\eta]$  25°C chloroform = 1.51 dl/g ( $M_w \approx 250,000$ ).

Cellulose acetate: (Eastman) acetyl content 39.4%. ASTM viscosity 45.

Solvents: reagent grade.

### Casting Solutions and Asymmetric Membrane Preparation

Cellulose acetate was dissolved in an acetone-formamide solvent mixture, while P<sub>4</sub>VPy solution was prepared separately in a methanol-chloroform mixture. The two solutions were mixed to give a clear casting dope.

The filtered polymer solution was poured evenly across one end of a glass plate and a casting knife (doctor blade) preset to give the desired thickness was drawn at an even rate down the entire length of the plate. After a predetermined

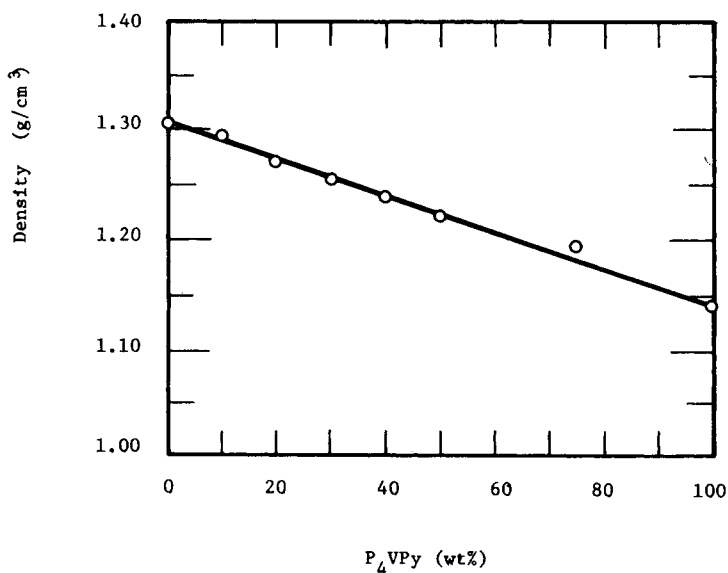


Fig. 1. Density vs. poly(4-vinyl pyridine) fraction in a dense P<sub>4</sub>VPy/CA alloy (cast from acetone/methanol/chloroform solution mixture).

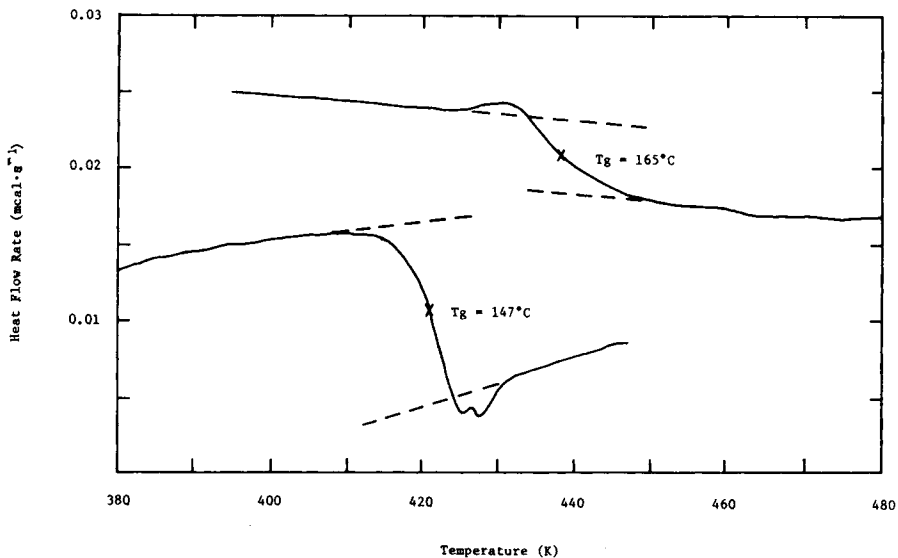


Fig. 2. Differential scanning calorimeter thermograms of poly(4-vinyl pyridine),  $T_g = 147^\circ\text{C}$ , and P<sub>4</sub>VPy/CA alloy (40/60 w/w),  $T_g = 165^\circ\text{C}$  (from samples shown in Fig. 1).

evaporation period, the plate was submerged in water and the polymer mix coagulated to yield a membrane which was stored wet. Selected casting conditions and component ratio are shown in Table I. Aspects considering selection of the solvents are discussed in the following.

### Scanning Electron Microscopy

Morphology of the membranes was determined employing AMR-1000 SEM. The specimens were gold-palladium coated. Cross sections of the membranes were obtained by freeze fracturing the sample under liquid nitrogen.

### Testing for Water/Salt Separation and Permeabilities in Reverse Osmosis

The membranes were tested on low (up to 15 atm) and high (up to 100 atm) pressure reverse osmosis rigs. The low-pressure rig was equipped with rectangular recirculating cells providing a membrane area of  $4.6 \times 10 \text{ cm}^2$ , the high-pressure rig equipped with round stainless-steel recirculating cells (Berghof America, Inc., Derry, NH) which provide a  $38.4 \text{ cm}^2$  effective membrane area. Flow rate of the saline solution above the membranes was maintained within the range of 100–250 liter/hr in a channel height of 0.0015 m. Recovery rates of less than 5% were maintained. Salt rejection and flux rate were determined by

$$R\% = 100 \left( 1 - \frac{\text{concentration of product}}{\text{concentration of feed}} \right)$$

$$J_v = \text{flux rate} = \frac{\text{volume permeated}}{\text{time} \times \text{membrane area}} \frac{\text{m}^3}{\text{m}^2 \text{ day}} \left( \text{or } \frac{\text{gal}}{\text{ft}^2 \text{ day}} = \text{gfd} \right)$$

Two feed solutions of 0.1 and 1 wt % NaCl in distilled water were prepared for

TABLE I  
Poly(4-Vinyl Pyridine)/Cellulose Acetate Alloy Membrane Fabrication Data

Membrane designation	PVPy in membrane (wt %)	Casting solution composition (wt %)			Clearance (mil)	Casting conditions				
		PVPy	CA	Chloroform		Acetone	Methanol	Formamide	Casting temperature (°C)	Quench temperature (°C)
7	29.4	6.2	14.8	14.4	35.4	12.7	16.5	20.0	20.0	20
8a	31.0	5.8	12.8	13.4	38.6	12.9	16.5	27.1	14.0	25
8b	31.0	5.8	12.8	13.4	38.6	12.9	16.5	27.1	14.0	25
9	27.0	5.0	13.7	11.7	40.8	11.2	17.6	24.8	14.5	25
10a	29.4	6.1	14.8	14.4	35.4	12.7	16.6	28.0	14.0	15
10b	29.4	6.1	14.8	14.4	35.4	12.7	16.6	28.0	14.0	15
10c	29.4	6.1	14.8	14.4	35.4	12.7	16.6	28.0	14.0	15
15a	42.8	8.0	10.7	13.3	37.7	11.8	18.5	24.0	14.0	20
15b	42.8	8.0	10.7	13.3	37.7	11.8	18.5	25.0	15.0	20
16	9.1	1.7	17.4	2.9	50.0	2.6	26.4	21.0	16.0	5
17	0	0	18.6	13.4	38.6	12.9	16.5	27.1	14.0	25

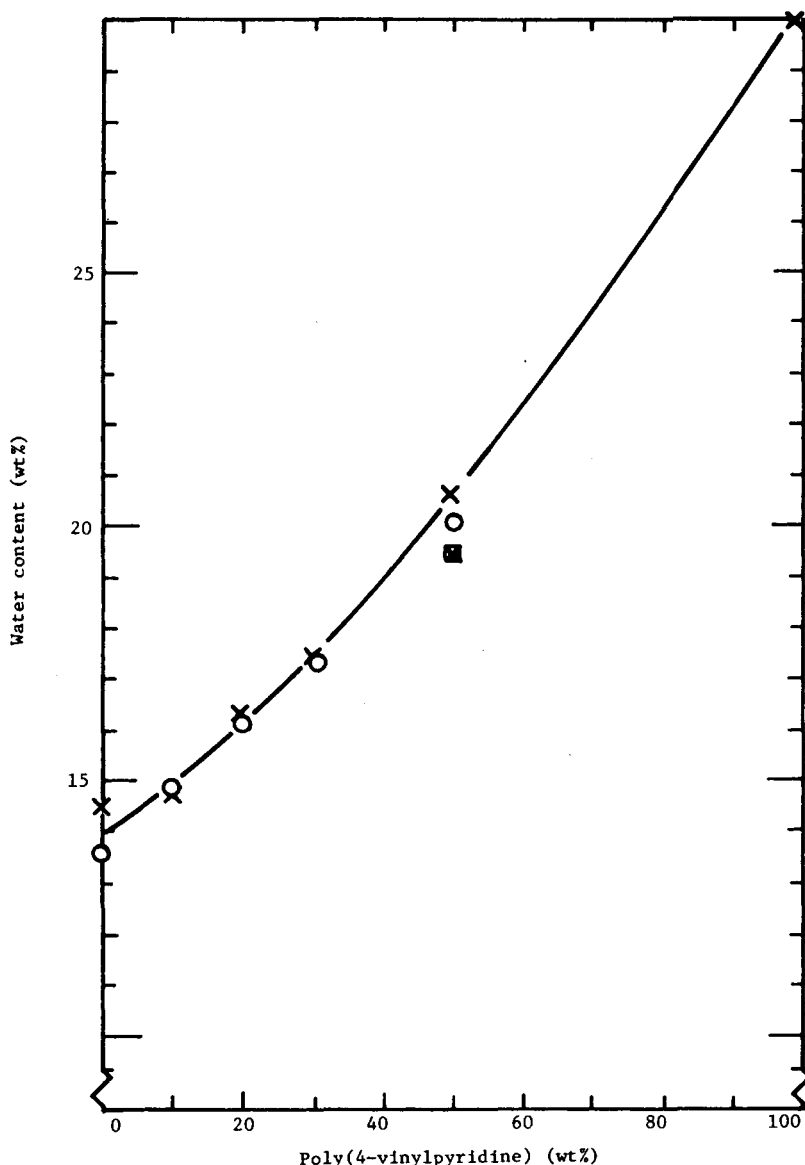


Fig. 3. Water content vs. PVPy fraction in water equilibrated dense PVPy/CA alloy membranes (same sample shown in Fig. 1). (x) 500  $\mu\text{m}$ ; (o) 250  $\mu\text{m}$ ; ( $\square$ ) 500  $\mu\text{m}$  annealed dry at 90°C for 15 min.

the low- and high-pressure rigs, respectively. The pH of  $6.5 \pm 0.4$  was maintained. The reflection coefficient ( $\sigma$ ) and the solute (NaCl) diffusive permeability ( $P$ ) were computed from the plots of  $R$  vs.  $J_v$  by the method described by Wendt et al.,<sup>12</sup> which is based on Speigler and Kedem's work,<sup>13</sup> in which quantitative relation between rejection and volume flux was first proposed through the following expressions:  $R = \sigma[\exp(\beta - 1)]/[\exp(\beta - \sigma)]$  and  $\beta = J_v(1 - \sigma)P$ . The reflection coefficient in this case reflects the maximum separation that can be obtained from each membrane in its specific testing system. Table II presents the  $\sigma$ ,  $P$ , and hydraulic permeability ( $L_p$ ) values for the membrane

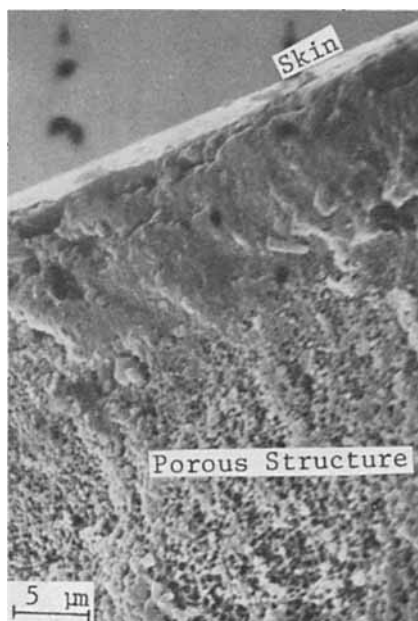


Fig. 4. Cross section of asymmetric alloy membrane of PVPy/CA (formula index 8a) displaying dense skin resting on porous structure.

TABLE II  
Transport Properties of the Membranes Listed in Table I as Obtained from Reverse Osmosis Experiments

Membrane designation and feed solution composition	Reflection coefficient ( $\sigma$ )	Permeability constant (NaCl) $P(\text{NaCl}) \times 10^5$ (cm/sec)	Hydraulic permeability ( $L_p$ ) (g/cm <sup>2</sup> atm) $\times 10^5$
7a (0.1% NaCl)	0.964 (+/-0.02)	2.87 (+/-0.2)	3.0
8a (0.1% NaCl)	0.915 (+/-0.003)	2.53 (+/-0.04)	4.4
8a (1% NaCl)	0.815 (+/-0.032)	7.59 (+/-2.3)	
8b (0.1% NaCl)	0.944 (+/-0.003)	1.06 (+/-0.02)	2.2
9a (0.1% NaCl)	0.960 (+/-0.006)	0.71 (+/-0.02)	1.4
9a (1% NaCl)	0.887 (+/-0.010)	4.27 (+/-0.3)	1.5
9a (quaternized) (0.1% NaCl)	0.721 (+/-0.004)	1.66 (+/-0.07)	2.3
9a (annealed) (0.1% NaCl)	0.907 (+/-0.068)	1.19 (+/-0.3)	0.2
10a (0.1% NaCl)	0.909 (+/-0.014)	1.28 (+/-0.1)	3.3
15a (0.1% NaCl)	0.911 (+/-0.009)	0.30 (+/-0.02)	0.8
15b (0.1% NaCl)	0.924 (+/-0.009)	2.69 (+/-0.1)	3.0
16 (0.1% NaCl)	0.813 (+/-0.020)	14.4 (+/-1.2)	8.0
17 (0.1% NaCl)	0.518 (+/-0.056)	14.4 (+/-4.5)	5.9

shown in Table I. The hydraulic permeability was computed from the volume flux equation,  $J_v = L_p(\Delta P - \sigma\Delta\pi)$ , where  $\Delta P$  is applied hydraulic pressure.

### Density Measurements

The density of P<sub>4</sub>VPy/CA alloys was determined in a density-gradient column equipped with calibrated glass beads exhibiting densities ranging from 0.600 to 1.600. The liquid mixture employed was carbontetrachloride/xylene. Readings

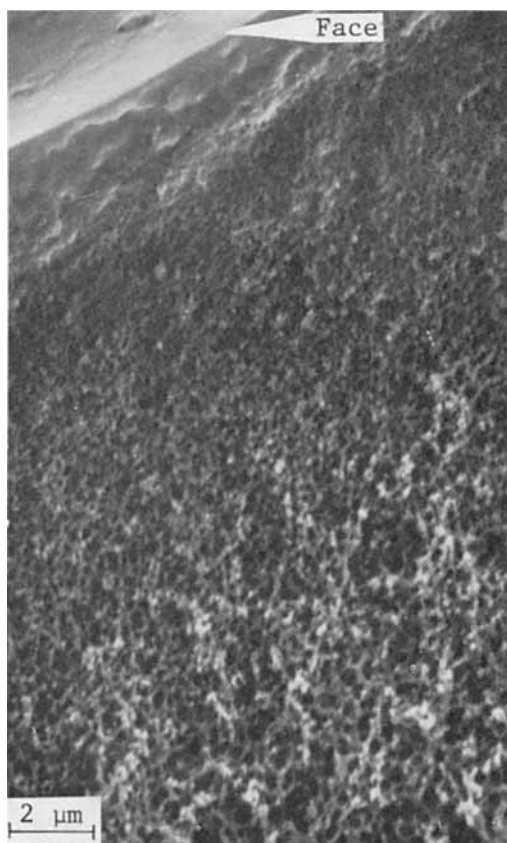


Fig. 5. Surface cross section of PVP/CA (formula index 10a) asymmetric alloy membrane, showing tight skin resting on a porous structure.

TABLE III  
Miscibility of Poly(4-Vinyl Pyridine) and Cellulose Acetate Solutions

CA	Solution of individual polymer (15 wt % P <sub>4</sub> VPy)	Solution mixture (1:1 w/w)	P <sub>4</sub> VPy/CA (1:1 w/w) Dense film (400 μm)
<i>N,N</i> -Dimethylformamide	<i>N,N</i> -Dimethylformamide	Clear	Opaque (multiphase)
Acetic acid	Acetic acid	Clear	Clear
Acetone	Methanol	Turbide (phase separate)	Opaque (multiphase)
Acetone	Methanol-chloroform (1:1 w/w)	Clear	Clear
Acetone	Acetone-acetic acid	Clear	Clear
Acetone/formamide/ (2:1 w/w)	Acetone/formamide (2:1 w/w)	Clear	Opaque (multiphase)

were taken in increments of 5 sec from submergent to assure no interference that was due to contingent interaction (i.e., swelling) of alloy samples with liquid. The above liquid mixture system exhibits minimum interaction, if any, with the dense P<sub>4</sub>VPy/CA films.





Fig. 6. Cross section of PVPy/CA (formula index 8a) alloy membrane.

### Glass Transition Temperature ( $T_g$ )

A Perkin–Elmer differential scanning calorimeter, DSC-2, was employed to obtain the  $T_g$  of the parent polymers and some of the alloys. Temperature rate increase was maintained at 10°C/min.

## RESULTS AND DISCUSSION

### Poly(4-Vinyl Pyridine)/Cellulose Acetate Blend

Polymer compatibility (or incompatibility) in solutions can, in most cases, be easily detected by physically mixing the polymeric solutions, especially when the pertinent solutions are relatively concentrated (10–30 wt %), as are most of the dope mixtures from which asymmetric membranes are cast. If the polymers are incompatible, the solution will separate into phases. The nature of the solvent in which compatible polymer pairs are dissolved does not affect phase separation in solution as long as the solvent molecules do not interfere with polymeric component interactions. For polymers and solvents that are identified by their activity as strong Lewis bases or acids (or as chelating agents), solvent–polymer interactions may change the polymer characteristics. Thus, with regard to specific interactions between two polymers, an active interacting solvent can either block an active site or become a bridge between sites, bringing together

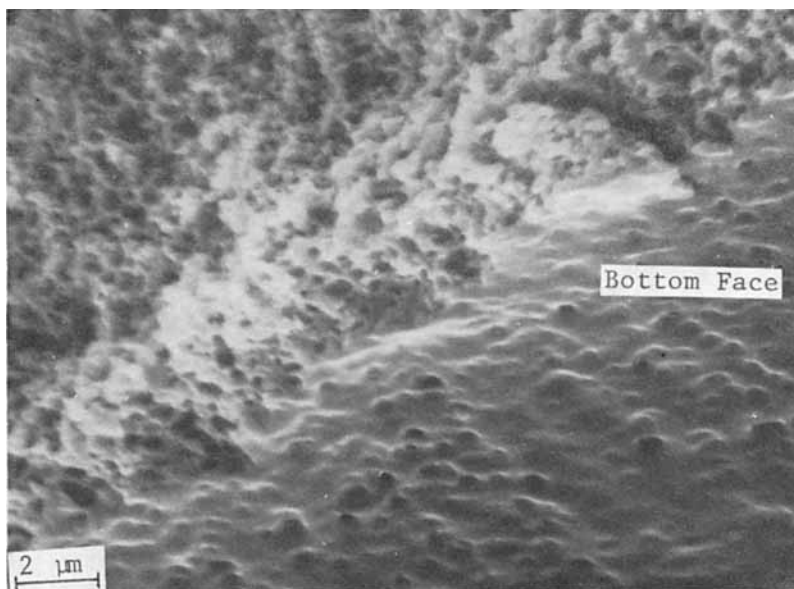


Fig. 7. Bottom face cross section of PVPy/CA (formula index 8a) alloy membrane displaying highly porous skin.

otherwise incompatible polymers; in the latter case, a homogeneous solid phase of the two polymers interlocked into a glassy (below glass transition temperature) matrix can be obtained by proper removal of the active solvent. Poly(4-vinyl pyridine), a strong Lewis base, when dissolved in a solvent system which contains a Lewis acid (or proton donors) would have a different chemical nature than if it were dissolved in a nonacidic solvent. This may well be regarded, in its extreme case, as the difference in the chemical nature between the poly(vinyl pyridine) and poly(vinyl pyridinium) ion. Studying the solubility properties of poly(4-vinyl pyridine), the polymer was found to be soluble in proton-donor-type organic solvents ranging from organic acids (e.g., acetic acid) to chloroform. It is also soluble in rather polar solvents such as DMF (dimethylformamide) or DMSO (dimethylsulfoxide); nonetheless, it is not soluble in less polar and common solvents such as acetone or dioxane. The polymer's affinity toward proton-donor-type solvents is also manifested by its solubility characteristics in water/organic solvent mixtures. While the polymer is insoluble in pure dioxane, acetone, or water, it is soluble in mixtures of either of the first two and water. In view of the above solubility characteristic, delineation of solubility parameter diagrams,<sup>6</sup> which often serve as solubility fingerprints of a polymer, has dubious merit.

Numerous solution mixtures of cellulose acetate and poly(4-vinyl pyridine) were prepared in order to identify the miscibility behavior of the two polymers (selected results are shown in Table III). The solvents selected and shown in the table were of special interest for the development of an asymmetric membrane by phase-inversion mechanism via water coagulation. All of these solvents, excluding chloroform, were employed successfully in the preparation of asymmetric membranes from cellulose acetate and its blends with polyphosphonates<sup>4</sup> and cellulose triacetate.<sup>14</sup> As for the compatibility of P<sub>4</sub>VPy with CA, the results shown in Table III indicate that it is conditional. The clear homogeneous so-



Fig. 8. Scanning electron micrograph of asymmetric PVPy/CA membrane (formula index 8a) showing surface of a membrane dried under ambient conditions. The membrane shrank less than 1% of its original size, displaying subtle wrinkles at the skin face. Although the overall flux rate of such a membrane decreases (~50%) the membrane retains its separation capability (~90% SR at 200 psi).

lution of P<sub>4</sub>VPy/CA in DMF yields a heterogeneous blend upon solvent removal. The mixture of acetone/methanol (in which each of the polymers is soluble) yields phase separation in the solution mixture. However, the addition of Lewis acids which specifically interact with pyridine moieties, yields homogeneous solutions and—what seems to be—a clear transparent single-phase polymer blend (optical clarity of a solid polymer blend does not necessarily prove compatibility on the molecular level; however, in most cases, it indicated a great deal of interpolymer mixing down to a range of ~50 nm and less).

The type of interaction between the two polymers has yet to be identified. Nonetheless, with respect to Table III, it should be remembered that the blended solution mixture, when cast from solution containing acetic acid, results in poly(vinyl pyridinium) moieties, while, when cast with chloroform, the dry blend consists of the poly(vinyl pyridine) interlocked with cellulose acetate in a thoroughly physical mix. The density of the latter was found to be the linear average of the individual polymer components, as plotted in Figure 1, which tends to indicate that while thorough intermixing prevails, specific interactions at this state of existence are relatively low (otherwise, an increase in the density—or rather decrease in specific volume—of the alloy would be expected).<sup>7</sup>

Glass transition ( $T_g$ ) measurement of the alloy cast from the acetone–methanol–chloroform mixture also infers a thorough intermixing. This is shown in Figure 2, where a P<sub>4</sub>VPy/CA—40/60 (w/w) blend—exhibits a glass transition temperature at 165°C, which is 18°C higher than that of pure poly(vinyl pyridine), which exhibits a  $T_g$  of 147°C. The  $T_g$  value of the above blend is lower

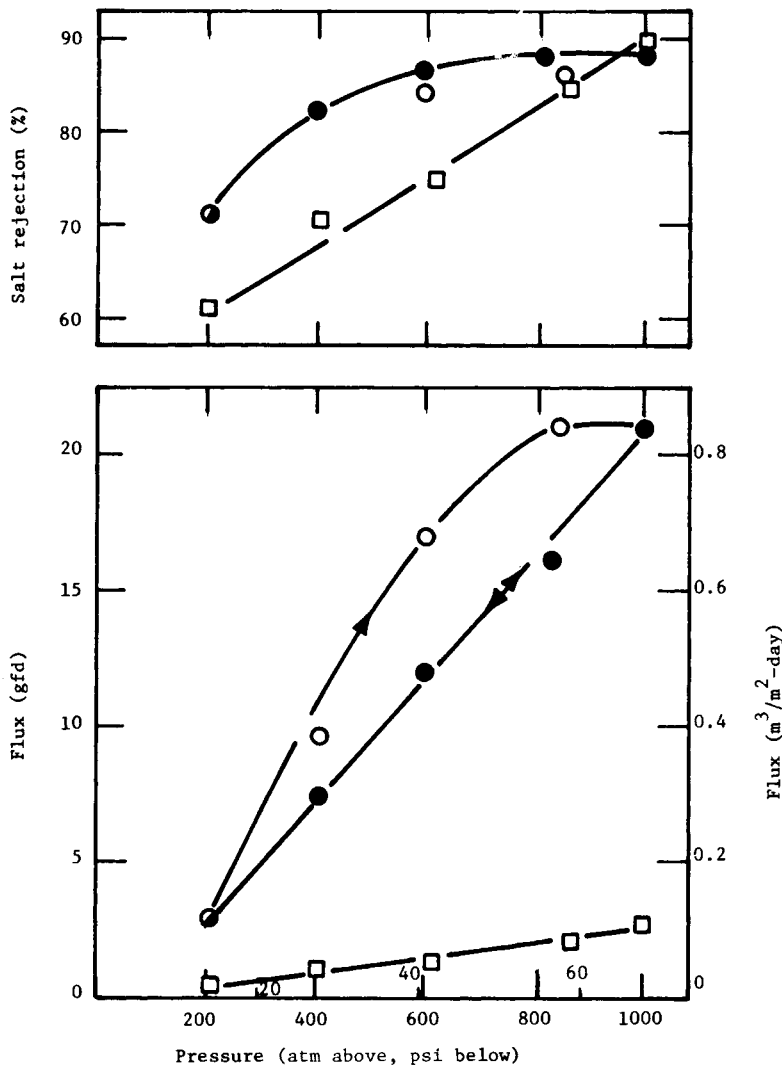


Fig. 9. Flux and salt rejection vs. pressure for PVPy/CA asymmetric alloy membrane (formula index 9a). Feed solution, 10,000 ppm NaCl. (O) Formula index 9a1 without annealing, increasing pressure (tested as cast); (●) formula index 9a1 without annealing, after conditioning at high pressure; (□) formula index 9a4 after annealing at 82°C.

than the mean average (or the reciprocal mean average) of the two polymeric components (the cellulose acetate employed in this study exhibits a  $T_g$  in the range of 190–200°C). A thorough thermoanalysis study of the P<sub>4</sub>VPy/CA alloy will be reported elsewhere.

The role of chloroform as a very effective ingredient in preparing the multi-component polymer solution is notable, especially since it is a nonsolvent for cellulose acetate. The fact that its presence provides the conditions for homogeneity of P<sub>4</sub>VPy/CA solutions may indicate that its interaction with the pyridine nitrogen provides the P<sub>4</sub>VPy chain with the proper conformation and chemical nature to interact with the cellulose acetate. The fact that poly(2-vinyl pyridine) does not yield a homogeneous blend when substituted for P<sub>4</sub>VPy—apparently because of steric hindrance—may support the above hypothesis.

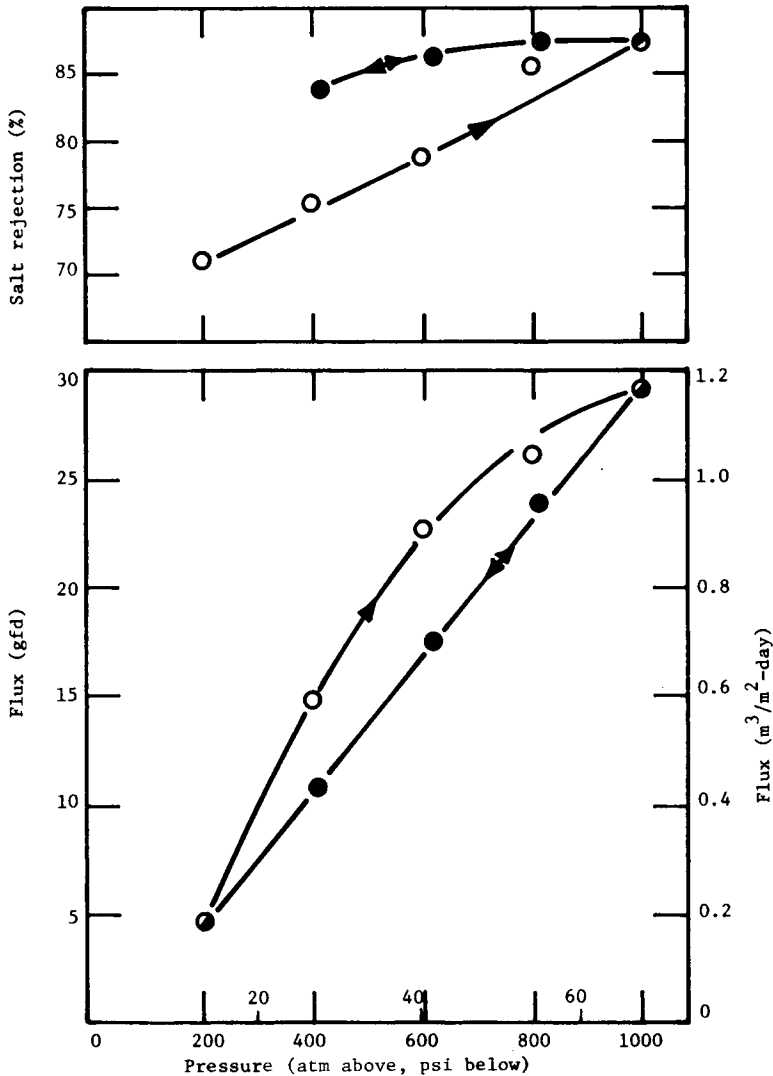


Fig. 10. Flux and salt rejection vs. pressure for PVPy/CA asymmetric alloy membrane (formula index 8a). Feed solution, 10,000 ppm NaCl. (O) Increasing pressure (first testing hour); (●) pressure-conditioned membrane.

The water content of P<sub>4</sub>VPy/CA dense membranes equilibrated in water (24°C) is shown in Figure 3. The increase in water content that accompanies an increase in the weight fraction of P<sub>4</sub>VPy in the alloy membrane is expected. However, a deviation from linearity is clearly seen. The ratio of bound and unbound water in the alloy matrix has yet to be determined. Despite the relatively high water uptake for P<sub>4</sub>VPy/CA [(1./l. by weight) membrane, up to 20 wt % water], no indication of catastrophic phase separation has been observed when running the samples through wet-dry cycles. Water permeability through such dense membranes was found to be high (self-diffusion coefficients determined with tracer are in the range of  $10^{-7}$  cm<sup>2</sup>/sec).<sup>15</sup>

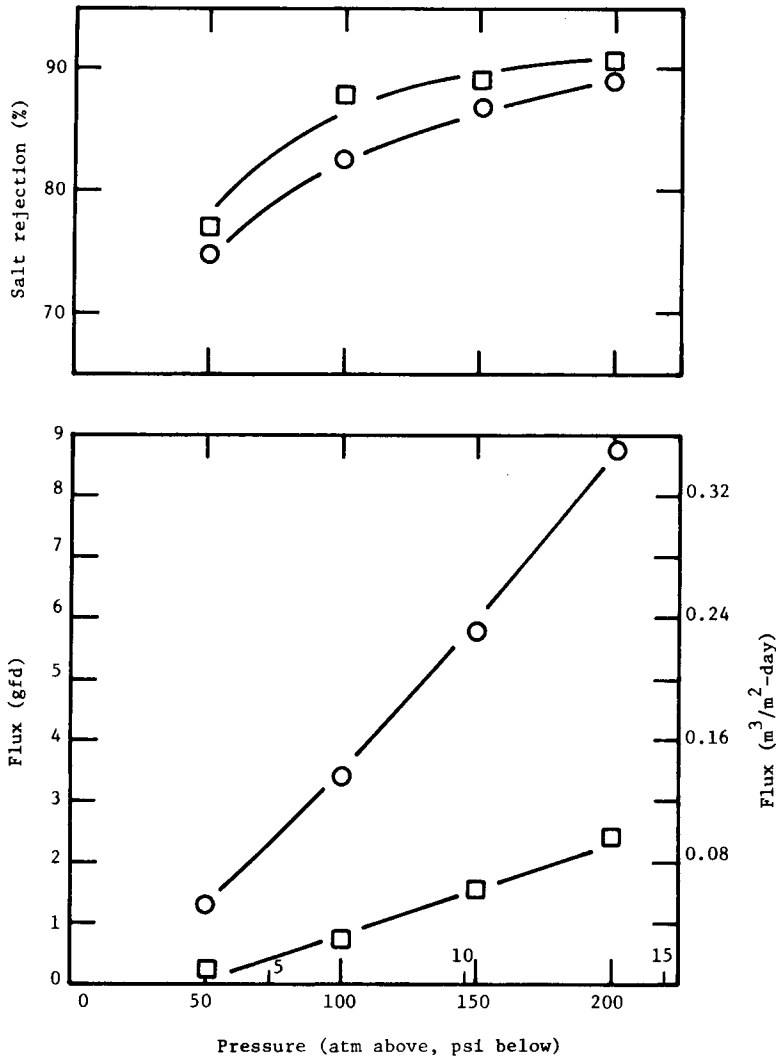


Fig. 11. Flux and salt rejection vs. pressure for PVPy/CA asymmetric alloy membrane (formula index 15). Feed solution, 1000 ppm NaCl. (○) Formula index 15a, casting thickness 5 mil; (□) formula index 15b, casting thickness 7 mil.

## Asymmetric Membranes

### Casting

Asymmetric membranes of  $P_4VPy/CA$  blends were prepared by anisotropic coagulation of the polymers solutions in water. The selection of the solvent shown in Table I was based on the well-known Manjikian<sup>16</sup> formulation for the preparation of anisotropic cellulose acetate membrane, which employs acetone-formamide solvent system. The methanol selected for dissolution of  $P_4VPy$  was used before<sup>14</sup> as a swelling agent that impedes macrovoid formation when added to the casting solutions of cellulose acetate-cellulose triacetate blends, and was employed as a solvent for poly(phosphonates) in the preparation of PPN/CA alloy membranes.<sup>4</sup> In general, the proportions among these three water

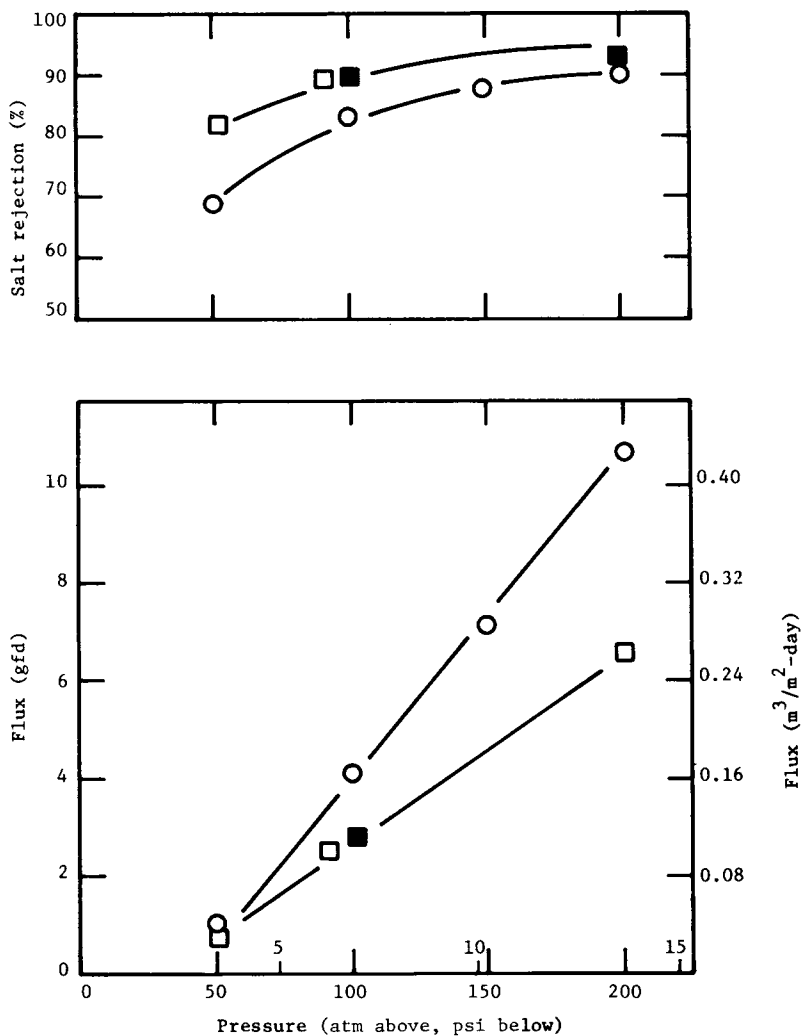


Fig. 12. Flux and salt rejection vs. pressure for PVPy/CA asymmetric alloy membrane (formula index 8). Feed solution, 1000 ppm NaCl. (○) Formula index 8a/2, casting thickness 5 mil; (□) formula index 8b, casting thickness 7 mil; (■) decreasing pressure.

compatible components (acetone, methanol, and formamide) were kept in that range (as shown in Table I), which would produce an asymmetric membrane for water-quenched cellulose acetate solutions.

The fact that addition of chloroform to  $P_4$ VPy/CA solutions (consisting of the above water-miscible solvents) yielded homogeneous solutions and clear translucent dense membranes prompts us to search for the condition by which asymmetric membranes would be produced from solutions containing chloroform. The latter has negligible solubility in water, which is considered an undesirable property if coagulation in water is sought. In this respect, we may point out that from the available compiled data, Klein and Smith<sup>17</sup> postulated some empirical laws in regard to the casting of asymmetric membranes—one of them stating that all solvent components of the system should be miscible with quench medium (i.e., coagulant). The prominent observation that had led to this pos-

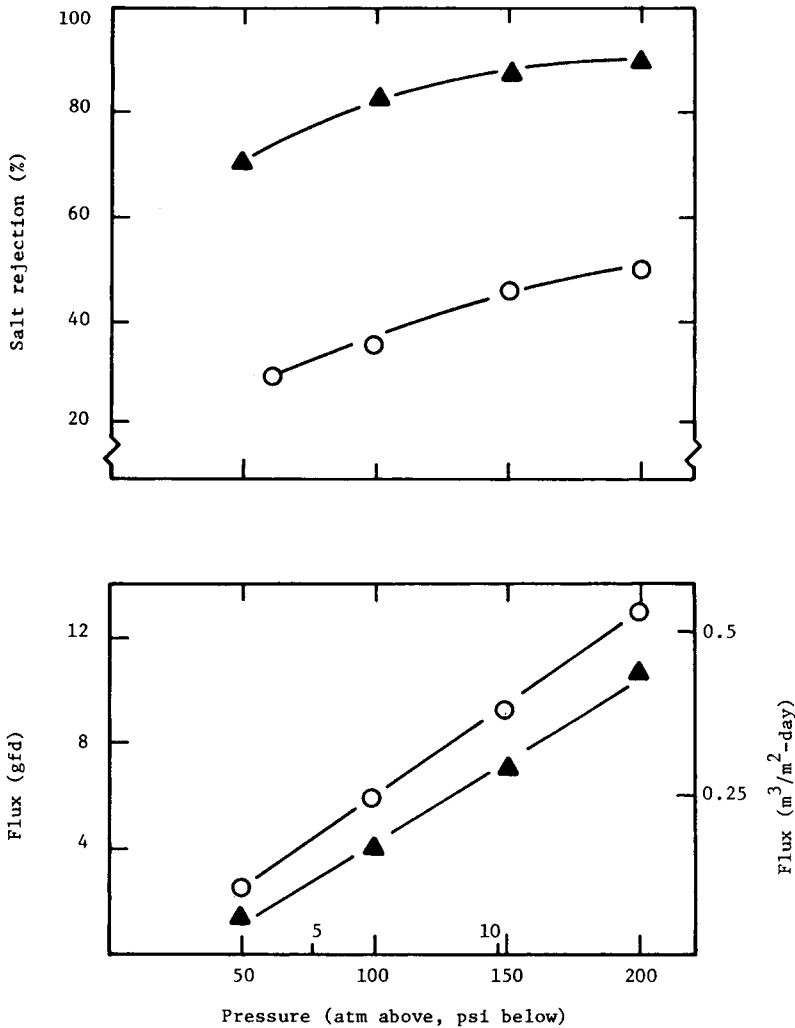


Fig. 13. Flux and salt rejection vs. pressure for asymmetric cellulose acetate (formula index 17) and P<sub>4</sub>VPy/CA alloy (formula index 8a) membranes. The latter shows improved semipermeability over the cellulose acetate membrane; both membranes were prepared from identical formulations (Table I). (▲) P<sub>4</sub>VPy/CA; (○) CA.

tulate is that the nonmiscible solvent retained in the polymer interferes with the coagulation process and impedes the formation of the porous substructure, or, by acting as a good plasticizer, leads to subsequent collapse of the porous substructure of the membranes.

The solution compositions shown in Table I contain up to ~18 wt % chloroform, which is a rather high fraction of the water-immiscible component. Nevertheless, asymmetric membranes were successfully cast employing water as quench medium. The chloroform fraction for each formulation was chosen to be that which would yield a single phase alloy P<sub>4</sub>VPy/CA if it were cast as a dense membrane from similar dopes that do not contain formamide. Hydraulic permeabilities and separation (in the form of reflection coefficients) obtained in reverse osmosis experiments (shown in Table II) indicate that permselective high-flux membranes were indeed obtained.



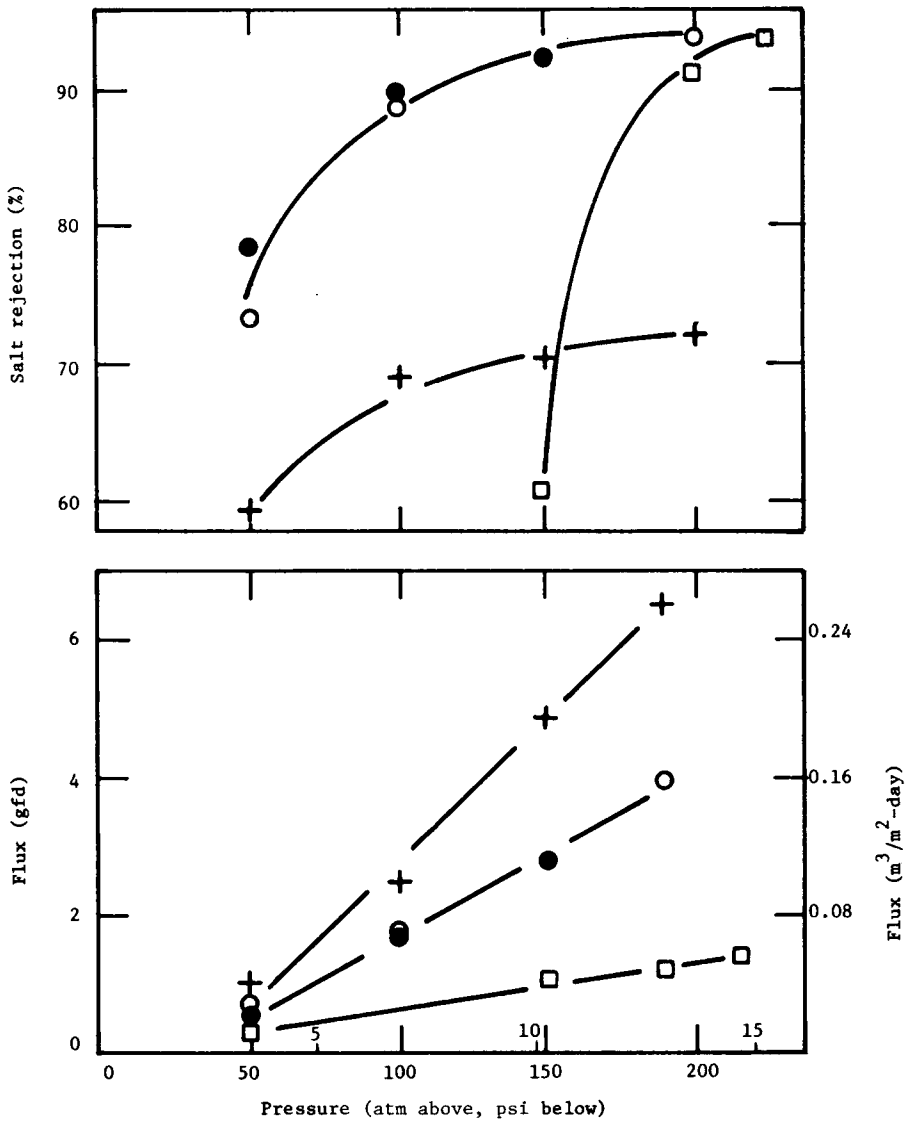


Fig. 14. Flux and salt rejection vs. pressure for PVPy/CA asymmetric alloy membranes (formula index 9a). Feed solution, 1000 ppm NaCl. (O) Wet sample 9a2, increasing pressure; (●) wet sample 9a2, decreasing pressure; (□) formula index 9a3 after drying; (+) formula index 9a3 after quaternization.

Preceding the discussion relating to the reverse osmosis experimental results, three notable observations should be summarized: (1) chloroform was successfully used in the casting solution; (2) the membranes were quenched in water at ambient temperatures (14–20°C); and (3) the membranes were tested as cast, without annealing.

There is no doubt that the addition of chloroform to the casting solution greatly influences the coagulation mechanism and membrane properties. Chloroform, having extremely low solubility in water, was retained for several days in the coagulated membrane matrix stored in water. Therefore, the membranes were

highly plasticized following the sol-gel transition. The plasticization of the membranes in this instance resembles the conventional annealing (in hot water  $>70^{\circ}\text{C}$ ) of the as-cast cellulose acetate asymmetric membrane. The phase inversion that occurs upon quenching the polymer solution does not—as expected—yield a “frozen” matrix (below glass transition temperature  $T_g$ ), and segmental translational motion of the macromolecules is allowed until most of the chloroform dissipates. At this intermediate stage, the dense skin reaches a structural stability which yields a highly packed, permselective dense skin. Membranes that were tested before the chloroform was allowed to fully dissipate exhibited high fluxes and low selectivity similar to the nonannealed Loeb-Sourirajan cellulose acetate membrane.<sup>1</sup>

The effect of the quenching temperature seems to be of minor importance in comparison with conventional conditions that are employed in the fabrication of cellulose acetate asymmetric membranes (which, for most formulations, require quenching temperatures in the range of  $-10$  to  $4^{\circ}\text{C}$ ). When sufficient time was given to allow full dissipation of the chloroform to the water, ambient quench temperatures, up to  $25^{\circ}\text{C}$ , could be employed.

### *Morphology*

Scanning electron microscopy studies revealed the asymmetric morphology (Figs. 4–6). The cross sections show a progressive decrease in pore size from the bottom face to the dense surface. The thickness of the dense skin cannot be determined from these photomicrographs, since the microporous structure beneath the skin apparently collapses when the membrane is dried. The bottom faces of these membranes display a highly porous skin, approximately  $250 \text{ \AA}$  thick (Fig. 7). A significant characteristic—regarding the casting condition and formation of tight skin—is that all the membranes are macrovoid-free. The fact that the entire membrane structure does not collapse upon drying is notable. For example, the asymmetric membrane designated No. 8a shrank less than 1% of its original surface area when dried in ambient conditions. Comparable cellulose acetate membranes that were cast and annealed to give the same transport performance (cast from acetone/formamide/cellulose acetate—45/30/25, annealed at  $85^{\circ}\text{C}$ ) lost 20% of their surface area when dried (a cellulose acetate membrane cast under the same conditions as 8a, which is shown as No. 17 in Table I, shrank more than 9% when dried in ambient condition). The dry  $\text{P}_4\text{VPy/CA}$  retains its permselectivity [ $\sim 90\%$  salt rejection at 200 psi ( $\sim 13.6 \text{ atm}$ )], but the overall flux rate decreases—because of the skin thickening—to about half the original wet flux rate, 11 gfd ( $0.45 \text{ m}^3/\text{m}^2 \text{ day}$ ) at this pressure. Close examination of the dry membrane reveals subtle wrinkling of the dry surface (Fig. 8). This is an important observation—especially since there is no indication of skin rupture as the permselectivity is retained—possibly indicating that the dense skin and the substructure may have different molecular packing densities (e.g., semicrystallinity) resulting in differences in their water absorption. The latter can also reflect differences in the alloy composition of the skin and substructure, which is an issue subject to further investigation.

### *Annealing in Water*

Annealing the membranes in water at 82°C had a significant adverse effect on membrane performance, as shown by Figure 9. The decrease in flux rate and separation indicates a collapse in the membrane structure. This is a probable outcome of the high water uptake—owing to the P<sub>4</sub>VPy/water interaction—of the membrane (Fig. 3), which results in lower glass transition temperature of the water-swollen P<sub>4</sub>VPy/CA alloy. In addition, untangling of the P<sub>4</sub>VPy and CA polymer chains under the above annealing conditions may result in microphase separation leaving imperfections in the selective skin. In comparison, it is of interest to note here that polyphosphonate/cellulose acetate membranes, where the phosphoryl ester is attached to a hydrophobic polymer chain,<sup>4</sup> require relatively high annealing temperatures (94°C) in order to upgrade the semipermeability of the membranes. Phase separation does not take place and water-phosphoryl group interaction hardly affects the structure of the hydrophobic skeleton, i.e., plasticization by water of these polyphosphonates is lower when compared to poly(vinyl pyridine).

### *Transport Properties*

In general, the membranes did not show any tendency to collapse or compact after the initial conditioning in a test cell; however, compaction characteristics of these membranes remain to be determined for long (several months) durability runs. Testing the membranes under elevated hydraulic pressure (Fig. 10) did not result in catastrophic collapse of the matrix, and after the conditioning period (designated by the open circle in the figure), linear relationship between flux and pressure is established. The thickness of the cast layer affects the resulting membrane performance, as shown in Figures 11 and 12; the trend is toward better separation, but lower flux rates for the thicker layer. The semipermeability and flux rates of cellulose acetate and poly(4-vinyl pyridine)-cellulose acetate alloy membranes prepared under the same conditions (Table I, formula indexes 8a, 8b, and 17)—were compared. The results are shown in Figure 13. The alloy membranes display much higher separations, while the product flux is slightly lower. Comparable cellulose acetate membranes that were cast and annealed to give the same salt rejection (cast from CA/acetone/formamide—25/45/30, annealed at 85°C) exhibited substantially lower flux (~0.1 m<sup>3</sup>/m<sup>2</sup> day) at a pressure of 200 psi (~13.6 atm). The higher salt rejection exhibited by the alloy composition, compared to the cellulose acetate (Fig. 13), may be attributed to the interaction between the two polymers.

The reflection coefficients, shown in Table II, comply with the theory of solution diffusion model for saline (NaCl) water through noncharged membranes,<sup>18-20</sup> which predicts that reverse osmosis membranes exhibiting water content in the range shown in Figure 3 might yield maximum salt separation of 85–95%.

The pH of the feed solution in all experiments ranged between 6.1 and 6.8. Lower pH (<4) alters the transport characteristics, since quaternization of the P<sub>4</sub>VPy takes place. The latter—as a hydrochloride quaternate—is a water-soluble polymer which is easily leached out from the membrane. However, crosslinking via quaternization of the P<sub>4</sub>VPy chains can easily be carried out with a dihalide reagent to give an insoluble quaternate. Plots showing transport

characteristics of three modifications—as cast, dried, and quaternized—of the P<sub>4</sub>VPy/CA asymmetric membrane (No. 9, Table I) are shown in Figure 14. The quaternization of the membrane was carried out on a sample previously dried in ambient atmosphere, then submerged in a solution containing 1,4-dichloro-2-butene (hexane/ethanol/C<sub>4</sub>H<sub>6</sub>Cl<sub>2</sub>—87.5/10/2.5). The results (Fig. 14) indicate that this treatment yields a substantial increase in flux rate; but separation decreases significantly, probably because the increase in water uptake of the treated membrane which swells beyond the point where the quaternary groups contribution to the membrane's semipermeability is detectable.

## CONCLUSIONS

Two dissimilar polymer chains, cellulose and ethylpyridine, have been combined into a homogeneous blend from which asymmetric membranes were cast. To our knowledge, only polyphosphonates and cellulose triacetate<sup>14</sup> had previously been blended successfully with cellulose acetate to yield high-pressure reverse osmosis membranes. The exact mechanism that is responsible for the interactions between the two polymers still requires further study.

The membranes introduced in this study do not qualify for seawater desalination because of their relatively high water absorption. The fact that poly(4-vinyl pyridine) is a more expensive polymer than the aromatic nylons and cellulose ester polymers employed at present would make the membrane less economically feasible at this stage, even for use with large-unit brackish water treatment systems. However, the use of asymmetric membranes has been very much diversified since originally conceived for the purpose of straightforward water desalination (to obtain drinking water). Two prominent advantages of the P<sub>4</sub>VPy/CA alloy membranes are that they are capable of maintaining a dry anisotropic structure (therefore, they are easy to sterilize, store, and pot), and they provide a source for a quaternized asymmetric membrane. Water and organic liquid absorption and diffusion characteristics in these alloy membranes will be reported in a subsequent article.<sup>15</sup>

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