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CONCERNING THE NATURE OF IONICALLY MODIFIED
AROMATIC POLYAMIDE MEMBRANES

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ABSTRACT

The application of cross-linking based on ionic bonds has been successfully demonstrated with aromatic polyamides for the improvement of long-term membrane flux stability. Flux decay values, expressed as $d \log J_1 / d \log t$, have been reduced to -0.02 compared with -0.12 for the untreated membrane control, operating at 102 atms. applied pressure, on a natural seawater feed solution. Selectivity to dissolved inorganic salts such as sodium chloride remains high, for membranes modified in this manner.

INTRODUCTION

The observation^{1,2} that membranes prepared from aromatic polyamides and polyamide-hydrazides possess a significant level of

selectivity to dissolved salts has resulted in considerable interest in these systems, as membrane compositions for desalting water by the process of reverse osmosis³.

Anisotropic membranes prepared from certain aromatic polyamides show⁴ total salt rejections ($r = 1 - \text{product concentration}/\text{feed concentration}$) of 0.998 and a product water flux (J_1) as high as 4×10^{-4} g/cm²-sec in field tests carried out with natural seawater at 102 atms. Observed compaction rates for some of these membranes, expressed as the flux decline parameter $\epsilon = d \log J_1 / d \log t$, were high, ca. -0.12. A portion of this water flux loss was attributable to membrane fouling in the form of iron oxide and biological growth at the membrane surface; however, much of the change appeared related to intrinsic membrane failure under the stresses of the applied hydrostatic load during reverse osmosis operation.

Several attempts⁵ at reducing membrane compaction through application of polymer cross-linking via reactions with aldehydes, and irradiation, alone or in the presence of mono and difunctional vinyl monomers, resulted in some increased stabilization. However, each measured improvement in flux stability was always accompanied by a reduction in the total membrane water flux, as shown in Table I.

As a result of this study, a unique method of membrane stabilization, based on an ionic modification procedure, has been demonstrated. It is believed that this process results in the formation of cross-links of an ionic nature^{6, 7, 8}.

TABLE I
Comparative Reverse Osmosis Data for Modified Polyamide Membranes

Polymer Type	Composition	Nature of Modification	$J_1, 10^{-4}(\text{g}/\text{cm}^2\text{-sec})$	r	$d \log J_1/d \log t$
amide	BABB/TCI	none	5.12	0.998	- 0.120
modified amide	BABB/TCI	Exposed to γ radiation (8.75×10^6 Rads)	3.25	0.997	- 0.034
modified amide	BABB/TCI	Irradiated as above in the presence of a (50:50) acrylic acid:ethylene glycol dimethacrylate aqueous mixture.	2.73	0.994	0.000
modified amide	(75:25) BABB:DABA/TCI	Ionically modified with p-phenylene diamine	4.80	0.994	- 0.020
amide-hydrazide	PABH/TCI	Annealed in water: 15 mins/100°C	1.13	0.990	- 0.004
amide-hydrazide	PABH/ICI	Annealed in water: 4 mins/87°C	3.35	0.995	- 0.030
amide-hydrazide	(50:50) PABH:MABH/ (50:50) ICI:TCI	Annealed in water: 4 mins/87°C	4.01	0.995	- 0.033

The process consists of incorporating carboxylic acid functional groups into the polymer backbone followed by exposure of these groups to difunctional amines. The resulting salt bridge or ionic bond provides the cross-linking. As far as the author is aware, this is the first known use of ionic bonds for membrane flux stabilization. The application of this technique has not only resulted in flux decline rates (ϵ) as low as -0.02 at 102 atms. applied pressure, but a simultaneous increase in the total membrane water flux. Such membranes show good hydrolytic stability.

EXPERIMENTAL

Polymer Synthesis

The aromatic polyamides used in this study were prepared by solution polymerization, at reduced temperature, in anhydrous dimethyl acetamide (DMAc) using the diamines: 1,3-bis(3-amino-benzamide)-benzene (BABB) and 3,5-diaminobenzoic acid (DABA) with terephthaloyl chloride (TCl) as the acid chloride.

Other intermediates used in the preparation of polymers included 3,4'-diaminobenzanilide (DAB), benzophenone dianhydride (BPDA), pyromellitic dianhydride (PMDA), isophthaloyl chloride (ICl), p-amino-benzhydrazide (PABH), and m-aminobenzhydrazide (MABH).

In addition to the incorporation of 3,5-diaminobenzoic acid, the use of pyromellitic dianhydride and benzophenone dianhydride in the

polymer chain afforded an alternate means of introducing the carboxyl groups, necessary to achieve the ionic modification.

The polymerization procedure used in this paper consisted of dissolving the diamine in the anhydrous dimethyl acetamide in a dry flask under a continuous nitrogen blanket. The temperature of this solution was then reduced to -10 to -15° C and the acid chloride added with stirring. The reaction was allowed to proceed for 30 minutes before raising the solution temperature to that of the ambient. After a three-hour mixing period, sufficient calcium carbonate, to neutralize 95 mol percent of the liberated HCl, was added. The resulting mixture was then stirred at ambient temperature for 30 minutes, 50° C for 30 minutes, and 75° C for 30 minutes to complete the reactions. The solution was then vacuum degassed (~ 500 mm Hg) at 75° C for 10 minutes.

The addition sequence used for polymerizations involving the dianhydride was: diamine dissolution in DMAc, followed by addition and dissolution of dianhydride, with subsequent solution temperature reductions (to -15° C), and the addition of TCl.

Membrane Preparation

Prior to membrane preparation, the polymer solution was pressure filtered through a double thickness of Whatman[®] No. 42 filter paper. The solution was then cast on to a clean, dry, polished glass plate by means of a Gardner[®] knife with an adjustable blade. The glass plate containing the film was immediately placed in a mechanical convection

McKINNEY

oven equipped with a filtered air intake set for 105° C. At the conclusion of this drying period, the glass plate was removed from the oven and quickly immersed in distilled water to effect coagulation. A membrane of anisotropic structure results from this procedure. Each membrane was washed for a minimum of 12 hours to remove solvent and dissolved salt. To insure complete elimination of any species associating with the polymer carboxyl groups as a result of the dope neutralization process, the membranes were exchanged in an aqueous hydrochloric acid bath (pH 2) followed by a second washing in high quality distilled water (specific resistance $\geq 10^6$ ohm-cm).

Ionic reaction was achieved in the following manner: After undergoing the second washing step, the asymmetric membrane was placed in an air-free aqueous solution containing 0.2-0.5 g dl⁻¹ of a difunctional amine, primarily paraphenylene diamine (pPD). The concentration of diamine was chosen to provide a level in excess of that necessary for reaction with the free-carboxyl groups in the membrane.

The reaction of pPD with the membrane was followed by the development of a blue color which became dark at the conclusion of the reaction. Once the reaction was complete (≤ 72 hours) the membranes were placed in distilled water to remove all unreacted pPD and were then ready for testing.

Membrane Testing

Membrane transport evaluations were made on an apparatus, previously described⁴, using 0.6M NaCl solutions at pressures to 102 atms. for a minimum of 10 days. A second test unit, constructed entirely from polyvinyl chloride components (except pump), permitted the evaluation of time-dependent transport parameters in the absence of unit corrosion and attendant membrane fouling. Testing was completed at 82 atms. applied pressure with the temperature of the test solutions regulated to within one degree centigrade during unit operation.

RESULTS AND DISCUSSION

Properties of the Ionic Reaction

The reaction between carboxyl groups of the membrane and p-phenylene diamine can be followed by the development of a blue color associated with the formation of the p-phenylene diammonium benzoate linkage, as suggested by Figure 1. The blue color appears to occur only when difunctional (complete) reactivity of the diamine is achieved. This can be demonstrated by the reaction of benzoic acid, as follows.

When benzoic acid is exposed to an aqueous solution containing p-phenylene diamine, the blue color is evident. When the mono-functional equivalent, aniline, is substituted for pPD, the blue color

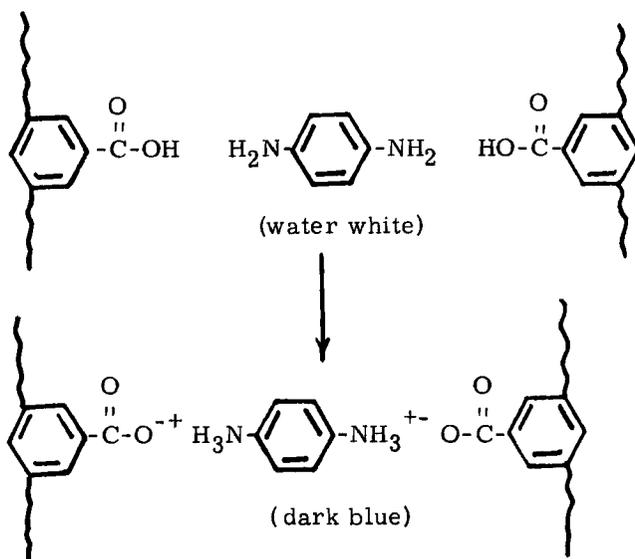


Figure 1. Proposed ionic cross-linking mechanism

does not occur. Similarly, when membranes containing the carboxyl functional group are exposed to aqueous aniline solutions, no color develops. This color relationship is illustrated in the photomacrograph of Figure 2. This suggests that the chromophore responsible for the color change is $\text{H}_3\text{N}^+ - \phi - \text{NH}_3^+$ and appears consistent with the concept of cross-linking via reaction with carboxyl groups of adjacent polymer chains. One might argue that such chromophoric structure could possibly be realized by reaction with carboxyl groups of the same chain, separated only by the terephthaloyl chloride group in the backbone. However, such logic is not consistent with other observations regarding polymer solubility and solution viscosity. Membranes

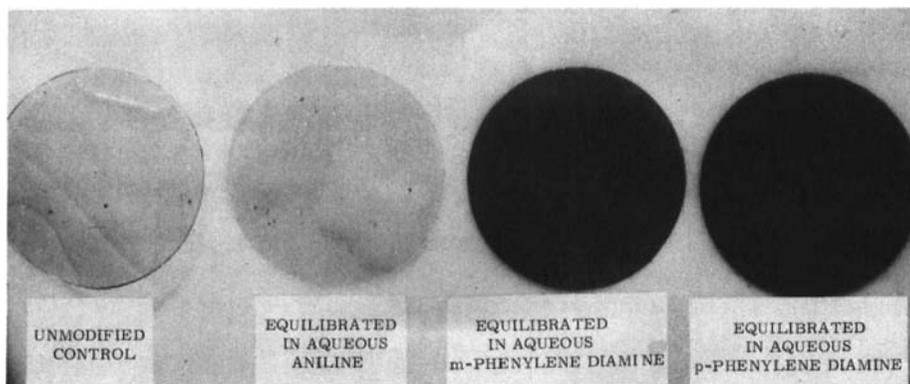


Figure 2. Membrane color development from exposure to selected amines.

containing the pPD bridge do not completely redissolve in dimethyl acetamide solutions. Such solutions contain large gel masses. Similar polymers not containing pPD dissolve readily. Also, viscosities of these polymer solutions have shown to increase ten-fold (to ca. 10^5 centipoise) on addition of pPD. Such evidence suggests, at least for systems containing pPD, the existence of intermolecular linkages. Prolonged heating (several hours) of the membrane containing pPD appears to result in the condensation of the salt bridge with the resulting formation of amide linkages.

Regardless of the exact mechanism, membranes ionically modified according to the above procedure exhibit increased resistance to hydraulically induced water transport (flux) decay under conditions of reverse osmosis. The extent of this resistance is a function of the degree of ionic cross-linking, expressed in terms of the available

cross-linking (carboxyl) sites in the polymeric membrane, as shown in Table II.

As the carboxyl group concentration in the membrane composition, expressed as the molar level of DABA, increases, the value of ϵ passes through an apparent minimum near 25 mole percent. At a concentration of 50 mole percent DABA, the membrane has become very swollen owing to the increased polar nature of this polymer. Also evident from this table is the nature of the water flux response to the level of DABA prior to, and after, ionic modification. While the ionic reaction with pPD reduces the level of J_1 at each level of DABA, this reduced flux level compares well with the unmodified control

TABLE II
The Effects of 3,5-Diaminobenzoic Acid Content
on Membrane Transport Properties

BABB/DABA ^b	Standard Membrane			Ionically Modified Membrane ^a		
	$J_1, 10^4(\text{g}/\text{cm}^2\text{-sec})$	r	ϵ	$J_1, 10^4(\text{g}/\text{cm}^2\text{-sec})$	r	ϵ
100/0	5.47	0.998	- 0.120	-	-	-
95/05	6.84	0.993	- 0.119	6.70	0.994	- 0.091
90/10	7.12	0.993	- 0.120	6.08	0.996	- 0.070
80/20	7.45	0.990	- 0.113	5.14	0.995	- 0.059
75/25	8.72	0.989	- 0.129	4.81	0.994	- 0.020
50/50	10.14	0.923	- 0.141	6.84	0.987	- 0.058

^a Membrane modified by exposure to an aqueous solution containing 0.3 g dl^{-1} p-phenylene diamine.

^b BABB is 1,3-bis(3-aminobenzamide) benzene and DABA is 3,5-diaminobenzoic acid. The acid chloride used was TCI .

(first entry, Table II). Sodium chloride rejection (r) remains high in all but one ionically modified membrane; the highly swollen system containing 50 mole percent DABA. The type of diamine used in forming the ionic bridge, during membrane stabilization, is an important variable, as shown in Table III. Paraphenylene diamine is the obvious choice of the candidate materials illustrated in this table. Solubility (in the membrane) and steric considerations are obviously important factors in diamine efficiency. The apparent decrease in membrane stability for the aniline treated sample is likely attributable

TABLE III
The Effects of Diamine Type on Membrane
Reverse Osmosis Performance^a

Diamine ^a	$J_1, 10^4(\text{g}/\text{cm}^2\text{-sec})$	r	$d \log J_1/d \log t$
none	7.12	0.993	- 0.120
p-phenylene diamine	6.08	0.996	- 0.070
m-phenylene diamine	5.89	0.996	- 0.089
1,3-bis(3-aminobenzamide) benzene	4.38	0.995	- 0.093
p-aminobenzhydrazide	4.81	0.997	- 0.088
1,3 diaminopropane	4.67	0.996	- 0.111
1,8 diaminooctane	3.58	0.997	- 0.173
1,12 diaminododecane	0.38	0.966	0
above membrane exposed 15 mins. to (1:3) ethanol:H ₂ O	0.42	0.985	+ 0.214
above membrane exposed 72 hours to (1:3) ethanol:H ₂ O	0.23	0.986	0
(aniline)	(3.87)	(0.991)	(- 0.137)

^a Reverse osmosis data taken with membranes prepared from the polymer: (90:10) BABB:DABA/TC1 at 102 atms.

^b Diamine exposure was effected from aqueous solutions.

McKINNEY

to the plasticizing effects of this solute which would act as a "bulky" side group to the polymer membrane. The positive flux decay value for one sample is related to membrane fouling and subsequent "in situ cleansing" during testing of the comparatively water-insoluble diaminododecane.

The use of ionic bridges in the stabilization of membranes raises questions of the hydrolytic stability of such systems when applied to operations under conditions of extremes in pH. To assess the stability of such systems, membranes were prepared from the polymer (90:10) BABB:DABA/TCI and modified with pPD in the usual manner. These membranes were placed in buffered solutions in the range: $2 \leq \text{pH} \leq 11$ for 24 hours, removed, rinsed with distilled water, and tested at 102 atms. These data are summarized in Table IV. Little change in stability ($d \log J_1 / d \log t$) is evident in the range $3 \leq \text{pH} \leq 8$. In order to further assess the stability question, additional membrane discs were prepared from the above material and exposed to 10-day reverse osmosis tests using pH-adjusted sodium chloride solutions in the range: $3.5 \leq \text{pH} \leq 8$ as illustrated in Table V. The system stability is clearly evident in this table.

The response of other aromatic polyamide structural variants to ionic modification is summarized in Table VI. While the BABB:DABA/TCI system has proven to be the most responsive to this modification process, similar treatment behavior is evident for the other structures given.

AROMATIC POLYAMIDE MEMBRANES

TABLE IV

The Effects of Storage at Selected pH Conditions of Ionically Modified Membrane Performance^a

Storage Media pH (buffered)	J_1 $10^4(\text{g}/\text{cm}^2\text{-sec})$	r	$d \log J_1/d \log t$
2.0	7.12	0.991	- 0.110
3.0	6.08	0.996	- 0.074
4.0	6.03	0.997	- 0.070
5.0	5.75	0.996	- 0.071
6.0	5.94	0.997	- 0.069
7.0	5.85	0.993	- 0.068
8.0	6.13	0.994	- 0.072
11.0	7.02	0.990	- 0.136

^a Reverse osmosis data taken with membranes, prepared from the polymer: (90:10) BABB:DABA/TCI ionically modified with p-phenylene diamine.

TABLE V

The Effects of Test Solution pH on Water Flux Stability for Ionically Modified Membranes^a

pH	Test Solution Composition	J_1 $10^4(\text{g}/\text{cm}^2\text{-sec})$	r	$d \log J_1/d \log t$
3.5	H ₂ SO ₄ /NaCl/H ₂ O	5.94	0.995	- 0.071
4.5	H ₂ SO ₄ /NaCl/H ₂ O	6.08	0.996	- 0.070
8.0	NaOH/NaCl/H ₂ O	5.80	0.995	- 0.069

^a Reverse osmosis data taken with a membrane prepared from the polymer (90:10) BABB:DABA/TCI ionically modified with p-phenylene diamine.

The temperature dependence of water flux and sodium chloride rejection for the ionically cross-linked membrane differs markedly from the non-modified control, as shown in Figures 3 and 4. Both

TABLE VI
Comparative Reverse Osmosis Data for Selected
Ionically Modified Membrane Compositions

Membrane Composition	Modifying Diamine	$J_1 \cdot 10^4$ (g/cm ² -sec)	r	d log J_1 /d log t
(97:03) TC1:BPDA/BABB	p-phenylene diamine	4.05	0.976	- 0.060
(95:05) BPDA:TC1/BABB	none	5.94	0.995	- 0.110
	p-aminobenzhydrazide	4.47	0.997	- 0.074
(97:03) IC1:BPDA/DAB	none	8.25	0.990	- 0.132
	m-phenylene diamine	6.69	0.994	- 0.075
	p-phenylene diamine	6.27	0.991	- 0.066
(97:03) TC1:PMDA/BABB	none	5.33	0.996	- 0.112
	m-phenylene diamine	4.90	0.996	- 0.069
	p-phenylene diamine	4.34	0.990	- 0.064
(90:10) DAB:DABA/IC1	none	7.83	0.985	- 0.123
	m-phenylene diamine	5.61	0.992	- 0.084

membranes exhibit a positive $d J_1/dT$ up to about 60° C. At this temperature, the non-linearity of the flux-temperature response of the control membrane (actually a decrease in flux) reveals the presence of transitions (Figure 3). This process is not evident in the ionically modified membrane (Figure 4). The observed decline in rejection suggests an increased degree of swelling, breakdown of the ionic bridges, or both.

The effectiveness of the ionic cross-linking process in maintaining membrane water flux can be explained in terms of membrane structure preservation, as illustrated by the results of transmission electron microscopy shown in Figures 5 through 8. Figure 5 is a transmission electron micrograph (TEM) of the active surface region of a high

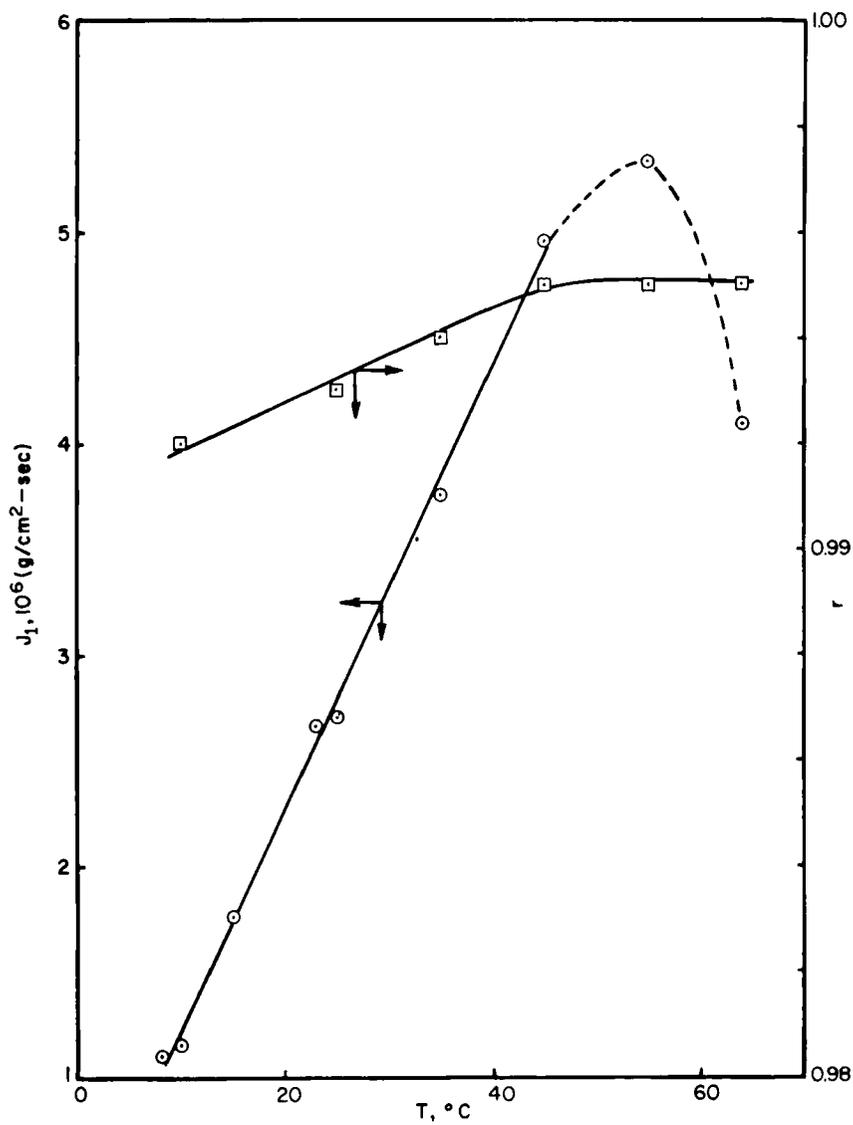


Figure 3. The flux, rejection-temperature dependence of a BABB/TCl membrane at 0.08M NaCl and 41 atms.

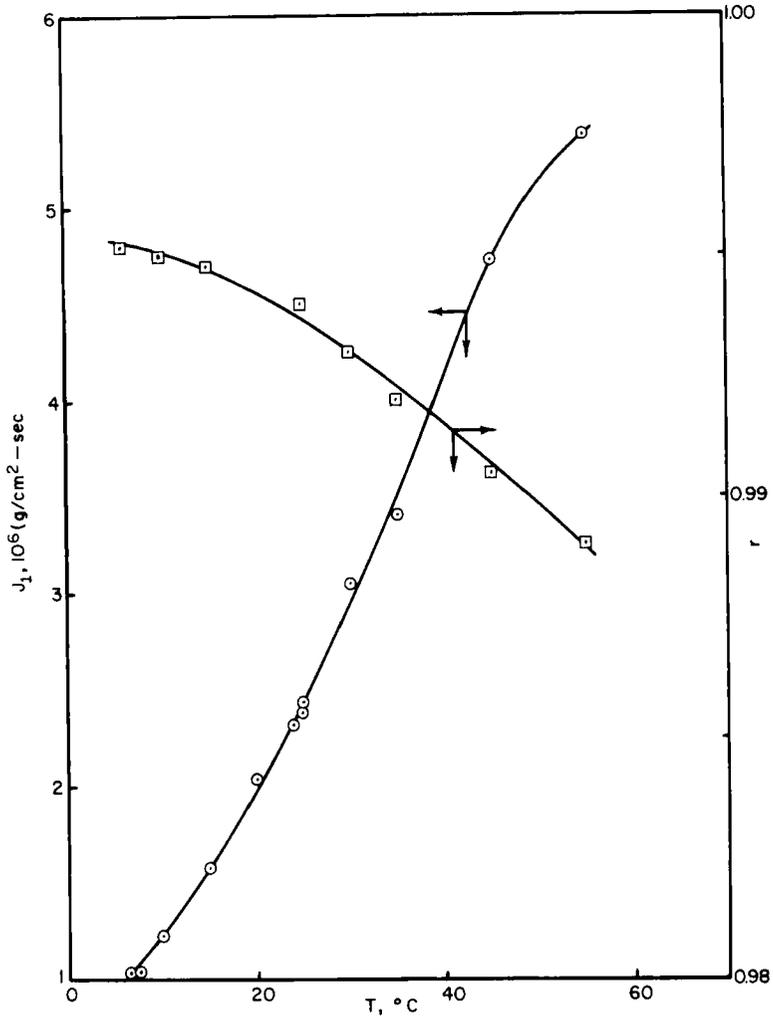


Figure 4. The flux, rejection-temperature dependence of a (90:10) BABB:DABA/TCl membrane modified with pPD at 0.08M NaCl and 41 atms.

performance control membrane. After 10 days of continuous reverse osmosis operation at 102 atms. applied pressure, a densification (loss of pore structure) is evident in the skin region (Figure 6). Such

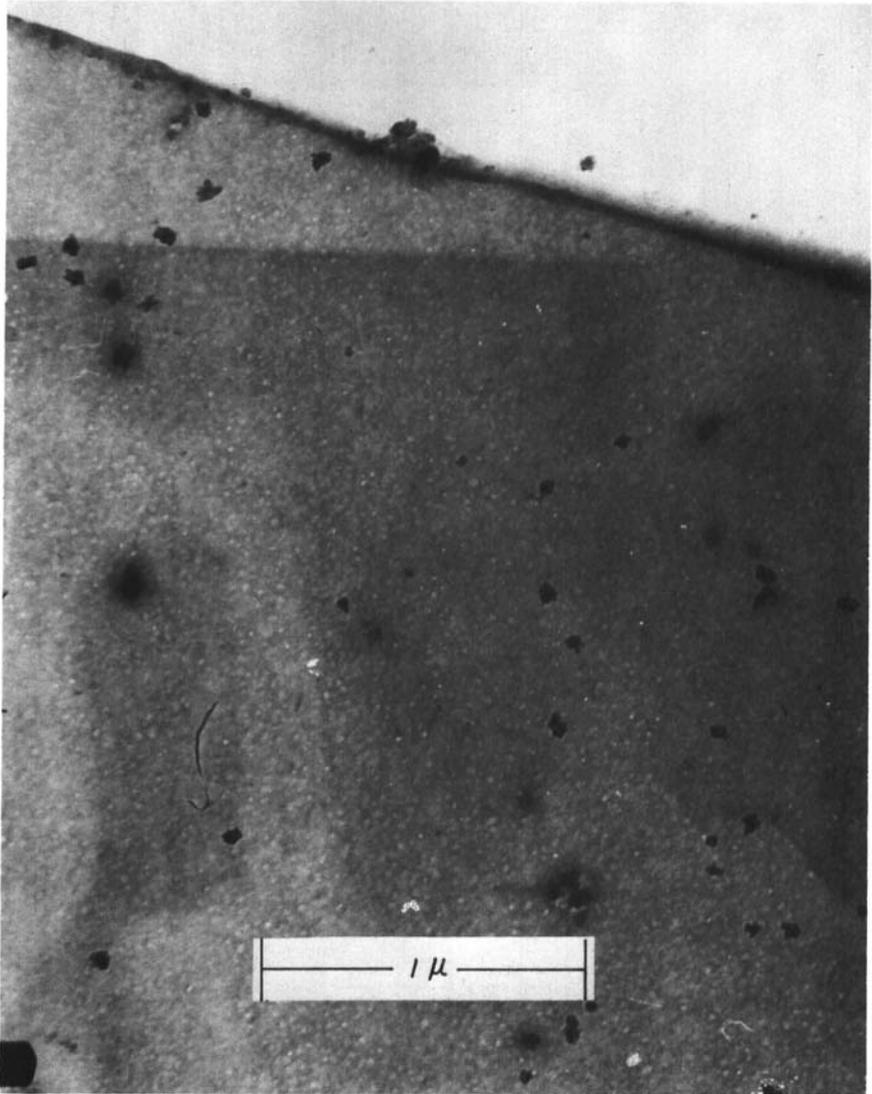


Figure 5. Electron photomicrograph of the skin region of an asymmetric BABB/TCl control membrane cross-section.

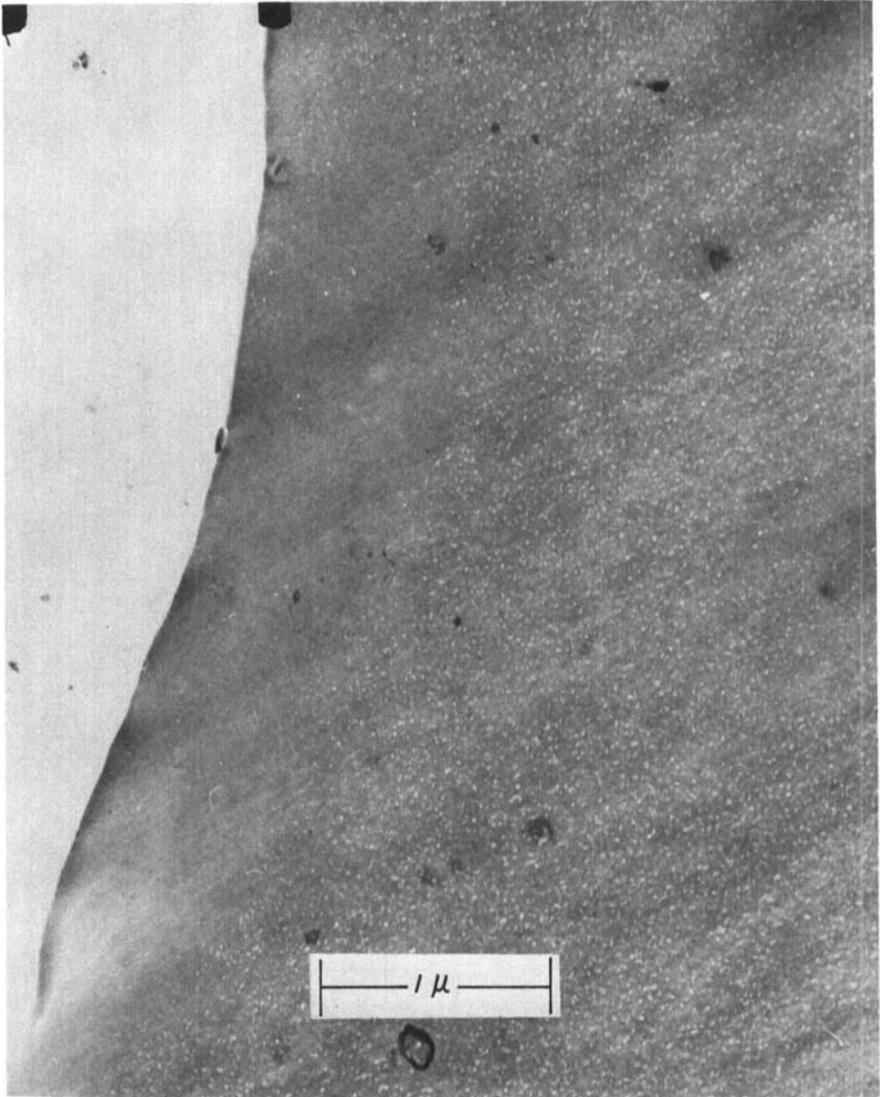


Figure 6. Electron photomicrograph of the skin region of an asymmetric BABB/TCI membrane cross-section after 10 days of RO at 102 atms.

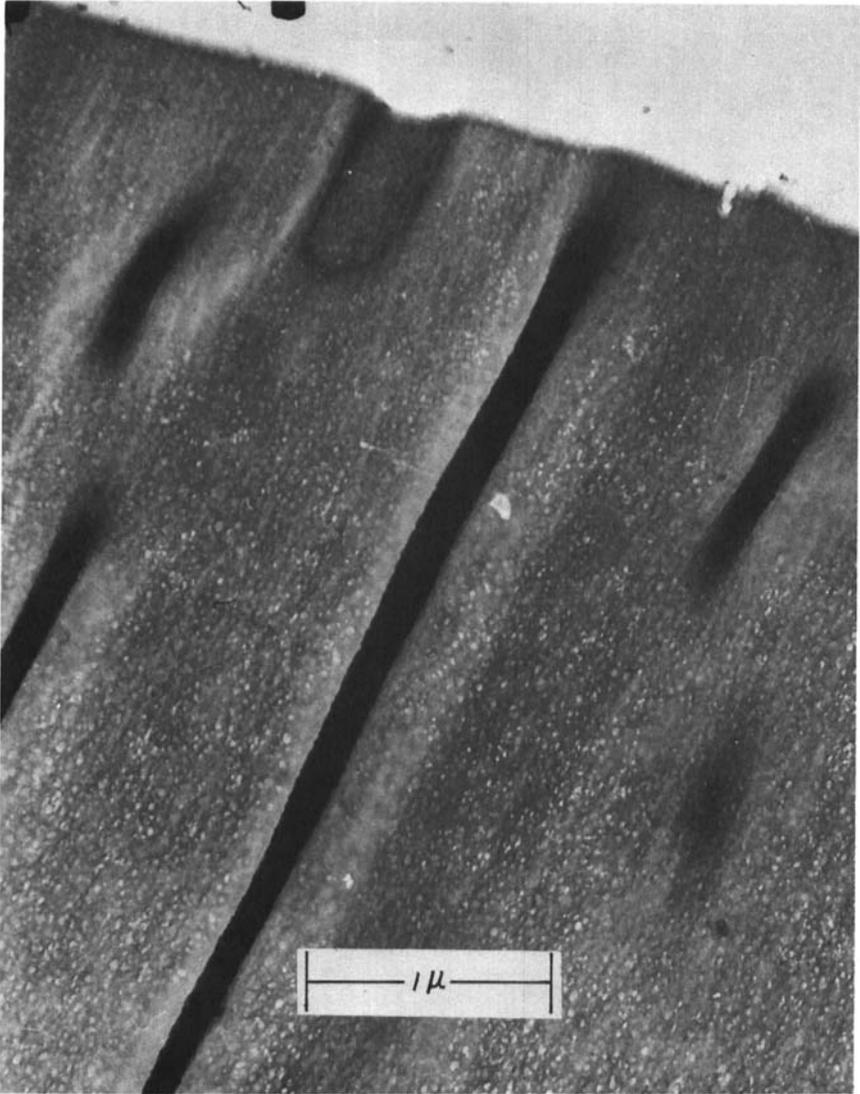


Figure 7. Electron photomicrograph of the skin region of an asymmetric (90:10) BABB: DABA/TCl + pPD control membrane cross-section.

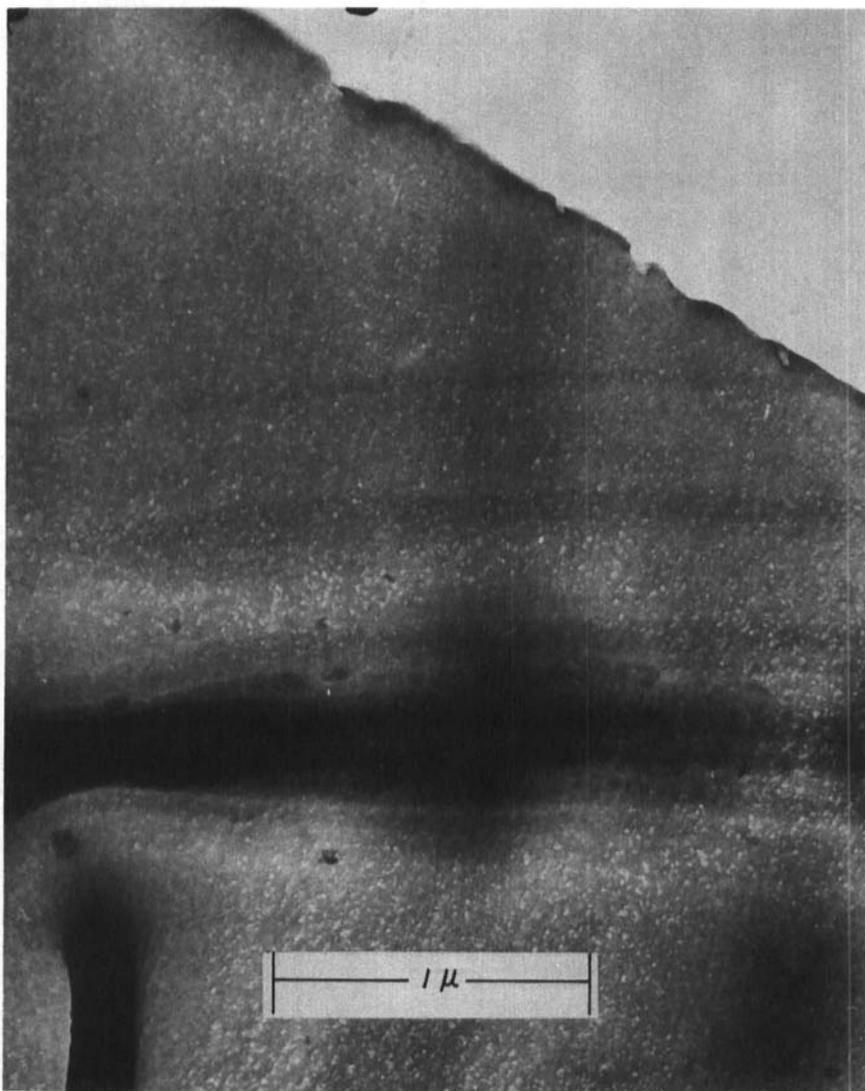


Figure 8. Electron photomicrograph of the skin region of an asymmetric (90:10) BABB:DABA/TCl + pPD membrane cross-section after 10 days of RO at 102 atms.

TABLE VII
Mechanical Property Data^a for Ionically Modified
Asymmetric Membranes

Polymer Composition (BAB:DABA)	Membrane Post Treatment	Membrane Thickness, 10 ² (cm)	Yield Stress 10 ⁻⁸ (dynes/cm ²)	Tenacity 10 ⁻⁸ (dynes/cm ²)	Elongation (%)	Modulus 10 ⁻⁹ (dynes/cm ²)
100:0	-	1.16	1.38	-	-	5.65
90:10	HCl washed above, plus 0.3% pPD	1.15 1.17	0.94 1.08	2.06 1.67	137 72	2.38 2.82
80:20	HCl washed above, plus 0.3% pPD	1.10 1.02	0.94 1.08	1.95 1.74	127 78	1.86 2.30
75:25	HCl washed above, plus 0.3% pPD	1.17 1.12	0.90 1.01	2.06 1.68	153 93	1.92 2.00
90:10	0.3% pPD added to membrane casting solution	0.57	1.47	2.24	80	3.20
Cellulose acetate	-	1.00	0.54	-	-	2.27

^a Mechanical property measurements carried out on an Instron[®] tester at 24±1°C with the asymmetric membrane positioned underwater.

McKINNEY

consolidation is not evident in the corresponding TEM of the ionically modified (90:10) BABB:DABA/TCl system shown in Figures 7 and 8. Such densification results in increased pressure drops at the membrane surface and, subsequently, a reduction in membrane water flux.

Less definitive are the results (Table VII) of mechanical property analysis carried out on water equilibrated membrane strips on an Instron tester. These data reveal an increase in yield stress and modulus and a decrease in elongation on cross-linking with pPD, as expected. However, surprising are the observations that, despite the cross-linking with pPD, higher levels of DABA result in greater degrees of water plasticization of the membrane, as evidenced by increases in elongation and decreases in modulus and yield stress. Also, the values of the yield stress and modulus of the ionically modified membrane are all below that found for the control. These data, together with observations made during reverse osmosis testing, indicate an apparent lack of agreement between time-dependent flux performance and measured mechanical properties.

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McKINNEY

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