Aromatic Polyamide Membranes for Reverse Osmosis Separations

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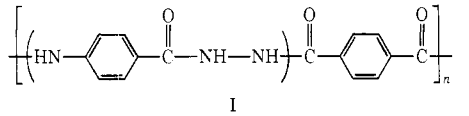
ABSTRACT: The reverse osmosis properties of asymmetric membranes prepared from a novel class of aromatic polyamides and polyamide–hydrazides are described. These materials are characterized by their unusually high degree of selectivity to dissolved salts (*ca.* ≥99.4% rejection) at moderately high levels of flux in the range $1 \leq J_1$ (gal ft^{-2} day^{-1}) ≤ 30, with excellent chemical stability and mechanical properties. The membranes are similar in structure to that reported for cellulose acetate, *i.e.*, they contain a thin dense surface layer supported on a porous matrix.

Considerable activity has been evident in the field of reverse osmosis since the early work of Reid and Breton.[1] Their discovery of cellulose acetate as a desalination membrane, along with the subsequent dramatic improvements in flux demonstrated by Loeb and Sourirajan,[2,3] has stimulated independent interest in reverse osmosis as an economic process in the desalination of brackish and sea waters. The search for new and improved membrane compositions has continued with moderate success, limited to cellulosics in general, and modifications of cellulose acetate in particular.

In this paper, the transport properties of a novel asymmetric membrane system based on a class of aromatic polyamides are described. These materials are characterized by their high degree of selectivity to dissolved salts at moderately high levels of water transport, good mechanical strength, and excellent chemical stability.

Experimental Section

Polymer Structure and Synthesis. The three polymers[4-7] evaluated during this study were a polyterephthalamide of *p*-aminobenzhydrazide (polymer I), poly(*m*-phenyleneisophthalamide) (polymer II), and a polyterephthalamide of 1,3-bis(3-aminobenzamide)benzene (polymer III). Structurally, they can be illustrated as I–III. The polyamide–hydrazide (polymer I) was prepared by ow-temperature (*ca.* 10°) solution polymerization in anhydrous dimethylacetamide from terephthaloyl chloride and *p*-aminobenzhydrazide. The polyamides (polymers II and III) were prepared at −20° in dimethylacetamide. Polymer II resulted from the polycondensation of *m*-phenylenediamine with isophthaloyl chloride, whereas polymer III was produced by the reaction of terephthaloyl chloride with the complex diamine 1,3-bis(3-aminobenzamide)benzene.



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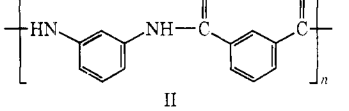

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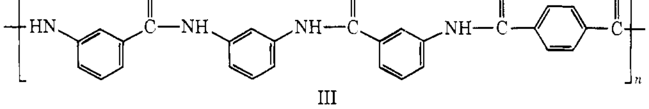

III

Once the polymerization reactions were complete, calcium carbonate, in quantities sufficient to neutralize 95 mol % of the HCl liberated during the polycondensation, was stirred into the polymer solution. The mixture was heated to 75–80° to achieve complete reaction of the $CaCO_3$ and then vacuum degassed. Polymer molecular weights in the range $20 \leq 10^{-3}\bar{M}_v \leq 70$ at concentrations of 6–20% (by weight) were prepared by this method.

Membrane Preparation. Asymmetric aromatic polyamides and polyamide–hydrazide membranes were prepared from the polymerization dopes previously described after careful filtration through a 5-μ pore-size filter. Membrane casting and thickness control were effected by use of a Gardner knife with adjustable blade. Solvent evaporation was achieved in either a mechanical convection (with air sweep) or vacuum oven (with nitrogen gas bleed). In all cases, precautions were taken to ensure exclusion of dust and other airborne contamination.

The polyamide–hydrazide (polymer I) membranes were prepared from polymer solutions containing 6–7% polymer ($\bar{M}_v \approx 34{,}000$) by casting onto clean, dry glass plates. The plate and contents were then placed in an oven, the solvent was allowed to evaporate for a specified period, usually 30–60 min, at a predetermined temperature, and the membrane was removed from the oven and immediately coagulated in deionized water. Each membrane was then allowed to float free of the glass plate and washed for a minimum of 12 hr to achieve complete solvent removal. The solvent-free membranes were then annealed in thermostated, deionized water at temperatures in the range $40° \leq t \leq 100°$) to increase membrane selectivity to sodium chloride.

The polyamide membranes (polymers II and III) were prepared in a manner similar to that used for the polyamide–hydrazide system, except that the water annealing process was omitted for polymer III. A high degree of selectivity (to salts) could be achieved as a direct result of the oven-controlled evaporative stage and subsequent coagulation for this polymer.

Reverse osmosis measurements with 0.5, 3.5, and 6.0 wt % NaCl were obtained with the membrane tester previously described.[8] Modifications (the addition of a pump) in the tester facilitated long-term reverse osmosis performance evaluation.

Results

Polyamide–Hydrazide Membranes. Among the important variables influencing membrane structure and subsequently transport properties of these polyamides and polyamide–hydrazides are temperature and duration of exposure in the oven evaporative step, coagulation temperature, and, if used,

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(1) C. E. Reid and E. J. Breton, Jr., *J. Appl. Polym. Sci.*, **1**, 133 (1959).

(2) S. Loeb and S. Sourirajan, "Sea Water Demineralization by Means of a Semipermeable Membrane," UCLA Report No. 60-60, July 1960.

(3) S. Loeb and F. Milstein, *DECHEMA* (*Deut. Ges. Chem. Apparatewesen Monogr.*), 47, 805 (1962).

(4) J. Preston and F. Dobinson, *J. Polym. Sci., Part B*, **2**, 1171 (1964).

(5) B. M. Culbertson, *ibid., Part B*, **5**, 805 (1967).

(6) (a) S. L. Kwolek, P. W. Morgan, and W. R. Sorenson, U. S. Patent 3,063,966 (1962); (b) J. W. Richter, *et al.*, U. S. Patent 3,567,632 (1971).

(7) W. B. Black and J. Preston, unpublished data.

(8) R. McKinney, Jr., *Anal. Chem.*, **41**, 1513 (1969).

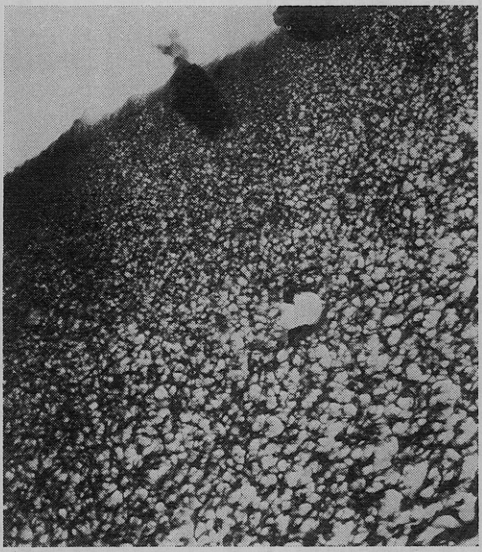

Figure 1. Electron micrograph of unannealed polymer I coagulated at 25°. Magnification is 19,000×.

annealing conditions which include the effects of both time and temperature.

The establishment of membrane anisotropy for polymer I occurs during the oven evaporative period, with the formation of a rudimentary skin or skin region at the air interface resulting from the rate difference for solvent evaporation and diffusion. Coagulation preserves this structure. The skin region extends into the membrane porous matrix for a depth of 3000–5000 Å, as shown in Figure 1, a transmission electron micrograph of a replicated polymer I membrane cross section. Here a pore gradient is observed, with the smaller pores residing in the skin region.

During the annealing step (posttreatment), a consolidation of the skin region occurs (Figure 2), with little effect on the membrane interior matrix evident. Accompanying this change in membrane morphology is a change in transport properties. An unannealed membrane prepared by oven drying at 100° for 50 min would typically have a flux of 30 gfd and 60% rejection for a 5000-ppm NaCl feed operating at 600 psi. The same membrane would demonstrate a 2-gfd flux at 98% rejection for similar test conditions after a thermal annealing for 15 min in deionized water at 100°.

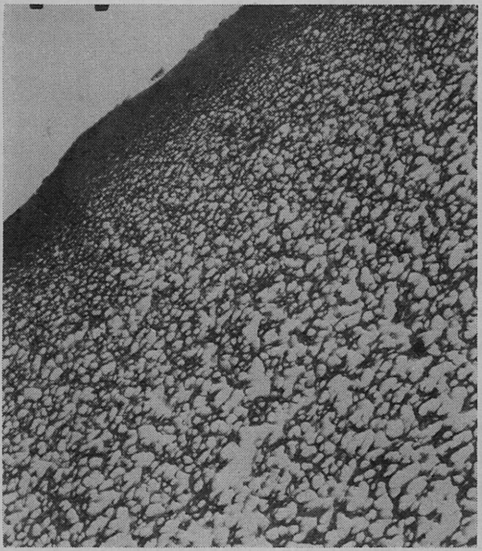

Figure 2. Electron micrograph of annealed polymer I coagulated at 25°. Magnification is 19,000×.

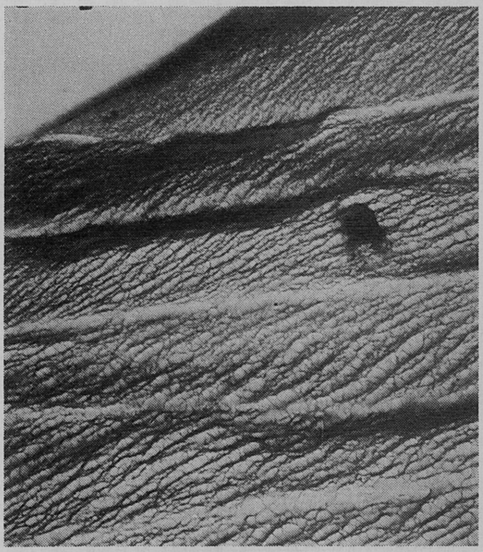

Figure 3. Electron micrograph of unannealed polymer I coagulated at 0°. Magnification is 19,000×.

The use of higher oven temperatures or extended drying intervals would result in a membrane of lower solvent content, consequently a denser structure on coagulation, and a reduced level of flux at comparable rejection.

Porosity of the membrane matrix for polymer I is controlled during the coagulation phase of membrane preparation, the process being very temperature sensitive. Membranes coagulated in an ice–water mixture possess a very porous open matrix, illustrated in Figure 3. The existence of a pore size gradient can be seen with the larger pores (*ca.* 0.25 μ) residing in the interior portion of the membrane matrix. Coagulation at ambient temperatures (*ca.* 25°) results in an equally porous structure (Figure 1) but generally smaller pore dimensions. Higher temperatures (*ca.* 50°) result in a collapsed, dense structure with pore diameters of approximately 0.05 μ evident from Figure 4. The corresponding effect on transport properties is illustrated in Table I. Here, one can observe a continual decrease of membrane flux with increase in coagulation temperature. Membrane selectivity to sodium chloride, as evidenced by rejection, is low (*ca.* 3–12%) owing to the lack of a continuous skin resulting from the brief 4-min oven exposure used in membrane preparation.

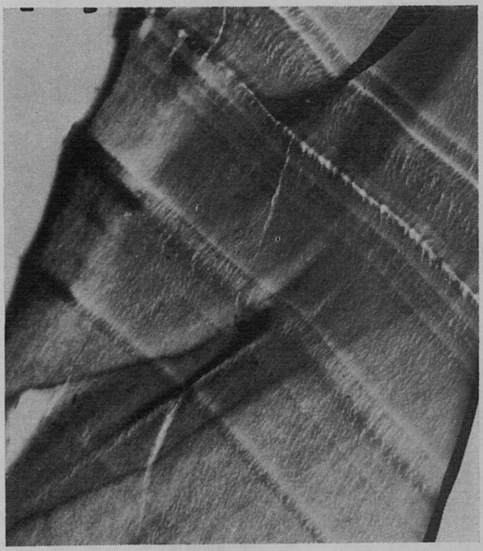

Figure 4. Electron micrograph of unannealed polymer I coagulated at 50°. Magnification is 19,000×.

TABLE I
EFFECTS OF COAGULATION CONDITIONS ON TRANSPORT PROPERTIES[a] OF UNANNEALED POLYMER I MEMBRANES[b]

Coagulation temp, °C	Flux, gal ft^{-2} day^{-1}	Rejection, %
0	47	9
0	42	12
25	30	10
25	31	9
50	10	3
50	15	7

[a] Reverse osmosis data taken at 600 psi and 5000-ppm sodium chloride feed. [b] Membrane heated 4 min at 100 ± 0.5° in mechanical convection oven.

Thermal annealing in water results in the establishment of a continuous skin at the membrane surface supported on a porous matrix, as illustrated in Figures 1 and 2. Further evidence for asymmetry can be observed through the directional reverse osmosis nature of the membranes. A typical membrane was observed to have a flux of 7.2 gal ft^{-2} day^{-1} at a rejection of 87% for 5000 ppm of NaCl at 600 psi. When reversed in its relation to the test brine, this membrane produced a flux of 7.4 gal ft^{-2} day^{-1} at a rejection of 77%. The absence of substantial increase in flux together with comparable losses in rejection typical of Loeb–Sourirajan cellulose acetate membrane[9] is attributable to the unusually high mechanical strength of the membrane system. The reduced selectivity on reverse operation is in part accounted for by concentration polarization in the porous membrane matrix. Air drying of this membrane resulted in an inward curling (top of membrane outside curl) with a reduced flux of 0.03 gal ft^{-2} day^{-1} at 98.5% rejection. Accompanying this change in transport properties was a reduction in membrane water content from 33 to 19% based on the wet membrane weight.

Each annealing temperature is associated with a membrane flux equilibrium which occurs in approximately 15 min depending upon the temperatures selected. Higher annealing temperatures (*ca.* 100°) result in a more rapid attainment (*ca.* 10 min) of steady-state conditions. The relationship between annealing temperature and membrane reverse osmosis properties is illustrated in Table II. A flux-rejection trade-off is possible, with the maximum rejection reaching 98% (for sodium chloride).

Aromatic Polyamide Membranes. The aromatic polyamides investigated do not require the postannealing step in water as do the amide–hydrazide systems previously discussed. A sufficiently selective, continuous skin (Figure 5) is established during the oven-drying phase. The principal variables influencing membrane reverse osmosis performance for these systems are membrane casting thickness, oven temperature, length of drying interval, and coagulation temperature.

TABLE II
RELATIONSHIP BETWEEN POSTANNEALING TEMPERATURE AND MEMBRANE REVERSE OSMOSIS PROPERTIES[a] FOR POLYMER I

Postannealing bath temp, °C	Flux, gal ft^{-2} day^{-1}	Rejection, %
40	28	69
60	12	79
70	7	82
85	4.5	96
100	2.5	98

[a] Reverse osmosis data taken at 600 psi with 5000-ppm NaCl feed.

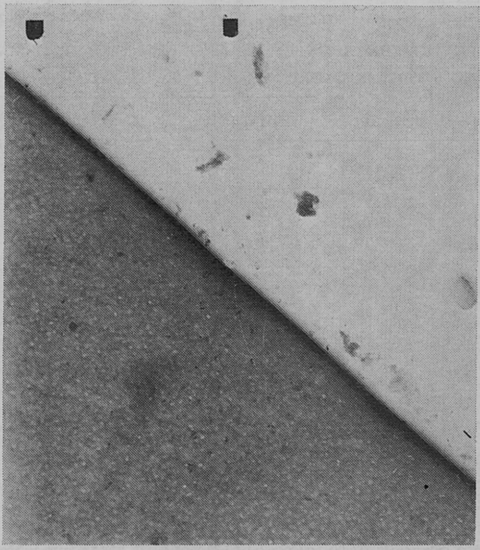

Figure 5. Electron micrograph of polymer III membrane. Magnification is 71,000×.

The effects of oven temperature and time, as well as membrane casting thickness, on membrane flux can be related to the residual membrane solvent at the time of coagulation. With each condition, there is associated a particular level of residual solvent which becomes asymptotic with oven-drying time under conditions of fixed membrane thickness and oven temperature, as shown in Figure 6. The overall level, however, is strongly dependent upon membrane thickness. Such dependency is related to the changes in membrane surface-to-volume ratio, the higher ratios (present in the thinner membrane) resulting in more rapid solvent loss. The solvent loss occurs quite rapidly during the first 10 min of oven exposure, after which the establishment of a skin retards further loss. The considerable reduction in solvent vapor pressure brought about by the relative increase in $CaCl_2$ salt present in the membrane is no doubt a dominating factor in maintaining the nearly constant solvent level. The level of residual solvent is important in its effect on the membrane morphology established during coagulation. Higher residual solvent levels result in a more open, porous matrix, whereas lower levels of

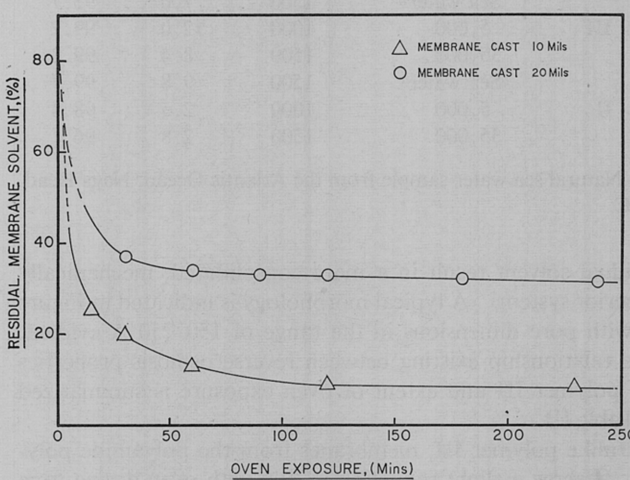

Figure 6. Residual membrane solvent *vs.* oven-drying period at 105° for polymer III.

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[9] U. Merten, "Desalination by Reverse Osmosis," MIT Press, Cambridge, Mass., 1966, p 131.

Table III
The Relationship between Reverse Osmosis Performance[a] and Oven Exposure for Polymer III Membrane[b]

Oven exposure, min	Flux, gfd	Rejection, %
15	3.1	93.2
30	6.1	99.7
60	5.1	99.5
120	5.7	99.6
	6.5	99.7
160	6.2	99.6
170	6.9	99.6
175	6.7	99.6
180	8.3	99.4
185	6.7	99.2
195	5.4	99.5
212	6.5	99.7
220	7.7	99.2
240	6.4	99.5

[a] Reverse osmosis data taken at 600 psi and 5000-ppm NaCl feed. [b] All membranes were cast 20 mils, dried for indicated period at 105° in a mechanical convection oven, then coagulated at 24.5 ± 0.5° in deionized water.

Table IV
Effect of Oven-Drying Time on Reverse Osmosis[a] Performance of Polymer II Membranes

Oven-drying time, min	Flux, gal ft^{-2} day^{-1}	Rejection, %
10	27	11
15	5.5	82
20	2.7	93
30	1.5	98
60	16	60
10[b]	3.5	26

[a] Reverse osmosis data taken 600 psi with 5000-ppm NaCl feed. [b] Membrane posttreated 15 min in 100° deionized water.

Table V
Reverse Osmosis Data for Aromatic Polyamides and Polyamide-Hydrazides with Various NaCl Feed Concentrations

Polymer	NaCl feed, ppm	Pressure, psi	Flux, gfd	Rejection, %
I	5,000	1000	6.5	96.5
	5,000	1000	8.7	98.0
	35,000	1500	8.3	92.8
	35,000	2000	10.8	94.6
	Sea water[a]	1500	7.0	95.7
III	5,000	1000	12.0	99.2
	35,000	1500	8.4	99.8
	Sea water[a]	1500	9.8	99.7
II	5,000	1000	2.5	98.4
	35,000	1500	2.8	96.7

[a] Natural sea water sample from the Atlantic Ocean, Nags Head, N. C.

residual solvent result in a more consolidated, mechanically superior system. A typical morphology is indicated in Figure 5, with pore dimensions in the range of 150–250 Å evident. The relationship existing between reverse osmosis properties for polymer III and extent of oven exposure is summarized in Table III.

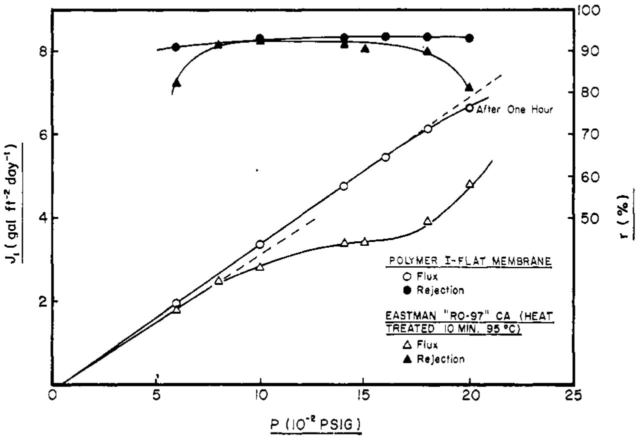

Figure 7. Flux-rejection-pressure experiment (reverse osmosis at 25° and 5000 ppm of NaCl).

Table VI
Typical Mechanical Properties[a] of Asymmetric Aromatic Polyamide Membranes at 100% Relative Humidity

Membrane	Modulus, psi	Yield stress, psi
Polymer I	250,000	7150
Polymer III	109,000	3930
Polymer II	82,000	2810
Cellulose acetate[b]	33,000	780

[a] Measurements carried out on an Instron tester with membranes positioned under water. [b] Eastman RO-97.

Table VII
Selectivity[a] of Polymer III Asymmetric Membranes to Various Solutes in Aqueous Solutions

Solute		Concentration, ppm Feed	Concentration, ppm Product	Rejection, %
$MgSO_4$		10,000	16	99
NH_4Cl		2,303	2	99
NaOH		2,000	430	83
Boron[b]	pH 3.5	67	11	83
	pH 10.2	67	1	98
HCl	pH 1.4	2,760	48	99
NH_4OH	pH 10.4	1,900	1349	29
Urea		18,000	1,500	92
Fructose		2,008	18	99
Poly(ethylene glycol) (400)		10,000	30	97
Poly(ethylene glycol) (1000)		10,000	20	98
Dimethylacetamide		100,000	64,000	36

[a] Reverse osmosis data taken at 600 psi and 25°, utilizing a polymer III membrane with a flux of 6–7 gal ft^{-2} day^{-1}. This flux was reduced to 0.2 gal ft^{-2} day^{-1} when the membrane was exposed to the dimethylacetamide solution. [b] Solution concentrations in the product and feed are expressed as parts per million of boron. Boric acid (with HCl) was used for the low-pH tests and sodium borate (with NaOH) was used for high-pH tests.

Unlike polymer III, membranes from the polyamide polymer II show a slight reduction in flux with oven-drying time in the range 10 ≤ oven time, min ≤ 60. Membrane integrity, as represented by defects and poor reproducibility in the level of selectivity, is less than observed for the polymer III, as shown in Table IV. This is perhaps related to the high potential for crystallinity for the all-meta-oriented polymer II system. Further evidence for crystallinity can be seen (Table IV) in the sample heated for 1 hr. The sudden drop in selectivity accompanied by an increase in flux is most likely the result of morphological changes resulting from increases in crystallinity. Water annealing at 100° (last entry, Table IV) produces similar reductions in membrane flux with modest improvements in selectivity. Such increases in selectivity must reflect a consolidation of the membrane skin region.

Coagulation behavior for the aromatic polyamides (polymers III and II) is similar. Rate of coagulation, as evidenced by the development of an opaqueness, occurs more rapidly for the aromatic polyamides than for the polyamide–hydrazide.

Conclusions

Typical flux-rejection data for the membrane systems described, with various feed solutions, are summarized in Table V. These aromatic polyamide membranes are characterized by their good mechanical strength, as illustrated in Figure 7. Here a comparison of flux-pressure response between polymer I and cellulose acetate is made. A straight line plot for flux is observed up to pressures of 1800 psi, with some departure from linearity evident after 1 hr. The deflection in the flux line for cellulose acetate is seen to coincide with a decrease in rejection, indicating development of a membrane defect.

Typical mechanical properties for asymmetric membranes prepared from these polymers are shown in Table VI. In addition to their good mechanical properties, these aromatic polyamides show remarkable chemical resistance, especially in the high-pH range. This is in marked contrast to the cellulose acetate systems.[9] Membrane reverse osmosis performance for aqueous salt rejections appears unaltered after 1 week of storage in 1 N solutions of H_2SO_4, HCl, HNO_3, CH_3COOH, NaOH, and NH_4OH.

Selectivity of these membranes to solutes other than NaCl is quite good, as illustrated by results for polymer III in Table VII.

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Liquid–Liquid Phase Separation in Multicomponent Polymer Systems. X. Concentration Dependence of the Pair-Interaction Parameter in the System Cyclohexane–Polystyrene

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ABSTRACT: The classical lattice theory of polymer solutions contains a concentration function of the pair-interaction parameter, normally represented as a truncated power series. The present study deals with the simple closed expression itself, $g(\varphi, T) = \alpha + (\beta_{00} + \beta_{01}/T)(1 - \gamma\varphi)^{-1}$, the constants of which can be evaluated conveniently with the aid of critical miscibility data. For the system cyclohexane–polystyrene the closed expression compares favorably with the power series representation reported by the present as well as other authors. Within the scope of the lattice theory the number of nearest neighbors z approximates $2\gamma^{-1}$. The value of z calculated for this system on the basis of the volume fraction seems quite acceptable ($z = 8.5$). At relatively low molecular weights there are indications that g depends on chain length. The present data can be reconciled with literature data when g is assumed to decrease with increasing number-average molecule weight, which, at temperatures below the Θ point, may well be the case.

It has become widely accepted in the literature on thermodynamic properties of polymer solutions that the pair-interaction parameter generally depends on the polymer concentration. This parameter, here denoted by g, arises in the lattice treatment of fluid macromolecular mixtures developed by Flory[1,2] and Huggins[3,4] when it is endeavored to reach quantitative agreement between theory and experiment. For this purpose Tompa[5,6] suggested using a power series in concentration with empirical coefficients. Such a description has indeed proved to be useful.[2,5–9]

This has also appeared from a recent study on the critical miscibility of the system cyclohexane–polystyrene.[10] In this work, as well as in all experimental studies on correlation functions, the series must be truncated because higher terms cannot be established with sufficient accuracy owing to experimental errors. This is not serious in itself, since, at any rate within the range of the measurements, the description of the measured quantities will be satisfactorily precise.

Yet, a closed expression, if available, would seem more elegant and be preferable to a truncated series. Such expressions have of late come forward from more refined molecular theories[11–13] yielding g functions in which many molecular parameters are included. The latter can often be obtained from independent measurements, but such an approach renders the modern expressions for g rather impracticable for routine use in cases where a relatively large number of varying systems must be described. One would then be inclined to make do with a simple closed expression even if its parameters

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(1) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942); **12**, 425 (1944).

(2) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

(3) M. L. Huggins, *Ann. N. Y. Acad. Sci.*, **43**, 1 (1942).

(4) M. L. Huggins, "Physical Chemistry of High Polymers," Wiley, New York, N. Y., 1958.

(5) H. Tompa, Comptes Rendu 2e Réunion de Chimie Physiques, Paris, 1952.

(6) H. Tompa, "Polymer Solutions," Butterworths, London, 1956.

(7) T. A. Orofino and P. J. Flory, *J. Chem. Phys.*, **26**, 1067 (1957).

(8) R. S. Jessup, *J. Res. Nat. Bur. Stand.*, **60**, 47 (1958).

(9) W. R. Krigbaum and D. O. Geymer, *J. Amer. Chem. Soc.*, **81**, 1859 (1959).

(10) R. Koningsveld, L. A. Kleintjens, and A. R. Shultz, *J. Polym. Sci., Part A-2*, **8**, 1261 (1970).

(11) M. L. Huggins, *J. Amer. Chem. Soc.*, **86**, 3535 (1964).

(12) P. J. Flory, *ibid.*, **87**, 1833 (1965).

(13) D. Patterson, *Rubber Rev.*, **40**, 1 (1967).