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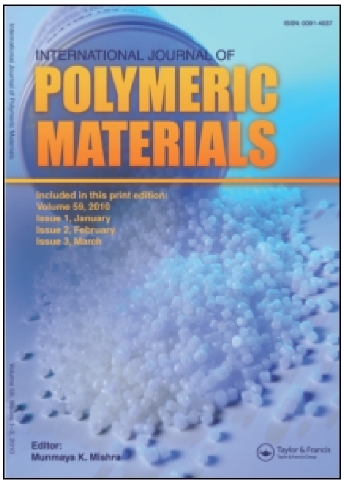

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Poly (*m*-Phenylene Isophthalamide) Membranes for Reverse Osmosis Separations

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Poly (*m*-phenylene isophthalamide) membranes were prepared by polycondensation of freshly prepared *m*-phenylene diamine and isophthaloyl chloride in chloroform solvent medium in presence of triethanol amine as acid acceptor. The reverse osmosis performance of the membranes prepared under varying conditions and the separation data for various solutes including urea and sucrose are presented.

INTRODUCTION

Aromatic polyamide class of polymeric membranes are well known[1,2] for their inherent mechanical, chemical and bacteriological stability compared to conventional cellulose acetate membranes for reverse osmosis (RO) separations. The synthesis, characterisation and membrane performance for a large number of aramid polymers are widely reported.[3–6] Synthesis of polyamide hydrazides containing ether and sulfone functional groups, capable of giving in excess of 98.5% solute separations under sea water test conditions have been reported from our laboratory.[7–8] This paper describes the synthesis by low temperature polycondensation of aromatic polyisophthalamide polymer in chloroform solvent in presence of triethanolamine (TEA) as acid acceptor. The experimental data on RO membrane performance of various solutes are presented in this paper.

MATERIALS AND METHODS

Synthesis of monomers and polymers

m-phenylene diamine (MPDA) was freshly prepared by reducing *m*-dinitrobenzene using hydrazine hydrate in presence of Raney's nickel as catalyst. It was recrystallised from ethyl acetate/petroleum ether (40/60). Isophthaloyl chloride (IPC) was commercially obtained and was purified by distillation followed by recrystallisation from dry hexane. Chloroform and triethanol amine (TEA) and TEA.HCL were commercially obtained and were purified by distillation. TEA was used as an acid acceptor and TEA.HCl was added to enhance the degree of polymerisation. The polymerisation reaction was carried out under N_2 atmosphere in the temperature range of -5 to -10°C in a reaction vessel equipped with mechanical stirrer. After completion of reaction, the reaction mixture, viscous solution, was poured into a large volume of petroleum ether yielding a fibrous polymer. It was washed with hot water and dried under vacuum. The precipitation of reaction mixture in petroleum ether ensures removal of TEA.HCl.

POLYMER CHARACTERIZATION

The polymer samples were characterised by measuring solution viscosity in dimethyl acetamide using Ubbelohde viscometer and the results are expressed as η_{inh}. The % moisture uptake was measured gravimetrically. The elemental composition of the polymer sample was determined by standard analytical methods.

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PREPARATION OF MEMBRANES AND PERFORMANCE EVALUATION

Asymmetric reverse osmosis membranes were prepared from these polymer samples by solution casting technique. Oven dried polymer samples were dissolved in freshly distilled dimethyl acetamide in presence of lithium chloride additive. After complete dissolution, the casting solution was pressure filtered and spread over a glass plate to obtain a smooth film. The thickness of the cast solution was controlled at 250 μ by the use of side runner tapes.

The film was subjected to partial solvent evaporation in an air circulating oven and later precipitated in demineralised water. The membrane samples were examined for dye penetration tests using Byebrich Scarlet red dye before subjecting them for RO test using 5000 ppm sodium chloride solution as the feed at 40 Kg/cm^2 pressure. The performance was evaluated in terms of water permeation velocity (cms/day) and % solute separation.

RESULTS AND DISCUSSIONS

Polymer characterisation

The polymer characterisation data are obtained in terms of elemental composition, inherent viscosity and moisture regain. The results are given in Table I.

Polymers with adequate molecular weight is a prime requirement to ensure membranes with mechanical integrity and performance stability. For aromatic

TABLE I

Characterisation of poly (*m*-phenylene isophthalamide) polymer

Sr. no.	Parameter	Data			
1.	Elemenral composition (%)	C	H	O	N
	Calculated	70.35	13.4	4.52	11.73
	Analysed	71.40	14.2	4.70	9.70
2.	Molecular formula	$(C_{14}O_2H_{10}N_2)_n$			
3.	η_{inh}	1.2 dl/g			
4.	Moisture regain (%)	4.53			

polymers of the class considered here, the minimum usable molecular weight is reported[9] to be about 25 000. The molecular weight of the polymer is related to intrinsic viscosity (η) (obtained by extrapolation of η_{inh} at infinite dilution) by Mark-Howink equation. The value of 1.2 dl/g in dimethyl acetamide in ambient temperature has been found to be adequate for film formation with stable barrier properties.

Membranes for use in reverse osmotic separation of aqueous systems require an optimum degree of polar groups superimposed on a nonpolar backbone. The degree of polarity is measured in terms of % moisture regain. It is reported[1] that polymers having a minimum of 4% moisture regain could be successfully fabricated into RO separation barriers. The % moisture regain data of 4.53% is comparable to 6% moisture regain data (1) for cellulose acetate polymers.

Membrane casting conditions

The role of polymer concentration, additives and thermal evaporation of solvents and gelling on the RO performance of membranes has been investigated. It was found that lithium chloride concentration in the casting solution of less than 0.5% (W) does not give a stable casting solution whereas higher concentrations of more than 6% (w) give membranes with poor RO performance. The performance of two different membrane samples I and II prepared from 20% polymer solution containing 4% lithium chloride and 18.5% polymer solution containing 5.5% lithium chloride respectively are shown in Figure 1. It can be seen that higher polymer and lower additive concentrations give lower water flux and better solute separation compared to membranes obtained from lower polymer and higher additive concentrations. It can be seen from Figure 1 that increasing evaporation time progressively improves membrane performance.

The performance data was also obtained for membrane films evaporated to different temperatures for a fixed period of times. It was found that the increase of evaporation temperature improves solute separation but reduces the water permeation rates. The possibility of using longer evaporation periods at relatively lower temperatures also give comparable membrane performance. The data obtained for membrane samples prepared for increasing evaporation periods of upto 50 minutes at 70°C are shown in Table II. It can be seen from the table that lower evaporation periods of upto 20 minutes give porous films with negligible solute separations. Performance improves gradually to a maximum value.

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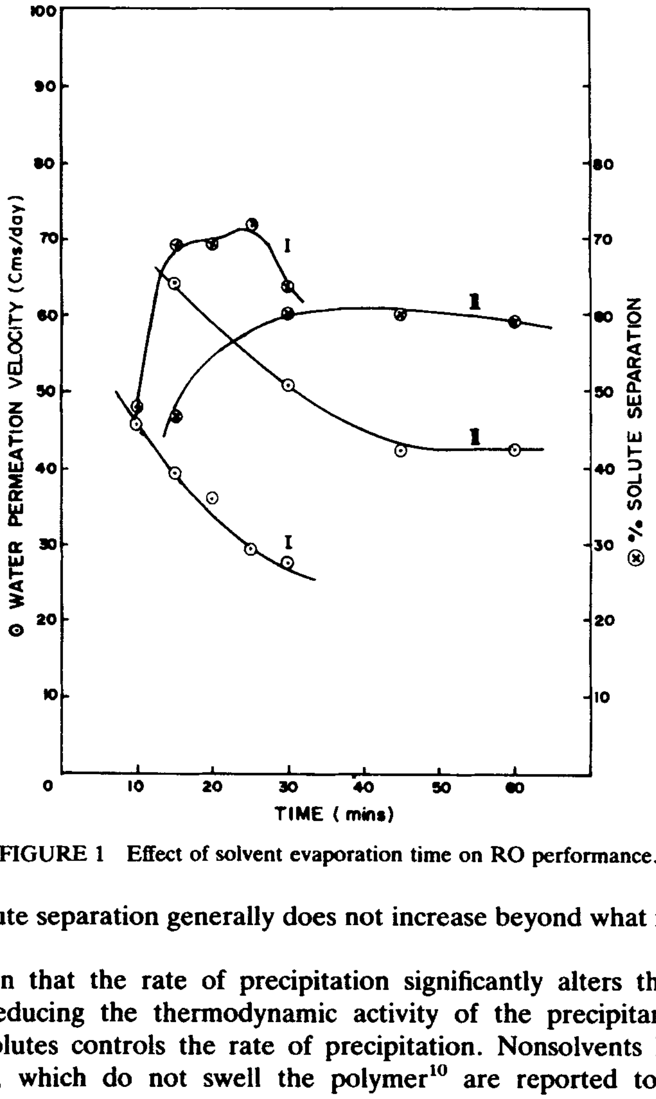

FIGURE 1 Effect of solvent evaporation time on RO performance.

However solute separation generally does not increase beyond what is reported in Table II.

It is known that the rate of precipitation significantly alters the membrane structure. Reducing the thermodynamic activity of the precipitant by adding solvent or solutes controls the rate of precipitation. Nonsolvents like glycerol, acetone etc., which do not swell the polymer[10] are reported to yield dense membrane structures. It can be seen from the data given in Table III that

TABLE II

Effect of evaporation time on membrane performance

Sr. no.	Time (mins.)	Water permeation velocity (cms/day)	%SR
1	10	194.4	8.8
2	20	129.7	11.2
3	30	63.6	30.5
4	40	50.8	21.7
5	50	37.3	66.5

Temperature of evaporation = 70°C.
Polymer, salt and solvent in the (W) ratio of 18:3:79.

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TABLE III

Effect of coagulation medium on membrane performance

Sr. no.	Coagulation medium	Water permeation velocity (cms/day)	% SR
1.	Demineralised water	39.7	64.0
2.	Glycerol	28.5	75.0

Polymer, salt and solvent in the (W) ratio of 20:4:76.
Evaporation: 100°C for 15 minutes.

coagulation in glycerol improves the solute separation. The membrane samples are coagulated however in demineralised water in all other cases.

Membrane morphology

The asymmetric polyamide membranes prepared under varying casting conditions have been examined[9] under electron microsope. The variation of structural defects observed have been explained in terms of casting variables.[11] Generally two kinds of structures namely, needle like and sponge like structure are noticed and reported. Membranes having large needle like pores supporting a dense skin layer are reported to give excellent RO performance. The sponge like structure is reported to give poor water permeation rate and high solute separation whereas structures with finger-like pores penetrating the skin layer are known to give poor solute separation and high water permeation. Between the two extremes, intermediate structures are also possible where reasonable water permeation with moderate solute separation is observed. The results of our present study point to the existence of intermediate morphological structures with few random defects penetrating into the skin layers.

Reverse osmosis performance of various solute systems

The effect of operating pressure on the membrane performance is shown in Figure 2. The water flux and solute separation are found to increase with increase

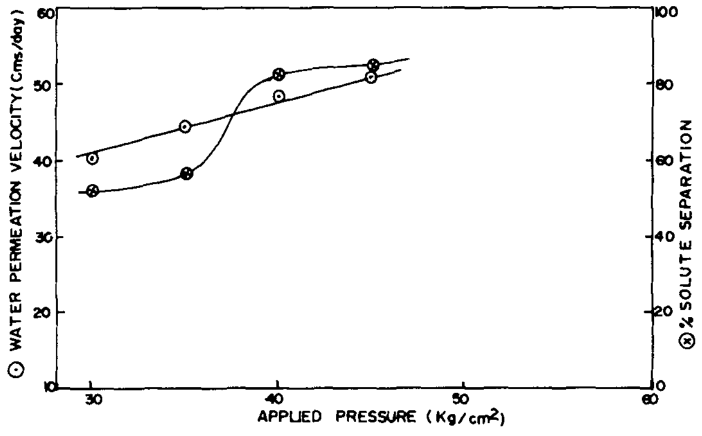

FIGURE 2 Effect of operating pressure on RO performance.

TABLE IV

Separation of various solute systems

Sr. no.	Solute	Conc. (ppm)	% SR	CA
1.	Sodium chloride	3000	65.9	89.9
2.	Sodium sulphate	2200	82.0	94.2
3.	Potassium permanganate	1000	86.9	—
4.	Potassium dichromate	1000	78.3	—
5.	Urea	500	75.7	26.0
6.	Sucrose	1000	89.2	—
7.	Potassium citrate	1000	72.3	—
8.	Byebrich Scarlet Dye	—	100	100

Polymer, salt and solvent in the (W) ratio of 20:4:76.
Evaporation: 100°C for 15 minutes.

in pressure as expected. The data obtained show that the membrane structure is not getting compacted although the maximum pressure employed is not very high. The separation data for various other solute systems are given in Table IV. It can be seen that % separation of other solutes is higher than that of sodium chloride. Urea and sucrose are also rejected as well as that of other inorganic solutes.

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CONCLUSIONS

Simple aromatic polyamide membranes were synthesized by low temperature polycondensation of *m*-phenylene diamine and isophthaloyl chloride in chloroform solvent medium in presence of triethanol amine as acid acceptor. The reverse osmosis performance data of membranes prepared under varying conditions are presented. It was found that these membranes give relatively lower solute separations with respect to sodium chloride compared to ether and sulfone containing polyamide hydrazides reported earlier from our laboratory. However these membranes offer better separation of urea, sucrose and other inorganic solutes and as such appear suitable for effluent treatment under reverse osmosis and also for ultrafiltration.

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