

Synthesis and Evaluation of Aromatic Polyamide Membranes for Desalination in Reverse-Osmosis Technique

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ABSTRACT: Reverse-osmosis membrane-grade aromatic polyamides have been synthesized by reacting 3,5-diaminobenzoic acid separately with three different acylchlorides, viz. isophthaloyl chloride, terephthaloyl chloride, and 4,4'-diphenyldicarboxylic acid chloride. Using these polyamides, asymmetric membranes were developed and characterized for various physical parameters, such as Staverman coefficient, membrane potential, and percent salt rejection using sodium chloride solution under high pressure. The effects of pressure, feed concentration, and feed flow rate have been studied on membrane transport parameters, viz. pure water permeability constant, product rate, solute transport parameter, and separation factor. The effects of annealing temperature and solvent evaporation time on the performance of the membranes were also studied. The analysis of the reverse-osmosis data revealed that the membranes prepared from the 3,5-diaminobenzoic acid and 4,4'-diphenyldicarboxylic acid chloride are superior to the membranes prepared from other polymeric materials. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 643–653, 1997

Key words: aromatic polyamides; desalination; reverse osmosis

INTRODUCTION

During the last few years, extensive efforts have been made to synthesize membrane-grade aromatic polyamides¹ as an economical substitute for the cellulose acetate which is routinely used in the preparation of membranes for desalination in the reverse-osmosis (RO) technique. With the discovery of aromatic membranes by Richter and Hoehn,² a number of useful aromatic polyamide-based membranes have been developed and evaluated for their performances in this RO technique.^{3,4} Subsequently, a theoretical model based on free-energy parameters has been developed to explain the transport of the ions in these membranes.⁵ Aromatic polyamide membranes based on piperazine showed high compaction on use at

high pressure and showed a significant reduction in the solvent flux.⁶ However, membranes prepared from the polyhydrazides, polysulphonamides, proved to be of great significance in the field of membrane technology.^{7–9} On analyzing both the experimental data reported in the literature and the mechanism of the transport of the solvent through the membranes, it has been concluded that the polymeric material with hydrophilic group would be of improved quality to develop RO membranes. In view of these observations, efforts have been made to develop membrane-grade polyamides having a pendant carboxylic group at their backbones. Three different polyamides have been synthesized and their RO performance has been investigated in detail and reported in this article.

EXPERIMENTAL

Synthesis and Characterization of Polyamides

Three polyamides were synthesized by low-temperature polycondensation of the monomers in

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N,N-dimethylacetamide (DMAC) solvent. The 3,5-diaminobenzoic acid, terephthaloyl chloride, isophthaloyl chloride, and DMAC were E. Merck (India) products and were purified through recrystallization and vacuum distillation before being used for the synthesis of polyamides. The DMAC was refluxed over barium oxide for about 4 h, distilled under reduced pressure, and subsequently stored over 4 Å-type molecular sieves. To prepare polyamides, a 10% (w/v) solution of 3,5-diaminobenzoic in DMAC was taken in three different 500-mL round-bottomed flasks, each fitted with thermometer, stirrer, and nitrogen bubbler, and the solution was cooled below 0°C by keeping these flasks in an ethylene-glycol cooling mixture. Subsequently, precooled stoichiometric solutions of isophthaloyl, terephthaloyl, and 4,4'-diphenyldicarboxylic acid chloride in DMAC were added dropwise, separately, to the flasks containing the 3,5-diaminobenzoic acid. During addition of the acylchlorides, rapid stirring was maintained to dissipate the heat generated by the reaction. At the end of the reaction, 3% (w/v) of the lithium carbonate (Li_2CO_3) was added to neutralize the acid liberated during the polycondensation process. Finally, the polyamides were precipitated by pouring the reaction mixtures into an excess amount of the methanol. These polyamides were washed with hot water to remove the remaining unreacted Li_2CO_3 , monomers, and trapped solvent molecules. The product was white in color and the yield was about 78%. The general scheme of the polymer synthesis is shown in Scheme 1.

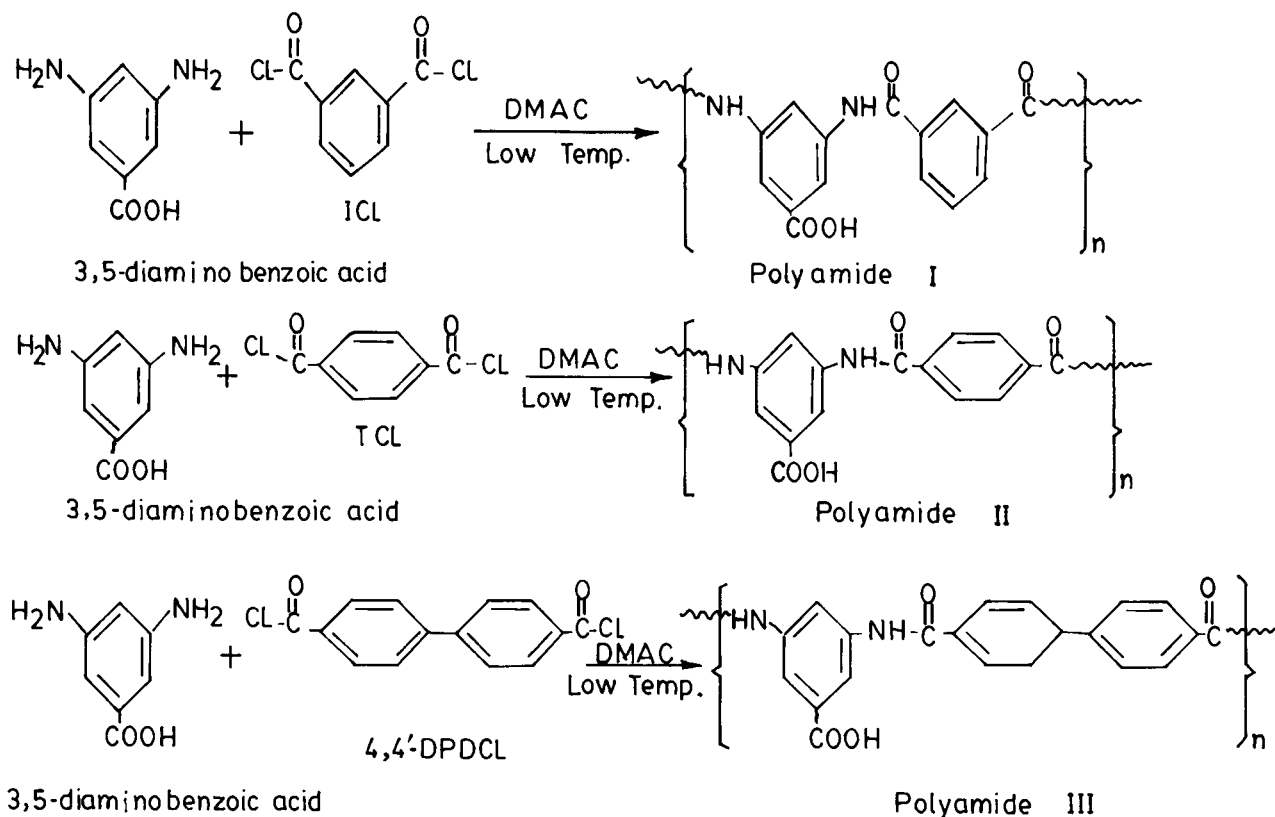
Solubility of the prepared polyamides was determined in different solvents by dissolving 1.0 g of the polyamide in 10 mL of the solvent at room temperature (Table I). The polyamides were found to be soluble in all amide-type solvents. The solubility increased on adding such salts as lithium chloride and calcium chloride. The prepared polyamides were also analyzed for C, H, and N elements, and the data were used to propose the structure of the repeat units in the prepared polyamides. The theoretical and experimental amounts of the elements were found to be in close agreement (Table II).

The molecular weight of the polyamides was determined with the help of the gel permeation chromatographic technique (GPC) using a 0.01% solution of synthesized polyamide in dimethyl acetamide at a flow rate of 3 mL/min. The GPC column was calibrated using aromatic polyamides (Nomex) of known molecular weight. These polyamides are structurally the same as the polyam-

ides prepared in the present studies. The intrinsic viscosity $[\eta]$ of the polyamides was determined by taking a 0.1–0.5% solution of polyamides in 5% lithium chloride solution in DMAC at room temperature using a Ubbelohde type of viscometer. The viscosity data are recorded in Table III. The thermal stability of the polyamides was determined by thermogravimetric analysis (TGA) in a nitrogen atmosphere at a heating rate of 5°C/min, up to a maximum temperature of 540°C, and the data are recorded in Table IV. The glass transition temperature (T_g) and melting point (mp) of the polyamides were determined with the help of a differential scanning calorimeter by taking a 20-mg sample of each polyamide and heating at a rate of 5°C/min in a nitrogen atmosphere. The results are recorded in Table III and Figure 1. The percent moisture regain (MR) of the prepared polyamides was determined as an amount of the moisture absorbed by the dried and weighed polyamide samples kept in the chamber, where the humidity was maintained to 62% at 25°C. The MR data are recorded in Table III. To examine the crystalline nature of the prepared polyamides, the wide angle X-ray diffraction (WAXD) measurements were made using $\text{CuK}\alpha$ radiation and a nickel filter. The WAXD patterns are shown in Figure 2. To determine the functional groups in the polyamides, the infrared (IR) spectra were recorded on a KBr disc, and the observed IR spectral frequencies were used to identify the functional groups in the polyamides.

Preparation and Characterization of Polyamide Membranes

To prepare the flat, asymmetric membranes from the synthesized polyamides, casting solutions of each polyamide were prepared by dissolving 14% (w/v) of polyamide along with 4% (w/v) of lithium chloride in 82% (w/v) of DMAC solvent. The lithium chloride was added to control the viscosity of the casting solution, to obtain membranes of uniform thickness, and to control the rate of evaporation of the solvent after casting the membranes. However, an excess amount of the lithium chloride was avoided to prevent the formation of opaque patches in the membranes. Before casting the membranes, it was insured that the casting solution was free from trapped air bubbles. Membranes were cast on flame-cleaned Pyrex glass plates and were subjected to solvent evaporation times ranging from 10 to 20 min, depending upon the pore size being targeted. The pore size is in-



Scheme 1. ICL = isophthaloyl chloride; TCL = terephthaloyl chloride; DMAC = dimethyl acetamide (solvent); 4,4'-DPDCL = 4,4'-diphenyl dicarboxylic acid chloride.

versely related to the evaporation time. From each polyamide three types of membranes were obtained, having evaporation times of 10, 15, and 20 min. Finally, these solvent-evaporated membranes were kept in ice-cold deionized water for about 24 h. During this gelation period the residual solvent diffuses out from the membrane matrix and the membrane pores are occupied by the water molecules. To provide strength, the membranes were annealed by being placed for about 10 min into the water bath maintained at temperatures of 75, 80, and 90°C. The differential scan-

ning calorimetry (DSC) data of the polyamide membranes were also recorded (Fig. 1) at a heating rate of 5°C/min in a nitrogen atmosphere using a 20-mg piece of each membrane. The endothermic peak in the DSC curve of each membrane was obtained at the same temperature as was found with the polyamide samples. This indicated that T_g and mp of the polyamides and their membranes are almost same. Performance of the membranes obtained at solvent evaporation time of 15 min and annealing temperature of 80°C was superior to the membranes obtained at other time peri-

Table I Solubility of the Synthesized Aromatic Polyamides

Polyamides	Solvents				
	DMAC	DMSO	NMP	DMF	MET
Polyamide I	+	+	+	+	-
Polyamide II	+	+	+	+	-
Polyamide III	+	+	+	+	-

DMAC, dimethylacetamide; DMSO, dimethylsulfoxide; NMP, *N*-methylpyrrolidone; DMF, dimethylformamide; MET, methanol.

Table II Analysis of C, H, N Elements in the Prepared Polyamides

Polyamides	Experimental (%)			Theoretical (%)		
	C	H	N	C	H	N
Polyamide I	62.34	3.42	9.20	63.83	3.55	9.93
Polyamide II	62.10	3.46	9.26	63.83	3.55	9.93
Polyamide III	76.60	4.10	7.86	77.30	4.29	8.59

ods of solvent evaporation and annealing (Table V). Therefore, results in this paper are from the membranes which were obtained at solvent evaporation of 15 min and annealing temperature of 80°C.

Before these membranes were used in the RO test experiments, they were subjected to various tests of characterization, namely specific water content (S , the amount of water present per cubic centimeter of the wet membrane in comparison to the dried membranes), interfacial water ($V_{s/m}$, the specific volume of the interfacial water present per unit weight of the membrane), and the membrane potential (ΔE_m , to test the semipermeability of the membranes by using the sodium chloride solutions across the membranes in different concentration ratios). The experimental data for the membranes are recorded in Table VI. The ΔE_m was determined by loading a 4-cm circular membrane in the specially designed electrochemical cell and putting the sodium chloride solution across the membrane in concentration ratios of 1 : 1 and 1 : 10M. The potential was determined with the help of the potentiometer, using silver chloride as the reference electrode. The permselectivity of the membranes was further tested by determining the value of the Staverman coefficient (σ) by mounting the 4-cm circular membrane in a specially designed cell and recording the flux (J_v) of the water at controlled hydrostatic pressure (ΔP). The following phenomenological transport equation of Kedem and Katchalsky¹⁰ was used for determining the value of σ , hydraulic permeability coefficient (L_p), and solvent flux (J_v).

$$J_v = L_p(\Delta P - \sigma\Delta\pi) \quad (1)$$

at $J_v = 0$, the value of σ would be

$$\sigma = \left(\frac{\Delta P}{\Delta\pi} \right)_{J_v=0} \quad (2)$$

The values of these parameters are recorded in Table VII, which clearly shows that the membranes are defect-free and permselective; otherwise, the value of σ would have been less than unity.

Reverse-Osmosis Test Experiments

To evaluate the RO test parameters of the prepared membranes, circular, flat membranes of 11.4 cm² effective area were fitted in the frame and plate module of the RO test unit and were initially subjected to a pure water pressure of 1,500 psig for about 2 h prior to performing the RO test experiments. Subsequently, the pure water permeability (PWP) was determined as a function of pressure, ranging from 500 to 1,500 psig at flow rates of 250 and 300 cm³/min. From the PWP, the pure water permeability constant (A) was determined as a function of pressure for each membrane prepared under different evaporation times and annealing temperatures. To evaluate the desalting specifications of the membranes, the sodium chloride water system was used and experiments were carried out at NaCl solution feed concentrations of 3,000 and 5,000 ppm at feed

Table III Physical Characteristics of the Synthesized Polyamides

Polyamides	MW	$[\eta]$ (dL/g)	T_g (°C)	mp (°C)	MR (%)
Polyamide I	34,096	1.70	235	286	8.9
Polyamide II	38,503	1.90	240	295	8.6
Polyamide III	56,101	2.80	291	308	8.4

Table IV Percent Weight Loss as a Function of Temperature

Polyamides	Temperature (°C)				
	300	360	420	480	540
Polyamide I	3.0	4.2	6.2	18.0	30.0
Polyamide II	2.8	3.2	5.7	14.0	22.0
Polyamide III	2.6	3.0	5.6	12.0	18.0

velocities of 250 and 300 cm³/min. The product rate (PR) as a function of pressure was recorded and from the permeate concentration, the percentage of salt separated was calculated. The conductivity measurements were made to measure the concentration of the salt in the feed and the product. The value of mass transfer coefficient corresponding to feed velocity, and the solute transfer parameter ($D_{AM}/K\delta$) were calculated using the Kimura–Sourirajan analytical equations. The specifications of the prepared polyamide membranes are shown in Table VIII. The variations in the values of A , f , and $D_{AM}/K\delta$ as a function of pressure for the different membranes are shown in Figures 3–5. The effects of operating pressure on the PWP and PR for the different polyamide membranes at feed flow rate of 250 cm³/min and feed concentration of 3,000 ppm of NaCl are shown in Table IX. A similar trend was obtained at high feed flow rate and at high feed concentration. The effects of feed flow rate and feed concentration on PR, $D_{AM}/K\delta$, and f were also studied and the data are recorded in Table

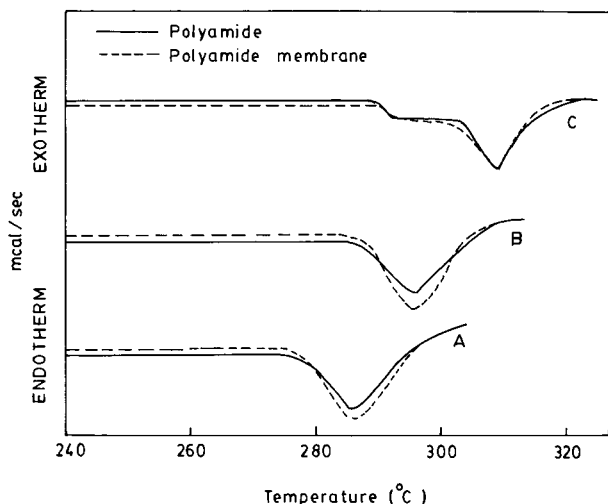


Figure 1 DSC curves of polyamides (—) and their membranes (· · · · ·) at their melting points: (A) polyamide I; (B) polyamide II; (C) Polyamide III.

X. The membranes' performance as a function of solvent evaporation time and annealing temperature were also determined and the data are presented in the form of A , PR, $D_{AM}/K\delta$, and f in Table V.

RESULTS AND DISCUSSION

Polymer Characterization

Prepared polyamides are of high molecular weights and high $[\eta]$. The molecular weight was found to be maximum in case of the polyamide

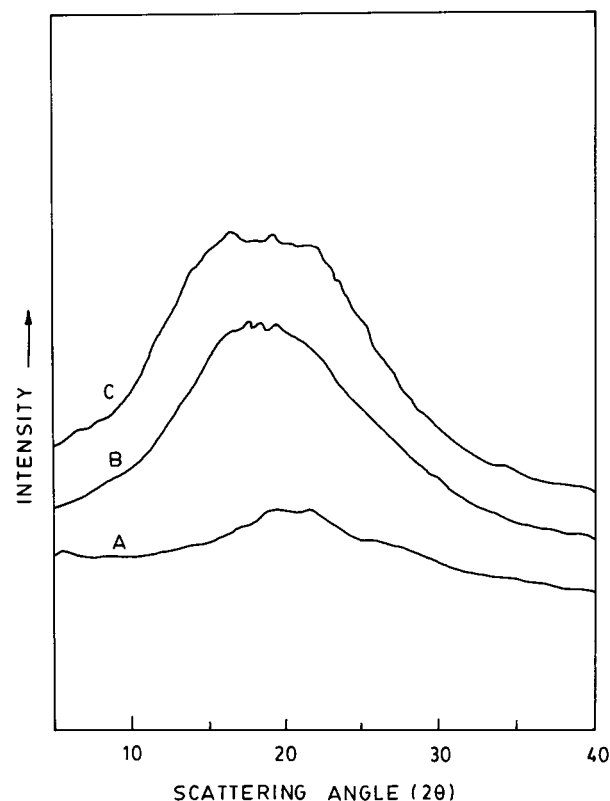


Figure 2 Wide angle X-ray diffractograms of polyamides: (A) polyamide I; (B) polyamide II; (C) polyamide III.

Table V Effects of Annealing Temperature and Solvent Evaporation Time on Membrane Parameters

Annealing Temperature (°C)	Solvent Evaporation Time (min)	A (g mol cm ⁻² s ⁻¹ atm ⁻¹)10 ⁻⁶	PR (g/h)	D _{AM} /Kδ (cm s ⁻¹)10 ⁻⁵	f
Membrane of Polyamide I					
80	10	2.86	70.0	33.40	80.01
75	15	2.02	51.0	15.00	86.00
80	15	1.27	31.2	2.31	96.20
90	15	1.19	29.0	1.37	97.60
80	20	1.20	28.2	1.65	97.00
Membrane of Polyamide II					
80	10	2.00	51.6	16.47	86.00
75	15	1.85	44.2	10.20	89.70
80	15	1.22	29.5	1.72	97.00
90	15	1.08	26.0	1.26	97.60
80	20	1.16	27.0	1.50	97.20
Membrane of Polyamide III					
80	10	1.70	41.2	9.48	89.80
75	15	1.19	29.0	1.81	96.80
80	15	1.16	28.8	1.57	97.20
90	15	1.04	26.0	1.02	98.00
80	20	1.14	28.0	1.23	97.80

Feed concentration: 3,000 ppm; feed flow rate: 250 cm³/min; operating pressure: 500 psig.

prepared from the 3,5-diaminobenzoic acid and 4,4'-diphenyldicarboxylic acid chloride (Table III). The high molecular weights and high $[\eta]$ of the prepared polyamides made these polymers suitable for casting the RO-grade membranes having optimum mechanical strength. The $[\eta]$ was found to be greater than that of Nomex (DuPont-USA) which is used as a suitable material for the preparation of the membranes¹¹ for RO tech-

nique. The high $[\eta]$ of the polyamides II and III was due to the *para*-orientation of the benzene ring in the polymer chain. The hydrophilic nature of the prepared polyamides is also an important factor for the high $[\eta]$ of the polyamides. The polymerization rate is usually high for the *para*-substituted compounds, and this was the reason for obtaining the high-molecular-weight polyamides from the terephthaloylchloride and 4,4'-diphenyldicarboxylic acid chloride monomers. The membranes prepared from polymers of high molecular weights and high $[\eta]$ were able to withstand the high pressure applied during the RO operation. The prepared polyamides I, II, and III were found to be soluble (Table I) in almost all solvents, due to the presence of the pendant —COOH group in the polymeric chains. To evaluate the composition of the repeat unit of the prepared polymers, the elemental analysis was carried out and the percentage of the different elements was matched with the calculated percentages of the elements in the polymers (Table II). The moisture regain data of the polyamides (Table III) clearly indicated that polymers possess the sufficient degree

Table VI Specific and Interfacial Water Content and Membrane Potential

Polyamides	Specific Water Content S (g/cm ³)	Interfacial Water Content V _{s/m} (cm ³ /g)	Membrane Potential ΔE _m (mv)
Polyamide I	1.35	0.96	60.2
Polyamide II	1.31	0.94	60.8
Polyamide III	1.20	0.85	61.2

Membrane annealing temperature: 80°C; solvent evaporation time: 15 min.

Table VII Phenomenological Parameters of the Membranes

Polyamides	Hydrostatic Pressure ΔP (kg/cm ²)	Water Flux J_v (mL cm ⁻² s ⁻¹)	Hydraulic Permeability L_p (cm s ⁻¹ atm ⁻¹) $\times 10^5$	Staverman Coefficient $\sigma_{J_v=0}$
Polyamide I	15.0	43.9	73.20	0.99
Polyamide II	15.0	38.10	62.28	0.99
Polyamide III	15.0	34.42	55.72	0.98

Membrane annealing temperature: 80°C; solvent evaporation time: 15 min.

of hydrophilicity necessary for making the membranes for RO technique. The MR was found to be within the range of 8.4–8.9% in the prepared polyamides and was found to be highest in polyamide I. The importance of the moisture regain has already been discussed.¹² The thermal parameters, such as T_g and MP were determined with the help of the differential scanning calorimeter; the data reported in Table III clearly indicate that the T_g and mp are highest for polyamide III due to the high molecular weight of this polymer in comparison with polyamides I and II. The thermal stability was also highest in case of polyamide III, as is clear from the weight-loss data recorded as a function of the temperature for all the prepared polyamides (Table IV). The X-ray diffractogram of the polyamides clearly indicates that the polyamides have low crystallinity (Fig. 2) compared with aliphatic and aromatic polyamides.^{13,14} The analysis of the IR spectra of the prepared polyamides reveals the presence of aromatic —CH(str) bands in the frequency range of 3008 to 3080 cm⁻¹ (w) and out of plane —CH(def) in the range of 1590 to 1600 cm⁻¹ (m). There were strong —NH bands in the frequency range of 3356 to 3480 cm⁻¹ for the amide group. The —C=O(str) and —N—H(def) coupled bands were observed near 1650 cm⁻¹ in the IR spectrum of all three polyamides. Sharp bands were observed at 802 and 908 cm⁻¹, which may be due to the presence of aro-

matic —NH and —CO groups. These tentative assignments of functional groups have been used as guidelines to identify the structure of the synthesized polyamides.

Membrane Characterization

Membranes of uniform thickness and free from any defects were prepared by the solvent-evaporation process. These membranes were found to be suitable for use in RO conditions. Thickness and the porosity of the membranes were found to be decreased on prolonged solvent evaporation. To evaluate the solvent transport properties of the membranes, the specific S and interfacial $V_{s/m}$ water content were calculated for each membrane prepared under different physical conditions. Results given in Table VI clearly indicate that the membranes prepared from polyamide III have less S and $V_{s/m}$ than the membranes prepared from polyamides I and II. However, the prepared membranes have higher S and $V_{s/m}$ in comparison with the other reported polyamides,¹⁵ probably due to the presence of the carboxylic group in the prepared polyamides. The lower S and interfacial $V_{s/m}$ water content values for polyamide III were due to the *para*-orientation of the benzene ring in the polyamide, which resulted in a more compact barrier than the one having ortho orientation. This has also been proved from the value of A

Table VIII Specifications of the Membranes Prepared from the Polyamides

Membranes	A (g mol cm ⁻² s ⁻¹ atm ⁻¹) 10^{-6}	$D_{AM}/K\delta$ (cm s ⁻¹) 10^{-5}	PR (g/h)	f (%)
Polyamide I	1.27	2.76	31.8	96.2
Polyamide II	1.22	1.72	29.5	97.0
Polyamide III	1.16	0.53	28.8	97.2

Feed concentration: 300 ppm; feed flow rate: 250 cm³/min; operating pressure: 500 psig; membrane annealing temperature: 80°C; solvent evaporation time: 15 min.

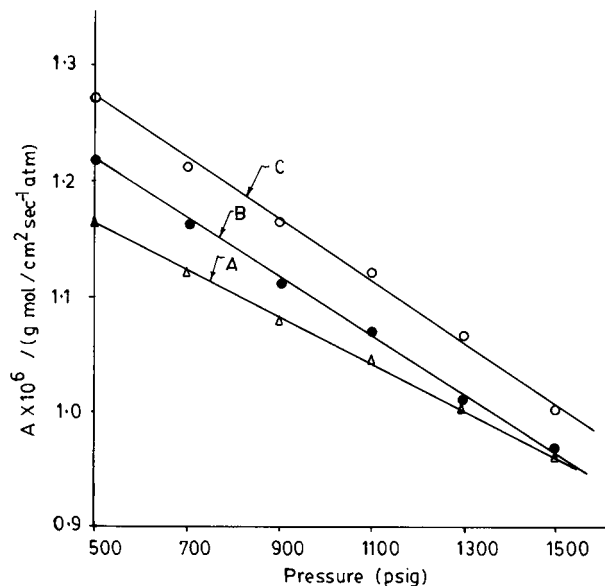


Figure 3 Effect of operating pressure on A . Feed concentration: 3,000 ppm; feed flow rate: 250 cm³/min; membrane annealed at 80°C; solvent evaporation time: 15 min. (A) polyamide I membrane; (B) polyamide II membrane; (C) polyamide III membrane.

determined from the RO data obtained by using these membranes (Table VIII). The overall porosity of the membranes prepared from polyamide III is low, as reflected from the values of the A

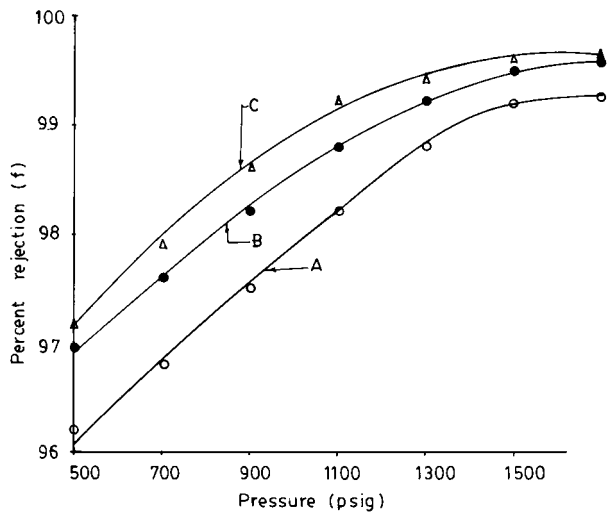


Figure 4 Effect of pressure on f . Feed concentration: 3,000 ppm; feed flow rate: 250 cm³/min; membranes annealed at 80°C; solvent evaporation time: 15 min. (A) polyamide I membrane; (B) polyamide II membrane; (C) polyamide III membrane.

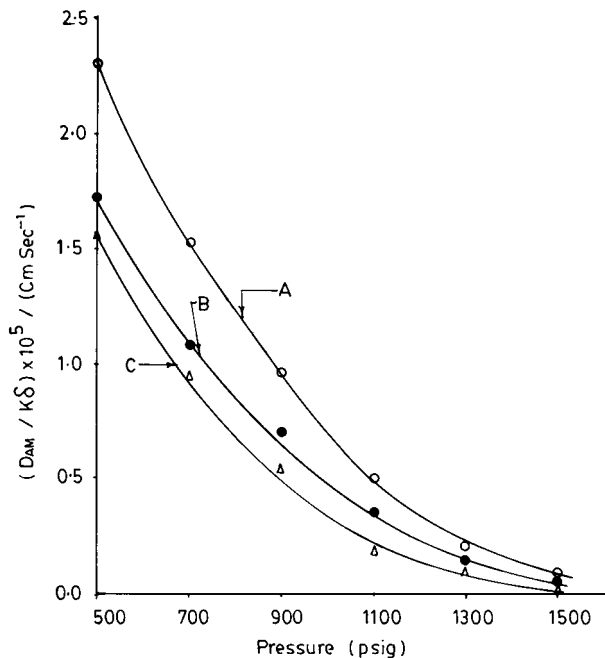


Figure 5 Effect of pressure on $D_{AM}/K\delta$. Feed concentration: 3,000 ppm; feed flow rate: 250 cm³/min; membranes annealed at 80°C; solvent evaporation time: 15 min. (A) polyamide I membrane; (B) polyamide II membrane; (C) polyamide III membrane.

obtained for the prepared membranes. The membranes prepared from polyamide III possess optimum pore size and the necessary water content required to maintain a continuous flow of the water across the membrane in RO technique.¹⁶ In RO technique, those membranes are more suitable which are hydrophilic but not highly porous, otherwise the salt rejection performance would be low. The *para*-orientation of the benzene ring in polyamide III membranes might also decrease the equilibrium distribution coefficient for the sodium chloride salt between the bulk of the solution and the interface of the membrane on the high-pressure side during RO operation, as is clear from the high salt rejection capacities of these polyamide III membranes in comparison with the other membranes. The constant value of the ΔE_m (Table VI) suggests that the membranes were permselective and defect free. The value of σ calculated for each type of membrane was found to be unity, as is shown from the values given in Table VII. This data provides experimental proof regarding the permselectivity of the membranes. The values of water flux (J_v) and L_p of the membranes were calculated by using eq. (1), and are recorded in Table VII. The high values obtained from the

Table IX Effect of Operating Pressure on PWP and PR

Pressure (psig)	Membrane I		Membrane II		Membrane III	
	PWP (g/h)	PR (g/h)	PWP (g/h)	PR (g/h)	PWP (g/h)	PR (g/h)
500	32.0	31.2	30.7	29.8	29.2	28.8
700	42.6	40.8	40.8	40.1	39.4	38.4
900	52.2	48.0	50.0	49.1	49.6	48.2
1,100	61.6	57.2	59.6	58.1	58.2	58.4
1,300	70.2	64.8	67.0	65.5	66.2	64.6
1,500	75.2	74.2	73.1	72.0	72.4	71.2

Feed concentration: 300 ppm; feed flow rate: 250 cm³/min; membrane annealing temperature: 80°C; solvent evaporation time: 15 min.

membranes prepared from polyamide I are an indication of that polyamide's high hydrophilicity.

Reverse Osmosis

RO data have been collected as a function of polymeric material and physical conditions of the preparation of the membranes, and of the operating parameters such as pressure, feed concentration, and feed flow rate. The values of A for the membranes at the operating pressure of 500 psig and feed concentration of 3,000 ppm of NaCl are

reported in Table VIII, which indicates that the overall porosities of the membranes prepared from polyamide III are lowest in comparison with the membrane I. The PWP has been found to vary from 32.0 to 29.2 g/h for the membranes I to III (Table IX). The PWP and A are characteristics of the membranes and were measured by taking pure water at a velocity of 250 cm³/min and an operating pressure of 500 psig. The effect of operating pressure on the values of A has also been studied by varying the pressure from 500 to 1,500 psig. It was found that the value of A decreased

Table X Effects of Feed Concentration and Feed Flow Rate on PR, $D_{AM}/K\delta$, and f

Feed Concentration (ppm)	Feed Flow Rate (cm ³ /min)	Membrane of		
		Polyamide I	Polyamide II	Polyamide III
Product Rate (PR) (g/h)				
3,000	250	31.20	29.50	28.80
5,000	250	18.80	17.68	17.30
3,000	300	37.40	35.38	34.52
5,000	300	22.43	21.28	20.82
Solute Transport Parameter ($D_{AM}/K\delta$) (cm/s)10 ⁻⁵				
3,000	250	2.305	1.72	1.57
5,000	250	9.77	6.55	3.97
3,000	300	2.04	1.27	0.63
5,000	300	7.94	4.73	1.78
Percent Salt Rejection (f)				
3,000	250	96.2	97.0	97.2
5,000	250	80.2	84.9	90.9
3,000	300	97.1	98.2	99.1
5,000	300	85.3	90.4	96.0

Operating pressure: 500 psig; membrane annealing temperature: 80°C; solvent evaporation time: 15 min.

on increasing the pressure. The effect of pressure on the value of A is shown in Figure 3 for all of the three membranes obtained from three different polymeric materials prepared under identical conditions. The decrease in the value of A was due to the compaction of the membrane on increasing the operating pressure from 500 psig to 1,500 psig. During this compaction, membrane stretching took place and the overall porosity was decreased. However, the PWP was found to increase with increasing pressure (Table IX), which was due to the increase in the chemical potential of the water on the high-pressure side of the membranes. After characterizing the membranes in terms of the A and PWP, the membranes' performance was also evaluated in terms of f , PR, and $D_{AM}/K\delta$ by carrying out experiments at room temperature under conditions of single-pass flow using a sodium chloride water system at known concentration and feed flow rate. The f was determined by estimating the concentration of the salt in the feed and permeate. The PR is expressed as the amount of the flux permeating per hour from the membrane at pre-set operating pressure. The values of these parameters for the prepared membranes are reported in Table VIII. From the results given in this table, it is clear that the membranes prepared from polyamide III are high salt-rejecting membranes. The PR is found to be high in the case of membranes prepared from polyamide I. The $D_{AM}/K\delta$, which is calculated by Kimura–Sourirajan analysis, has also been found highest in the case of membranes prepared from polyamide I. The effect of the pressure on f has been determined by varying the operating pressure from 500 to 1,500 psig for all three different types of membranes. The results were recorded at a feed concentration of 3,000 ppm of NaCl and feed flow rate of 250 cm³/min, and are given in Figure 4. Observation of the figure clearly indicates that the salt rejection increases on increasing the operating pressure; however, the rate of increase in the salt rejection decreased after attainment of the maximum value of f in each types of the membranes. This increase in the value of f on increasing the operating pressure is due to the compaction¹⁷ of the membranes. A similar effect of pressure on f has been reported by Kimura and Sourirajan.¹⁸ The effect of operating pressure on PR has also been studied, and from the results given in Table IX, it has become clear that PR has increased on increasing the pressure from 500 to 1,500 psig. With increased pressure the permeability of the solvent is increased, hence the PR was found to

increase on increasing the pressure. The effect of the pressure on $D_{AM}/K\delta$ has also been studied and the results are shown in Figure 5. The $D_{AM}/K\delta$ in each membrane was found to decrease on increasing the pressure; however, the net decrease in the value of $D_{AM}/K\delta$ for the polyamide I membrane is high in comparison with the membranes prepared from polyamide III. This indicates that the membranes of polyamide III are high salt-rejecting membranes. The effect of the pressure on $D_{AM}/K\delta$ is similar to the trend reported in the literature.¹⁸ The effects of feed concentration and feed flow rate on the PR, $D_{AM}/K\delta$, and f have also been studied and the results are reported in Table X. Observation of the results clearly indicates that the PR was found to decrease on increasing the feed concentration from 3,000 to 5,000 ppm of NaCl. This decrease in PR was due to the concentration polarization of the membranes, which ultimately decreased the effective operating pressure on the membrane, as reported in the literature.¹⁹ However, the PR has been found to increase on increasing the feed flow rate, as is clear from the results given in Table X. This increase of PR on increasing the flow rate is assumed to be due to the disturbance in the concentration profile at the membrane surface on the high-pressure side. The $D_{AM}/K\delta$ found to increase on increasing the feed concentration from 3,000 to 5,000 ppm (Table X) which is due to the increase in the transport of the salt through the membranes. However, its value decreases on increasing the feed flow rate. Similar observations were reported by Sourirajan.²⁰ The effect of feed concentration and feed flow rate on f was also determined, and the results given in Table X clearly indicate that the solute rejection decreases on increasing the feed concentration and increases on increasing the feed flow rate. The effect of feed concentration and feed flow rate on the value of f can be explained considering the variation in the values of $D_{AM}/K\delta$ as a function of feed concentration and feed flow rate. The effects of annealing temperature and solvent evaporation time on the values of the membranes parameters A , PR, $D_{AM}/K\delta$, and f are shown in Table V; from the data it is clear that the optimum temperature is 80°C and the solvent evaporation time was almost 15 min. On increasing the annealing temperature and the time of solvent evaporation, the f value was increased at the expense of the product rates, hence it is not economical. Similarly, on decreasing the annealing temperature and the time of solvent evaporation the PR increased but the f was poor. These observations of the RO data

suggest that the membranes prepared at 80°C and at solvent evaporation of 15 min are suitable for the optimum product rate and maximum salt rejection for all the membranes.

CONCLUSIONS

The synthesized aromatic polyamides were of high molecular weights and high $[\eta]$, and hence found suitable to prepare membranes for RO technique. The polyamide III prepared from 3,5-diaminobenzoic acid and 4,4'-diphenyldicarboxylic acid chloride gave membranes of superior quality in comparison with polyamides I and II. The pendant carboxylic acid group of the prepared polyamides, due to its hydrophilic nature, was helpful in improving the product rate.

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