Synthesis of Highly Selective Copolymer Membranes and Their Application for the Dehydration of Tetrahydrofuran by Pervaporation

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ABSTRACT: Acrylonitrile was copolymerized with 2-hydroxyethyl methacrylate (HEMA) at three different copolymer compositions by emulsion polymerization to produce polyacrylonitrile–2-hydroxyethyl methacrylate (PANHEMA) copolymer membranes containing increasing amounts of HEMA from PANHEMA-1 to PANHEMA-3. The dehydration of tetrahydrofuran (THF) over a concentration range of 0–14 wt % water in the feed was studied by pervaporation with these three copolymer membranes. The permeate water flux and separation factor for water was measured over the same concentration range at 30, 40, and 50°C. Among the copolymer membranes, PANHEMA-1 exhibited a reasonable water flux (34.9 g m^{-2} h^{-1}) with a very high water selectivity (264), whereas PANHEMA-3 showed a higher water flux (52 g m^{-2} h^{-1}) but a lower water selectivity (176.5) for highly concentrated THF (0.56 wt % water in the feed) at 30°C. The permeation factors of water for all of the membranes were much greater than unity, which signified a strong positive coupling effect of THF on water permeation. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 728–737, 2007

Key words: copolymerization; membranes; selectivity; separation techniques

INTRODUCTION

Pervaporation (PV) is a fast-growing membrane process involving the separation of a binary liquid mixture with a nonporous dense membrane. In PV, separation takes place by the preferential sorption and diffusion of one component through the membrane under reduced pressure, which creates a chemical potential gradient in the liquid phase.

In recent years, extensive research work has been done on PV for the separation of traces of organics from aqueous solutions, dehydration of organics, and organic–organic separation. PV is very effective in the separation of these liquid mixtures, which are difficult to separate by conventional means of separation due to azeotrope formation, low relative volatility, or the presence of microorganisms that require a mild process of separation.[1] Various polymeric membranes have been used for these separations, depending on how close their solubility parameter values were to the component to be separated.[2,3]

Hydrophilic membranes have been widely used for the dehydration of many organics by PV. Poly-acrylonitrile (PAN)-supported crosslinked poly(vinyl alcohol) membranes have already been commercialized for the dehydration of alcohols.[4] However, this membrane failed when used for the dehydration of corrosive acids, such as glacial acetic acid.[5] As a stable dehydrating membrane, copolymers of acrylonitrile (AN) have been used with consistent results.[5,6] These copolymer membranes show high water selectivities along with reasonable fluxes when used for the dehydration of corrosive liquids.[5,7] The dehydration of highly volatile organics such as tetrahydrofuran (THF) is also very important. The aqueous solution of THF is encountered in many chemical processes.[8] THF reacts readily with oxygen on contact with air to produce an unstable hydroperoxide. Distillation of peroxides containing THF increases the peroxide concentration and results in a serious risk of explosion.[8] THF also forms an azeotrope with water (5.3 wt % water), and the THF–water mixture needs dehydration during the manufacture of THF.

PV would be a better candidate for the dehydration of THF because, unlike distillation, it can be carried out at low temperatures, and the azeotropic composition encountered in distillation can be separated by PV without the requirement of a third entrainer. In this study, a copolymer of AN with 2-hydroxyethyl methacrylate (HEMA) was used for the dehydration of THF. In this case, the AN moiety of the copolymer gave the mechanical strength of the membrane, and its hydrophilicity was provided by its HEMA moiety.

EXPERIMENTAL

Materials

The monomer HEMA was given by M/s Berger Paints (Kolkata, India). The other monomer (AN), the emulsifier (sodium lauryl sulfate), and the initiator (potassium peroxodisulfate) were obtained from M/s E. Merck, Ltd. (Mumbai, India).

Synthesis of the polymer

The copolymerizations of AN and HEMA at three different comonomer compositions were carried out by emulsion polymerization in a three-necked reactor at 70°C for about 6 h. The reactor was fitted with a stirrer, a thermometer pocket, and a condenser. Water was used as the dispersion medium. Sodium lauryl sulfate and potassium peroxodisulfate were used as the emulsifier and initiator, respectively. After polymerization, the polymer was precipitated with common salt and was washed repeatedly with distilled water. The copolymer was then dried at 70°C for 4 h in a vacuum drier. The structure of the polyacrylonitrile–2-hydroxyethylmethacrylate (PAN-HEMA) copolymer is shown in Figure 1.

Membrane casting

The PANHEMA copolymer membranes were prepared by casting from a dimethylformamide (DMF) solution (6 wt %) of the copolymers with an applicator on a clean smooth glass plate and dried at 60°C for 2 h. Subsequently, the membranes were annealed at 80°C for an additional 6 h. Both of these drying and annealing operations were carried out in a vacuum oven under 1 mmHg of pressure. The membrane thickness for the copolymers was maintained at about 30 μm. The thickness was measured by ASTM D 374 with a standard dead-weight thickness gauge (Baker, type J17, Japan).
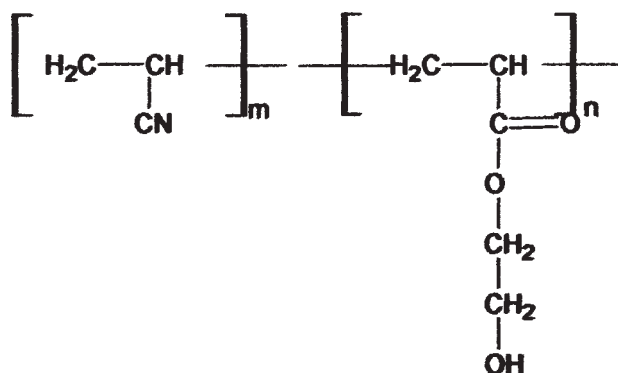
Figure 1 Structure of the repeating units of the PAN-HEMA copolymer.

TABLE I
Copolymer Composition of the Pervaporation Membranes

Name of the copolymer	Comonomer composition (mole fraction)		Reactivity ratio		P_1/P_2 peak ratios
	AN	HEMA	AN	HEMA	
PANHEMA-1	0.971	0.029	0.2	1.0	0.9573
PANHEMA-2	0.955	0.045			1.5035
PANHEMA-3	0.899	0.101			1.922

Copolymer composition

The three PANHEMA copolymers, that is, PAN-HEMA-1, PANHEMA-2, and PANHEMA-3, were prepared with various copolymer compositions on the basis of their relative reactivity ratios. The theoretical copolymer compositions of the copolymers were calculated from a standard equation.[9] The molar concentration of the comonomer and the resulting copolymers along with their reactivity ratio values are given in Table I. The three copolymer of PANHEMA, that is, PANHEMA-1, PANHEMA-2, and PANHEMA-3, with three different compositions as obtained from the previous experiments were characterized by the following methods.

Copolymer (membrane) characterization

Fourier transform infrared (FTIR) studies

The FTIR spectra of the copolymer membranes were recorded on a Jasco FTIR spectrometer (FT/IR-460 Plus, Jasco Corp., Japan) with a thin film (10 μm) of the polymer. The sample film was prepared by solvent casting from its solution in DMF. The film was dried under reduced pressure (~1 mmHg) in a vacuum oven for 8 h at 80°C. film of the polymer.

Intrinsic viscosity studies

The intrinsic viscosities of the copolymer were determined with an Ubbelohde-type viscometer. Four dilute solutions of the polymers (0.25, 0.5, 0.75, and 1 g/dL) in DMF were taken in the viscometer, and the specific viscosities were determined from the relative times taken by the polymer and the solvent itself in the viscometer. Reduced viscosity, which is the specific viscosity per unit concentration, was plotted against concentration of the polymer solution, and from the plot, the intrinsic viscosities of the copolymer membranes were obtained by extrapolation to zero concentration.

Glass-transition temperature (T_g)

T_g was measured by a differential scanning calorimetry (DSC) analyzer (DSC822[e] Mettler Toledo,

Switzerland). The temperature range for these experiments was 30–125°C at a scanning rate of 10°C/min.

Mechanical strength testing

The tensile strength and elongation at break of the polymer films were determined with an Instron tensile tester (model 4301). The experiment was performed according to ASTM D 882-97. In our system, the length of the specimens was 250 mm, the thickness of the specimens was around 0.1 mm, and the thickness was uniform to within 5% of the thickness between the grips. The width of the specimens was 20 mm, and the edges were parallel to within 5% of the width over the length of the specimen between the grips.

Sorption studies

Membranes of known weights were immersed in different known concentrations of aqueous THF solutions and were allowed to equilibrate for 96 h at 30°C. Each sample was weighed periodically until no weight change was observed. These membranes were taken out from the solutions and weighed after the superfluous liquid was wiped out with tissue paper. The increment in weight was equal to the total weight of water and THF sorbed by the membrane.

Permeation studies

PV experiments were carried out in a batch-stirred cell (Fig. 2) with an adjustable downstream pressure that was maintained at 1 mmHg. The effective membrane area in contact with the feed solution was 19.6 cm^2, and the feed compartment volume was 150 cm^3. PV experiments were carried out at constant temperature of 30°C. The water content of the permeate was determined by an Abbe-type refractometer (model AR600, MISCO) at 25°C for all the samples.

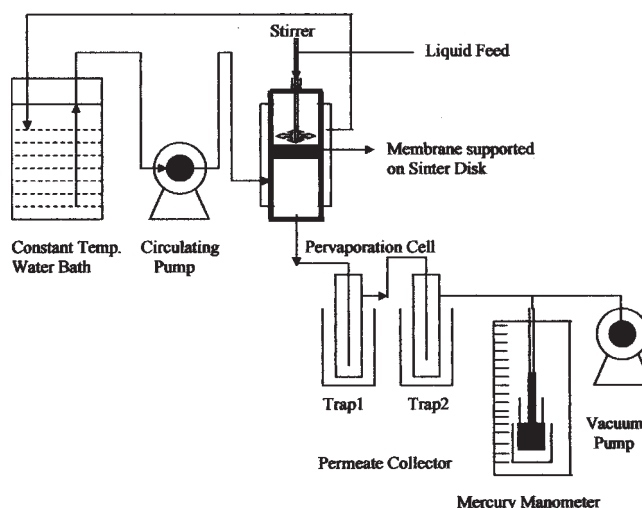The selectivity (α) for THF dehydration may be expressed as a separation factor:

$$\alpha_{\text{water}} = \frac{\dfrac{Y_{\text{Water}}}{Y_{\text{THF}}}}{\dfrac{X_{\text{Water}}}{X_{\text{THF}}}} \qquad (1)$$

where y_i and x_i are the weight fractions of the i components in the permeate and feed, respectively.

RESULTS AND DISCUSSION

Synthesis of the polymer

The copolymerization of AN with vinyl monomers has been carried out by bulk,[10] solution,[11] and sus-

Figure 2 Schematic diagram of the permeation setup for PV.

pension[12] methods by various authors. In bulk polymerization, viscosity builds up rapidly at a low conversion,[13] which leads to a low-molecular-weight gelled polymer in which membrane preparation is impossible. In bulk polymerization, the control of reaction also becomes difficult because of the poor dissipation of the high heat of vinyl polymerization in the absence of any other solvent; this results in a runaway reaction. Solution polymerization also requires highly polar solvents, such as DMF, dimethyl sulfoxide, and N-methylpyrrolidone, and the reaction is sluggish in nature because of the interaction of these solvents with the propagating polymer chain.[14] In contrast, in emulsion polymerization, an easily dispersed medium, such as water, leads to a high-molecular-weight polymer with minimum contamination.[15] In emulsion polymerization, apart from a high-molecular-weight product, a polymer with low polydispersity is obtained; this results in a membrane of better mechanical strength and consistent permeation behavior. In this study, AN and HEMA were thus copolymerized by emulsion polymerization to obtain a PV membrane with desired qualities.

Copolymer (membrane) characterization

FTIR study

The FTIR spectra of the three PANHEMA copolymers were obtained with very thin films of the polymers. The FTIR spectra of PANHEMA-1, PANHEMA-2, and PANHEMA-3 copolymers are shown in Figure 3(a–c). The strong band at 2241.84 cm^{-1} corresponded to the CN stretching vibration of the AN comonomer. The ester stretching vibration band at 1725.01 cm^{-1}, the C—O stretching band at 1212.04 cm^{-1},
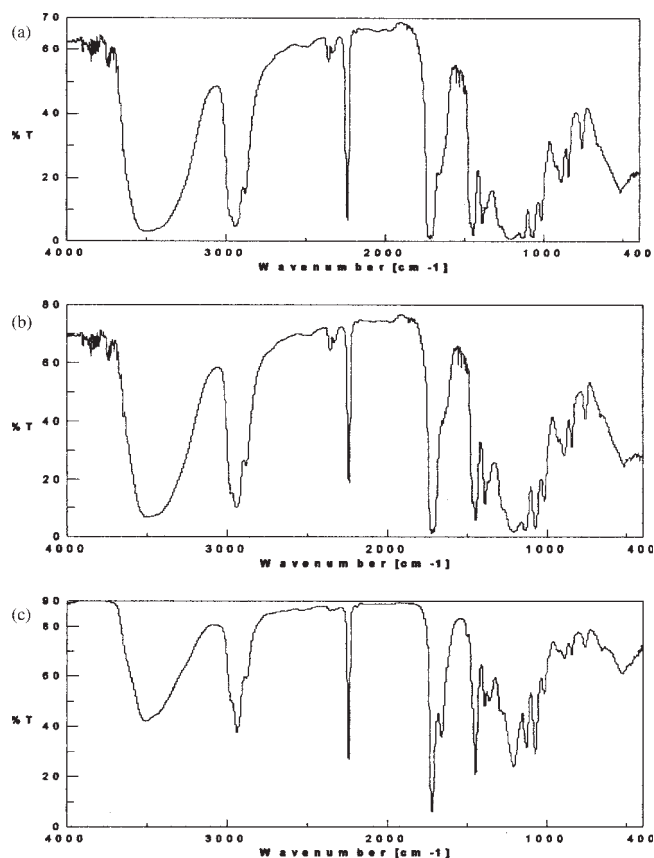
Figure 3 FTIR spectra of the PANHEMA copolymers with various compositions: (a) PANHEMA-1, (b) PAN-HEMA-2, and (c) PANHEMA-3.

and the O—H bending vibrations of 1078.01 cm^{-1} corresponded to the hydroxyethyl methacrylate comonomer of the copolymer.[5] The other strong bands at 1454.06 and 2940.91 cm^{-1} corresponded to the C—H bending (alkane, —CH$_3$, alkane, —CH$_2$—) and C—H stretching of alkane, respectively.[16]

FTIR spectra and copolymer composition

We mentioned earlier that each of the three PAN-HEMA copolymers was synthesized with various comonomer compositions on the basis of their relative reactivity ratio values. The three different copolymer compositions of PANHEMA were characterized with three different FTIR spectra. Figure 3(a–c) shows the FTIR spectra of the three different copolymers of PANHEMA, that is, PANHEMA-1, PANHEMA-2, and PANHEMA-3, with various copolymer compositions. It is quite clear from these figures that the ratio of band intensities due to carbonyl and nitrile of the copolymer were different, which signified the various copolymer compositions. As shown in Figure 3 and Table II, the ratio of band intensities of carbonyl (P$_1$ for HEMA) to nitrile (P$_2$ for AN) decreased from PANHEMA-3 (1.922)

to PANHEMA-2 (1.5035) and PANHEMA-1(0.9573); this indicated a decreasing amount of HEMA in the copolymer. However, the exact copolymer compositions were not obtained in the absence of any standard sample of the copolymer.[17]

Intrinsic viscosity studies

The intrinsic viscosities of the copolymers as obtained by extrapolation of reduced viscosity against concentration are given in Table II. The viscosity-average molecular weight of the copolymers could not be measured because of the nonavailability of the Mark–Houwink constants of the copolymers. However, from the literature,[18] the intrinsic viscosities of the corresponding homopolymers were calculated as given along with the experimental intrinsic viscosities of the copolymer (Table II). When we compared these values, it was evident that the membrane copolymers were of high molecular weight.
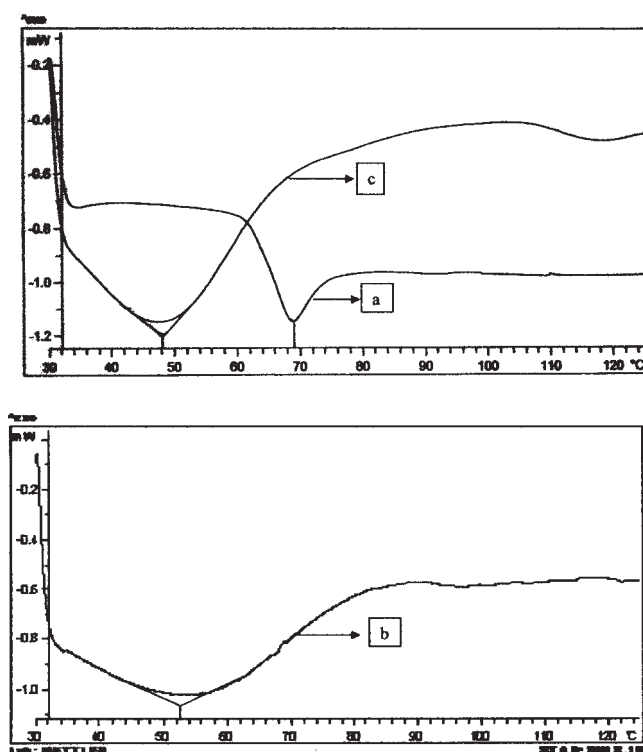
T_g

Evaluation of T_g characterizes a copolymer in that a copolymer always shows a single T_g in contrast to a blend of two homopolymers, which show two different T_g's. In this study, a single characteristic T_g was shown by all three PANHEMA copolymers, as shown by the DSC curves in Figure 4 for the PANHEMA-1 and PANHEMA-3 membranes. Similar types of DSC curves were also obtained for the other PANHEMA copolymer. The shifting of T_g from PANHEMA-1 to PANHEMA-3 with increasing HEMA content is clearly shown in Figure 4. T_g plays an important role in the determination of membrane performance, as high and low T_g's make a polymer tough and rubbery, respectively, which affect the permeability of the membrane differently. PAN is a glassy polymer with a T_g as high as 95°C and a very low water permeability. Apart from increased hydrophilicity, the incorporation of the hydrophilic comonomer, that is, HEMA, also enhanced the water permeability of the resulting copolymer membranes through intramolecular plasticization, as apparent

TABLE II
Physical Properties of the Homo- and Copolymers

Name of the copolymer	Tensile strength (MPa)	Elongation at break (%)	Glass transition temperature T_g(°C)	Intrinsic viscosity (dL/g)
Polyacrylonitrile	78	2.5	92	1.06
Poly(HEMA)	—	—	45	2.06
PANHEMA-1	30.56	3.9	71	1.05
PANHEMA-2	16.72	9.6	52	1.2
PANHEMA-3	11.92	13.8	48	1.6

Figure 4 DSC curves of the PANHEMA copolymers with various compositions: (a) PANHEMA-1, (b) PANHEMA-2, and (c) PANHEMA-3.

from the decreased T_g of these copolymers from PANHEMA-1 to PANHEMA-3 in comparison to homopolyacrylonitrile. The T_g values of the polymers are given in Table II.

Mechanical strength testing

For a good PV membrane, there should be an optimum balance between TS and EAB. The three copolymer membranes of PANHEMA synthesized for this study had different TS and EAB in comparison to homopolyacrylonitrile, as shown in Table II. The incorporation of HEMA increased EAB at the cost of TS, as shown by the values given in Table II.

Sorption studies

Effect of feed concentration on the sorption isotherm. Figure 5(a) shows the variation of the total sorption of water and THF of all three copolymer membranes with the feed concentration of water at 30°C. As shown in Figure 5, with increasing feed concentration of water, the total sorption of all of the membranes increased, which signified the water selectivity of theses membranes in sorption. It is evident from the figures that these sorption isotherms closely resembled Rogers type-III sorption; that is, the mutual interaction of the sorbed THF and water mole-

cules was greater than their interaction with the copolymer membranes, and these sorbed particles formed clusters within the membrane matrix.[19] As also shown in Figure 5, the total sorption increased for the same feed concentration of water with increasing HEMA content from PANHEMA-1 to PANHEMA-3 along with usual increase of sorption with increasing feed concentration of water. The increased sorption of these copolymers for the same feed concentration was ascribed to the increased hydrophilicity of the copolymers due to the incorporation of more hydrophilic comonomer, that is, HEMA.

Effect of temperature on the sorption isotherms. The sorption isotherms of PAMHEMA-1 at 30, 40, and 50°C are shown in Figure 5(b). Similar types of isotherms were also obtained with the other two copolymer membranes. As shown in Figure 5(b), with increasing temperature, the total sorption increased for this membrane. The increased sorption of the

(a)

(b)
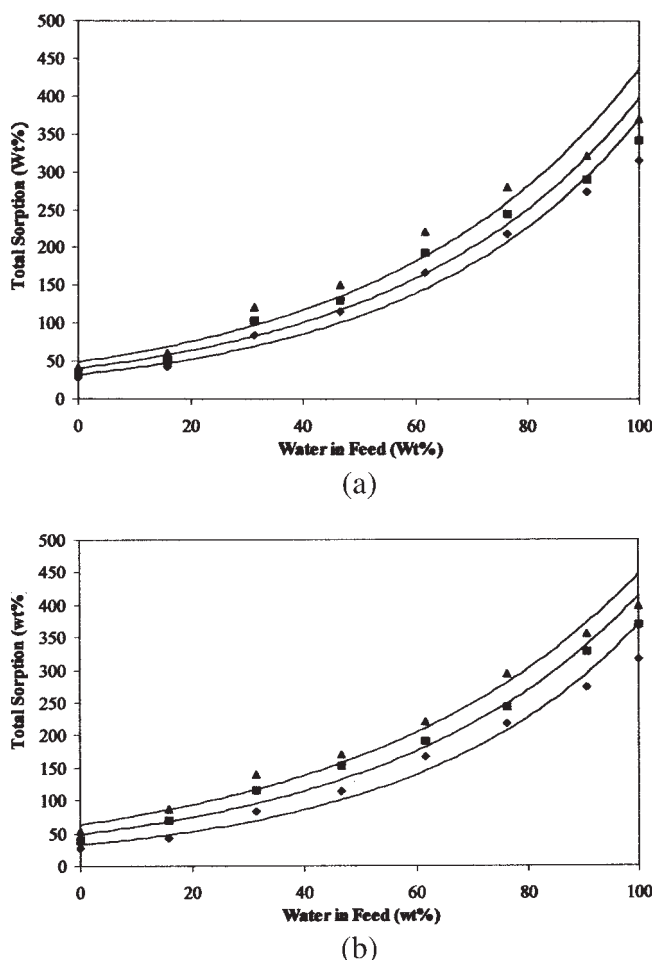
Figure 5 (a) Sorption isotherms of the copolymer membranes at 30°C: (◆) PANHEMA-1, (■) PANHEMA-2, and (▲) PANHEMA-3. (b) Total sorption of the PANHEMA-1 membranes at different temperatures: (◆) 30, (■) 40, and (▲) 50°C.

(a)

(b)
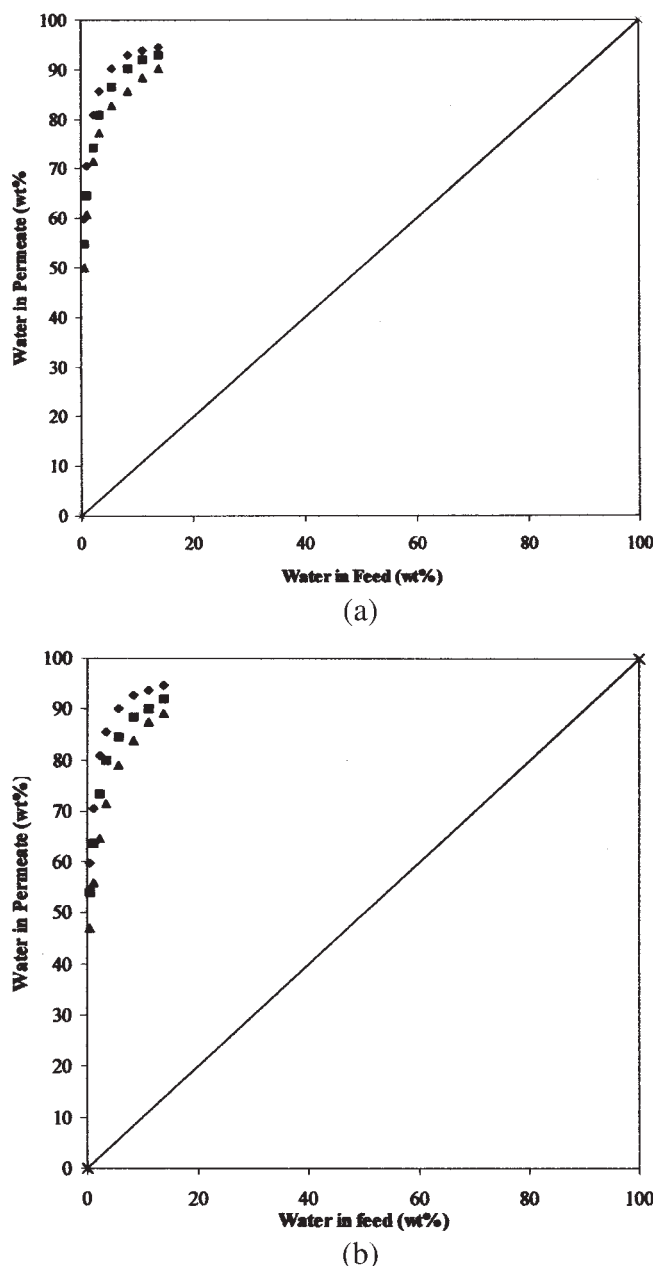
Figure 6 Variation of the permeate concentration of water (a) with its feed concentration at 30°C [(◆) PANHEMA-1, (■) PANHEMA-2, and (▲) PANHEMA-3] and (b) for the PANHEMA-1 membrane with its feed concentration at different temperatures [(◆) 30, (■) 40, and (▲) 50°C].

membranes at higher temperatures may have been due to the increased solubility of the organics in the membranes at higher temperatures.

Permeation studies

Effect of feed concentration and temperature on the THF dehydration. Figure 6(a) shows the variation of the weight percentage of water in the permeate against the weight percentage of water in the feed for dehy-

dration of THF with all the three PANHEMA membranes. It appears from these McCabe–Thiele-type *xy* diagrams that these PANHEMA membranes showed measurable dehydration characteristics over the entire concentration range without any pervaporative azeotrope, and their dehydration characteristics showed the following order: PANHEMA-1 > PANHEMA-2 > PANHEMA-3. With increasing HEMA content in the AN moiety from PANHEMA-1 to PANHEMA-3, the dehydration characteristic of the membranes decreased due to increased hydrophilicity and, hence, plasticization of the membranes.

As shown in Figure 6(b), the dehydration characteristics of the PANHEMA-1 membrane decreased with increasing feed temperature. Similar types of curves were also obtained for the other two copolymers. This may be attributed to the increased permeation rate of THF along with water at high temperatures.

Effect of feed concentration on the flux and selectivity. Figure 7(a) shows the effect of the feed concentration of water on its flux and separation factor for all three PANHEMA copolymer membranes. As shown in Figure 7(a), for these PANHEMA membranes, with increasing water concentration in the feed, water flux increased linearly at the cost of the separation factor. For the same feed concentration, the flux increased from the PANHEMA-1 to the PANHEMA-3 membrane, whereas the separation factor followed the opposite order. As shown in the figure, initially, the separation factor also decreased almost exponentially with increasing feed concentration of water up to around 3–3.5 wt % in the feed, which may be attributed to the plasticization of the hydrophilic membrane with water. However, above this concentration of water in the feed, the dehydration separation factors decreased marginally with a linear trend for all of the membranes. In this case, the plasticization effect was partially offset by the fact that the presence of hydrophilic carbonyl and hydroxyl groups in the membranes formed preferential hydrogen bonds with the sorbed water molecules[5] and caused the preferential permeation of water molecules through the membranes.

Effect of feed temperature on the flux and selectivity. As shown in Figure 7(b), the water flux increased with increasing temperature at the cost of the separation factor for the PANHEMA-3 membrane. Similar results were also obtained for the other two PANHEMA membranes. This may have been due to increases in both the total sorption and diffusion coefficient of water with increasing temperature. Again, the thermal motion of the polymer chains increased with increasing temperature, which may have facilitated the permeation of the sorbed molecule through the membrane.

(a)

(b)
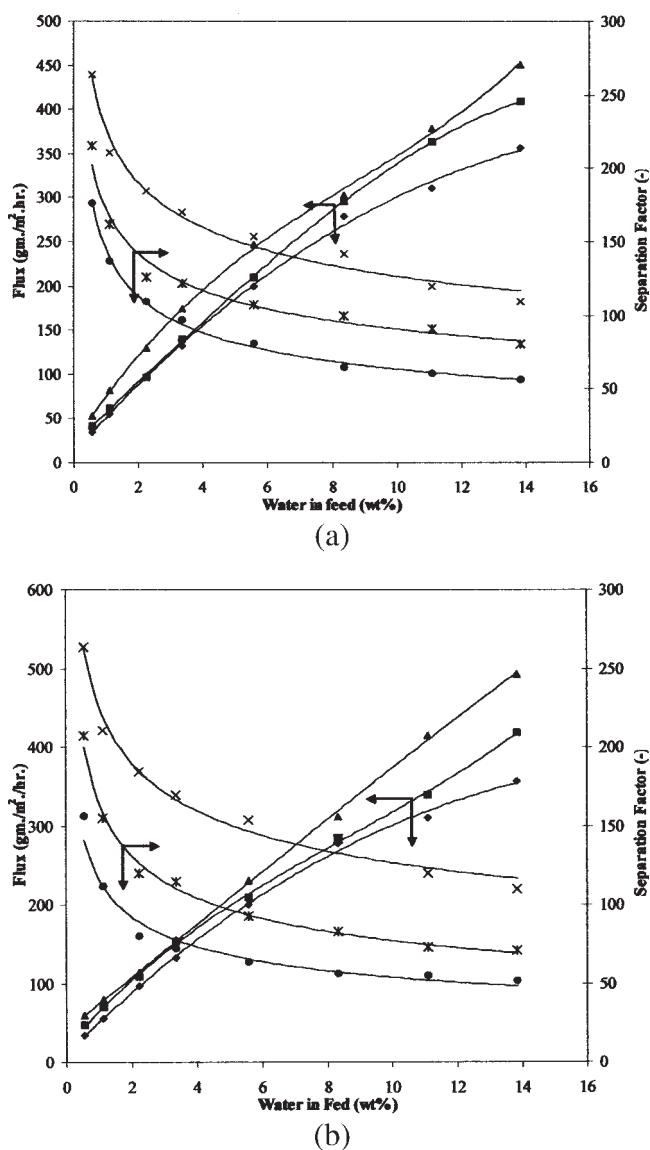
Figure 7 Variation of the flux and separation factor of water (a) with its feed concentration at 30°C [(◆ and ×) PANHEMA-1, (■ and *) PANHEMA-2, and (▲ and ●) PANHEMA-3] and (b) for PANHEMA-1 with its feed concentration at different temperatures [(◆) flux at 30°C, (■) flux at 40°C, (▲) flux at 50°C, (×) separation factor at 30°C, (*) separation factor at 40°C, and (●) separation factor at 50°C].

Effect of feed concentration on the activation energy. Activation energies for permeation (ΔE_P's) can be compared with the rate constant of a chemical reaction, and thus, it may be defined from an Arrhenius type equation:

$$\ln F = -\frac{\Delta E_P}{RT} + \ln A \qquad (2)$$

where R is the universal gas content and A is a pre-exponential factor. The activation energies for permeation of all three copolymer membranes at differ-

ent feed concentrations of water were obtained from the previous Arrhenius-type plot of the logarithm of flux (F) against the inverse of the absolute temperature ($1/T$). These activation energies for permeation were then plotted against the feed concentration of water for all three membranes, as shown in Figure 8. As shown in this figure, initially, up to around 3–3.5 wt % water in the feed, the activation energy decreased almost exponentially. However, above this concentration, the change in activation energy with feed concentration was marginal. The initial drastic fall of activation energy with feed concentration may be ascribed to the extensive plasticization of the highly hydrophilic membrane with even very low concentrations of water in the feed, which resulted in easy permeation and, thus, demanded less activation energy. Further plasticization above 3–3.5 wt % water in the feed was low, as reflected in the marginal fall of activation energy above this feed concentration.

Effect of feed concentration and temperature on the diffusion coefficient. From Fick's law

$$J = D\frac{dc}{dx} \qquad (3)$$

$$or\ D = \frac{J}{\frac{dc}{dx}} \qquad (4)$$

The Fickian diffusion coefficient (D) of water and THF were obtained from the previous equation, that is, by the division of water or THF flux (J) by the difference in its concentration in the feed and permeate and the multiplication of the same by the thickness (x) of the membranes, which was maintained at 30 μm for this study. The diffusion coefficient is a strong function of concentration and changes across the thickness of a membrane. However, true diffu-
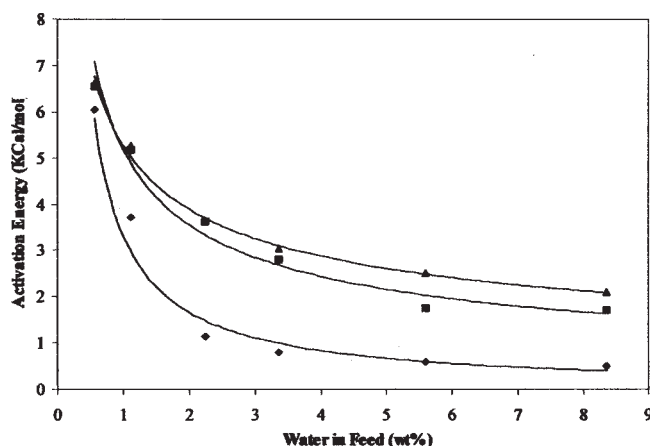
Figure 8 Variation of the activation energy with the feed concentration of water for PANHEMA membranes: (◆) PANHEMA-1, (■) PANHEMA-2, and (▲) PANHEMA-3.

(a)

(b)
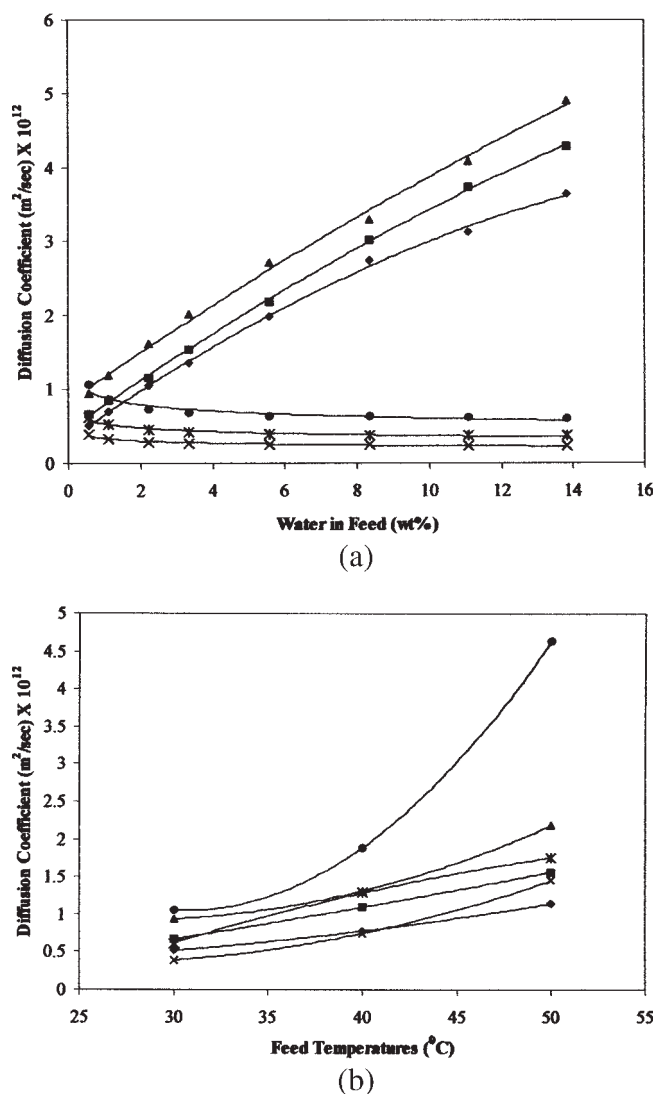
Figure 9 Variation of the diffusion coefficient of (a) the membranes at 30°C [(◆) water–PANHEMA-1, (■) water–PANHEMA-2, (▲) water–PANHEMA-3, (×) THF–PANHEMA-1, (∗) THF–PANHEMA-2, and (●) THF–PANHEMA-3] and (b) the PANHEMA membranes with feed temperatures [(◆) water–PANHEMA-1, (■) water–PANHEMA-2, (▲) water–PANHEMA-3, (×) THF–PANHEMA-1, (*) THF–PANHEMA-2, and (●) THF–PANHEMA-3].

sion coefficients across the thickness of a membrane cannot be measured with a high level of accuracy due to the difficulties of obtaining concentrations at different regions of the membrane along its thickness. In this study, the Fickian diffusion coefficient was calculated[20] to get an approximate idea about the influence of diffusion on the permeation selectivity of the membranes. The diffusion coefficients of water increased more or less linearly with the feed concentration of water for all three membranes, as shown in Figure 9(a). The effect of copolymer composition on the diffusion coefficient is also shown in this figure in that diffusion coefficient of water increased with increasing HEMA content from PANHEMA-1

to PANHEMA-3. Increased plasticization of the membranes with increasing feed concentration of water in the feed or HEMA content in copolymer caused a faster permeation and, hence, higher diffusion coefficient of water through the membranes. As shown in Figure 9(a), the diffusion coefficient of THF was much lower than that of water, and with increasing feed concentration of water, the diffusion coefficient of THF through the membranes remained marginally constant. The much bigger kinetic diameter[21] of THF in comparison to the water molecule resulted in a lower diffusion coefficient of THF.

The diffusion coefficients of water and THF also increased linearly with temperature except for THF permeation through the PANHEMA-3 membrane, as shown in Figure 9(b), where the diffusion coefficient of all three membranes are plotted against the feed temperature for 0.56 wt % feed in water.

(a)

(b)
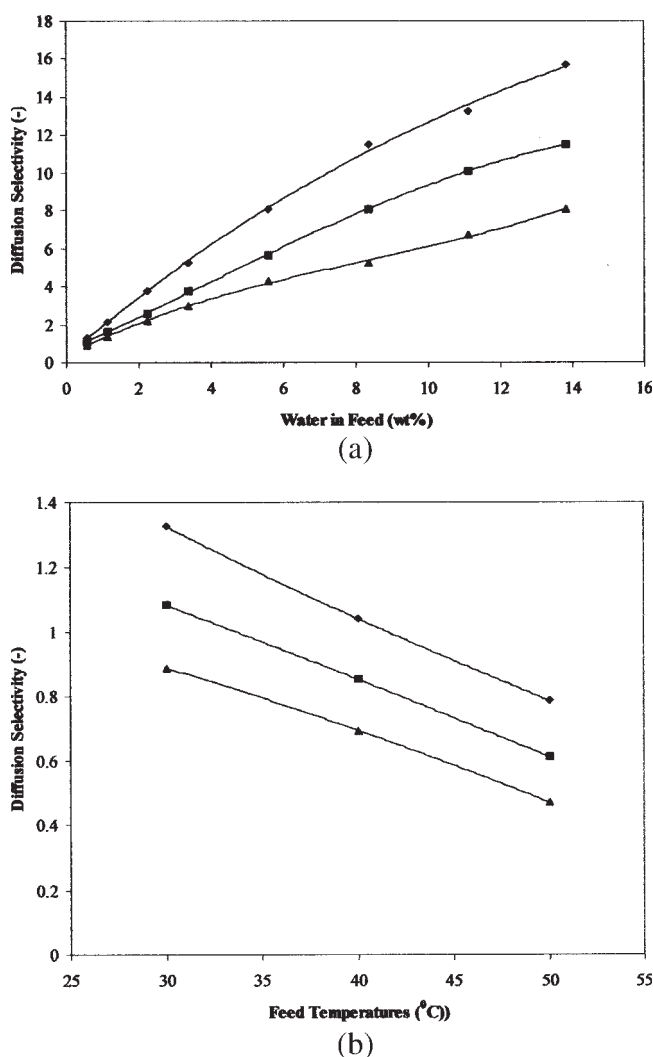
Figure 10 Variation of DS of the PANHEMA membranes at (a) 30°C [(◆) PANHEMA-1, (■) PANHEMA-2, and (▲) PANHEMA-3] and (b) at different temperatures [(◆) PANHEMA-1, (■) PANHEMA-2, and (▲) PANHEMA-3].

Effect of feed concentration and temperature on the diffusion selectivity (DS). The ratio of the diffusion coefficients of water to THF was considered as the DS of water, and the DS of water increased with increasing feed concentration of water, as shown in Figure 10(a). As also shown in this figure, for the same feed concentration, the DS of water increased with decreasing HEMA content from PANHEMA-3 to PANHEMA-1; this was in agreement with the overall dehydration selectivity order of the membranes.

The effect of temperature on the DS of water for 0.56 wt % water in the feed is shown in Figure 10(b). As shown in this figure, DS decreased drastically with a linear trend for all three membranes. At higher temperatures, the diffusion of THF through the membrane also increased; this resulted in a decrease in the DS for water.

Effect of feed concentration on the permeation ratio. Huang and Lin[22] defined the permeation ratio (θ), which was a measure of the deviation of the actual permeation rate ($J_{i, \text{exp}}$) from the ideal rate (J^0), to explain interactions between polymer and permeants:

$$\theta_i = J_{i \text{ expt at } x \text{ concentration}} / J^0_{i \text{ expt at } x \text{ concentration}} \qquad (5)$$

$$J^0_{i \text{ (at } x \text{ concentration)}} = J^0_{\text{(pure } i)} x_i \qquad (6)$$

Similarly, for component *j*, the equations become

$$\theta_j = J_{j \text{ expt at } x \text{ concentration}} / J^0_{j \text{ expt at } x \text{ concentration}} \qquad (7)$$

$$J^0_{j \text{ (at } x \text{ concentration)}} = J^0_{\text{(pure } j)} x_j \qquad (8)$$

where *i* and *j* denote the individual components in the binary mixture, *x* is the weight fraction in the feed mixture, and the superscript 0 denotes the ideal permeation.

The variation in the permeation factors of both water and THF with respect to the feed concentration of water is given in Figure 11 for the three copolymer membranes. As shown in this figure, THF had a strong positive coupling effect on water flux, as the individual water fluxes of all three membranes were much higher than the ideal flux (i.e., when instead of a THF–water mixture, only pure water was present in the feed). Also, water had also a positive coupling effect on THF permeation. Furthermore, the coupling effect of THF on water permeation decreased drastically up to 3–3.5 wt % feed concentration of water and then linearly with increasing feed concentration of water. However, the coupling effect of water on THF permeation through the membrane was independent of the feed concentration of water; this signified the strong hydrophilic nature of the membranes.
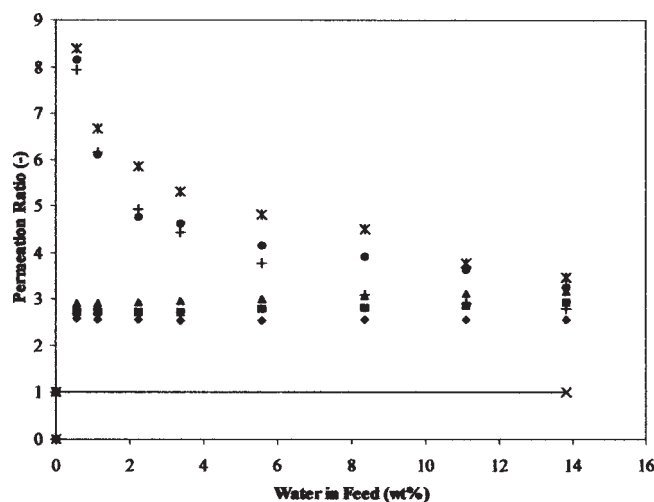
Figure 11 Variation of the permeation ratio with the feed concentration of water at 30°C: (◆) THF–PANHEMA-1, (■) THF–PANHEMA-2, (▲) THF–PANHEMA-3, (×) water–PANHEMA-1, (●) water–PANHEMA-2, and (+) water–PANHEMA-3.

CONCLUSIONS

The copolymerization of AN with HEMA with various comonomer compositions by emulsion polymerization yielded three different copolymer membranes. These membranes were used for the dehydration of THF over the entire concentration range 0–14 wt % feed water at various feed temperatures by PV. All of these membranes gave a high degree of water permeation and dehydration selectivities. The copolymer membranes showed both sorption and DS for water. The activation energy for permeation for all of the membranes decreased exponentially with increasing water concentration in the feed up to around 3.4 wt % water in the feed, and then, it decreased linearly with feed concentration. The DSs of all the membranes were also a strong function of the feed concentration of water, feed temperature, and copolymer composition.

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