Pervaporative Separation of a 1-Methoxy Propanol and Water Mixture

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ABSTRACT: The pervaporative dehydration of ether derivatives of alcohol, such as 1-methoxy propanol (MP) and water mixtures, was studied with polyimide (PI), cellophane, poly(vinyl alcohol) (PVA), cellulose diacetate (CDA), cellulose triacetate, two separate blends of cellulose acetate and CDA with cellulose acetate propionate, and PVA crosslinked with multifunctional crosslinkers. The effects of different substitution derivatives of cellulosic materials were investigated. Membranes of PVA and citric acid and of PVA and maleic anhydride were studied with respect to the effect of the crosslinker and its loading. Among all the hydrophilic membranes, PI gave the best selectivity but poor flux. Poly(dimethylsiloxane) (PDMS) and linear low-density polyeth-

ylene (LLDPE) membranes were invoked for the selective permeation of comparatively weaker hydrophilic components. PDMS showed acceptable results for MP separation in terms of both flux and selectivity. LLDPE yielded better selectivity but very poor MP flux. All these membranes were stable, and no changes in their properties were observed over the entire range of concentration at 30°C. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2194–2210, 2002

Key words: differential scanning calorimetry (DSC); NMR; polysiloxanes; crosslinking; blends; membranes; morphology; selectivity; swelling; separation techniques

INTRODUCTION

The pervaporative dehydration of alcohol or its ether derivatives, such as 1-methoxy propanol (MP) with water, is important because most of these mixtures form azeotropes or yield a pinch on the vapor–liquid equilibrium curves. Pervaporation (PV) is a membrane-based separation process and a well-established route for producing absolute alcohol by the removal of water from an alcohol–water mixture. The pervaporative dehydration of ethanol has been studied by a number of investigators with various types of polymeric membranes.[1,2] Besides these, the sorption and permeation of aqueous alcohol (C1–C4) through poly(vinyl alcohol) (PVA) membranes or PVA crosslinked with multifunctional crosslinkers have been reported.[3–5] MP is extensively used in the pharmaceutical, biochemical, and electrical industries. The selective separation of water from aqueous mixtures of MP or the dehydration of MP can be carried out with different membranes that contain polar groups, either in the backbone or as pendant moieties. For the pervaporative dehydration of such a mixture, cellophane[6] and PVA and PVA-based membranes[7,8] can be used. Cellophane contains a polar oxygen atom in its glucosidic unit, as well as —OH, —CH$_2$OH groups as side groups, and PVA is a well-known hydrophilic polymer, containing —OH groups as pendant moieties on the ethylene unit. PVA is affected less at lower water concentrations,

but at higher water concentrations it swells substantially, and so the selectivity is lost. To overcome this problem, Huang and coworkers grafted[9] and crosslinked[5] PVA with different reagents. Subsequently, a number of investigators have reported different methods for modifying PVA membrane to achieve better stability and performance under operating conditions. Crosslinking with aldehyde acids was carried out by Burshe and coworkers.[3,7] Besides PVA, different cellulosic derivatives can be used. These are very effective for the separation of strongly hydrophilic compounds. Polyimide (PI) membranes were also extensively used by several investigators.[10–12] PI gave excellent selectivity for more polar compounds with very poor flux.

In this study, results for the pervaporative dehydration of MP are reported. A variety of polar membranes were used, mainly based on cellulose, PI, and different derivatives of PVA. Besides this, the performances of poly(dimethylsiloxane) (PDMS) and linear low-density polyethylene (LLDPE) were also evaluated. The purpose of this article is to summarize the potential applications of PV with membranes of various solubility parameters (14.9–32.28 MPa$^{1/2}$) and to discuss the performances in terms of selectivity and flux with different cellulosic blends and variations in the crosslinker loading. This study was done for a concentration range of 0–100 wt % water–MP.

THEORY

The transport of components of a binary mixture through a dense membrane can be explained by the

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sorption-diffusion model.[12] According to this model, the transport of a given species takes place as follows:

- Sorption of the permeants at the liquid side of the membrane.
- Diffusion of these permeants through the membrane.
- Desorption at the low-pressure side of the membrane.

The relative sorption or the extent of solubility can be explained by two theories:

- Solubility parameter theory.
- Interaction parameter or Flory–Huggins theory.

The interaction parameter theory reveals the extent of the attraction or affinity of a solvent with a matrix. According to the Flory–Huggins theory,[13] the free energy of mixing (ΔG_m) of a binary mixture consisting of a solvent (subscript s) and a polymer (subscript p) is given by

$$\Delta G_m / RT = \ln(1 - \phi_p) + \phi_p + \chi_{ip}\phi_p^2 \qquad (1)$$

For equilibrium sorption, the enthalpy of mixing is zero, and χ_{ip} is obtained as follows:

$$\chi_{ip} = -\,(\ln\phi_s + \phi_p)/(\phi_p)^2 \qquad (2)$$

χ is a dimensionless parameter that characterizes the interaction between the polymer segments and the solvent molecules and between one polymer segment and one solvent molecule. With decreasing affinity between the polymer and the penetrant, the value of χ_{ip} increases. Therefore, a lower value of χ_{ip} means higher sorption. Generally, a completely miscible solvent–polymer system[13] has a value less than 0.5

The dissolution of an amorphous polymer in a solvent is governed by the free energy of mixing:

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

where ΔH_m is the enthalpy change on mixing and ΔS_m is the entropy change during mixing. A negative value of the free energy change on mixing implies that the mixing process will occur spontaneously. Because the dissolution of a high molecular weight polymer is always connected to a small and modest increase in the entropy, the enthalpy term (the sign and magnitude of ΔH_m) is the deciding factor in determining the sign of Gibb's free energy change.

Hildebrand et al.[14] proposed that

$$\Delta H_m = V[(\Delta E_1/V_1)^{1\,2} - (\Delta E_2/V_2)^{1\,2}]^2\phi_1\phi_2. \qquad (3)$$

Equation (3) can be rewritten to give the heat of mixing per unit volume for a binary mixture:

$$\Delta H_m / V = (\delta_1 - \delta_2)^2\phi_1\phi_2 \qquad (4)$$

where $\delta_i = (\Delta E_i/V_i)^{1/2}$ is called the solubility parameter, which describes the attractive strength between the molecules of the two materials. When $\delta_1 = \delta_2$, the free energy of mixing will always be less than zero and the components will be miscible in all proportions. In general, the solubility parameter difference must be small for miscibility over the entire volume fraction range.

EXPERIMENTAL

Materials

Elastosil LR 7660 A and B solutions were kindly supplied by Wacker Chemie (Germany) for the preparation of the PDMS membranes. Cellulose acetate propionate (CAP; average molecular weight = 15,000) was obtained from Acros Organics (New Jersey), and cellulose diacetate (CDA; 52.8% acetyl content) was obtained from Ion Exchange, Ltd. (Mumbai, India). Cellulose acetate (CA; 40% acetyl content) was supplied by Sigma–Aldrich. Dimethylformamide (DMF) was procured from S.D. Fine Chemicals (Mumbai, India). CA (40% acetyl content), CDA (52.8% acetyl content), cellulose triacetate (CTA; 59.6% acetyl content), and LLDPE films (70–100 μm) were used. The PVA used, polynol 117 (average molecular weight = 75 kD; 99% hydrolyzed) was kindly supplied by Polychem, Ltd. (Mumbai, India). A PI film 40 μm thick was supplied by ABR Organics (Hydrabad, India). Citric acid (Ca; analytical reagent) and maleic anhydride (Manh) were supplied by Himedia Laboratories Pvt., Ltd. (Mumbai, India), and Loba Chemie Pvt., Ltd. (Mumbai, India), respectively. Span Chemicals (Mumbai, India) supplied MP.

Membrane preparation

Different types of membranes were prepared. Table I provides a summary of these membrane preparations.

Blend synthesis and membrane preparation

CA and CDA are fully compatible with CAP. Physical blending was carried out with 10 g of CA dissolved in DMF and 1 g of CAP and mixing. In a similar CA solution, 2 g of CAP was mixed thoroughly. After homogenization, each solution was spread on a glass plate separately. Then, it was kept at 60°C for 4 h. The membrane thickness was 50 μm. The 10:1 and 10:2 blends of CA and CAP are named blend 1 (B1) and blend 2 (B2), respectively. Similarly, the 10:1 and 10:2 blends for CDA and CAP are designated blend 3 (B3) and blend 4 (B4), respectively.

Polymer	Solvent	Curing temperature (°C)	Curing time (h)
CA, CDA, CTA	DMF	60°	4
CA + CAP and CDA + CAP	DMF	60°	4
PVA	Water	100	6
PVA + crosslinker	Water	120	6
PDMS	Mixture of 7760 (A) and (B) at a ratio of 9:1, respectively.	80	8

PVA is soluble in hot water. For the preparation of crosslinked PVA membranes, two solutions of PVA were prepared in distilled water. PVA (5 g) was put in a beaker with 45 g of water for the preparation of a 10% solution. Similarly, another 10% PVA solution was prepared. In these solutions, 1 (10:1 membrane) and 2 g (10:2 membrane) of Ca were added and mixed thoroughly. After being kept overnight, each solution was cast on a glass plate. A gradual change in the heat treatment was carried out, first at 100°C for 1 h and then at 120°C for 1 h. Similarly, another membrane set with the same concentration of Manh was prepared. The 10:1 and 10:2 membranes are designated membrane 5 (B5) and membrane 6 (B6) for Ca and B7 and B8 for Manh, respectively. The crosslinking was due to a reaction between —OH and —COOH groups.

Membrane characterization

Fourier transform infrared (FTIR) studies

The FTIR spectra of the blend membranes were recorded [Fig. 1(A)] on a PerkinElmer Paragon 500 FTIR instrument with a thin (10-μm) film of each polymer.

Differential scanning calorimetry (DSC) studies

The DSC studies were performed [Fig. 1(B)] with a PerkinElmer DSC-7 instrument.

^{1}H-NMR studies

The ^{1}H-NMR studies were performed (Fig. 2) with a 200-MHz Bruker AC-200 FT-MHz spectrometer.

Determination of the interaction parameter

Samples of dry membranes of known weights were immersed in a pure solvent and allowed to equilibrate for 3 days. These membranes were taken out from the solvent, and the superfluous liquid was wiped off with tissue paper. Then, the swollen membrane was weighed. For the equilibrium sorption of a pure solvent in a polymer, the binary interaction parameter χ_{ip} can be calculated with eq. (2).

Permeation studies

Experiments were carried out in a batch-stirred cell maintaining a downstream pressure of 2 mmHg. The cell[12] had two flanged compartments. The upper compartment containing the liquid had a capacity of 500 cm^3 and was provided with an outer jacket for temperature control. The effective membrane area in contact with the feed solution was 19.6 cm^2. The membrane was placed on a porous (stainless steel) supporting disc and sealed with a rubber O-ring. The permeate vapor was collected in a trap cooled with liquid nitrogen.

The permeation selectivity is defined as

$$\alpha = (Y_i/Y_j)/(X_i/X_j)$$

where X and Y represent the weight fractions of the solute in the feed and the permeate, respectively. Subscript i refers to the desired component (the selectivity of which is to be determined), and j refers to the second component.

Analysis of permeants

The feed and permeate concentrations of all the mixtures were analyzed by the measurement of the refractive indices of these solutions on a Bausch and Lomb refractometer. The precision of this method was ±0.05 wt %.

RESULTS AND DISCUSSION

Characterization of blend membranes by FTIR studies

The FTIR traces of PVA and Manh, PVA and Ca, and PVA are given in Figure 1(A). A peak at 1706 cm^{-1} in Figure 1(b) and a peak at 1710 cm^{-1} in Figure 1(a) correspond to carbonyl group stretching. The presence of an alkene (—C=C—) group in the Manh-crosslinked structure shows an electron-withdrawing tendency from the attached carbonyl carbon of the ring structure [shown later in Fig. 4(C)]. However, in a Ca-crosslinked PVA membrane, a carbonyl carbon is attached to an alkyl (—C—C—) group. Therefore, the
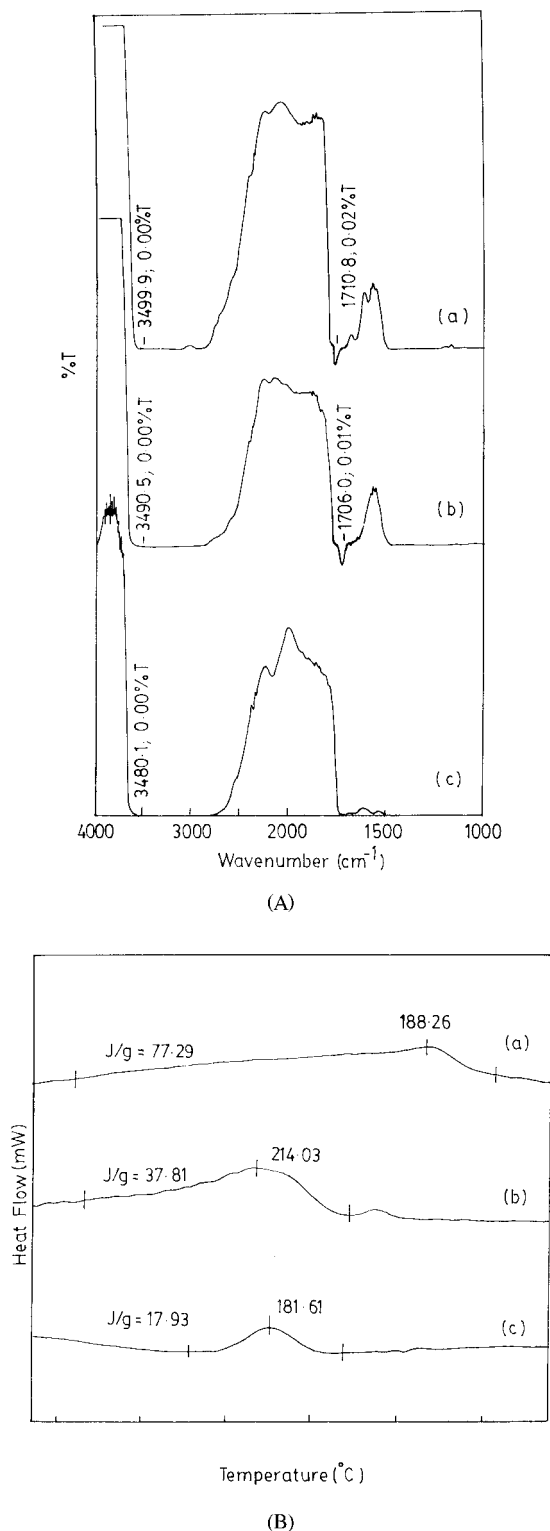
Figure 1 (A) FTIR spectra of virgin PVA and its crosslinked membranes: (a) PVA crosslinked with Manh, (b) virgin PVA, and (c) PVA crosslinked with Ca. (B) DSC studies of virgin PVA and its crosslinked membranes: (a) PVA crosslinked with Manh, (b) virgin PVA, and (c) PVA crosslinked with Ca.

wave number or frequency value for the PVA and Manh membrane increases in comparison with the normally expected carbonyl stretching frequency.

Membrane characterization through DSC

DSC can be used to determine[15] the crystallinity of a crosslinked membrane. The values of the heat of fusion at melting were directly obtained for each crosslinked membrane from DSC plots. The crystallinity was calculated with the following equation:

$$Crystallinity \ (\%) \ = \ (\Delta H_{fs}/\Delta H_{fr}) \times 100$$

where ΔH_{fs} is the change in the heat of fusion of the unknown sample and ΔH_{fr} is that of the reference sample.

The heat of fusion at melting for standard PVA has been reported[16] to be 167 J/g.

From this relation, the crystallinity values [Fig. 1(B)] of crosslinked PVA/Ca and PVA/Manh (10:4 blends for both) were 10.7365 and 46.28%, respectively. The virgin PVA membrane crystallinity was 22.64%. From these data, it is concluded that crystallinity obeys the following order: PVA and Manh > PVA > PVA and Ca.

Interpretation based on interaction parameters

The affinity between a polymer and a solvent can be expressed (Table II) in terms of an interaction parameter.[17,18] In a mixture of A and B, where A is present in a very low amount and is to be separated, component A should have a solubility parameter closer to that of the membrane material than B. Alternatively, the interaction parameter χ of A must be lower than that of the other component B for a particular membrane polymer.

CA and other cellulosic derivatives

The difference between CA and other cellulosic derivatives such as CDA and CTA lies in the substitution of cellulosic —OH groups with acetyl groups. When a cellulosic —OH group reacts with acetic acid and acetic anhydride, acetylation takes place. This substitution reduces the hydrophilicity of the polymer matrix in polar solvents and creates a remarkable difference (Table III) in the interaction performance. CA with 40% acetylation implies less substitution than CDA (52.8% acetyl content) and CTA (59.6% acetyl content). Therefore, CA ($\chi_w = 0.934$) provides better interaction with water than CDA ($\chi_w = 1.078$) and CTA ($\chi_w = 1.355$). The presence (Fig. 3) of acetyl groups not only reduces the polarity but also increases the free volume, and the increase in the gap helps to accommodate MP in this order: CTA > CDA > CA. Therefore, CTA shows more affinity for MP ($\chi_{MP} = 1.719$) than CDA ($\chi_{MP} = 1.739$) and CA ($\chi_{MP} = 1.824$).
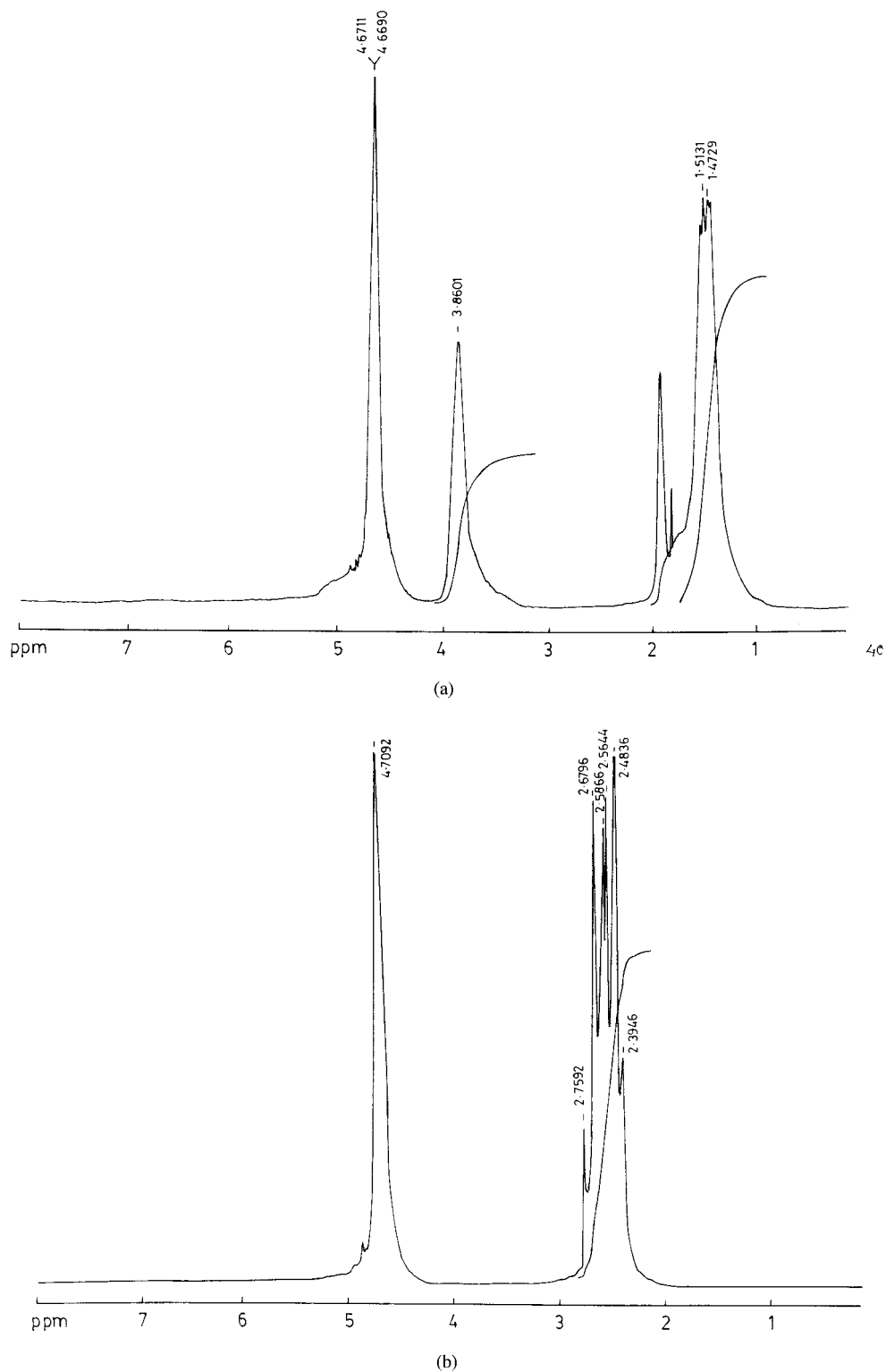
(a)

(b)

Figure 2 Monitoring the course of crosslinking between PVA and crosslinking agents by NMR spectroscopy: (a) pure PVA, (b) pure Ca, (c) pure Manh, (b1) a blend of PVA and Ca after 4 h, (b2) a blend of PVA and Ca after 7 days, (c1) a blend of PVA and Manh after 4 h, and (c2) a blend of PVA and Manh after 7 days.

Cellulosic blends

CAP contains both acetate and propionate groups; not only do these reduce polarity, but the propyl group of

the propionate moiety increases void space more than the acetate group. A blend of CA and CAP (Fig. 3) should exhibit less polarity than CA, so the interaction

(c)
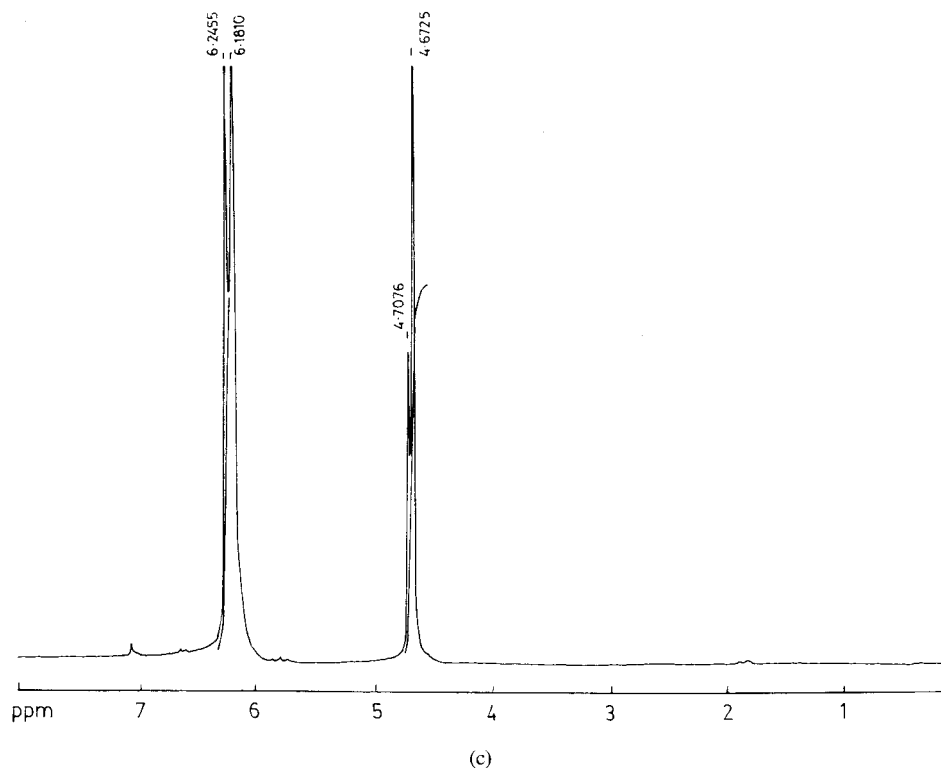
Figure 2 (*Continued from the previous page*)

with water decreases ($\chi_{CA} = 0.934$, $\chi_{B1} = 1.068$) and that with MP increases ($\chi_{CA} = 1.824$, $\chi_{B1} = 1.588$). In B3, CDA was used instead of CA, and the interaction parameter with water ($\chi_{CDA} = 1.078$, $\chi_{B3} = 1.194$) supports this. Similarly, B3 (Table II) shows poorer results than B1, but MP affinity increases ($\chi_{B1} = 1.588$, $\chi_{B3} = 1.405$). This is also evident in B2 ($\chi_w = 1.17$, $\chi_{MP} = 1.471$) and B4 ($\chi_w = 1.228$, $\chi_{MP} = 1.363$).

Regenerated cellulose or cellophane membrane

Cellophane contains (Fig. 3) two hydroxyls and one —CH₂OH group in each monomer moiety, and each six-membered cyclic repeating unit contains an oxygen atom with other carbon members. Another oxygen atom is present as a bridging/linking agent between two glucopyranosidic units, making cellophane more hydrophilic in nature. Therefore, a cellophane membrane contains a maximum number of —OH groups and produces a high affinity for polar compounds. Because of this, the interaction value of cellophane with water (0.0838) is lower. However, MP is less polar and shows a comparatively lower affinity for polar polymers, and χ_{MP} (1.412) becomes much higher.

PVA membranes

The interaction parameter of water ($\chi_w = 0.504$) with PVA suggests that it is an excellent hydrophilic membrane and can be used for dehydration. The interaction

parameter value with MP (3.356) is sufficiently higher, implying less affinity toward the membrane. This observation can be explained by the membrane structures. Almost regular arrangements (Fig. 3) of the monomer moiety of PVA, containing an —OH group attached to an ethylene moiety, exhibit more attraction to water.

Crosslinked PVA membranes

Ca (used as a multifunctional crosslinker) contains two —CH₂COOH groups, one —COOH group, and another —OH group, among which the —COOH group is acidic and the —OH group is also acidic [Fig. 4(A)]. It is assumed that all these groups react with alcoholic —OH groups [Fig. 4(B)] of PVA. With an increasing amount of Ca, crosslinking increases, and polarity decreases. Therefore, the attraction of water to B6 ($\chi_w = 0.5401$) is less than that to B5 (0.5235). In contrast, MP shows the reverse trend. However, Manh contains two carboxylic groups and shows less reduction in polarity than Ca [Fig. 4(C)]. Therefore, from B7 to B8, the interaction increases for water, but the amount of interaction (Table II) is higher than for B5 and B6, respectively. The increase in the interaction parameter is an indication of decreased swelling, which is due to crosslinking.

When Ca- or Manh-crosslinked membranes are compared with PVA, the former crosslinked type ($\chi_{w/B5} = 0.5235$, $\chi_{w/B6} = 0.5401$) shows less of an affinity for water than PVA ($\chi_w = 0.504$), whereas an
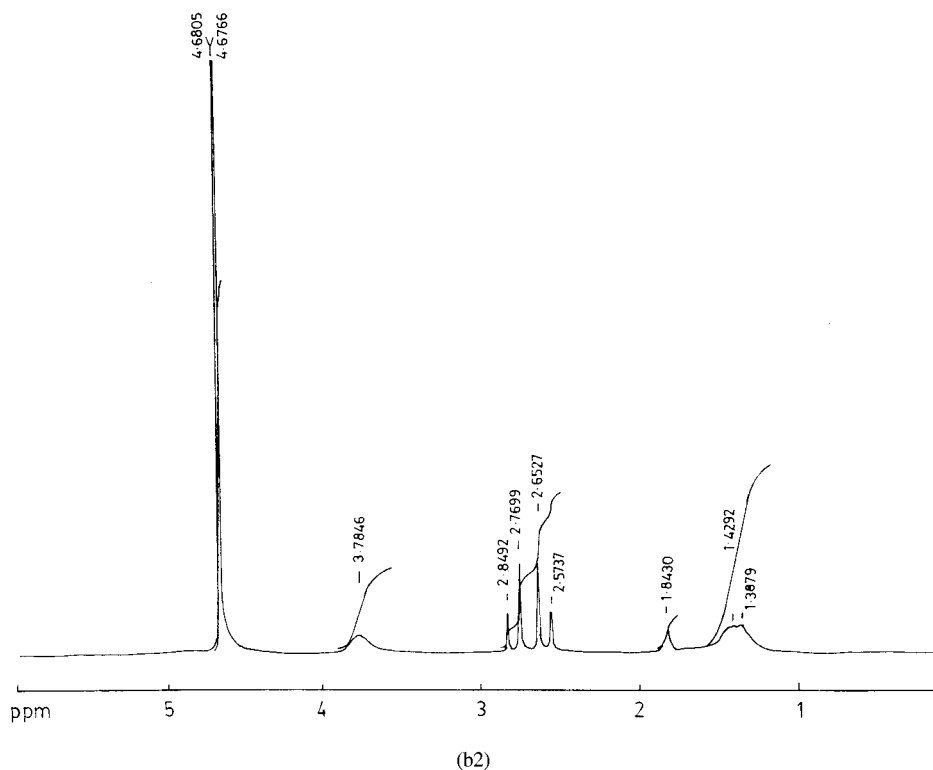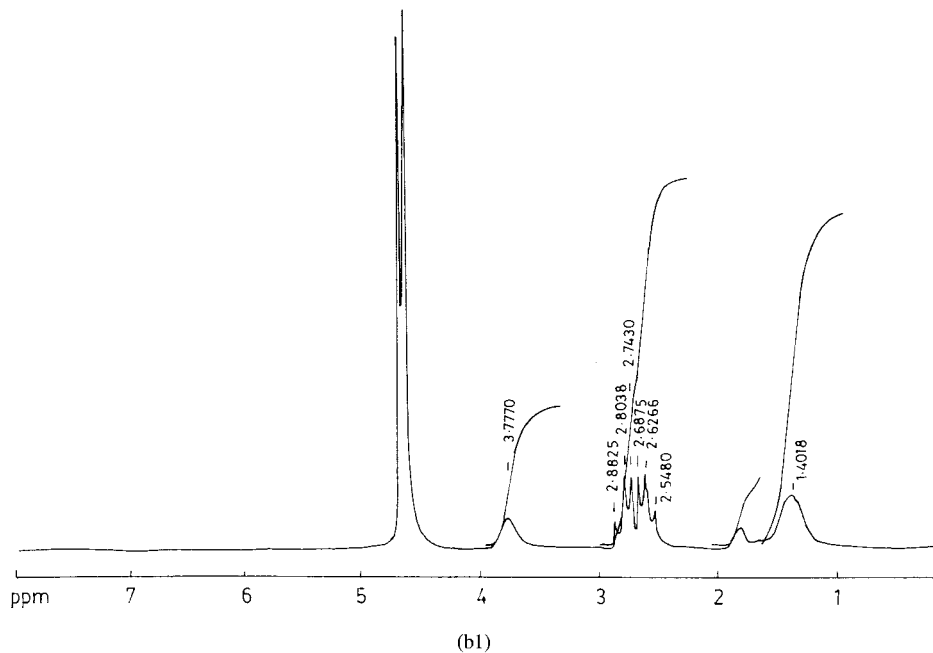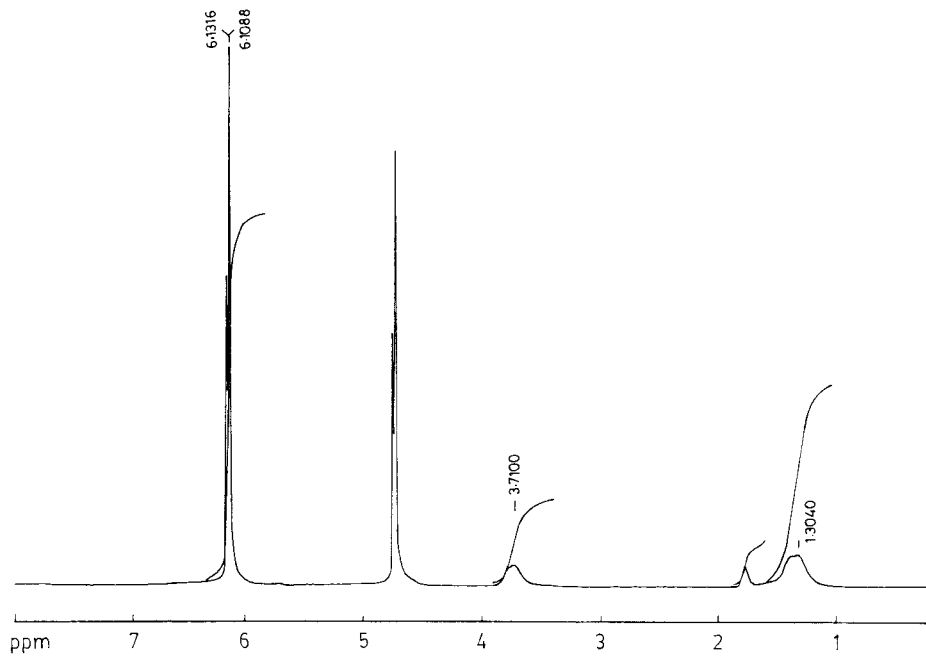
Figure 2 (*Continued from the previous page*)

Manh-crosslinked matrix ($\chi_{w/B7} = 0.5136$, $\chi_{w/B8} = 0.5283$) is expected to be more permselective than a Ca-crosslinked type.

PI

Each monomer unit of PI contains (Fig. 3) two imide groups, in which two carbonyl groups are attached to nitrogen, satisfying two valences, and the third valance is satisfied with para-substituted ether benzene. The presence of all the polar groups makes it sufficiently hydrophilic in nature, but the membrane is highly crystalline [glass-transition temperature (T_g) = 380°C]. Because of the dense structure (ρ = 1700 kg/m^3) and reluctance toward politicization, the amount of sorption decreases.

(c1)
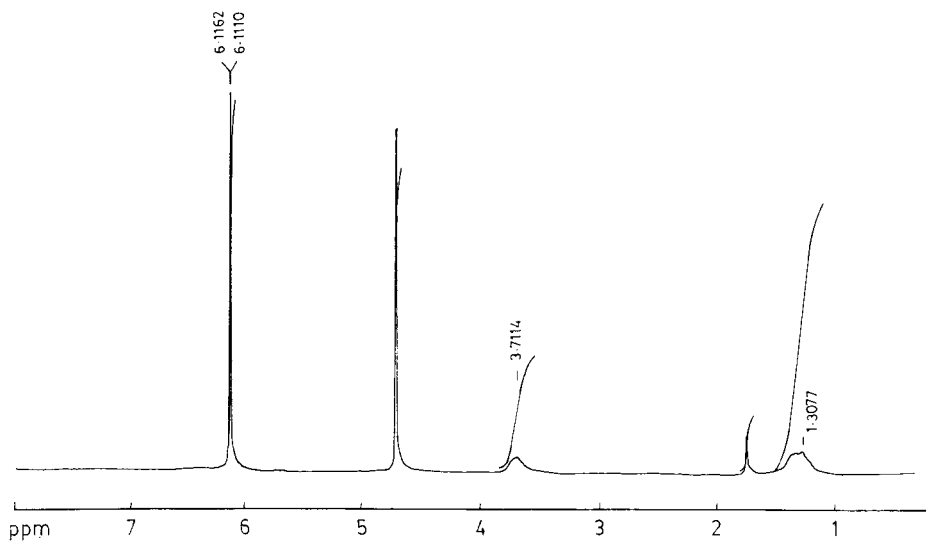
(c2)

**Figure 2** (*Continued from the previous page*)

PDMS membrane

PDMS is a hydrophobic membrane that contains (Fig. 3) a skeleton of —Si—O—Si—, and the other two valences of the silicon atom are satisfied with —CH₃ groups. As it has affinity toward the weaker hydrophilic component, MP shows better interaction (χ_{MP} = 2.021) than water (2.887). However, the hydrophobic layer (made with —CH₃) of PDMS helps to repel water and possibly favors the interaction with the CH₃—O— group of MP. Therefore, a difference in the interaction arises.

LLDPE

In Table II, it is found that the affinity of weakly polar MP toward LLDPE (χ_{MP} = 1.348) is much higher than that of the polar component water (χ = 2.375). The repetition (Fig. 3) of the —CH₂—group either in the backbone or in a side chain converts (Table III) LLDPE into a hydrophobic membrane. From the difference in the χ values, it is found that MP is sorbed much more than water because LLDPE has an affinity toward less polar compounds. It is also noticed that the interaction of MP with LLDPE (1.348) is more than that for PDMS
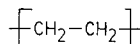
TABLE II
Interaction Parameters

| Membrane	χ_{MP}	χ_w
CA	1.824	0.934
CDA	1.739	1.078
CTA	1.719	1.355
CA + CAP (10:1) B1	1.588	1.068
CA + CAP (10:2) B2	1.471	1.1703
CDA + CAP (10:1) B3	1.405	1.194
CDA + CAP (10:2) B4	1.363	1.228
Cellophane	1.412	0.0838
PVA	3.356	0.5041
PVA + Ca (10:1) B5	3.213	0.5235
PVA + Ca (10:2) B6	3.134	0.5401
PVA + Manh (10:1) B7	3.424	0.5136
PVA + Manh (10:2) B8	3.487	0.5283
PI	2.396	1.695
PDMS	2.021	2.887
LLDPE	1.348	2.375
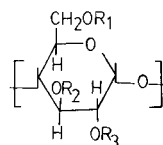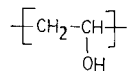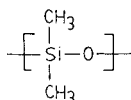
(2.021). This fact is expected to be reflected in the permselective behavior.

Monitoring the course of crosslinking between PVA and crosslinking agents with NMR spectroscopy[19]

The spectra of pure PVA [Fig. 2(a)], Ca [Fig. 2(b)], and Manh [acid in D_2O; Fig. 2(c)] and the structures of the mixtures (separate blends) of PVA with Ca [Fig. 2(b1,b2)] and Manh [Fig. 2(c1,c2)] were obtained after 4 h and after 7 days, respectively, by ^{1}H-NMR spectroscopy (Table IV) with D_2O as a solvent. For pure PVA, Ca, and Manh in D_2O, the following results were obtained: δ (ppm) = 3.8601 (s, 1H, $\rangle\hat{C}H$—OH) and
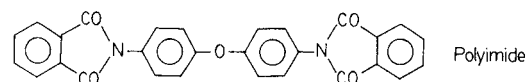
Figure 3 Repeating monomer units of the polymers.

1.5131–1.4729 (m, 2H, —$\hat{C}H_2$—) in Figure 2(a), δ (ppm) = 2.7592–2.3946 (m, 4H, —$\hat{C}H_2$—) in Figure 2(b), and δ (ppm) = 6.2455–6.1810 (m, 2H, —$\hat{C}H$═$\hat{C}H$—) in Figure 2(c). The peaks around 4.7–4.5 ppm are due to the solvent exchange of D_2O. The two peaks, instead of the characteristic single peak in Figure 2(c), for Manh are due to the different environment during

TABLE III
Properties of the Polymers Related to Pervaporation

| Property	PDMS	LLDPE	PVA	Cellophane	CA	CDA	CTA
Solubility parameter (MPa)[1,2]	14.9	16.01	25.78	32.24	25.08	23.22	18.84
Selective sorption	Aromatic	Aromatic	Alcohol	Alcohol	Alcohol	Alcohol	Alcohol
Specific gravity	1.268	0.916	0.838	0.676	1.285	1.297	1.001
T_g (°C)	−123	−20 to −50	70	250–330	165	182	190
Polymeric backbone/ repeat unit	(structure)	(structure)	(structure)	(structure)	Same as cellophane	Same as cellophane	Same as cellophane
Side group(s)	—CH_3	Butane/ olefinic chains	—OH	—OH and —CH_2OH	—OH, —CH_2OH, and —$OCOCH_3$	—$OCOCH_3$ increases	—$OCOCH_3$ increases
Features of interest affecting T_g	Flexible backbone	Flexible backbone	Polar interaction	Extensive polar–polar interaction	Interchain interaction	Polar interaction decreases	Stiff backbone

Cellophane Regenerated cellulose

TABLE IV
^{1}H-NMR Spectroscopy Study of PVA and Crosslinked PVA (on a 200-MHz Bruker AC-200 FT-MHz Spectrometer)

| Sample	Characteristic Peaks	>CĤ—OH of PVA	—CĤ$_2$— of PVA	—CĤ$_2$— of Ca	—CĤ=CH— of Manh
a	PVA (Pure)	3.8601	1.5131–1.4729		
b	Ca (Pure)			2.7592–2.3946	
c	Manh (Pure)				6.2455–6.1810
b1	Ca (after 4 h) [Blend (B)]	3.7770	1.4018	2.8825–2.5480	
b2	Ca (after 7 days) B	3.7846	1.3879	2.8492–2.5737	
c1	Manh (after 4 h) B	3.7100	1.3040		6.1316–6.1088
c2	Manh (after 7 days) B	3.7114	1.3077		6.1162–6.1110

solvent exchange. The initial position of the characteristic peaks in Manh was at 6.2455–6.1810 ppm.

After 4 h, this shifted to 6.1316–6.1088 ppm [Fig. 2(c1)], and after 7 days, it was at 6.1162–6.1110 ppm [Fig. 2(c2)]. The initial changes and differences in the values were due to the reaction of one —COOH group

and the different chemical environments. However, after several days (7 days), two —COOH groups appear to have reacted, and they are gradually becoming equivalent protons. Therefore, it is expected that the difference [Fig. 2(c2)] will gradually diminish and, after the proper arrangement, convert into a singlet

Poly(vinyl alcohol)(PVA)

Citric Acid (Ca)
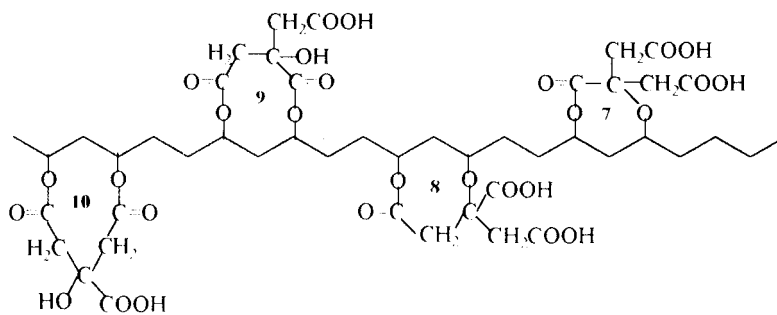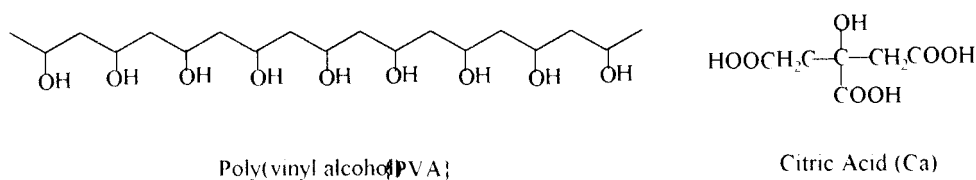
(A)
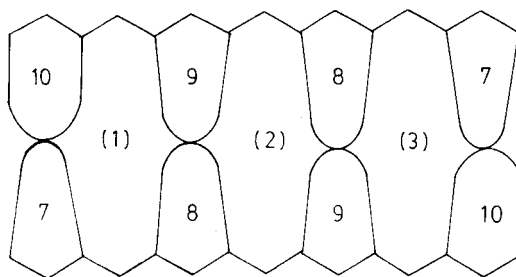
(B)

Figure 4 Expected morphology of crosslinked PVA membranes: (A) the first step of the crosslinking of Ca with PVA, (B) the interring (7,8,9,10) and intraring cavity (1,2,3) formation of the Ca-crosslinked PVA membrane, (C) the crosslinking of Manh with PVA, and (D) the compact structure of the Manh-crosslinked PVA membrane.

(with a small hump). However, those at 3.8601 ppm ()CĤ—OH of PVA) and 1.5131–1.4727 ppm ()CĤ$_2$— of PVA) have shifted to 3.7100 ppm and the multiplet at 1.3040 ppm (after 4 h), respectively [Fig. 2(c1)], and again (although to a small degree) to 3.7114 and the multiplet at 1.3077, respectively [Fig. 2(c2)].

For Ca, the aforementioned groups changed from 3.8601 ()CĤ—OH of PVA) and 1.4729 (—CĤ$_2$— of PVA) to 3.7770 and 1.4018 after 4 h [Fig. 2(b1)]. After 7 days [Fig. 2(b2)], the values changed to 3.7846 and 1.3879, respectively, for the reason mentioned previously. The multiplet of Ca in Figure 2(b)) changed to a better rearrangement after 4 h [Fig. 2(b1)], and with time it reacted further and rearranged itself in a much better way, exhibiting an excellent double doublet (2.8492–2.5737) with a coupling constant (j) of approximately 12 Hz due to —CĤ$_2$— groups of crosslinked Ca, which is a characteristic feature of that group [Fig. 2(b2)].

An NMR spectroscopy study shows that the —OH group of PVA is progressively crosslinked. This curtails polymer chain flexibility and, therefore, lowers the diffusion coefficient of the solute. This lowering is more marked for the larger MP molecule than for the smaller water molecule. Therefore, although the flux for the solutes decreases, the sharp decrease in the flux of MP increases the selectivity for water.

HYDROPHILIC MEMBRANES

Effect of the feed concentration on permeation

CA, CDA, and CTA membranes

Figure 5 gives the variation of the concentration of water in the feed versus the permeate for an MP–water mixture when CA, CDA, and CTA membranes are invoked. This figure is an example of the effect of the variation of acetylation percentages of different cellulosic derivatives. Pervaporative behavior was studied with various contents of sulfonate groups by Hamada and coworkers.[20–22] They found that the flux of water and 2-propanol increased with an increasing molar fraction of sulfonate groups in the membrane. Here, all the membranes are selectively permeating water, and among these, CA (40% acetylation) is the best. The results could be explained by the polarity, hydrogen bonding, and percentage of acetylation of the membrane material. Membrane hydroxyls have sufficient attraction for —OH groups of the feed components. The solubility is dependent on both the polymer penetrant interaction and the volume available[23] for hole filling. Between MP and water, the sorption is greater for water because of the polarity, the effect of hydrogen bonding, and the volume available for accommodation. For instance, the energy for hydrogen
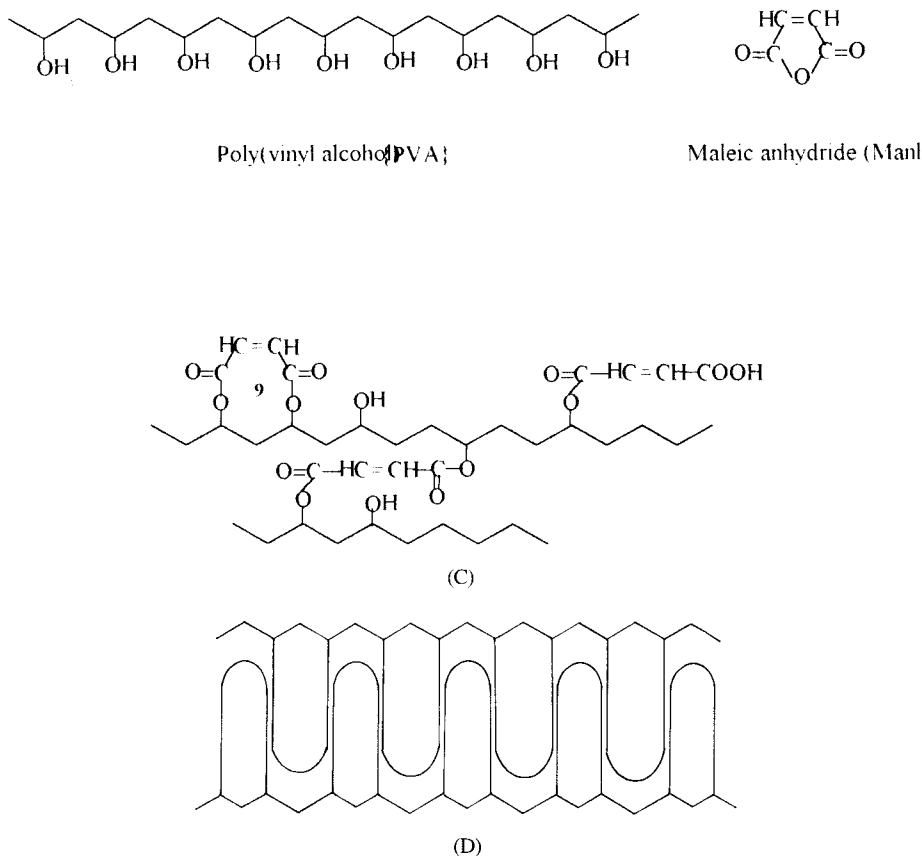
Poly(vinyl alcohol) (PVA)

Maleic anhydride (Man)

(C)

(D)

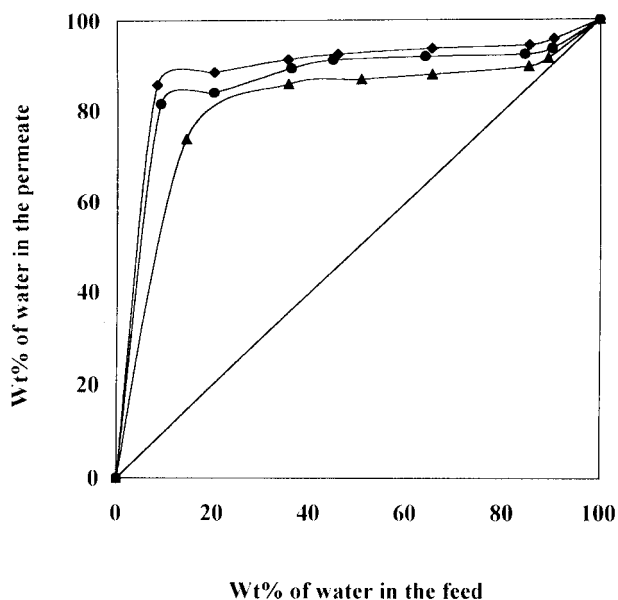**Figure 4** (*Continued from the previous page*)

Figure 5 Variation of the concentration of water in the permeate with its feed concentration for the MP–water system with different cellulose derivatives: (♦) CA, (●) CDA, and (▲) CTA.

bonding between the membrane and permeant hydroxyls is $E_h = 20{,}000$ (J mol^{-1}),[24] indicating a favorable interaction. The interaction parameter values (Table II) indicate water sorption in the following order: CA > CDA > CTA. The secondary bonding also facilitates sorption, which depends on the presence of hydroxyl groups in the membrane. CA (40% acetylation) contains a larger number of hydroxyl groups on its backbone, and CDA (52.8% acetylation) contains more hydroxyl groups than CTA (59.6% acetylation). However, because of an increase in substitution, the free volume in the membrane matrix increases, and the likelihood of penetration of a comparatively weakly polar component increases as the degree of substitution increases. Therefore, the amount of water permeation follows the aforementioned order.

CA and its blends

Figure 6 shows the feed concentration of water versus the permeate concentration for the entire range of concentrations with CA and its blends. A comparison of the permeation values of CA and CA and CAP in different blends (B1 and B2) is shown. CAP reduces the hydrophilicity (as discussed in the CA and Other Cellulosic Derivatives section) and increases the free volume of the membrane matrix. The less polar propionate group helps with the greater permeation of MP, and separation decreases. This effect is very distinct in the lower feed concentration region, and it also indicates how water permeation decreases with an increasing amount of CAP in the blends.
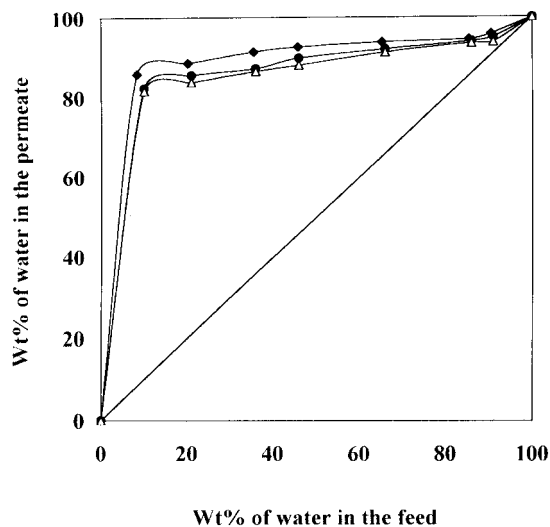

Figure 6 Variation of the concentration of water in the permeate with its feed concentration for the MP–water system with CA and its blends: (♦) CA, (●) B1, and (△) B2.

CDA and its blends

Figure 7 shows variations in the concentration of water in the feed versus the permeate when CDA, B3 (10:1 CDA/CAP), and B4 (10:2 CDA/CAP) are invoked. CDA is a sufficiently hydrophilic membrane for use in dehydration. CAP not only decreases hydrophilicity but also increases the free space, because of which water separation decreases, as explained in the previous case (see the CA and Its Blends section).
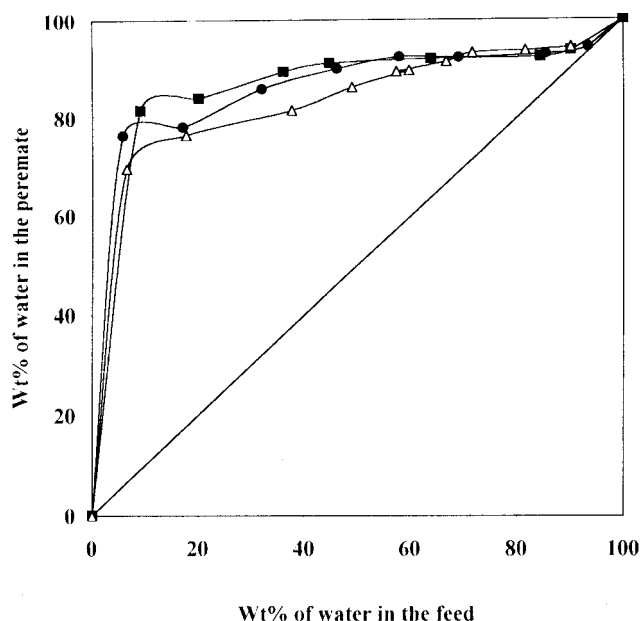

Figure 7 Variation of the concentration of water in the permeate with its feed concentration for the MP–water system with CDA and its blends: (■) CDA, (●) B3, and (△) B4.
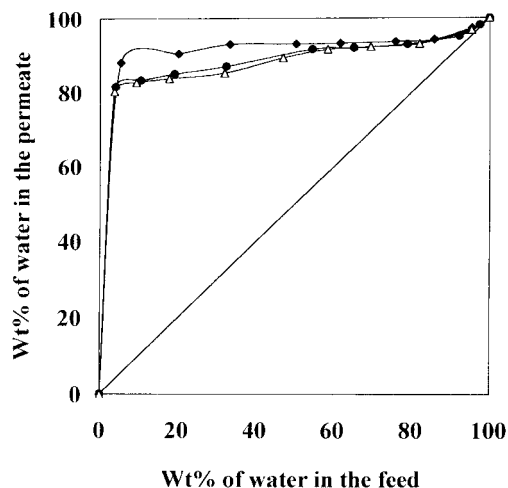
Figure 8 Variation of the concentration of water in the permeate with its feed concentration for the MP–water system with PVA and Ca-crosslinked PVA: (◆) PVA, (●) B5, and (△) B6.

Figure 9 Variation of the concentration of water in the permeate with its feed concentration for the MP–water system with PVA and Manh-crosslinked PVA: (◆) PVA, (●) B7, and (△) B8.

PI and cellophane membranes

Figure 8 shows the weight percentage of water in the feed versus that in the permeate for PI and cellophane membranes. Between these two membranes, PI shows a better PV selectively. The compactness in the structure of PI produces a hindrance for the permeation of the larger MP molecule. However, the cellophane membrane is more flexible and swells substantially,[18] increasing the void space and facilitating MP permeation. Therefore, although both membranes are hydrophilic, PI gives better permeation separation.

Figure 10 shows weight percent of water in the feed versus that in the permeate for PI and cellophane membranes. Between these two membranes, PI shows a better pervaporation selectively.

PVA and its crosslinked membranes

PVA is an excellent hydrophilic membrane, but its swelling tendency in the presence of polar compounds (mainly water) increases, and the longevity of the PVA membrane drastically decreases. To produce a sufficient hindrance for MP, Manh (bifunctional) or Ca (multifunctional) as a crosslinker can be used. Figures 8 and 9 present a comparison of the permeation behaviors of PVA/Ca and PVA/Manh crosslinked membranes, respectively. Before the comparison and explanation of the permeation curves, the following points should be considered.

Ca has four functional groups, and all these groups are capable of reacting with PVA hydroxyls. In Figure 4(A), it is shown that first any two functional groups of Ca react with PVA hydroxyls and form a stable ring. The remaining groups of the crosslinker still do not react with the nearest possible hydroxyls groups
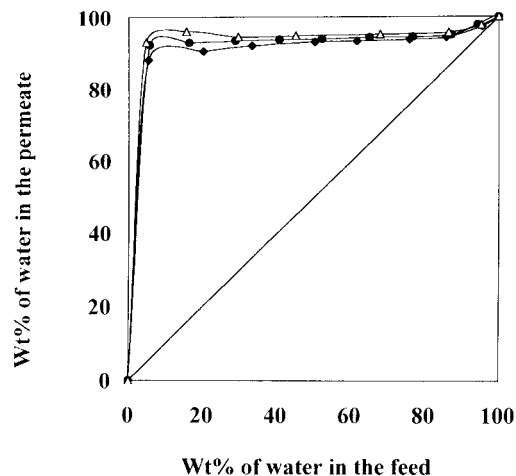
of another crosslinked PVA chain. Under these conditions, four possible ring structures have been found that are 7,8,9,10-numbered rings, and according to the ring number, the intraring spaces increase. Numbers such as 7,8,9,10 in these ring structures indicate the number of atoms present in the ring.

In Figure 4(B), it is shown that the remaining two functional groups of Ca react with the —OH groups of another PVA molecule and form a 7,8,9,10-membered ring. Here, another three large rings are formed, that is, 1, 2, and 3, which are later called interring cavities, defined as void spaces facilitating MP permeation. Besides this, the material of structure B is less polar than that of structure A, as all the functional groups of Ca are exhausted or converted from polar hydroxyl or acidic groups into less polar ester groups.
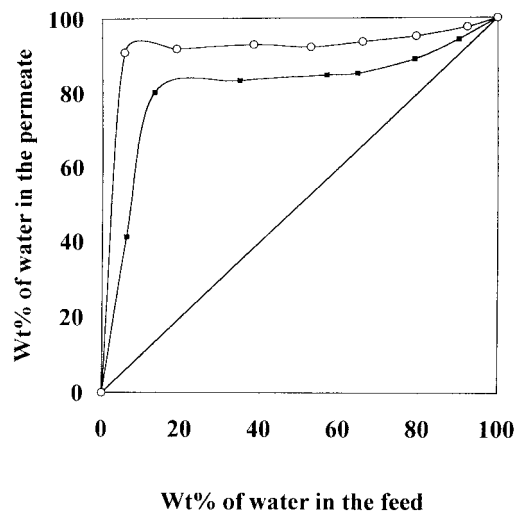

Figure 10 Variation of the concentration of water in the permeate with its feed concentration for the MP–water system with (○) PI and (■) cellophane.
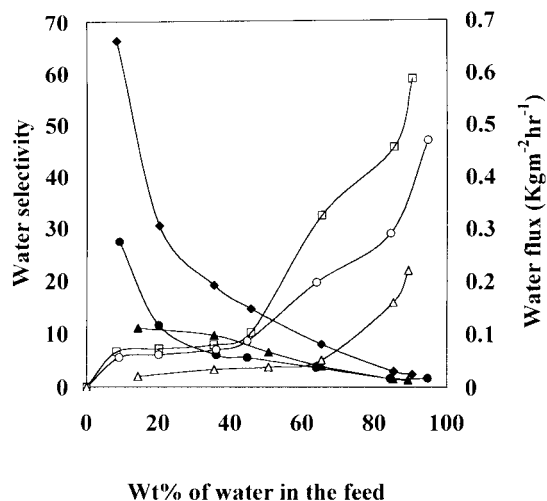
Figure 11 Variation of the water selectivity and flux for the MP–water system with its feed concentration with different cellulosic derivatives: (♦) CA, (●) CDA, and (▲) CTA (water selectivity versus feed concentration) and (◇) CA, (○) CDA, and (△) CTA (water flux versus feed concentration).

However, the bifunctional Manh-crosslinked membrane yields structures [Fig. 4(C,D)] in which C is a 9-membered ring structure, with two functional groups of anhydride links with the —OH groups coming from PVA hydroxyls. In Figure 4(C), one Manh unit reacts between two lateral PVA hydroxyls and implies closer proximity or the introduction of linearity within the membrane matrix. Another possible structure is shown in Figure 4(D), where two arranged C-type structures are present at such an equilibrium position that the liberated energy will be maximum. The latter implies a more linear configuration and a decrease in the free space in comparison with the structure in Figure 4(B). There is no chance of interring cavity formation. The presence of an alkene double bond (—C=C—), instead of an alkyl (—C—C—) structure (see Fig. 1 and the Characterization of Blend Membranes by FTIR Studies section) with two attached —O—C=O groups, increases ring polarity and rigidity. With its rigidity, it exhibits less motion under applied force, and a better crystalline structure (D) is obtained (see the Membrane Characterization through DSC section). Therefore, Manh-crosslinked PVA creates less void space, and the probability of crystal fitting (D) increases.

The results of the permeation and DSC [Fig. 1(B)] studies confirm the structure of the crosslinked membranes. It is expected that a comparatively less crystalline structure will produce less hindrance toward the permeation of a bigger solute and increase the void space [Fig. 4(B); interring cavities], helping in permeating the larger component. However, in Figure 4(C,D), the voids are less and become tortuous, and so MP does not get any chance to pass through. Therefore, a PVA membrane crosslinked with Manh permeates water better than virgin PVA or PVA crosslinked with Ca.

Effect of the feed concentration on selectivity and flux

CA, CDA, and CTA membranes

Figure 11 gives the selectivity versus the flux with respect to the weight percentage of water in the feed when membranes such as CA, CDA, and CTA are invoked. As already mentioned, CA (40% acetylated) contains more hydroxyl groups than CDA (52.8% acetylated) and CTA (59.6% acetylated). CA suffers a severe polar–polar attraction to water and selectively sorbs it. Interaction parameter values of water (Table II) also give an indication of polar–polar interactions, with CA showing the maximum affinity for water. However, the χ_{CA} value is quite high for MP, and this makes a big difference in the χ value with water for CA. This difference is gradually lowered for CDA and CTA as the interaction with MP increases in the order CTA > CDA > CA. Therefore, sorption selectivity and permeation gradually decrease for water in the same order, and the flux obeys the reverse.

Cellulosic blend membranes

Figures 12 and 13 show the trade-off relationship in water selectivity and flux when plotted against the weight percentage of water in the feed with CA and its blend membranes or CDA and its blend membranes, respectively. These figures represent the effect of blending CAP in different proportions. CAP contains both acetate and propionate groups, and the latter group is less polar than the former and increases the free space. Therefore, B2 or B4 possesses more affinity for MP than water in comparison with B1 or B3, respectively. Here, the less polar nature of the propyl group allows more MP to pass through because of the
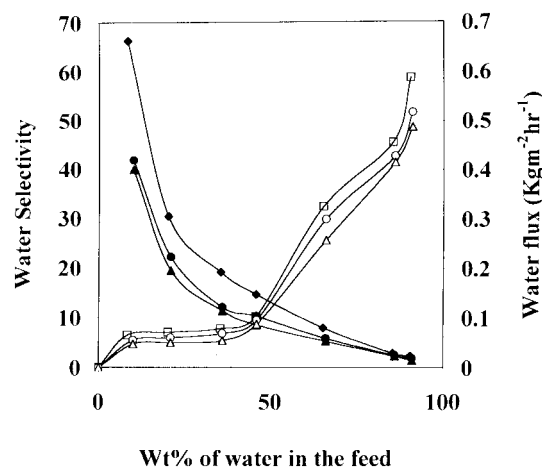

Figure 12 Variation of the water selectivity and flux for the MP–water system with its feed concentration with CA and its blends: (♦) CA, (●) B1, and (▲) B2 (water selectivity versus feed concentration) and (□) CA, (○) B1, and (△) B2 (water flux versus feed concentration).
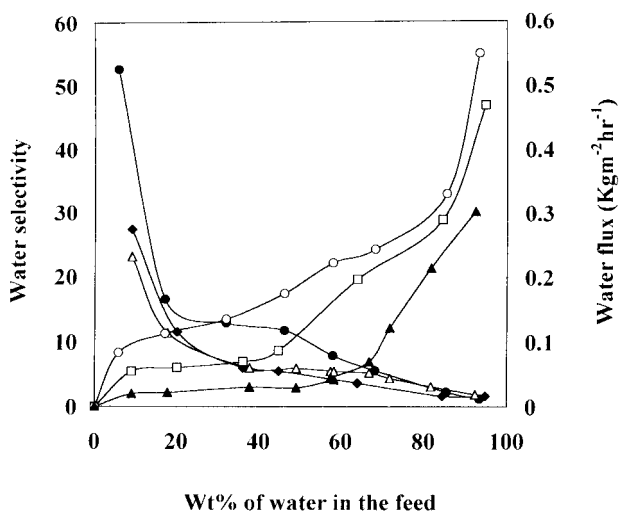
Figure 13 Variation of the water selectivity and flux for the MP–water system with its feed concentration with CDA and its blends: (●) CDA, (♦) B3, and (△) B4 (water selectivity versus feed concentration) and (○) CDA, (◇) B3, and (▲) B4 (water flux versus feed concentration).

Figure 14 Variation of the water selectivity and flux for the MP–water system with its feed concentration with PVA and Ca-crosslinked PVA: (♦) PVA, (●) B5, and (△) B6 (water selectivity versus feed concentration) and (◇) PVA, (○) B5, and (▲) B6 (water flux versus feed concentration).

increase in void space. Therefore, selectivity decreases. The effect becomes more pronounced with an increasing amount of CAP in the blend.

Again, in Figure 12, it is seen that the flux gradually increases with an increase in water in the feed. As CA contains a high percentage of hydrophilic hydroxyls, it yields more water flux. With an increasing percentage of CAP, the membrane polarity decreases, and the MP flux increases with a concomitant water flux decrease. The same is true for CDA and its blends.

PI and cellophane

Figure 14 gives the water selectivity and flux with respect to the weight percentage of water in the feed when PI or cellophane membranes are invoked. Here, PI exhibits higher selectivity and lower flux, but cellophane shows comparatively lower selectivity with high productivity. The facing liquid (mainly water) extensively swells the cellulose film, and it no longer behaves[25,26] as a homogeneous and dense material. Therefore, mass transport through the barrier becomes significantly high but is, therefore, much less selective than that of PI.

PVA and its crosslinked membranes

Figures 15 and 16 show the trade-off relationship between water selectivity and flux for a water–MP mixture with the aforementioned PVA with Ca-crosslinked membranes and Manh-crosslinked membranes, respectively. From Figure 16, it is clear that with an increasing percentage of Manh, water selectivity increases, whereas with an increase in Ca, selectivity decreases(Fig. 15). The
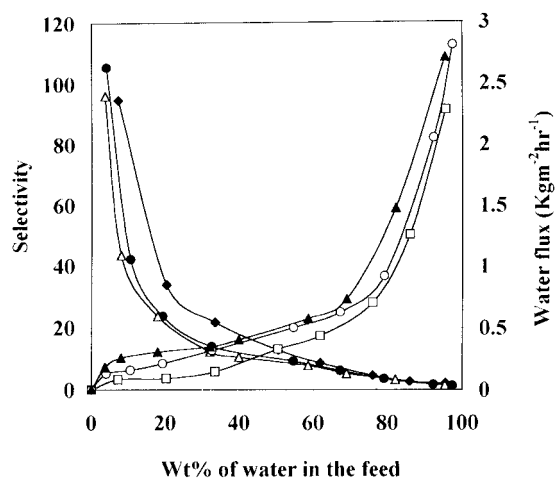
effect of the crosslinker loading can be divided (1) by the number of functional groups and (2) by the nature of the groups. Ca contains one acidic hydroxyl group, two —CH_2COOH groups, and one —COOH group. Manh contains two —COOH group attached with a —C=C— and condensed to an anhydride group. Here, Manh after curing produces a more crystalline or compact structure (as obtained from DSC studies) than Ca-crosslinked membranes (see the PVA and Its Crosslinked Membranes section). Figure 4(D) exhibits a more crystal fitting morphology than Figure 4(B). The large interring spac-
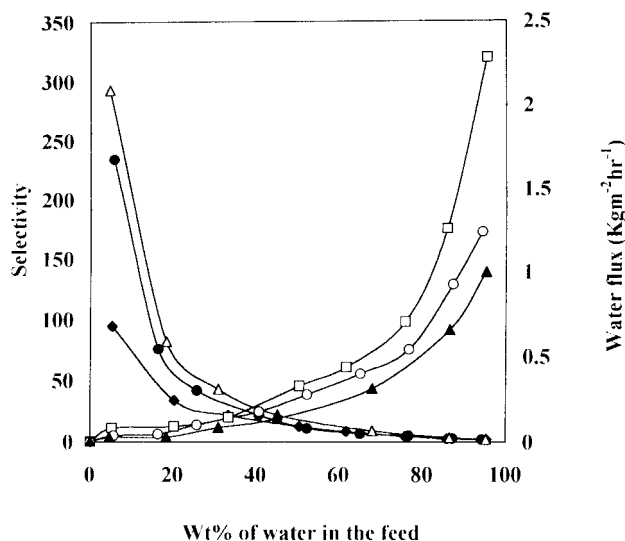

Figure 15 Variation of the water selectivity and flux for the MP–water system with its feed concentration with PVA and Manh-crosslinked PVA: (♦) PVA, (●) B7, and (△) B8 (water selectivity versus feed concentration) and (◇) PVA, (○) B7, and (▲) B8 (water flux versus feed concentration).
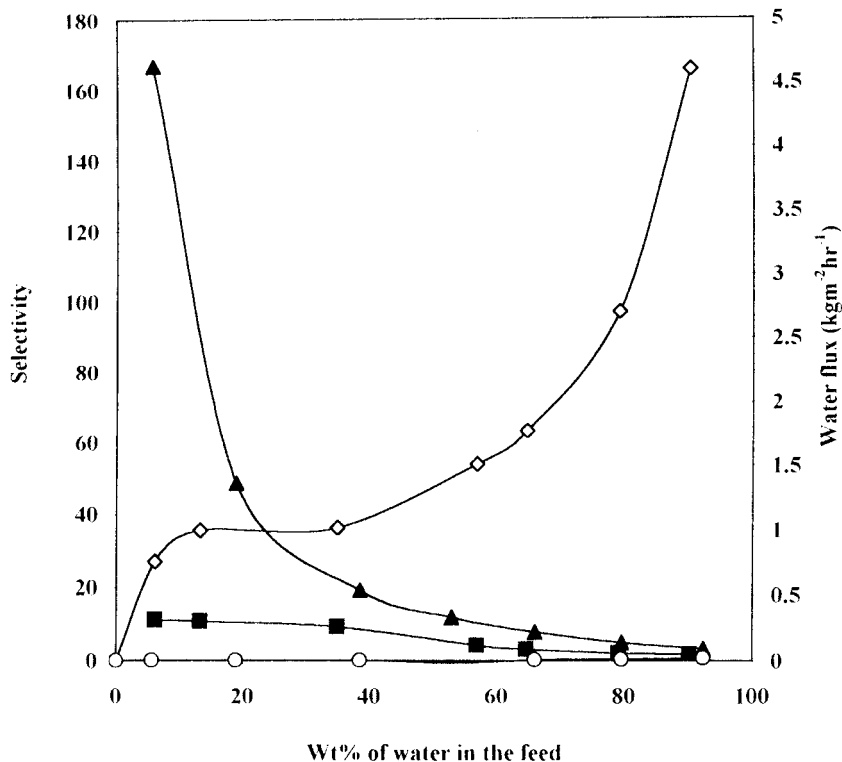
Figure 16 Variation of the water selectivity and flux for the MP–water system with its feed concentration with PI and cellophane: (▲) PI and (■) cellophane (water selectivity versus feed concentration) and (○) PI and (◇) cellophane (water flux versus feed concentration).

ing [numbered 1–3 in Fig. 4(B)] suggests an easy penetration of MP, and so selectivity decreases.

Hydrophobic membranes

To separate the less polar compound, PV of MP and water was carried out with PDMS and LLDPE. The solubility parameter values of PDMS (14.9 MPa$^{1/2}$) and LLDPE (16.01 MPa$^{1/2}$) favor the sorption of MP, as indicated from the interaction parameter values (Table II).

Effect of the feed concentration on permeation

Figure 17 shows the weight percentage of MP in the feed versus that in the permeate for PDMS and LLDPE membranes. From this figure, it is evident that LLDPE permeates MP more than PDMS. LLDPE contains linear ethylene long chains as side chains and in the polymer backbone. There is no polar group or moiety in any part of its structural unit. PDMS, however, contains an oxygen atom in its main repeating unit as —Si—O—, and the rest of the valences of the silicon atom are satisfied with —CH$_3$ groups. Comparatively, the more nonpolar structure of LLDPE helps with the permeation of MP more than PDMS. A lower interaction character of LLDPE ($\chi_{LLDPE} = 1.3848$, $\chi_{PDMS} = 2.0212$) also indicates the fact that LLDPE sorbs MP better than PDMS.

Effect of the feed concentration on selectivity and flux

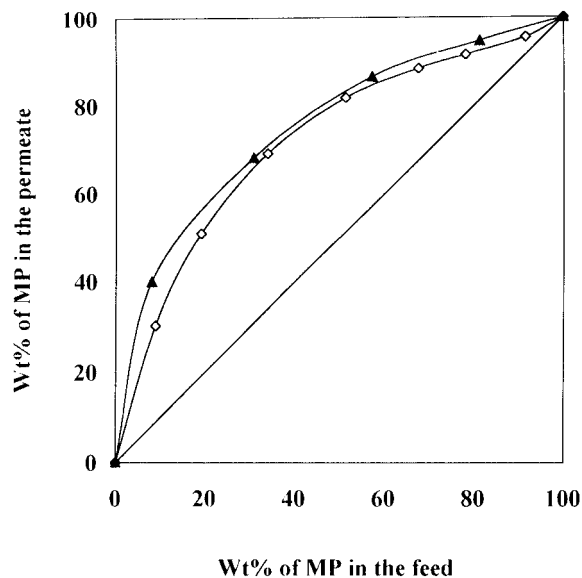Figure 18 shows the trade-off relationship between selectivity and flux for MP and water with PDMS and

Figure 17 Variation of the concentration of MP in the permeate with its feed concentration for the MP–water system with (▲) LLDPE and (◇) PDMS membranes.
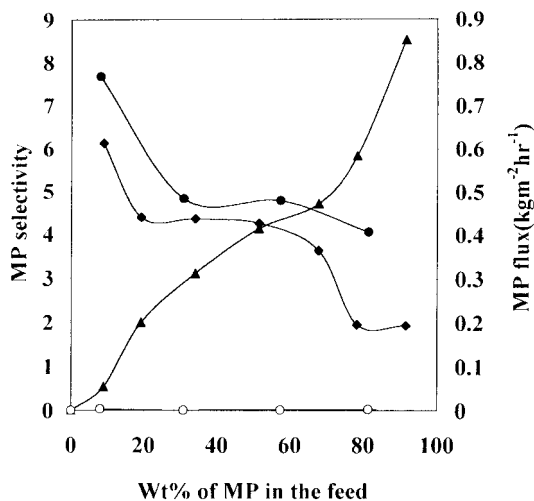
Figure 18 Variation of the MP selectivity and flux for the MP–water system with PDMS and LLDPE membranes: (●) LLDPE and (♦) PDMS (MP selectivity versus feed concentration) and (○) LLDPE and (▲) PDMS (MP flux versus feed concentration).

LLDPE. With an increase in the MP concentration in the feed, flux increases but selectivity decreases. The permeation of a strongly sorbed compound through a hydrophobic membrane is believed to be diffusion-controlled. The membrane morphology, including the constituted groups, and free volume determine the selectivity. The nature of LLDPE favors the sorption and permeation of MP more than PDMS. Therefore, the former shows higher selectivity, whereas the linear, more dense nature of LLDPE allows less MP to pass through, and the flux is lower. The flexibility of PDMS becomes pronounced at a higher concentration of MP, permeating more MP with a distinct increment in the flux. The swelling of LLDPE, however, is suppressed, and it exhibits a very low flux.

CONCLUSIONS

A detailed study of the interaction parameter and solubility parameter and a structural analysis of polymer membranes for the permeation of a water–MP mixture were carried out. Among the various membranes used, the PI membrane was the most water-selective but showed very low flux, whereas cellulosic membranes were good in both respects. PVA crosslinked with Manh was excellent in the selective permeation of water and had reasonable flux. Therefore, this membrane appears to be the best among the various types studied in this work. The removal of MP from an aqueous solution was also performed, and LLDPE was more MP-selective than PDMS.

NOMENCLATURE

R	universal gas constant (L atm/K)
T	absolute temperature (K)
ϕ_s	volume fraction of the solute in the polymer
χ_{ip}	interaction parameter for the ith component with polymer p
ΔG_m	Gibb's free energy change on mixing
ΔH_m	enthalpy change on mixing
ΔS_m	entropy change during mixing
V	molar volume of the mixture
ΔE_i	total energy of vaporization of the ith species
ϕ_i	volume fraction of the ith species in the mixture
δ_i	solubility parameter
ΔH_{fs}	change in the heat of fusion of the unknown sample
ΔH_{fr}	change in the heat of fusion of the reference sample

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