Dehydration of Glycerin/Water Mixtures by Pervaporation Using Homo and Copolymer Membranes

D.B. Khairnar and V.G. Pangarkar*

Mumbai University Institute of Chemical Technology, Matunga, Mumbai–400019 India.

ABSTRACT: Separation characteristics of glycerol/water mixtures were studied using hydrophilic poly(acrylonitrile-co-methacrylic acid) (PANMAC), poly(acrylonitrile-co-hydroxyethyl methacrylate) (PANHEMA), Poly(vinyl alcohol) GFT-1001, and poly(vinyl alcohol) (PVA) crosslinked with maleic anhydride (PVAManh) membranes. All membranes were found to be highly water selective. PVAManh membrane yielded the highest permeation flux for water over the entire range of water concentration studied. Homopolymers (PVAManh and GFT-1001) gave better permeation rates than copolymer membranes (PANHEMA and PANMAC). But the swelling of homopolymers is much greater than that of copolymers, which is why PVA membranes have poor longevity. No effect on selectivity of the membrane was observed with a change in operating parameters. No decomposition/polymerization of glycerin was observed, as there was no involvement of high temperatures as there is with distillation. A comparison of pervaporation with vapor–liquid equilibrium data showed that pervaporation of glycerin/water mixtures yielded better selectivity than vapor–liquid equilibrium, particularly for glycerol concentrations above 90 wt%.

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KEY WORDS: Comparison, copolymer, crosslinked homopolymer, dehydration, glycerin, membranes, pervaporation.

Pervaporation has found significant industrial application in the dehydration of organic compounds (1–3). In the past, exclusively polymeric membranes were used. However, because of the poor longevity of these membranes, inorganic membranes are being developed as a long-lasting alternative (4). Many companies have introduced inorganic membranes (e.g., Sulzer Chemtech, Winterthur, Switzerland; and Mitsui Engineering and Shipbuilding Co., Tokyo, Japan). Although inorganic membranes are temperature and wear resistant, they are brittle and more expensive than organic polymeric membranes.

Glycerin is one of the most versatile chemicals. Recovery of glycerin from the sweetwater obtained from the fat splitting process is an important step. Because of its high boiling point (290°C) and low decomposition temperature (190°C), the final traces of water from glycerin are removed by vacuum distillation. Even vacuum distillation cannot prevent damage to glycerol due to inherently long residence times during distillation (5). So pervaporation, which can achieve dehydration at much lower temperatures by using hydrophilic membranes, is an attractive alternative to the vacuum distillation process.

Dehydration studies of glycerin/water mixtures by pervaporation have been performed using homogeneous polymeric membranes (6–8). However, despite its importance, dehydration of glycerin by pervaporation is not advanced. The probable reason for this is that polymeric membranes have poor stability and longevity. Polymeric membranes have limited life because they attract the water molecule selectively. Most polymeric membranes, e.g., based on poly(vinyl) alcohol (PVA), have a high affinity for water, swell extensively, and ultimately dissolve in water. The swelling can be controlled by crosslinking. However, the degree of crosslinking must not be high since highly crosslinked membranes yield very low fluxes.

An alternative to the above crosslinked homopolymer membranes is a copolymer membrane using suitable monomers (9,10). Thus, acrylonitrile, which is a tough and strong monomer but has poor hydrophilicity, can be copolymerized with carefully chosen monomers that have functional groups that can interact with water and make the copolymer sufficiently hydrophilic yet resist excessive swelling. This concept has the added advantage that, by changing the monomer ratio, the degree of hydrophilicity can be varied. Such copolymers have sufficient hydrophilicity and, owing to the strong acrylonitrile backbone, a long life (11).

The present work deals with the pervaporation performance of homopolymer and copolymer membranes for dehydration of glycerol/water mixtures. Polymeric membranes of poly(acrylonitrile-co-methacrylic acid) (PANMAC) and poly(acrylonitrile-co-hydroxyethyl methacrylate) (PANHEMA), Poly(vinyl alchohol) GFT-1001, and PVA crosslinked with maleic anhydride (PVAManh) were tested. The effect of feed concentration, feed temperature, and downstream pressure were studied. Pervaporation performance was evaluated in terms of selectivity and flux. Selectivity is defined as

$$\alpha_{AB} = \frac{(Y_A/X_A)}{(Y_B/X_B)} \qquad [1]$$

where α = selectivity, X = concentration in feed, Y = concentration in permeate, A = water, and B = glycerin. Overall performance of the membrane is evaluated in terms of pervaporation separation index (PSI), given as

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*To whom correspondence should be addressed. E-mail: vgp@udct.ernet.in

$$\mathrm{PSI} = J_p[(C_{p,\mathrm{water}}/C_{f,\mathrm{water}}) - 1] \qquad [2]$$

where $C_{p,\mathrm{water}}$ and $C_{f,\mathrm{water}}$ are water concentrations in the permeate and feed, respectively, and J_p is the permeate flux (kg/m^{2}h).

EXPERIMENTAL PROCEDURES

Materials. Analytical grade glycerin was procured from S.D. Fine Chemicals (Mumbai, India). PVA flakes were procured from Sigma-Aldrich (Diesenhofen, Germany). Poly(vinyl alcohol) GFT-1001 membrane was kindly supplied by Sulzer Chemtech (Winterthur, Switzerland). All chemicals were used without further treatment.

Membrane preparation. Membranes used in this work were prepared by the solution casting method except for Poly (vinyl alcohol) GFT-1001. Copolymers of acrylonitrile using monomers such as 2-hydroxyethyl methacrylate and methacrylic acid were prepared by the emulsion polymerization method described by Ray *et al.* (9) and Mandal and Pangarkar (10), respectively. PANHEMA and PANMAC membranes were prepared by casting from dimethyl formamide (DMF) solution of the respective polymer with an applicator on a clean, smooth glass plate and dried at 60°C for 2 h. Subsequently, the membrane was annealed at 80°C for an additional 6 h. For preparing membranes of PVA crosslinked with maleic anhydride, PVA flakes were gradually dissolved in deionized water at 80°C and boiled for 2 h to a transparent 8% by weight solution. To crosslink PVA, a calculated amount of maleic anhydride (3 wt%) was added to the PVA solution with constant stirring. The resultant solution was then cast on a glass plate with an applicator. Water was allowed to evaporate by keeping these membranes in an oven at 60°C for 2 h to obtain films of crosslinked PVA membrane. The resultant films were cured at 150°C for 4 h.

Sorption studies. Sorption studies were carried out for PANHEMA, PANMAC, and PVAManh membranes, but not for Poly(vinyl alcohol) GFT-1001 since it is a composite membrane. Pieces of prepared membranes of known weight were immersed in aqueous solutions of glycerin of different known concentrations. The membranes were allowed to equilibrate for 48 h at 30, 50 and 70°C. The membranes were then removed and weighed after the superfluous liquid had been wiped off with a tissue paper. The increase in weight was due to the water and glycerin sorbed by the membrane. The weight of the membrane after and before sorption was used to calculate the sorption coefficient. Approximately 70% of the experiments were replicated on a random basis. Reproducibility of the experimental data for sorption was ±5%.

Analysis of sorbed material. The amount of water sorbed in the membrane was analyzed by using a Karl Fischer Titrator Model Auto-1 (Veego, Mumbai, India). The procedure was as follows: The membrane to be analyzed was equilibrated with anhydrous methanol for 1 h to extract sorbed water from the membrane in an airtight chamber. After this, the extracted water was titrated *in situ* using a Karl Fischer (KF) reagent. Water content was calculated by using Equation 3,

$$\text{wt of water} = (\text{mL of KF reagent required for end point}) \times (\text{KF factor}) \qquad [3]$$

where the KF factor is the amount of water in mg/mL of KF reagent, i.e.,

$$\text{KF factor} = 10 \text{ mg water/KF reading} \qquad [4]$$

The amount of glycerin sorbed was obtained by material balance.

Permeation studies. The setup used for pervaporation experiments was the same as described by Netke *et al.* (12). The membrane was allowed to equilibrate with the feed solution for 1 h before the commencement of the pervaporation experiments. It is not beneficial to provide a longer equilibration time as no significant change was observed after 30 min of equilibration. The desired vacuum was maintained in the permeate side in all the experiments by using a vacuum pump. The permeate sample collected in the condenser was weighed and analyzed. The water concentration in feed was varied from 5 to 40 wt%. The downstream pressure was varied from 5 to 25 mm of Hg. The feed temperature was varied from 30 to 70°C. The permeate weight and composition were used to calculate flux, selectivity, and other parameters. The flux values reported in this work were normalized to 5 μm membrane thickness. Approximately 70% of the experiments were replicated on a random basis. Reproducibility of the experimental data for permeation was ±3%.

Permeate analysis. Permeate was analyzed by the refractive index (RI) method. A Bausch and Lomb refractometer was used for the RI analysis. Standard calibration charts of water/glycerin mixtures were prepared from 0–100 wt% by plotting RI vs. concentration of water.

RESULTS AND DISCUSSION

Sorption. (i) Effect of feed concentration. Figure 1 shows sorption data for water for all membranes used except the GFT membrane. The sorption of glycerin for all the membranes except PVAManh was negligible; therefore, these data would lie practically on the $Y = 0$ line and hence were not shown. Thus, although the water sorption of PANHEMA and PANMAC was not as high as for PVAManh, the glycerin sorption (not shown in Fig. 1) being negligible, the former membranes also showed good sorption selectivity for water. From Figure 1 it can be observed that the PVAManh membrane yielded high sorption values for water as compared to PANHEMA and PANMAC membranes. Owing to the higher intermolecular space between PVA chains, the free volume available in a PVA membrane is higher, thus allowing high sorption of water as well as glycerin. In the PVAManh membrane, sorption occurs because of hydrogen bonding between the OH group of PVA and water. Thus, water/polymer pair formation as well as plasticization of the polymer is greater

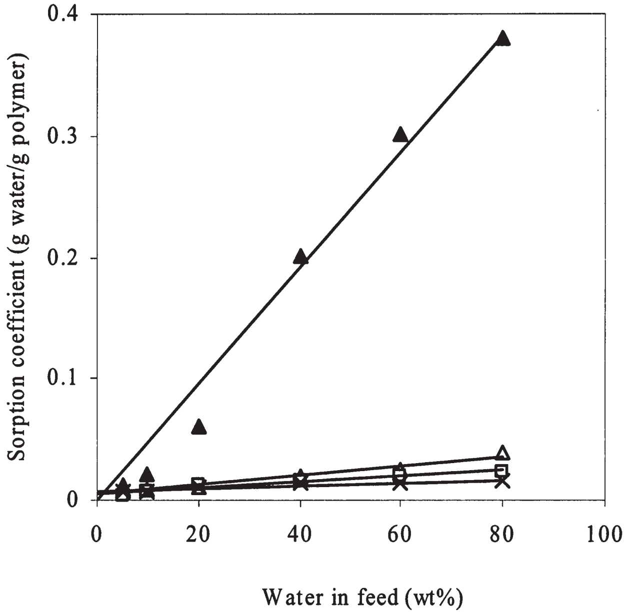

FIG. 1. Sorption isotherms of water and glycerin for various membranes at 30°C. For water: (▲) Poly(vinyl alcohol) GFT-1001 crosslinked with maleic anhydride (PVAManh) (R^2 = 0.98); (△) poly(acrylonitrile-co-hydroxylethyl methacrylate) (PANHEMA) (R^2 = 0.96); (□) poly(acrylonitrile-co-methacrylic acid) (PANMAC) (R^2 = 0.92). For glycerin: (×) PVAManh (R^2 = 0.96).

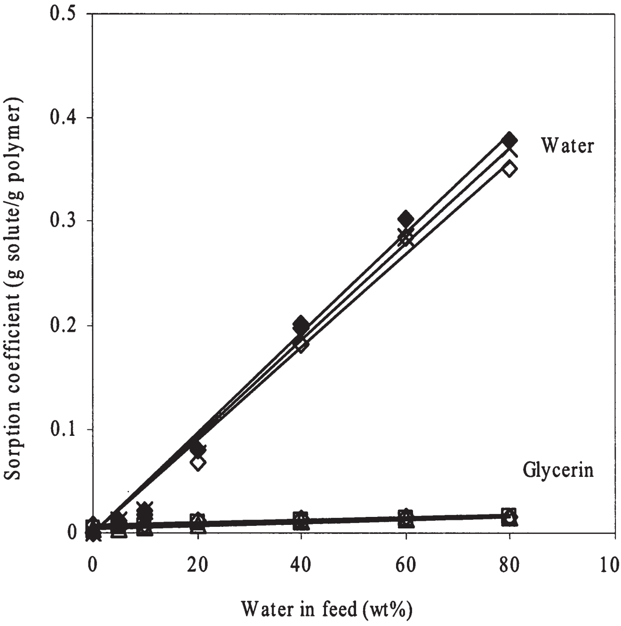

FIG. 2. Sorption isotherms of water and glycerin at 30, 50, and 70°C for the PVAManh membrane. For water: (◆) 30°C (R^2 = 0.99); (×) 50°C (R^2 = 0.99); (◇) 70°C (R^2 = 0.98). For glycerin : (△) 30°C (R^2 = 0.94); (□) 50°C (R^2 = 0.95); (◇) 70°C (R^2 = 0.98). For abbreviation see Figure 1.

and therefore polymer sorption capacity is also greater. Although the free volume available in a PVAManh membrane is higher, sorption of glycerin is much lower because of the high molar volume of glycerin. The component with the smaller molar volume will be sorbed preferentially (13). The sorption coefficient of water for PANHEMA and PANMAC membranes is nearly the same. PANHEMA and PANMAC membranes showed low sorption of water compared with PVAManh. These membranes have a highly compact and rigid structure. Thus, water/polymer pair formation as well as plasticization of the polymer is less and polymer sorption capacity is less. These membranes show negligible sorption of glycerin, probably because of the very compact structure of these polymers and the large difference in molar volume between water and glycerin. From Figure 1 one can see that the sorption coefficient for water increases linearly with the increase in concentration of water in feed for PVAManh, PANHEMA, and PANMAC membranes. The sorption isotherm of water for the membranes can be described by Roger's type I isotherm (14). The sorption coefficient for the permeants in various membranes follows the order: PVAManh > PANHEMA ≅ PANMAC.

(ii) Effect of feed temperature. Figure 2 shows the variation in sorption coefficient of water for PVAManh membrane at different temperatures. The sorption coefficient shows a marginal decrease with an increase in temperature, implying that although the heat of sorption is negative, its value is very low. Similar results were obtained for other membranes. The sorption of glycerin by the membrane is very poor. When the sorption data for glycerin are shown along with the water sorption data on a common scale, the effect of temperature on glycerin sorption is not evident. For instance, the sorption of glycerin decreased by a maximum of 10% in the range of 30 to 50°C. Heats of sorption for water for various membranes at 5 wt% of water in the feed are given in Table 1. These values can be used to predict the sorption at elevated temperatures.

Permeation. (i) Effect of feed concentration. Figure 3 shows the effect of feed concentration on the total flux for various membranes at 30°C. It can be observed that the flux increased with an increase in the concentration of water in the feed ($y = mx^n$, $n < 1$). This is due to the increase in plasticization of the membrane. From Figure 3 one can see that PVAManh yielded the highest flux over the entire range of concentration studied as compared with other membranes. The probable reason for this is that the interchain mobility of this polymer is high and also that crosslinking density of this polymer (3 wt% maleic anhydride) is less meaning more free volume is available. The flux values in PANHEMA and PANMAC membranes are low

TABLE 1
Energy of Activation for Permeation (ΔE_p), Diffusion (ΔE_d), and Heat of Sorption (ΔH_S) for Water for Various Membranes (5 wt% of water in the feed)

Membrane[a]	ΔE_P (kJ/mol)	ΔE_d (kJ/mol)	ΔH_S (kJ/mol)	R^2
PANHEMA	43.5	49.2	−5.730	0.99
PANMAC	40.0	48.9	−8.87	0.99
PVA (GFT-1001)	56.5	—	—	0.89
PVAManh	50.2	54.2	−4.01	0.91

[a] PANHEMA, poly(acrylonitrile-co-hydroxyethyl methacrylate); PANMAC, poly(acrylonitrile-co-methacrylic acid); PVA (GFT-1001), Poly(vinyl alcohol) proprietary membrane of GFT company, now owned by Sundar Chem. Tech.; PVA Manh, poly(vinyl alcohol) crosslinked with maleic anhydride.

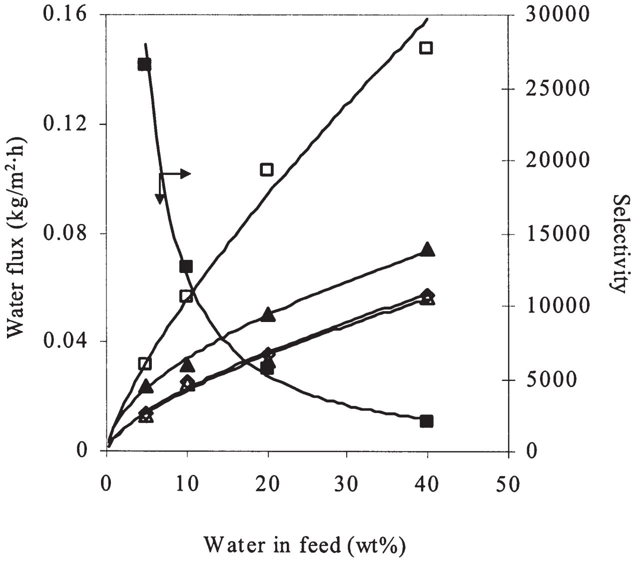

FIG. 3. Variation of water flux and selectivity with concentration of water in the feed for various membranes at 30°C. (■) PVAManh (R^2 = 0.99); (▲) Poly(vinyl alcohol) GFT-1001 (R^2 = 0.99); (△) PANHEMA (R^2 = 0.98); (◇) PANMAC (R^2 = 0.98); (◆) selectivity. For abbreviations see Figure 1.

because of the compact structure of these polymers. The presence of the $-COOCH_2CH_2OH$ group in PANHEMA lowers the compactness, and the $-CH_3$ group decreases the hydrophilicity (10). The presence of a methyl group in PANHEMA and PANMAC imparts less rotational freedom of the side chain (9). Therefore, these membranes yielded low fluxes. The permeation rates of PANHEMA and PANMAC membranes were nearly same. Figure 3 also shows the effect of feed concentration on selectivity for water by various membranes at 30°C. All the membranes were highly water permselective over the entire range of concentration studied. Permeate composition over a wide range of feed composition was greater than 99.9 wt% of water with only traces of glycerol. At high concentrations of glycerol, higher selectivities were obtained (Table 2). Comparison of the sorption values and the results for permeation show that preferential sorption of water contributes to a large extent to selective water transport. The water permeation rate of various membranes follows the order: PVAManh > PVAGFT > PANHEMA ≅ PANMAC.

The effect of feed concentration on the pervaporation separation index (PSI), which is a measure of the separation ability of the membrane, is shown in Figure 4. PVAManh yielded highest PSI values as compared to the other membranes.

TABLE 2
Effect of Water Concentration in Feed on Selectivity at Different Temperatures

Water concentration in feed (wt%)	Selectivity	R^2
5	26,600	1
10	12,596	1
20	5,598	1
40	2,099	1

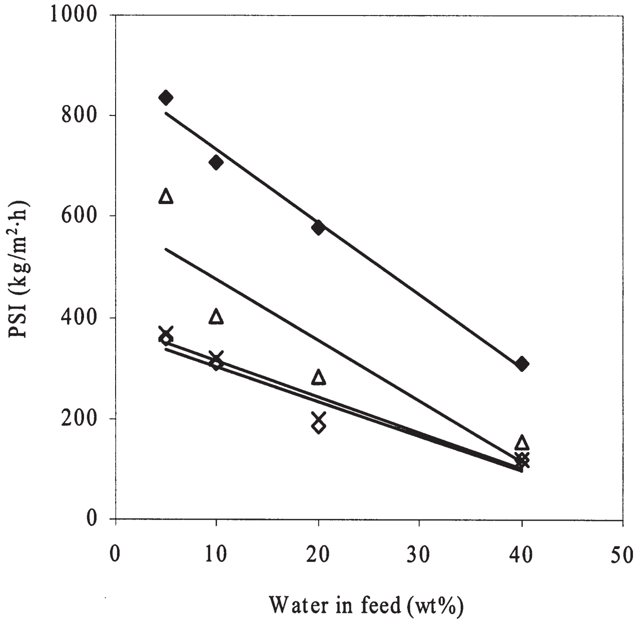

FIG. 4. Variation of pervaporation separation index (PSI) with concentration of water in the feed at 30°C. (◆) PVAManh (R^2 = 0.99); (△) Poly(vinyl alcohol) GFT-1001 (R^2 = 0.81); (x) PANHEMA (R^2 = 0.93); (◇) PANMAC (R^2 = 0.91). For abbreviations see Figure 1.

(ii) Effect of feed temperature. Since solubility and diffusivity of the feed mixture components in polymeric membranes are generally dependent on the operating temperature, pervaporation characteristics in terms of flux are dependent on the temperature (15). Figure 5 shows the effect of feed temperature on water flux through the PVAManh membranes. Water flux was observed to increase linearly with an increase in temperature. Similar trends were observed for other membranes.

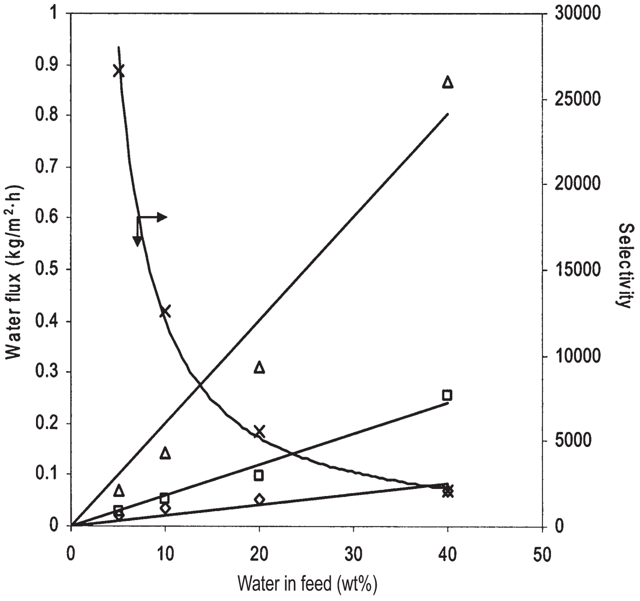

FIG. 5. Variation of water flux with feed temperature for PVAManh membrane. (◇) 30°C (R^2 = 0.92); (□) 50°C (R^2 = 0.98); (△) 70°C (R^2 = 0.94); (x) selectivity. For abbreviation see Figure 1.

This occurs because an increase in temperature increases the chain mobility in the polymer and thereby the diffusion coefficient of the solute in the polymer matrix. The increases in flux with temperature for PVAManh and Poly(vinyl alcohol) GFT-1001 were due to more flexible polymer chains compared to PANHEMA and PANMAC. The sorption and diffusion steps involved in permeation are activated processes, and the temperature effect is described by an Arrhenius-type relationship $J = J_0 \exp(-\Delta E_P/RT)$. The energy of activation for diffusion is given by Equation 5:

$$\Delta E_d = \Delta E_P - \Delta H_S \qquad [5]$$

where ΔE_d = energy of activation for diffusion (kJ/mol), ΔE_P = energy of activation for pervaporation (kJ/mol), and ΔH_S = heat of sorption (kJ/mol). The activation energies for permeation and diffusion of water in various membranes at 5% water concentration in feed are given in Table 1. Activation energy values for PVAManh and Poly(vinyl alcohol) GFT-1001 membranes are high compared with those for PANHEMA and PANMAC membranes. This is because PANHEMA and PANMAC membranes have a glassy, dense structure. For polymers with a more glassy and dense structure, less activation energy is required for permeation, as in the glassy state the jump lengths are less, demanding less entropy of activation (16). The selectivity is strongly dependent on temperature; in most cases, a decrease in selectivity is found at increasing temperature. According to Eyring's hole theory of diffusion, diffusive holes are produced with thermal motion of the polymer chains. These diffusive holes become larger with increasing temperature, which allows more solute to diffuse through the membrane. In the present case, it was observed that, although the permeation rate increased with an increase in temperature, there was no effect of temperature on the selectivity of the membrane for all membranes (Fig. 5). The probable reasons for this are that the polymer structure of the membranes used in this work were compact, and although diffusive holes became large with an increase in temperature, these were not large enough to accommodate the glycerol molecule owing to its higher diffusive cross section.

(iii) Effect of downstream pressure. As the downstream pressure was increased beyond a limiting threshold value, desorption at the membrane interface slowed and the downstream layer of the membrane became swollen. Both feed components could therefore easily diffuse through it, and the selectivity decreased (17). Figure 6 shows the variation in the permeation rate with downstream pressure for the PVAManh membrane ($y = mx^n$, $n < 1$). With increasing permeate pressure from 5 to 25 mm of Hg, permeation remained practically constant up to 25 wt% water. Above 40 wt% water in the feed, the increase in permeate pressure caused about a 20% decrease in the flux of the water. Similar trends were observed for other membranes. The decrease in permeation rate at higher downstream pressure (25 mm Hg) was not more than 10–12% compared with that at 5 mm Hg at 30°C. At high concentrations of glycerin, the decrease in permeation rate was very small. But the condensation temperature, in the case of 25 mm Hg downstream pressure, will be much higher, which can reduce the load on the refrigeration unit. No effect of downstream pressure on selectivity was observed, indicating that the limiting threshold pressure is greater than 25 mm Hg.

From these observations, it is evident that all membranes

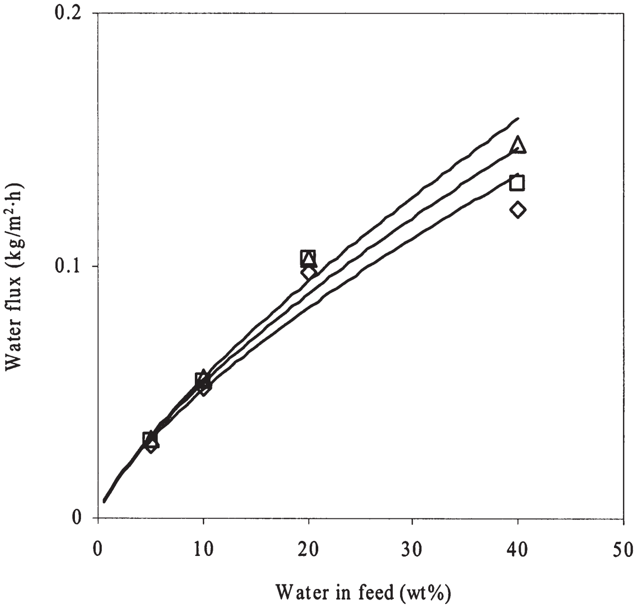

FIG. 6. Variation of water flux with a change in downstream pressure for PVAManh membrane at 30°C. (△) 5 mm Hg (R^2 = 0.99); (□) 15 mm Hg (R^2 = 0.97); (◇) 25 mm Hg (R^2 = 0.97). For abbreviation see Figure 1.

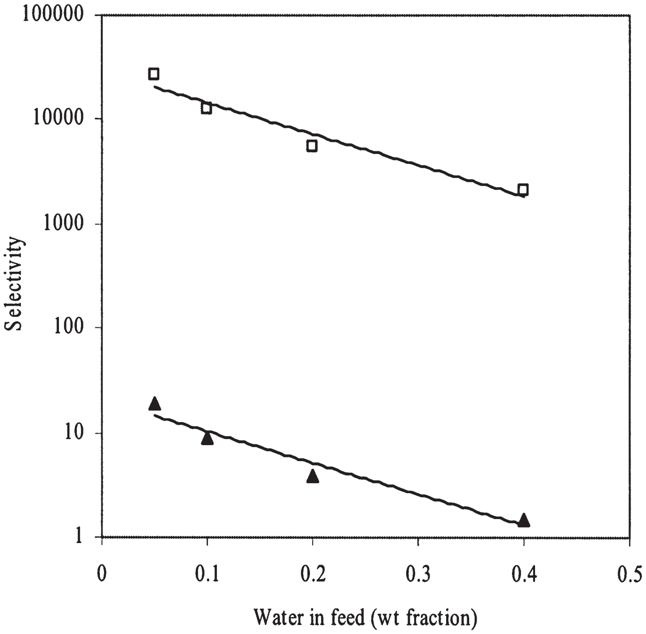

FIG. 7. Comparison between pervaporation selectivity for PVAManh membrane with vapor–liquid equilibrium (VLE) selectivity at 70°C. (□) Pervaporation selectivity (R^2 = 0.95); (▲) VLE selectivity (R^2 = 0.95). For abbreviation see Figure 1.

are highly permselective for water. There is no effect of operating parameters on the selectivity for water. Also homopolymers PVAManh and Poly(vinyl alcohol) GFT-1001 gave better permeation rates than copolymer membranes (PANHEMA and PANMAC). But the swelling of homopolymers is much more than copolymers of polyacrylonitrile, which is why PVA membranes have poor longevity. Although the swelling can be controlled by crosslinking, it reduces the permeation rate and makes the membrane brittle. Copolymers of polyacrylonitrile have lower permeation rates, but owing to the presence of strong acrylonitrile backbone, the stability and longevity of these membranes make them attractive when an overall economic scenario is considered.

Comparison of pervaporation with vapor-liquid equilibrium (VLE) data for evaporation/distillation. Figure 7 shows a comparison between pervaporation selectivity for the PVAManh membrane and VLE selectivity at 70°C. VLE selectivity for a glycerin/water mixture was estimated by the Universal Quasi Chemical Theory Functional Group Activity Coefficient Model (UNIFAC) (18,19). From Figure 7, it was observed that the pervaporation selectivity for a glycerin/water mixture was approximately 1000 times higher than for VLE selectivity.

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