Sodium Alginate–Poly(hydroxyethylmethacrylate) Interpenetrating Polymeric Network Membranes for the Pervaporation Dehydration of Ethanol and Tetrahydrofuran

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ABSTRACT: Interpenetrating polymeric network (IPN) membranes of sodium alginate (NaAlg) and various amounts of poly(hydroxyethylmethacrylate) (PHEMA) have been prepared and tested for the pervaporation dehydration of ethanol and tetrahydrofuran (THF). The presence of hydrophilic PHEMA in the IPN matrix was found to be responsible for increase in membrane selectivity to water. NaAlg–PHEMA IPN membrane containing 20 wt % of PHEMA exhibited a selectivity of 571 to water for the water–ethanol mixture and 857 for water–THF mixture. These data are much better than those observed for the pristine NaAlg membrane. However, flux of the IPN membranes was smaller than that of pristine NaAlg membrane. Comparatively higher flux values were observed for water–THF mixture than for water–ethanol mixture. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3324–3329, 2006

Key words: interpenetrating polymer networks (IPNs); sodium alginate; hydroxy ethylmethacrylate; pervaporation

INTRODUCTION

Preparation of polymeric membranes from interpenetrating network (IPNs) structures provide improved properties over those of conventional polymeric materials.[1–6] IPN has many advantages over the pristine membranes in terms of providing multifunctional groups by a combination of hydrophilic and hydrophobic components, soft and hard segments, etc., to enhance its preferential affinity to a particular component of the feed mixture. In the literature,[7] IPN membranes of cellulose–poly(acrylamide or acrylic acid) have been used for the pervaporation (PV) separation of water–ethanol mixtures. A semi-IPN membrane prepared from of poly(ethyleneglycol dimethacrylate) network with cellulose propionate or butyrate was used in the PV separation of ethanol-ethyl-*t*-butyl ether.[8] Various types of IPN membranes including those prepared from polyurethane–poly(methylmethacrylate)-acrylic acid copolymers have also been used in the PV separation of water–ethanol mixture.[4,9,10] Highly selective IPNs of poly(acrylamide)-poly(vinyl alcohol) copolymers have been proved to be efficient as PV separation membranes.[6]

In PV, a liquid feed stream from the upstream side of the membrane interacts with the membrane surface and transports across the barrier membrane as a vapor on the permeate side under the influence of vacuum. PV technique has been well recognized as an energy-intensive process when compared with simple distillation because it can be performed at ambient temperature and requires lesser energy than distillation, in addition to being an environmentally clean process. In PV, the membrane acts as a third phase in achieving azeotropic separation, whereas in distillation, benzene (a deadly carcinogen) is used as an entrainer for the same purpose. However, key to the success of PV process is to fabricate suitable membranes that yield high permeability flux and good selectivity, in addition to reasonable mechanical strength.

Sodium alginate (NaAlg) has been widely used as a membrane in PV separation of aqueous-organic mixtures because of the presence of carboxylic and hydroxyl groups, which play an important role in preferential removal of water from organic solvents. Particularly, NaAlg and its blend membranes have been extensively used in the PV separation of water–isopropanol, water–1,4-dioxane and water–ethanol mixtures.[11–13] Poly(hydroxyethyl methacrylate) (PHEMA) is a hydrophilic polymer that swells, but is insoluble,

in water and it has the ability to retain water molecules. In this work, novel IPN polymer containing NaAlg and PHEMA has been prepared by combining the properties of NaAlg and PHEMA. HEMA was polymerized in an aqueous solution of NaAlg under reduced pressure and membranes have been prepared. IPN membranes thus prepared have been crosslinked with glutaraldehyde and used for the PV separation of water–ethanol and water–THF mixtures. The effect of concentration of HEMA on flux and selectivity has been investigated.

EXPERIMENTAL

Materials

Sodium alginate (low viscosity grade sample), 2-hydroxyethylmethacrylate, potassium persulfate, ethanol, tetrahydrofuran, and glutaraldehyde (25% aqueous solution) (GA) were purchased from S.D. Fine Chemicals, Mumbai, India. Deionized water, having a conductivity of 20 μS/cm, was produced in the laboratory itself using the Permeonics pilot plant (Vadodara, India) on a nanofiltration membrane module.

Membrane preparation

Sodium alginate and 2-hydroxyethylmethacrylate IPN membranes have been prepared by polymerizing 2-hydroxyethylmethacrylate in an aqueous solution of NaAlg using potassium persulfate ($K_2S_2O_8$) as an initiator. In brief, 4 wt % aqueous solution of NaAlg was prepared by dissolving NaAlg in water under constant stirring overnight. Passing nitrogen gas for 30 min degassed the solution. To this solution, different amounts (10 and 20 wt %) of 2-hydroxyethylmethacrylate were added and stirred thoroughly for 1 h. The membranes were designated, respectively, as NaAlg–HEMA-10 and NaAlg–HEMA-20. The initiator solution containing 50 mg of $K_2S_2O_8$ was added to the above mixture and stirred for 1 h at 40°C under a vacuum pressure of 10 Torr. The resulting solution was poured on a clean glass plate to cast the membranes and dried at room temperature. The membranes were peeled of from the glass plate and immersed in a crosslinking bath containing water–acetone mixture (30 : 70) with 2.5 mL of glutaraldehyde and 2.5 mL of conc. HCl for about 8–10 h. The crosslinked membranes have been washed with deionized water and dried at ambient temperature.

Swelling experiments

Swelling experiments were performed gravimetrically[14] on all the membranes in 5, 10, and 15 wt % water containing feed mixtures at 30°C. Initial mass of the circularly cut (diameter = 2.5 cm) NaAlg and NaAlg–

PHEMA IPN membranes (containing 10 and 20 wt % HEMA) was measured on a single-pan digital microbalance (model AE 240, Mettler, Switzerland) sensitive to ±0.01 mg. The samples were placed inside the specially designed airtight test bottles containing 20 cm^3 of the test solvent. Test bottles were transferred to an oven maintained at a constant desired temperature. Dry membranes were equilibrated by soaking in different compositions of the feed mixture in a sealed vessel at 30°C for 48 h. The swollen membranes were weighed immediately after carefully blotting and weighing on a digital microbalance. The % degree of swelling, DS, was calculated as follows:

$$DS = \left(\frac{W_\infty - W_0}{W_0} \right) \times 100 \qquad (1)$$

where W_∞ and W_0 are weights of the swollen and dry membranes, respectively.

Pervaporation experiments

PV experiments were carried out in a 100 mL batch mode with an indigenously constructed manifold operated at a vacuum level as low as 0.05 mmHg in the permeate line. Membrane area of the PV cell assembly was approximately 20 cm^2. PV experiments were carried out in triplicate at 30°C using the freshly prepared feed solutions each time to check the reproducibility of the measurement. The collected permeate was weighed on a Mettler electronic balance (Model AE 240) to an accuracy of 10^{-4} g to calculate flux and then analyzed using gas chromatography to evaluate membrane selectivity.

Feed and permeate samples were analyzed using a Nucon Gas Chromatograph (GC Model 5765) installed with a thermal conductivity detector (TCD) and Tenax packed column of 2 m length. Oven temperature was initially kept at 70°C and then raised to 210°C at the heating rate of 25°C/min. Injector and detector temperatures were maintained at 150°C each. The sample injection size was 1 μL and pure hydrogen was used as a carrier gas at a pressure of 0.75 kg/cm^2. GC response was calibrated for this particular column and conditions, with the known compositions of water + ethanol and water + THF feed mixtures. Calibration factors were fed into the software to obtain the correct analysis for unknown samples. From the PV experiments, the total permeation flux (J_p) and selectivity (α) were computed using,

$$J_p = W_P/At \qquad (2)$$

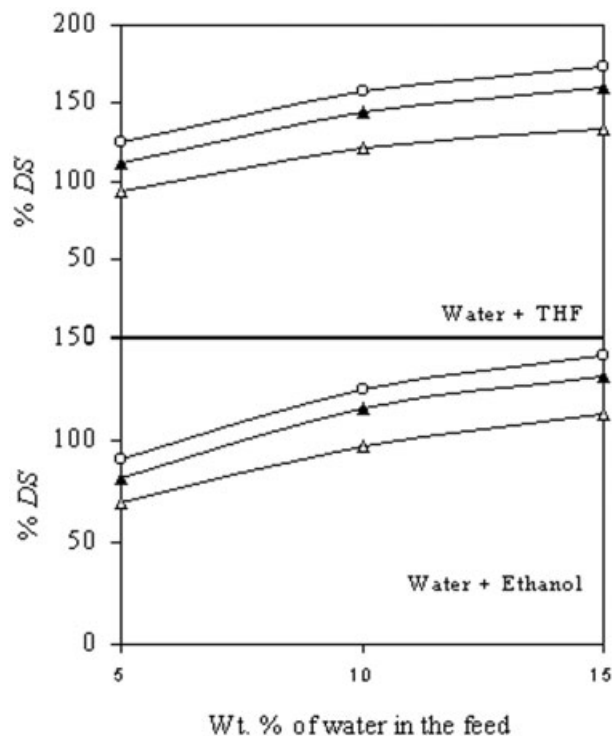$$\alpha = (P_w/P_{\text{org}})/(F_w/F_{\text{org}}) \qquad (3)$$

Figure 1 Degree of swelling versus wt % of water in feed. (○) pristine NaAlg, (△) NaAlg–HEMA-10, and (▲) NaAlg–HEMA-20 membranes.

Here, W_p is mass of permeate (in g), A is effective membrane area (in m^2), t is time (in h) required for liquid permeation; P and F are mass fractions of permeate and feed, respectively. Subscript w stands for water and org stands for ethanol or THF.

RESULTS AND DISCUSSION

Degree of swelling

Equilibrium degree of swelling, obtained from sorption experiments at 30 °C, for the three membranes as a function of wt % of water in the feed are displayed in Figure 1 for 5, 10 and 15 wt % water in the feed. Swelling kinetics depends on the mutual diffusion of solvent molecules in response to polymer chain relaxation.[15] Polymer swelling showed a clear-cut dependence on permeation flux and selectivity data. For instance, swelling is higher for NaAlg–HEMA-20 IPN membrane than observed for NaAlg–HEMA-10 IPN membrane, but lower swelling is observed for pristine NaAlg membrane than for both the IPN membranes. Degree of swelling is higher for THF than for ethanol, suggesting more interacting nature of THF than ethanol.

Membrane performance

Membrane performance is judged by the flux and selectivity data of a particular component of the mix-

ture. In pervaporation, molecular transport occurs across a membrane as a result of concentration gradient existing between the feed and the permeant mixtures as envisioned by the solution-diffusion principles.[16,17] Permeating molecules first dissolve into the membrane and diffuse out on the downstream side as a result of the concentration gradient. In case of NaAlg–HEMA IPN membranes of this present study, the overall separation can be explained by the hydrophilic interaction of HEMA with NaAlg and their affinity to the water molecules. Considering the PV separation of water–ethanol and water–THF mixtures, the relative affinity of ethanol, THF, or water molecules towards the membranes can be assessed from the sorption (swelling) results. In the present study, when a hydrophilic HEMA is polymerized in the presence of another hydrophilic NaAlg, permeation flux of the IPN membrane is enhanced in proportion to the amount of HEMA added (see Table I). This observation is identical to the swelling results. For instance, when a higher amount of HEMA (20 wt %) is present in the IPN matrix, a greater degree of swelling and higher permeation flux are observed. On the other hand, when 10 wt % HEMA is present in the IPN matrix, swelling of the membrane is lower than that observed for 20 wt % HEMA in the IPN.

TABLE I
Pervaporation Results of the Membranes at 30°C

wt % of water in feed	Normalized water flux (10 μm thickness)	Selectivity	wt % of water in permeate
WATER–ETHANOL			
Pristine NaAlg membrane			
5	0.170	73	79.33
10	0.270	34	78.99
15	0.355	18	75.66
NaAlg–HEMA (10 wt %)			
5	0.106	310	94.23
10	0.210	56	86.21
15	0.306	17	75.35
NaAlg–HEMA (20 wt %)			
5	0.132	571	96.78
10	0.245	79	89.76
15	0.328	23	80.21
WATER–THF			
Pristine NaAlg membrane			
5	0.189	619	97.02
10	0.300	280	96.89
15	0.345	103	94.78
NaAlg–HEMA (10 wt %)			
5	0.149	720	97.43
10	0.264	294	97.03
15	0.299	113	95.21
NaAlg–HEMA (20 wt %)			
5	0.168	857	97.83
10	0.285	340	97.42
15	0.326	147	96.28

Compared with IPN matrix containing 10 wt % HEMA, the membrane containing 20 wt % HEMA exhibited a higher degree of swelling because of the higher amount of hydrophilic HEMA present in the matrix, which absorbs more of water molecules. Moreover, hydrogen-bond type interactions between water molecules and the hydrophilic HEMA moiety as well as the hydrophilic NaAlg polymer are responsible for providing higher selectivity to water, compared with pristine NaAlg membrane, even though the flux is lower. A substantial increase in selectivity and a moderate increase in permeation flux for both 10 and 20 wt % HEMA–NaAlg IPN membranes is due to the fact that in the swollen state, hydrophilic HEMA would preferentially allow more of water molecules to be sorbed much faster than ethanol or THF, and this would increase the selectivity as well flux values at higher amounts of water in the feed. Notice that flux and selectivity values of THF are higher than that of ethanol, which agree with the trends observed for degree of swelling. The decrease in permeation flux of the IPN membranes may be due the presence of more number of crosslinking units in the IPN membranes than the pristine NaAlg membrane. The effect of HEMA on water transport has helped in improving membrane performance. It is worth mentioning that varying effects of flux and selectivity are attributed to different amounts of HEMA present in the NaAlg matrix.

Normalized water flux and selectivity results are displayed in Figures 2 and 3, respectively. The normalized water flux for pristine NaAlg membrane has increased from 0.170 to 0.355 kg/(m^2 h) for feeds containing 5 to 15 wt % of water in case of water + ethanol mixtures and 0.189–0.345 kg/(m^2 h) for water + THF feed mixtures. However, selectivity of the pristine NaAlg has decreased from 73 to a much smaller value of 18 when water content in the feed mixture increased from 5 to 15 wt % in case of water + ethanol mixture and 619 to 103 for water + THF mixture. Parallel to this effect, the wt % of water in permeate also decreased from 79.33 to 75.66 for water + ethanol, while a negligible decrease is observed (97.02 to 94.78) for water + THF mixture. Increase in flux with increasing amount of water in the feed is attributed to the plasticization effect of the membrane as a result of membrane swelling, thus permitting more of water molecules (than organic component) from the feed mixture to permeate through the membranes. After the addition of HEMA (10 and 20 wt %), the combined membrane properties have changed. For instance, normalized water flux for NaAlg–HEMA-10 IPN membrane increased from 0.106 to 0.306 kg/(m^2 h) for water + ethanol feed and 0.149–0.299 kg/(m^2 h) for water + THF feed, while for NaAlg–HEMA-20 IPN membrane, the normalized water flux has increased from 0.132 kg/(m^2 h) to 0.328 kg/(m^2 h) for water +
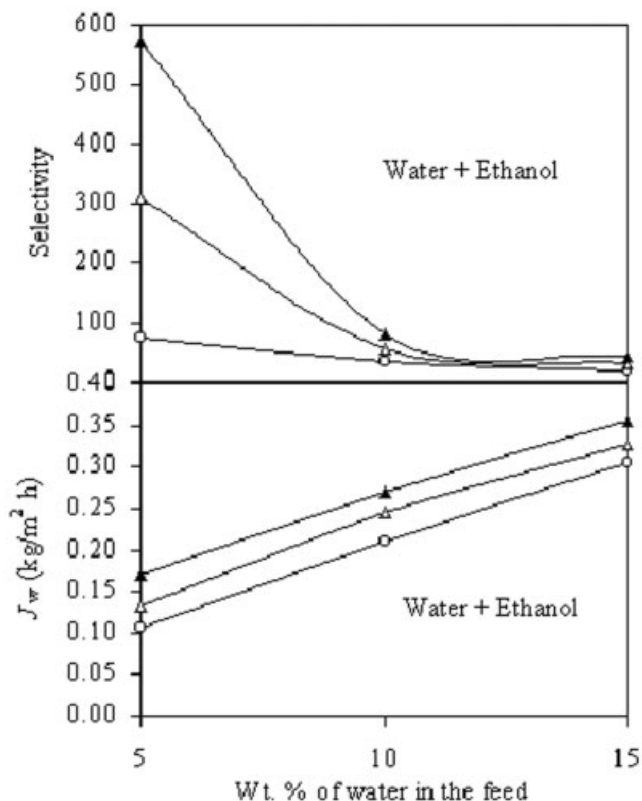

Figure 2 Normalized water flux and selectivity versus wt % of water in feed for water + ethanol. (○) pristine NaAlg, (△) NaAlg–HEMA-10, and (▲) NaAlg–HEMA-20 membranes.

ethanol and 0.168–0.326 kg/(m^2 h) for water + THF mixtures as a result of increasing amount of water in the feed from 5 to 15 wt %.

Water in permeate for NaAlg–HEMA-10 IPN membrane ranged between 94.23 and 75.35% for water + ethanol mixture, while it was 97.43–95.21% for water + THF feed; however, in case of NaAlg–HEMA-20 IPN membrane, these values ranged between 96.78 and 80.21% for water + ethanol feed. In case of water + THF mixture, water in permeate was 97.83–96.28% over the range of water compositions of the feed mixtures. This is due to the hydrophilic nature of HEMA, which has exerted a high affinity to water molecules than ethanol or THF, since water has higher polarity than ethanol or THF. The decrease in selectivity with increasing concentration of water in the feed varies depending upon the amount of HEMA present in the NaAlg matrix. For instance, with NaAlg–HEMA-10 IPN membrane, selectivity dropped rapidly from 310 for 5 wt % of water in feed to about 17 for 15 wt % water in the feed for water + ethanol mixture. On the other hand, for water + THF feed mixtures, at 5 wt % of water, the selectivity was as high as 720, which dropped drastically to 113 at 15 wt % of water in the feed. On the other hand, for NaAlg–HEMA-20 IPN
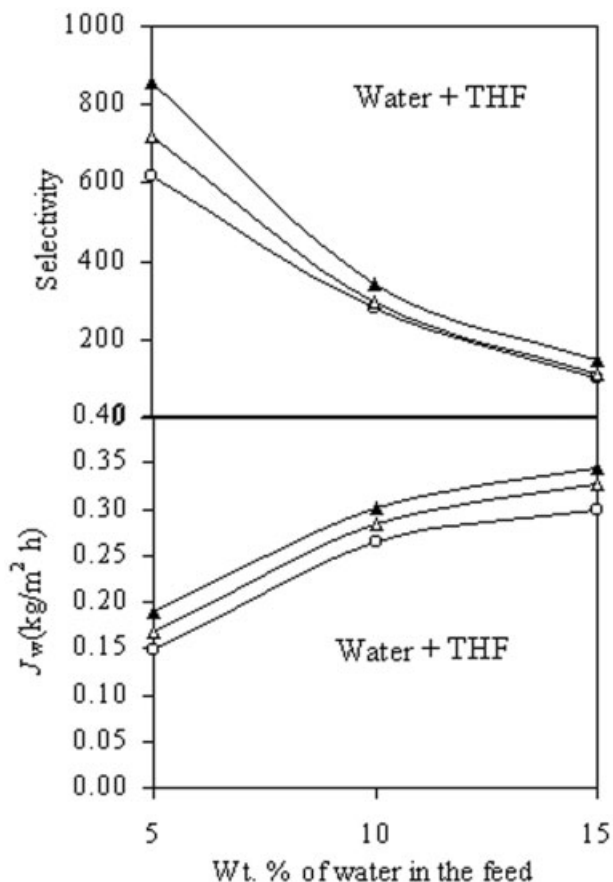
Figure 3 Normalized water flux and selectivity versus wt % of water in feed for water + THF. (○) pristine NaAlg, (△) NaAlg–HEMA-10, and (▲) NaAlg–HEMA-20 membranes.

membrane, both flux and selectivity have increased more than that of NaAlg–HEMA-10 IPN membrane (see Table I). It is thus evident that the presence of higher amount of HEMA in NaAlg–HEMA IPN matrix allows more of water molecules to pass through because of its hydrophilic nature; this explains the observed increase in selectivity. A highest selectivity of 857 was found for NaAlg–HEMA-20 IPN membrane at 5 wt % water in the feed mixture. However, for 15 wt % water-containing feed mixture, selectivity has dropped to147. The amount of water extracted was also quite high, i.e., it ranged between 97.83 and 96.28% in the investigated range of feed concentrations.

Comparison of PV results with VLE data

Water + ethanol and water + THF mixtures have the azeotropic compositions at 4 and 6.7 wt % of water, respectively. It is however, difficult to separate such mixtures by using distillation without adding an entrainer such as benzene, which makes the process environmentally hazardous. In contrast, PV could separate the azeotropes because here, vapor–liquid equi-

librium (VLE) is not the controlling mechanism for separation. In PV, a trade-off exists between flux and selectivity. Balancing these parameters is difficult and thus, for large scale applications, PV could be effective in separating azeotropes. It is demonstrated here that it is possible to increase simultaneously both flux and selectivity to water by membrane modification, i.e., preparing IPNs of HEMA with NaAlg. See data displayed in Figure 4 for 10 wt % water-containing feed mixture plotted versus wt % HEMA, wherein, the normalized water flux is smaller than found for pristine NaAlg, but selectivity is enhanced much more after the modification of NaAlg membrane. In PV, membrane acts as a third phase and breaks the azeotrope.

Figure 5 compares the results of water concentration obtained in permeate by PV (NaAlg–HEMA-20) IPN membrane and that obtained in the vapor phase by VLE for the feed mixtures of this study. It is, however, common to the express selectivity as a product of VLE selectivity and membrane selectivity. From Figure 5, it is seen that membrane selectivity is high, because permeate is primarily composed of water over the entire concentration range.[18] Thus, PV is an environmentally clean process and more efficient when compared with simple distillation. Even the NaAlg used is of natural origin, thereby adding to the environmental cleanliness.
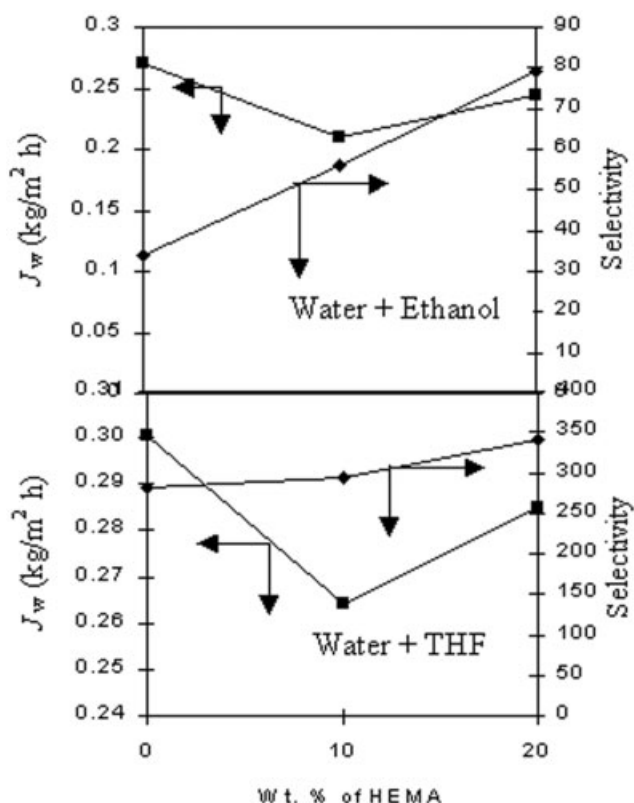

Figure 4 Normalized water flux and selectivity versus wt % of HEMA (0, 10, and 20 wt %) for 10 wt % of water in feed.
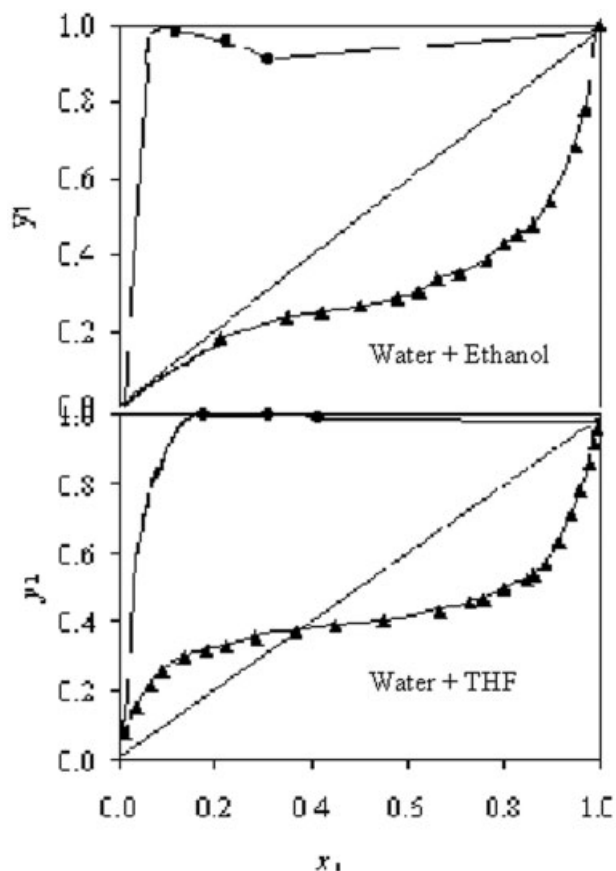
Figure 5 Comparison of vapor liquid equilibrium curve (▲) with PV data (●) for aqueous (1) + organic (2) mixtures at 30°C for NaAlg–HEMA-20 membrane.

CONCLUSIONS

Interpenetrating polymeric network membranes comprising of sodium alginate and poly(hydroxyethylmethacrylate) have been prepared and tested for pervaporation dehydration of ethanol and THF. These IPN membranes are found to be superior over that of the pristine NaAlg membrane for the dehydration of ethanol and THF. The presence of hydrophilic HEMA in the IPN membranes might have enhanced the se-lectivity of IPN membranes when compared with pristine sodium alginate. It is also observed that selectivity has increased with increasing amount of HEMA in the IPN matrix.

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