

# Comparison of the Pervaporation Separation of a Water–Acetonitrile Mixture with Zeolite-Filled Sodium Alginate and Poly(vinyl alcohol)–Polyaniline Semi-Interpenetrating Polymer Network Membranes

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**ABSTRACT:** The pervaporation (PV) separation performance of ZSM-5- and Na-Y-type zeolite-filled sodium alginate (NaAlg) membranes were compared with those of pure NaAlg and semi-interpenetrating polymer network (semi-IPN) membranes of poly(vinyl alcohol) (PVA) with polyaniline (PANI) for the dehydration of acetonitrile. The PV separation characteristics of the zeolite-filled membranes showed a dependence on the nature of the zeolites. The variation of the acidity function of the ZSM-5 zeolite had an influence on the flux and selectivity of the membranes when compared to unfilled membranes. The crosslinked membranes were characterized by differential scanning calorimetry, X-ray diffraction, scanning electron microscopy, and Fourier transform infrared spectroscopy. Increasing the PANI content of the semi-IPN network increased the separation selectivity. Among the NaAlg membranes, the plain NaAlg membrane showed the highest selectivity of 414 at 30 mass % water in the feed mixture, whereas the Na-Y- and

ZSM-5 (40)-filled NaAlg membranes exhibited much lower values of selectivity, that is, 7.3 and 4.3, respectively for 30 mass % water in the feed. When the flux and selectivity data of ZSM-5 (250)-filled NaAlg membranes were compared with that of Na-Y- or ZSM-5 (40)-filled NaAlg membranes, a noticeable increase in the selectivity for the ZSM-5 (250)-filled NaAlg membrane was observed, but a somewhat comparable flux was observed compared to the plain NaAlg membrane. For the first time, PANI was polymerized with PVA to yield a semi-IPN. The total flux and water flux increased systematically, whereas the selectivity decreased greatly from 251.87 to 5.95 with increasing amounts of water in the feed. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1968–1978, 2005

**Key words:** diffusion; interpenetrating network (IPN); zeolites

## INTRODUCTION

Zeolites are highly crystalline inorganic structures having uniform molecular size pores and are used in a variety of separation problems. Because of the small pore size, the diffusion rates of some molecules with different sizes and adsorption strengths inside the zeolite crystals differ by orders of magnitude. Zeolites have been used as fillers to develop polymeric mem-

branes to take advantage of the adsorption and diffusion differences to separate liquid mixtures.<sup>1</sup> The majority of laboratory-scale studies on zeolite-filled membranes have focused on gas separation and liquid separation by the pervaporation (PV) technique; the latter uses a liquid feed and a vacuum on the permeate side of the membrane. The PV technique has a greater potential for saving energy than conventional distillation. Zeolite-filled membranes for PV separation have been widely studied in recent years.<sup>2–9</sup> Because of their unique structural properties, zeolites can selectively separate a wide range of compounds, depending on their size, shape, and chemical characteristics. During PV, the adsorbed coverages are higher than those present in gas separation studies, whereas with the liquid feed, the total coverage at the feed side of the membrane is usually near to saturation.

Particularly, when aqueous–organic mixtures are separated, hydrophilic or hydrophobic membranes have been used.<sup>10–15</sup> The hydrophilicity and hydro-

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phobicity of the membranes can be varied by the incorporation of zeolites of different polarities. This can help to simultaneously increase the flux and selectivity. In this study, a comparative investigation on the PV separation characteristics on a water-acetonitrile (ACN) mixture was made with zeolite-filled and unfilled membranes. The water-ACN mixture is widely used in organic synthesis and electrochemical studies. Therefore, it would be of interest to separate these mixtures by the PV technique. Conventionally, distillation can be used, but the method is not feasible at azeotropic compositions of the mixture. The water-ACN mixture forms an azeotrope at the water composition of 12.3 mass %. To tackle this issue, we developed six membranes, namely, plain sodium alginate (NaAlg), three zeolite [(Na-Y, hydrophilic; ZSM-5 (40) hydrophilic; and ZSM-5 (250) hydrophobic)]-filled NaAlg membranes, and two semi-interpenetrating polymer networks (semi-IPNs) of polyaniline (PANI) with poly(vinyl alcohol) (PVA). Interest in PANI as a material for membrane separations has stemmed from its high selectivity toward many liquids because it has shown a high separation selectivity.<sup>16-19</sup> However, PANI can be tailor-made through a doping/undoping processes, but we prepared semi-IPNs of PANI with PVA to compare their PV separation characteristics for water-ACN mixtures. The results of this study are discussed in terms of the flux and selectivity of water over that of ACN. The importance of zeolite-filled membranes over those of unfilled membranes is discussed.

## EXPERIMENTAL

### Materials

NaAlg, aniline, ACN, aluminum sulfate, silica acid, glutaraldehyde, acetone, ethanol, hydrochloric acid, sodium hydroxide, and sulfuric acid were purchased from S. D. Fine Chemicals (Mumbai, India). Tetrapropylammonium bromide was purchased from Aldrich Chemicals (Milwaukee, WI). Double-distilled water was used throughout the study.

### Zeolite synthesis

ZSM-5 comes under the pentasil family and is a medium-pore zeolite with high thermal and catalytic stabilities. It was synthesized hydrothermally from an aqueous gel prepared from silica acid, aluminum sulfate, NaOH, sulfuric acid, and tetrapropylammonium bromide (TPA). Concentrated H<sub>2</sub>SO<sub>4</sub> was applied to adjust the gel pH. Here, TPA was used as a template, whereby zeolites crystallized around it. After standing at 160°C for 44 h, the mixture gave a yield of about 80–90% ZSM-5. Its composition was approximately 1.8 (TPA)<sub>2</sub>O:1.2 Na<sub>2</sub>O:1.3 Al<sub>2</sub>O<sub>3</sub>:100 SiO<sub>2</sub>:7 H<sub>2</sub>O. Then

by taking an appropriate amount of an alumina source, we synthesized ZSM-5 (40) (hydrophilic) and ZSM-5 (250) (hydrophobic) with in-house facilities at the National Chemical Laboratory (Pune, India). Na-Y zeolite was synthesized from sodium aluminate, NaOH, and silica sol with the approximate gel composition of Na<sub>2</sub>O: Al<sub>2</sub>O<sub>3</sub>:5.3 SiO<sub>2</sub>:5 H<sub>2</sub>O.

### Membrane preparation

Zeolite-filled NaAlg and pure NaAlg membranes

NaAlg (3 g) was dissolved in 80 mL of water with continuous stirring. Zeolite (0.3 g) was dispersed in 20 mL of water, and the solution was sonicated for about 30 min. This was added to the already prepared NaAlg solution with continuous stirring for 24 h and poured on a dust-free flat glass plate to cast the membranes and dried overnight. The membranes were peeled off from the glass plate and immersed in a crosslinking bath containing a water-acetone mixture (30:70) with 2.5 mL of glutaraldehyde and 2.5 mL of concentrated HCl for about 12–14 h. The crosslinked membrane was removed from the bath and dried in an oven at 40°C. The pure NaAlg membrane was prepared in the same manner without the zeolite. The membrane thickness, as measured by a screw gauge, was 40 μm.

PVA-PANI semi-IPN membranes

A solution of PVA (3 mass %) was prepared in water. To this, 0.6 or 0.9 mL of aniline was added. The pH of the solution was adjusted to 1 by the addition of concentrated HCl. To this mixture, we added an aqueous solution of ammonium persulfate at 5°C under constant stirring by maintaining an aniline-to-ammonium persulfate ratio of 1:1. Stirring was continued for 4 h, and the resulting solution was poured directly onto a glass plate to cast the membranes. The dried membranes were crosslinked in a similar manner as before. The thickness of the membrane (60 μm) was measured by means of a screw gauge.

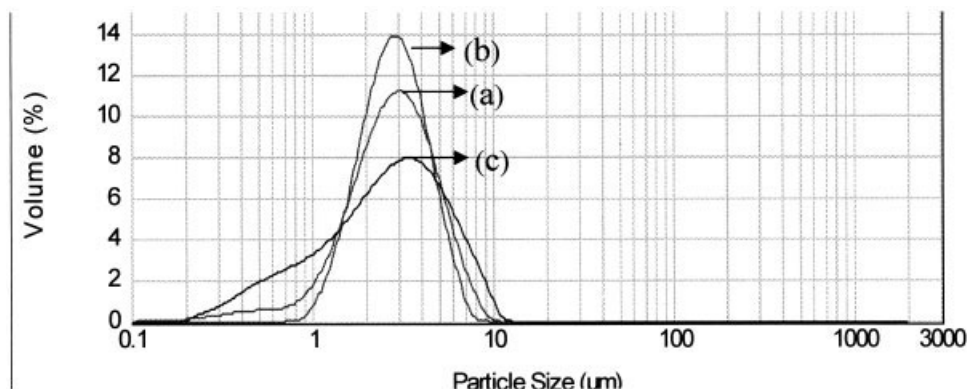
### Particle size measurement of the zeolites

The volume mean diameter and size distribution of different zeolites were measured with a particle size analyzer attached with the dry accessory system (model SCIROCCO-2000, Malvern).

### Characterization of the membranes

Fourier transform infrared (FTIR) spectroscopy

FTIR spectral measurements were performed with a Nicolet (model Impact 410) spectrophotometer to confirm the presence of zeolites in NaAlg and PANI in



**Figure 1** Particle size distribution curves of (a) ZSM-5 (40), (b) ZSM-5 (250), and (c) Na-Y zeolites.

PVA-PANI membranes. Membranes were finely ground with KBr to prepare the pellets under a hydraulic pressure of 400 kg, and spectra were scanned between 4000 and 400  $\text{cm}^{-1}$ .

#### Scanning electron microscopy (SEM)

Scanning electron micrographs of zeolite-filled NaAlg membranes were performed on a Leica Stereoscan-440 scanning electron microscope (Cambridge, UK) equipped with Phoenix energy dispersive analysis of X-rays available at the National Chemical Laboratory.

#### Differential scanning calorimetry (DSC)

Thermal analysis of the zeolite-filled NaAlg and PVA-PANI membranes were performed on a differential scanning calorimeter (model DSC SP, Rheometric Scientific, Surrey, UK). Thermograms were recorded from 25 to 400°C at the heating rate of 10°C/min under a nitrogen atmosphere.

#### X-ray diffraction (XRD)

The XRD measurements of the zeolite powder and zeolite-filled NaAlg membranes were recorded with a Rigaku Geigerflex diffractometer (Tokyo, Japan) equipped with Ni-filtered  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The dried membranes of uniform thickness were mounted on a sample holder, and the patterns were recorded in the range 0–50° at a speed of 5°/min.

#### PV experiments

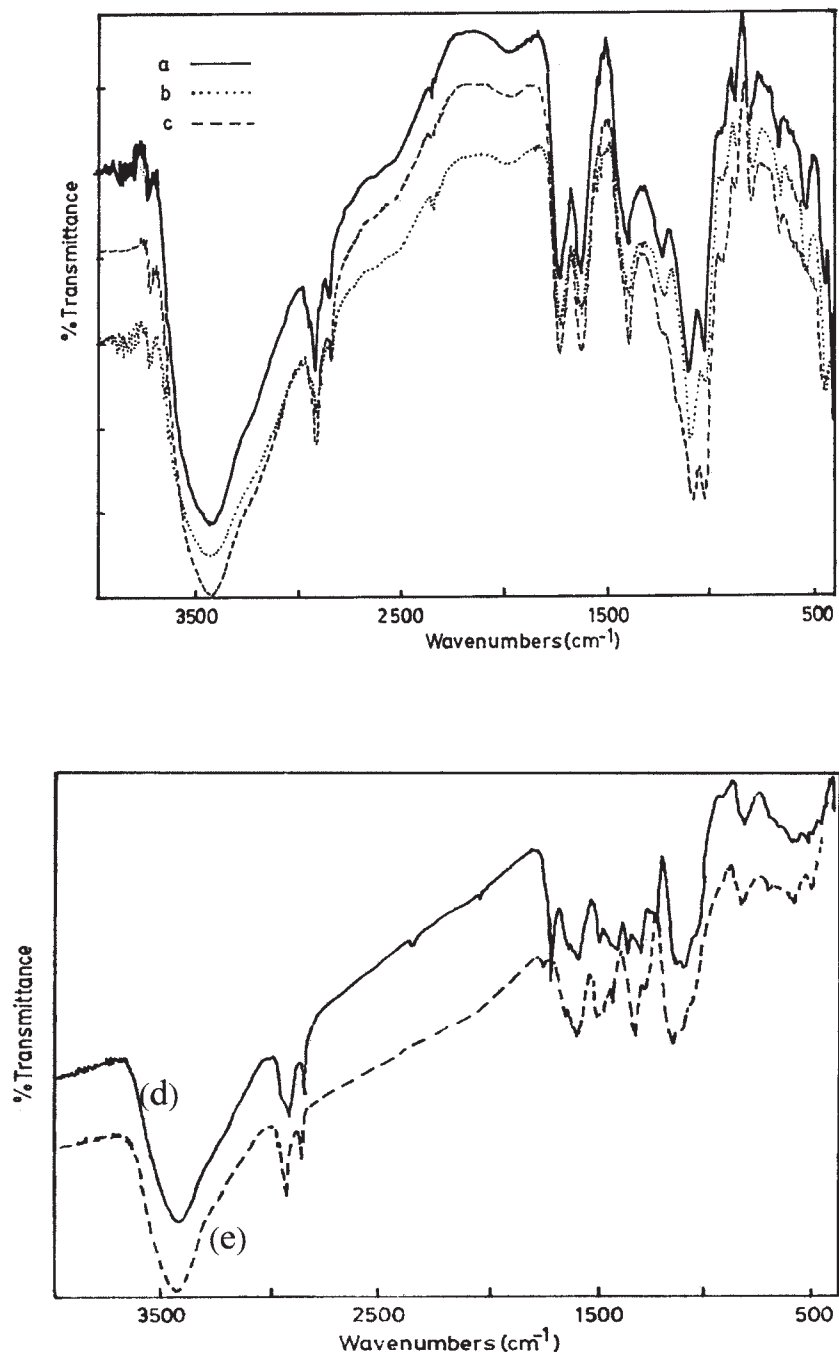
PV experiments<sup>20</sup> were performed in an apparatus consisting of a stirred stainless steel cell with an effective membrane area of 28.27  $\text{cm}^2$  and a diameter of 6.0 cm. The volume capacity of the cell was about 250 mL. The temperature of the feed mixture was maintained constant by a thermostatic water jacket. The PV cell had an efficient three-blade stirrer powered by a di-

rect-current motor in the feed compartment. Turbulent flows were obtained even at low rotation of the stirrer, that is, below 200 rpm. Mass-transfer limitations due to concentration polarization effects were negligible. The downstream side of the PV apparatus was evacuated with a vacuum pump (Toshniwal, Mumbai, India) at a pressure of less than 10 torr. The test membrane was equilibrated for 2 h with the feed mixture before the PV experiment was started. After the establishment of steady state, liquid permeate was collected in traps immersed in liquid nitrogen. The permeate was condensed in traps with liquid nitrogen. Experiments were performed for the feed mixtures ranging from 10 to 50 mass % water. Depleted water and makeup water for the next composition was enriched by the addition of the required amount of fresh water, and the mixtures were further equilibrated for 1 h. The mass of permeate in the trap was collected, and its composition was determined by the measurement of the refractive index with a Abbe refractometer (Atago, model 3T, Tokyo).

## RESULTS AND DISCUSSION

### Zeolite synthesis

ZSM-5 is a medium-pore zeolite and is unique for its high thermal and catalytic stabilities. This zeolite has a high silica ratio. The primary building units of ZSM-5 are Si/Al atoms that are tetrahedrally linked to four oxygen atoms. These primary units join to form the secondary building units, which in turn, form a linked tetrahedral structure. These tetrahedral units join through the edges to form chains. The chains are connected to form sheets, and the linking of sheets leads to the three-dimensional framework structure. The unit cell of ZSM-5 crystal is orthorhombic with the dimensions:  $a = 20 \text{ \AA}$ ,  $b = 19 \text{ \AA}$ , and  $c = 13.4 \text{ \AA}$ . As the Si/Al ratio increases, the cation density and electrostatic field strengths decrease. The affinity of the zeolite surface for nonpolar sorbates increases, as silica-rich zeolites prefer organics to water.



**Figure 2** FTIR spectra of NaAlg membranes containing (a) ZSM-5 (40), (b) ZSM-5 (250), and (c) Na-Y and (d) PVA-PANI-I semi-IPN and (e) PVA-PANI-II semi-IPN membranes.

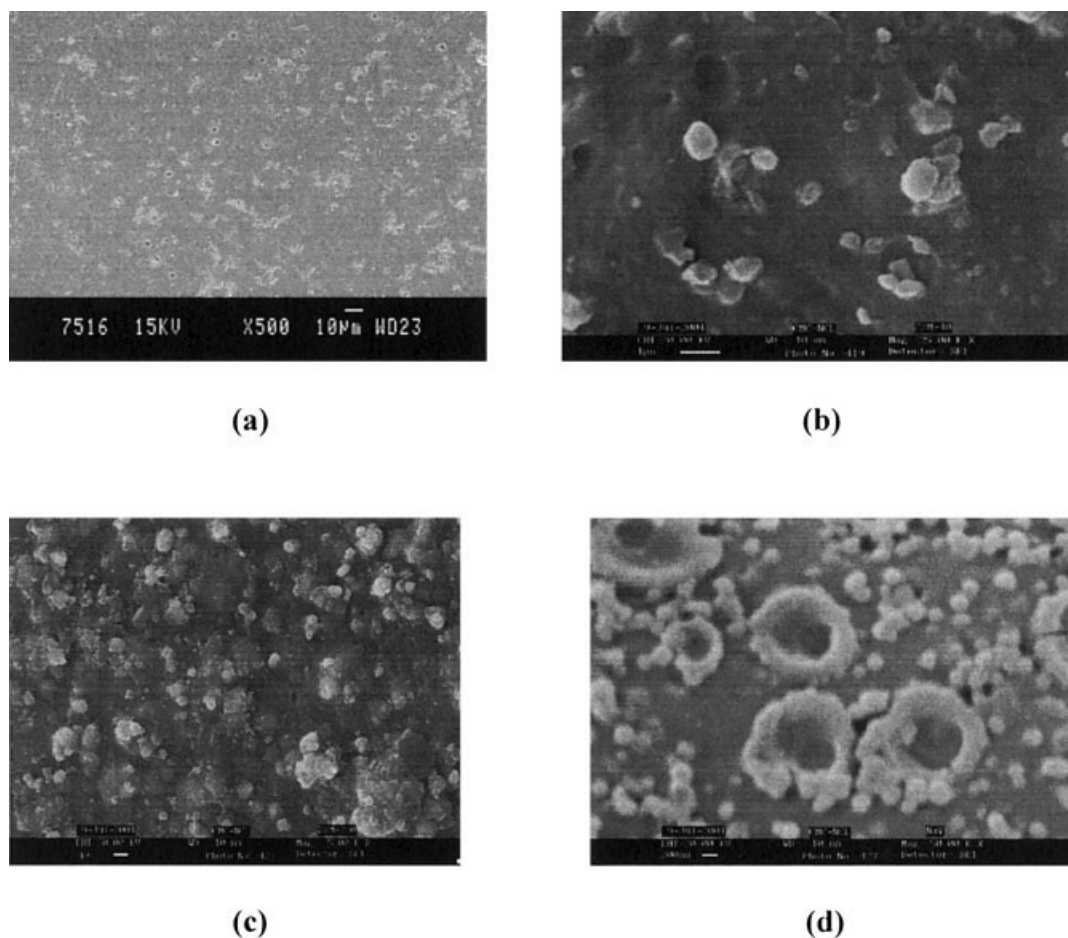
The prepared samples were of high purity, and the  $d$ -values in the XRD analysis were in good agreement with those reported. The as-synthesized sample had the most intense peak at  $2\theta = 23.2^\circ$ , whereas the peaks at  $8.05$  and  $8.95^\circ$  were relatively weak. No other change was noticed after the various thermal treatments at various stages. Na-Y type zeolites find large-scale applications in catalysis; these had  $0.74$ -nm apertures (12-membered oxygen rings) and a three-dimensional pore structure. The Na-Y zeolite was

synthesized from sodium aluminate, NaOH, and silica sol with an approximate gel composition of  $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:5.3\text{ SiO}_2:5\text{ H}_2\text{O}$ .

#### Particle size analysis

The particle size of the zeolites was useful when these zeolites were incorporated into the membranes. The particle size distribution curves of the different zeolites used in this research are displayed in Figure 1.





**Figure 3** Scanning electron micrographs of the (a) pure NaAlg membrane and the (b) ZSM-5 (40)-, (c) ZSM-5 (250)-, and (d) Na-Y-filled NaAlg membranes.

The volume mean diameters of the zeolites were ZSM-5 (40) =  $3.044\ \mu\text{m}$  [Fig. 1(a)], ZSM-5 (250) =  $3.091\ \mu\text{m}$  [Fig. 1(b)], and Na-Y =  $3.101\ \mu\text{m}$  [Fig. 1(b)]. In all of the zeolites, 50% of the particles had a diameter of less than  $2.8\ \mu\text{m}$ . In ZSM-5 (40), about 90% of particles were below  $5.3\ \mu\text{m}$ , whereas in case of ZSM-5 (250), nearly 90% of the particles were below  $4.8\ \mu\text{m}$  in size. In the case of Na-Y, 90% of the particles were less than  $6.2\ \mu\text{m}$  in size. This size range appeared to be appropriate for their incorporation into the NaAlg matrix. In this study, we incorporated 10 mass % of each zeolite (with respect to mass % of NaAlg) into the NaAlg solution and studied its effect on the PV separation characteristics of the filled membranes.

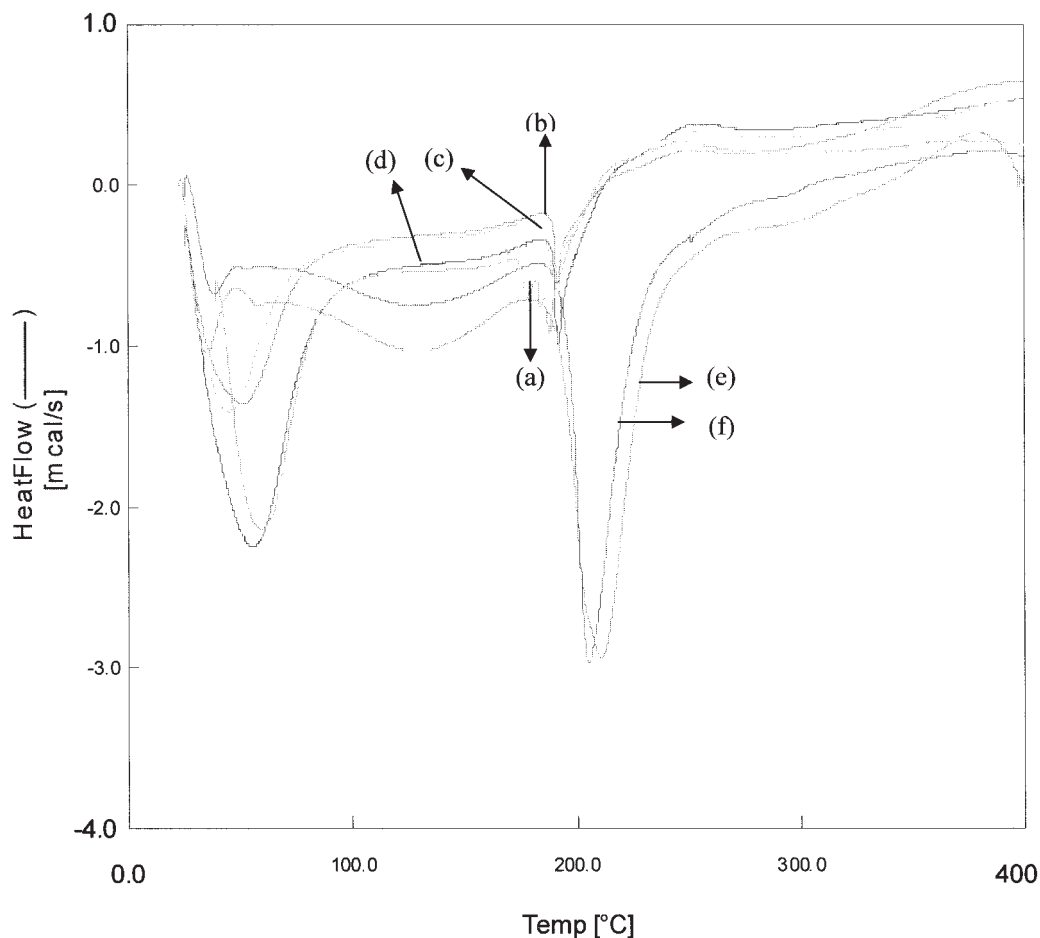
#### FTIR analysis

The FTIR spectra of the crosslinked zeolite-filled NaAlg and semi-IPNs of PVA-PANI membranes are displayed in Figure 2. In the case of zeolite-filled NaAlg membranes, the characteristic broad band appearing at about  $3442\ \text{cm}^{-1}$  corresponded to O—H stretching vibrations of the NaAlg backbone. The

sharp peaks observed around  $1628\text{--}1634$  and  $1394\text{--}1399\ \text{cm}^{-1}$  corresponded, respectively to the asymmetric and symmetric stretching of the carboxyl group of NaAlg. A sharp peak around  $1090\text{--}1101\ \text{cm}^{-1}$  corresponded to the C—O stretching of NaAlg and also for the Si—O bonds in zeolites. Peaks appeared between  $410$  and  $1000\ \text{cm}^{-1}$ , corresponding to the Al—O stretching vibrations of the zeolites. In case of the semi-IPNs of PVA-PANI, the vibrational bands observed for PANI were in accordance with literature reports on the FTIR spectra of PANI.<sup>21</sup> These data confirmed the presence of zeolite in the zeolite-filled NaAlg membranes and PANI in the PVA-PANI semi-IPN membranes.

#### SEM analysis

Figure 3 compares the surface SEM images of the zeolite-filled membranes with that of the NaAlg membrane. The zeolite-filled NaAlg membranes showed uniform molecular-level distribution. The pore size of the Na-Y-filled NaAlg membrane [Fig. 3 (d)] appeared to be much larger than those of the ZSM-5 (40)- and



**Figure 4** DSC curves for the (a) pure NaAlg membrane; the (b) ZSM-5 (40)-, (c) ZSM-5 (250)-, and (d) Na-Y-filled NaAlg membranes; and the (e) PVA-PANI-I semi-IPNs and (f) PVA-PANI-II semi-IPNs.

ZSM-5 (250)-filled membranes shown, respectively, in Figures 3(b) and 3(c).

### DSC analysis

DSC curves of all of the membranes are displayed in Figure 4. A sharp peak around 157°C indicated the crosslinking of NaAlg. A similar peak was also observed in the zeolite-filled membranes, indicating the crosslinking of NaAlg even in the presence of zeolites. However, the zeolites did not show any melting transition in the recorded range of the DSC thermogram. In the case of the PVA-PANI semi-IPN membranes, a baseline shift around 85°C and a sharp peak at 200°C indicated the glass-transition temperature and melting point of PVA, respectively. On the other hand, PANI did not show any melting transition in the studied temperature range.

### XRD

The X-ray diffractograms of the ZSM-5 (40)- and ZSM-5 (250)-filled NaAlg membranes along with the

pure zeolite are shown in Figure 5. Sharp peaks around 5–6 and 23–25° represented the crystalline nature of both of the zeolites. However, similar peaks with lesser intensity also appeared in the zeolite-filled NaAlg membranes, confirming the incorporation of the zeolites in NaAlg, but the peak intensities were somewhat lower due to the surrounding NaAlg matrix. The X-ray diffractograms of the Na-Y-filled NaAlg membrane along with pure Na-Y zeolite are displayed in Figure 6. All of the peaks match with those reported by Kita et al.<sup>22</sup> and Yeom and Lee<sup>23</sup> for the X-type crystal of the Na-Y zeolite with respect to the positions and intensities of the observed reflections, but no additional peaks were observed. Similar peaks with very low intensities also appeared for the Na-Y-filled NaAlg membranes confirmed the presence of the amorphous NaAlg matrix along with the zeolites.

### Membrane performance

According to the solution-diffusion mechanism, membrane selectivity depends on the partition of two

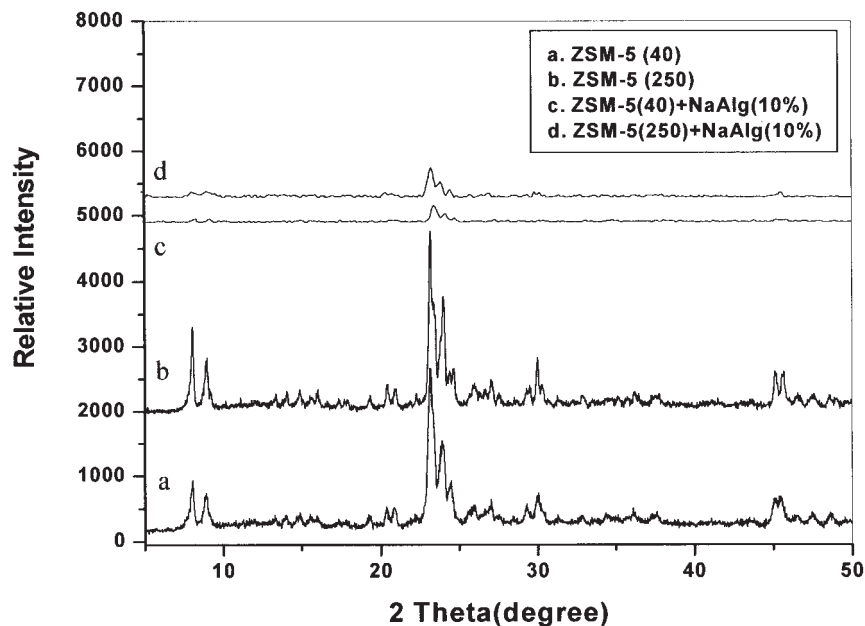


Figure 5 XRD tracings of the zeolites and zeolite-filled NaAlg membranes.

components between the feed mixture and the upstream layer of the membrane and on the difference of their diffusivities across the membrane. Several experiments have indicated that the PV separation of a dense membrane can be determined by its preferential adsorption properties.<sup>24</sup> In the case of the zeolite-filled NaAlg membrane, selectivity depended mainly on the adsorption selectivity of the zeolite. Thus, the nature of zeolite determined the membrane performance. In a previous study by Ping et al.,<sup>24</sup> the relationship between the properties of the ZSM-5 zeolite and its

performance in filled silicone rubber membranes for the extraction of alcohol was studied. The higher the Si/Al ratio was, the more hydrophobic the zeolite became, thus increasing its affinity to organics rather than water.

In this study, we have selected two ZSM-5 zeolites, namely, ZSM-5 (40), that is, a hydrophilic zeolite with an Si/Al ratio of 40, and ZSM-5 (250), that is, a hydrophobic zeolite with a Si/Al ratio of 250. The permeation of a mixture through the membrane involves (1) the transport of molecules from the bulk liquid phase

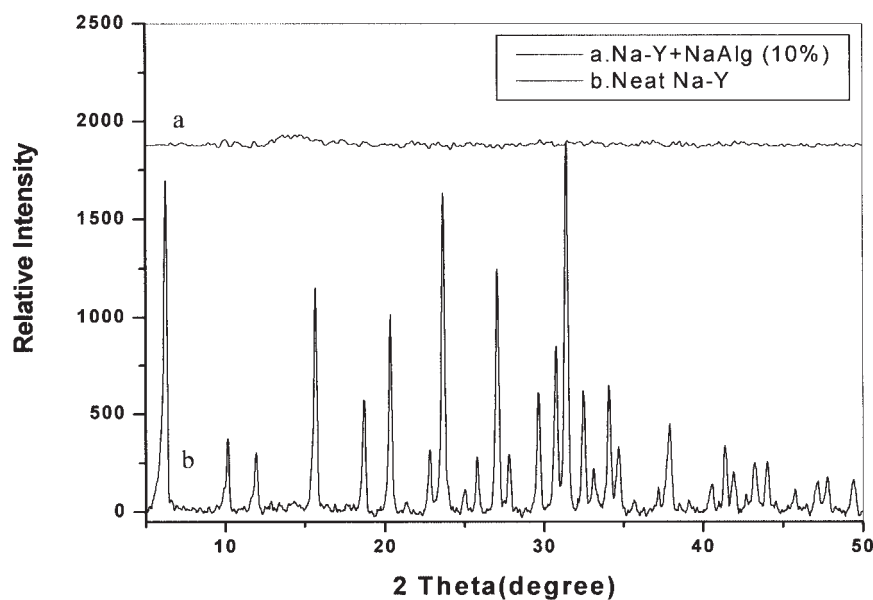


Figure 6 XRD tracings of the zeolites and zeolite-filled NaAlg membranes.

TABLE I  
Pervaporation Results of Water-ACN Mixtures for Different Membranes at 30°C

Mass % of water in feed	Total flux $\times 10^2$ (kg m <sup>-2</sup> h <sup>-1</sup> )	Water flux $\times 10^2$ (kg m <sup>-2</sup> h <sup>-1</sup> )	ACN flux $\times 10^2$ (kg m <sup>-2</sup> h <sup>-1</sup> )	Selectivity	Mass % of water in permeate	Mass % of ACN in permeate
NaAlg						
10	21.76	20.75	1.01	184.55	95.35	4.65
20	90.00	88.06	1.94	181.19	97.84	2.16
30	89.27	88.77	0.50	414.33	99.44	0.56
40	55.07	45.07	10.00	6.76	81.84	18.16
50	38.20	24.54	13.66	1.80	64.24	35.76
Na-Y (hydrophilic)-filled NaAlg membrane						
10	33.58	29.69	3.89	68.73	88.42	11.58
20	78.27	59.47	18.80	12.65	75.98	24.02
30	83.26	63.11	20.15	7.31	75.80	24.20
40	90.22	68.39	21.83	4.70	75.80	24.20
50	91.52	69.37	22.15	3.13	75.80	24.20
ZSM-5 (40) (hydrophilic)-filled NaAlg membrane						
10	29.46	27.52	1.94	127.36	93.40	6.60
20	64.41	49.79	14.61	13.63	77.31	22.69
30	257.59	166.84	90.75	4.29	64.77	35.23
40	185.62	120.23	65.39	2.76	64.77	35.23
50	214.89	137.19	77.70	1.77	63.84	36.16
ZSM-5 (250) (hydrophobic)-filled NaAlg membrane						
10	21.81	17.53	4.28	36.86	80.38	19.62
20	47.65	35.44	12.21	61.44	74.38	25.62
30	70.13	59.45	10.68	94.15	84.77	15.23
40	54.74	44.95	9.79	68.82	82.11	17.89
50	54.45	50.13	4.32	68.82	92.06	7.94
PVA-PANI-I membranes						
10	8.59	8.29	0.30	251.87	96.55	3.45
20	9.59	5.43	4.16	5.23	56.64	43.36
30	24.52	17.85	6.66	6.25	72.82	27.18
40	24.80	20.53	4.27	7.21	82.77	17.23
50	34.31	29.37	4.93	5.95	85.62	14.38
PVA-PANI-II membranes						
10	12.19	11.52	0.67	154.93	94.51	5.49
20	15.85	9.74	6.11	6.37	61.44	38.56
30	35.21	33.15	2.06	37.55	94.15	5.85
40	36.90	25.40	11.51	3.31	68.82	31.18
50	41.13	28.31	12.83	2.21	68.82	31.18

to the feed membrane interface, (2) the preferential sorption of molecules at the feed-membrane interface (upstream), (3) the diffusion of molecules through the membrane, and (4) the desorption of molecules at the membrane-permeate interface. Solubility is a thermodynamic quantity, whereas diffusivity is a mass-transfer quantity. Both solubility and diffusivity affected the membrane selectivity toward a particular component.

The membrane performance was studied by the calculation of flux ( $J_p$ ) and selectivity ( $\alpha$ ). Flux represents the permeate flow rate per unit membrane area per unit time for a given membrane thickness, which was calculated as

$$J_p = W_p / At \quad (1)$$

where  $W_p$  is the mass of permeate,  $A$  is effective area of the membrane, and  $t$  is time. Selectivity describes the ability of the membrane to separate the higher

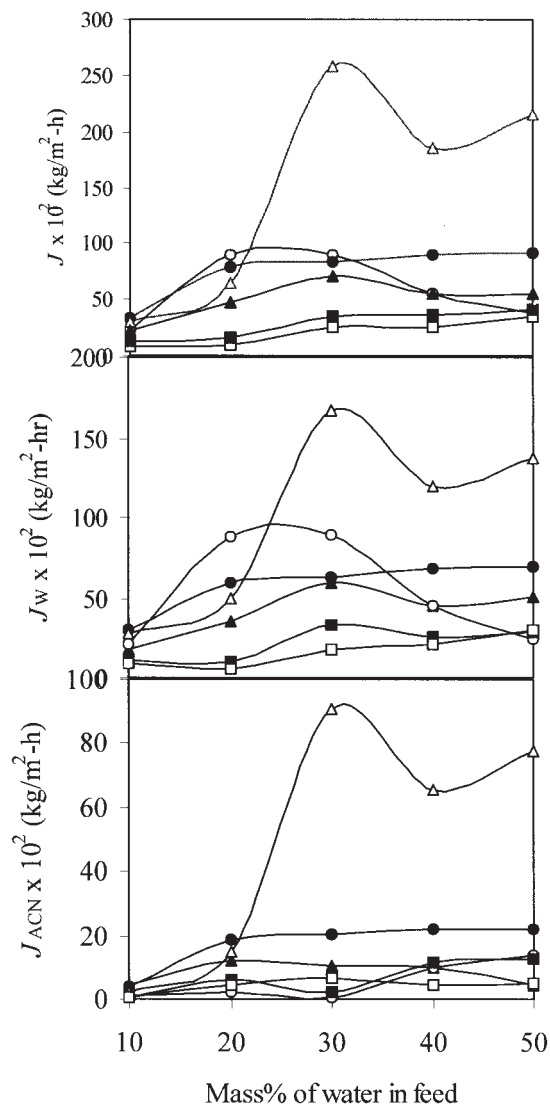
permeating component from the mixture. It was computed with the equation

$$\alpha = (P_w F_{ACN}) / (P_{ACN} F_w) \quad (2)$$

where  $P_w$  and  $P_{ACN}$  are the mass percentages of water and ACN in the permeate, respectively, and  $F_w$  and  $F_{ACN}$  are the mass percentages of water and ACN in the feed, respectively. The PV data of all of the membranes for the water composition ranging from 10 to 50 mass % in the feed are compared in Table I. Zeolites with low and medium Si/Al ratios are preferred for the dehydration of water. In this study, we varied the Si/Al ratio from 40 to 250 in the case of ZSM-5, thereby increasing its hydrophobicity.

The results of flux ( $J_{total}$ ,  $J_{water}$ , and  $J_{ACN}$ ) and selectivity versus the mass percentage of water in the feed mixture are displayed in Figures 7 and 8, respectively. For the plain NaAlg membrane, the water flux was slightly lower than the total flux but was considerably



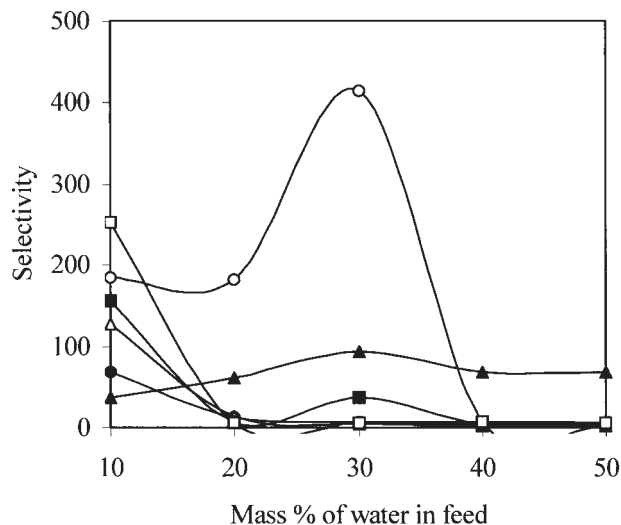


**Figure 7**  $J_{total}$ ,  $J_{water}$ , and  $J_{ACN}$  flux versus mass percentage of water in the feed at 30°C: (○) pure NaAlg, (●) Na-Y-filled NaAlg, (Δ) ZSM-5 (40)-filled NaAlg, (▲) ZSM-5 (250)-filled NaAlg, (□) PVA-PANI-I semi-IPN membranes, and (■) PVA-PANI-II semi-IPN membranes.

higher than ACN flux. This was due to the hydrophilic nature of the NaAlg membrane. Selectivity decreased after it reached a maximum of 414.33 at 30 mass % water in the feed. The mass percentage of water in the permeate was as high as 99.44%, indicating the water-selective nature of the plain NaAlg membrane. The introduction of the hydrophilic Na-Y zeolite into the NaAlg matrix has increased the water flux but with a decrease in selectivity with increasing amount of water in the feed mixture. The total flux also increased quite considerably from 0.336 to 0.915 kg m<sup>-2</sup> h<sup>-1</sup>, indicating the water-selective nature of the zeolite-filled membranes. Because both water (ca. 0.28 nm) and ACN (ca. 0.41 nm) molecules were smaller than the pore size of either Na-Y (ca. ~ 0.7 nm) or ZSM-5

zeolite (ca. ~ 0.6 nm), a molecular sieving effect due to the presence of zeolites might have played a minor role in the PV separation of water.

One could also interpret the PV results as due to the difference in either the adsorption or diffusion properties of water and ACN. Water permeation was also considerably affected by the presence of ACN molecules. Thus, when the ZSM-5 (40) hydrophilic zeolite was added to the NaAlg membrane, water flux increased significantly from 0.275 to 1.37 kg m<sup>-2</sup> h<sup>-1</sup>, whereas selectivity decreased from 127.4 to 1.8 over the studied range of water composition in the feed. This might have been due to preferential adsorption of ACN molecules, resulting in a significant number of adsorbed molecules onto the membrane polymer. On the other hand, the number of adsorbed water molecules was less than the adsorbed ACN molecules at lower compositions of water in the feed. Thus, adsorbed water molecules could diffuse faster than the adsorbed ACN molecules due to their smaller molecular size, leading to the separation of water from ACN. In addition, ACN molecules entering the zeolite pore might have hindered the diffusion of water molecules because the pores of ZSM-5 or Na-Y zeolites were not large enough in the swollen state to allow the ACN molecules to pass through. Hence, the flux for ACN was significantly smaller than that observed for the water flux in pure NaAlg and Na-Y or ZSM-5 (40) zeolite-filled NaAlg membranes. From a comparison of flux and selectivity values between ZSM-5 (40)- and ZSM-5 (250)-filled NaAlg membranes, we noted that both flux and selectivity increased, probably due to the hydrophobic nature of ZSM-5 (250), which prefer-



**Figure 8** Selectivity versus mass percentage of water in the feed mixtures for different membranes: (○) pure NaAlg, (●) Na-Y-filled NaAlg, (Δ) ZSM-5 (40)-filled NaAlg, (▲) ZSM-5 (250)-filled NaAlg, (□) PVA-PANI-I semi-IPN membranes, and (■) PVA-PANI-II semi-IPN membranes.

entially allowed more ACN molecules to permeate through than water molecules.

The PV separation characteristics of the PANI-PVA semi-IPN membranes were quite different than the NaAlg-based membranes. For instance, the flux values were quite low, which increased with increasing amount of water in the feed. On the other hand, the selectivity results were quite high (i.e., 251.87) at 10 mass % water in the feed; these values decreased considerably with increasing amount of water in the feed mixture. An increasing amount of PANI in the matrix showed a slight increase in flux with a decrease in selectivity. This was obvious due to the presence of a lesser amount of hydrophilic PVA in the membrane matrix.

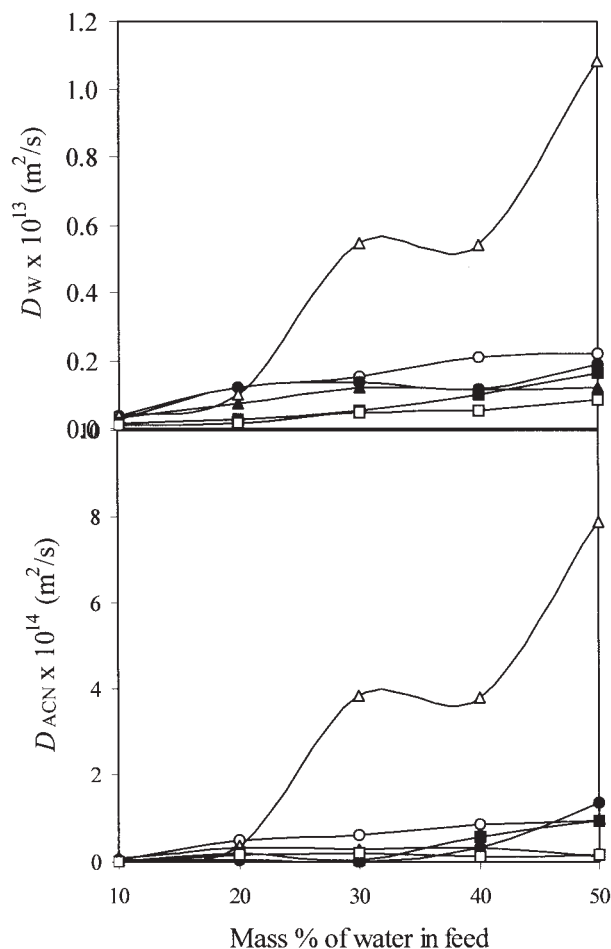
Generally, in most PV separation studies,<sup>17-20</sup> as the mass percentage of water in the feed increases, the water flux will increase. However, no regular trends of flux were observed with increasing water content in the feed for all of the membranes, indicating an unusual type of thermodynamics operative in the water-ACN mixtures. Similarly, the PV separation data for the semi-IPNs of PVA-PANI membranes exhibited no regular trends for flux with the increasing amount of water in the feed. This could again be attributed to the unusual thermodynamic behavior of the water-ACN mixtures. In the case of semi-IPNs, the water flux was always higher than the ACN flux (see Fig. 7) due to the hydrophilic nature of PVA; the flux increased with increasing aniline content in the semi-IPN membrane.

### Diffusion coefficients

Diffusion in a PV process results because of a concentration gradient. This can be explained by the solution-diffusion theory.<sup>26</sup> Describing the Fickian transport equation for PV process,<sup>27</sup> we can write

$$J_i = P_i [p_{i(\text{feed})} - p_{i(\text{permeate})}] = \frac{D_i}{h} [C_{i(\text{feed})} - C_{i(\text{permeate})}] \quad (3)$$

where  $J_i$  is flux of component  $i$ ;  $h$  is the thickness of membrane;  $C_{i(\text{feed})}$  and  $C_{i(\text{permeate})}$  are, respectively, the composition of liquids in the feed and permeate sides. Diffusion coefficients were computed as described before.<sup>28</sup> The computed values of  $D_i$  (where the subscript  $i$  stands for water or ACN) at 30°C are displayed in Figure 9. The values of  $D$  for water were higher for ZSM-5 (40) membranes than for the other membranes. This was due to the hydrophilic nature of the ZSM-5 (40) zeolite, which allowed a large number of water molecules to diffuse through the membrane. However, the  $D$  values did not show any systematic dependence on the amount of water present in the feed mixture. The  $D$  values for water were higher than those for ACN by an order of magnitude.



**Figure 9** Diffusion coefficients of water ( $D_w$ ) and ACN ( $D_{ACN}$ ) versus mass percentages of water in the feed for different mixtures: (○) pure NaAlg, (●) Na-Y-filled NaAlg, (△) ZSM-5 (40)-filled NaAlg, (▲) ZSM-5 (250)-filled NaAlg, (□) PVA-PANI-I semi-IPN membranes, and (■) PVA-PANI-II semi-IPN membranes.

### CONCLUSIONS

Separations play a major role in industrial processing operations. Of the several separation techniques, membrane-based separations are often the fastest and most energy efficient. In this study, the PV separation of a water-ACN mixture was attempted with different zeolite-filled NaAlg and semi-IPN membranes of PVA-PANI. Higher flux values were attributed to the more hydrophilic nature of the membranes. Flux values increased enormously (almost double) after the incorporation of hydrophilic zeolites in NaAlg. In case of semi-IPN membranes prepared by the addition of a higher amount of aniline, the PV performance in terms of flux and selectivity was better than for the other membranes prepared by the addition of a lower amount of aniline.

With regard to membrane selectivity toward water, the plain NaAlg membrane showed the highest selectivity at 30 mass % water in the feed compared to all

of the other membranes. Among the zeolite-filled membranes, the ZSM-5 (40)-filled NaAlg membrane showed the highest selectivity compared to other membranes at 10 mass % water in the feed. Because hydrophilicity decreased from ZSM-5 (40) to ZSM-5 (250), the membrane selectivity was also affected. Among the semi-IPN membranes, the membrane prepared with a higher amount of aniline (0.9 mL) showed more efficient PV separation characteristics than the membrane prepared with a lower amount of aniline (0.6 mL).

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