

# Pervaporation Dehydration of Isopropyl Alcohol with NaY Zeolite Incorporated Hybrid Membranes

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**ABSTRACT:** With a solution technique, NaY zeolite incorporated, tetraethylorthosilicate-crosslinked poly(vinyl alcohol) membranes were prepared. The resulting membranes were tested for their ability to separate isopropyl alcohol/water mixtures by pervaporation in the temperature range of 30–50°C. The effects of the zeolite content and feed composition on the pervaporation performance of the membranes were investigated. The experimental results demonstrated that both flux and selectivity increased simultaneously with increasing zeolite content in the membranes. This was explained on the basis of the enhancement of hydrophilicity, selective adsorption, and establishment of a molecular sieving action attributed to the creation of pores in the membrane matrix. The membrane containing 15 mass % zeolite exhibited the highest separation selectivity of 3991 with a flux of  $5.39 \times 10^{-2}$  kg/m<sup>2</sup> h with 10 mass % water in the feed at 30°C. The total flux and flux of water were close to each other for almost all the studied membranes, and this suggested that the membranes could be used effectively to break the

azeotropic point of water/isopropyl alcohol mixtures to remove a small amount of water from isopropyl alcohol. From the temperature-dependent diffusion and permeation values, the Arrhenius activation parameters were estimated. The activation energy values obtained for water were significantly lower than those for isopropyl alcohol, and this suggested that the developed membranes had a higher separation efficiency for water/isopropyl alcohol systems. The activation energy values for total permeation and water permeation were found to be almost the same for all the membranes, and this signified that coupled transport was minimal because of the highly selective nature of the membranes. Positive heat of sorption values were observed in all the membranes, and this suggested that Henry's mode of sorption was predominant. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2043–2053, 2008

**Key words:** activation energy; diffusion; membranes; selectivity; zeolites

## INTRODUCTION

The purification and concentration of isopropyl alcohol from a water solution are necessary for many chemical processes such as acetone production, solvent extraction, and the manufacture of hydrogen peroxide.<sup>1</sup> Isopropyl alcohol is also used as a cleaning agent in the modern semiconductor and electronic industries, in which the recycling of waste isopropyl alcohol is essential from both environmental and economic standpoints.<sup>2,3</sup> Unfortunately, isopropyl alcohol and water form an azeotrope at an isopropyl alcohol concentration of 85.3 mass %, <sup>4</sup> and so the separation of these mixtures by conventional

methods such as solvent extraction and rotavapor or by distillation could prove uneconomical. To overcome this difficulty, the pervaporation (PV) technique has attracted considerable attention because of its high efficiency and low cost. PV is a membrane-based separation technology used to treat multicomponent liquid solutions.<sup>5–7</sup> It is especially promising for the separation of organic liquid mixtures such as azeotropes<sup>8,9</sup> and close-boiling components.<sup>10,11</sup> Unlike distillation processes, the separation mechanism in PV is based not on the relative volatility of the components but on the difference in the sorption and diffusion properties of the feed components as well as the permselectivity of the membrane.

The successful performance of the PV process largely depends on the physical and chemical properties of the membrane material. Generally, a membrane material that contains a large number of hydrophilic groups is preferred for the dehydration process because the hydrophilic groups absorb water molecules preferentially, leading to a high flux and a high separation factor. However, the incorporation of hydrophilic groups sometimes causes the membrane to swell significantly because of its plasticizing

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action, and this reduces the selectivity. Among the hydrophilic membranes available, poly(vinyl alcohol) (PVA) is particularly attractive because of its good chemical stability and film-forming ability; unfortunately, its stability in aqueous solutions is poor. As a result, PVA needs to be made insoluble by crosslinking (or via some other modification) to get a stable membrane with good mechanical properties and selective permeability toward water. Insolubilization of PVA by crosslinking with maleic acid, glutaraldehyde, and phenylene diamine has been well documented by many investigators.<sup>12–17</sup> The resulting membranes give a better PV performance but still fail to achieve satisfactory results; the crosslinking density is too high, or at lower crosslinking density, the degree of swelling is too high. A possible solution to this problem is to introduce inorganic crosslinking segments between the linear polymer chains to improve the membrane toughness. In this way, with a minimum degree of crosslinking density, it is possible to retain a greater number of hydrophilic groups in the polymer matrix and so improve the overall PV performance. Hybrid materials based on organic and inorganic materials, ideally in a homogeneous system, have recently been investigated in a variety of fields.<sup>18–23</sup> In terms of organic–inorganic hybridization, the sol–gel method is particularly important as the starting materials may be in solution and syntheses at a low temperature are possible. Thus, we recently have successfully used this sol–gel technique to produce a hybridized organic and inorganic material with improved PV performance.<sup>4</sup>

Another efficient method for improving the PV performance is to incorporate a selective zeolite into a membrane matrix. Zeolites have a high surface area (up to 1000 m<sup>2</sup>/g), a high void volume (30% of the total volume of zeolite), and a uniform pore size distribution, and consequently, they have been used widely in chemical and physical processes such as shape-selective catalysis and separation media.<sup>24</sup> The incorporation of such zeolites into dense membranes can improve the separation performance of PV membranes<sup>24–26</sup> by virtue of the combined effects of molecular sieving action, selective adsorption, and differences in diffusion rates. In addition, zeolites have high mechanical strength and good thermal and chemical stability. Thus, the membranes into which these zeolites are incorporated can be used over a wide range of operating conditions. For instance, Gao et al.<sup>27</sup> and Chen et al.<sup>28</sup> studied the PV separation of hydrophilic zeolite-filled PVA and chitosan membranes for organic–water systems, respectively. In our previous studies, we have reported hydrophobic zeolite-filled PVA and poly(dimethylsiloxane) membranes<sup>29,30</sup> and hydrophilic zeolite-filled sodium alginate and chitosan membranes<sup>31,32</sup> for the separation of water/isopropyl alcohol mixtures. In all

the membranes except PVA, we have successfully increased both the separation factor and flux simultaneously, although this is uncommon in PV processes.

On the basis of the aforementioned results, we recently attempted to control membrane swelling by introducing an inorganic group as a crosslinker into a PVA matrix via hydrolysis followed by condensation with the sol–gel technique.<sup>33</sup> In addition, an effort was also made to enhance both the flux and the separation factor simultaneously by judicious incorporation of the NaY zeolite into a sol–gel solution. The resulting membranes demonstrated excellent performance for the separation of water/acetic acid mixtures.<sup>33</sup> This prompted us further to study these membranes for the dehydration of isopropyl alcohol/water systems at different temperatures. The values of the permeation flux, separation factor, and diffusion coefficients were evaluated. From the temperature dependence of the permeation flux and diffusion coefficients, the Arrhenius activation parameters were estimated. The results are discussed in terms of the PV separation efficiency of the membranes.

## EXPERIMENTAL

### Materials

PVA (weight-average molecular weight  $\sim$  125,000, degree of hydrolysis = 86–89%), isopropyl alcohol, and hydrochloric acid (HCl) were purchased from S.D. Fine Chemicals, Ltd. (Mumbai, India). Tetraethylorthosilicate (TEOS) was procured from E. Merck, Ltd. (Mumbai, India). NaY zeolite was kindly supplied by Indian Petrochemicals Corp., Ltd. (Baroda, India). The characteristic properties of NaY zeolite are given in Table I. All the chemicals were reagent-grade and were used without further purification. Double-distilled water was used throughout the study.

### Membrane preparation

PVA (4 g) was dissolved in 100 mL of deaerated–distilled water at 60°C. To the hot solution, 6 g of TEOS and 1 mL of concentrated HCl as an acid catalyst were added for the sol–gel reaction. The reaction mixture was stirred overnight at room temperature. The solution was then filtered with a fritted glass disc filter to remove undissolved residue particles, and the solution was left overnight so that the effervescence could be completed. The resulting homogeneous solution was spread onto a glass plate with the aid of a costing knife in a dust-free atmosphere at room temperature. After being dried for about 48 h, the membrane was subsequently peeled off and was designated M.

**TABLE I**  
**Physicochemical Properties of Hydrophilic NaY Zeolite**

Counterion	Na <sup>+</sup>
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	2.6
Density	1.27 g/mL
Pore size	0.5–2.0 μm
Pore volume	0.47 mL/g
Topology	FAU (Faujasite)
Nature	Hydrophilic

The data were taken from refs. 32–35.

To prepare the zeolite-incorporated hybrid PVA membranes, a known amount of NaY zeolite was added to the aforementioned sol–gel reaction. The mixed solution was stirred overnight at room temperature, and then it was kept in an ultrasonic bath at a fixed frequency of 38 kHz (Grant XB6, Grants Instruments (Cambridge) Ltd., Herts, United Kingdom) for about 30 min to break the aggregated crystals of zeolite and to improve the dispersion of zeolite in the polymer matrix. The rest of the procedure was followed as mentioned previously. The amount of NaY zeolite with respect to PVA was varied (5, 10, and 15 mass %), and the membranes thus obtained were designated M-1, M-2, and M-3, respectively. The resulting membranes were characterized with Fourier transform infrared spectroscopy, wide-angle X-ray diffraction, and differential scanning calorimetry, and the data thus obtained are in good agreement with results reported previously.<sup>33</sup> The thickness of these membranes was measured at different points with a Peacock dial thickness gauge (model G, Ozaki Mfg. Co., Ltd., Tokyo, Japan) with an accuracy of ±2 μm, and the average thickness was considered for calculation. The thickness of the membranes was found to be 40 ± 2 μm.

### Scanning electron microscopy (SEM)

Membranes' surfaces were observed at 15 kV with a JSM-840A scanning electron microscope (JEOL, Tokyo, Japan). All specimens were coated with a conductive layer (400 Å) of sputtered gold.

### Swelling measurements

The membrane swelling measurements were carried out with water/isopropyl alcohol mixtures of different compositions with an electronically controlled oven (WTB Binder, Tuttlingen, Germany). The masses of the dry membranes were first determined, and these were equilibrated through soaking in different compositions of the feed mixture in a sealed vessel at 30°C for 24 h. The swollen membranes were weighed as quickly as possible after careful blotting on a digital microbalance (Mettler B204-S, Mettler-

Toledo International Inc., Zurich, Switzerland) with an accuracy of ±0.01 mg. All the experiments were performed at least three times, and the results were averaged. The degree of swelling (DS) was calculated as follows:

$$DS(\%) = \left( \frac{W_s - W_d}{W_d} \right) \times 100 \quad (1)$$

where  $W_s$  and  $W_d$  are the masses of the swollen and dry membranes, respectively.

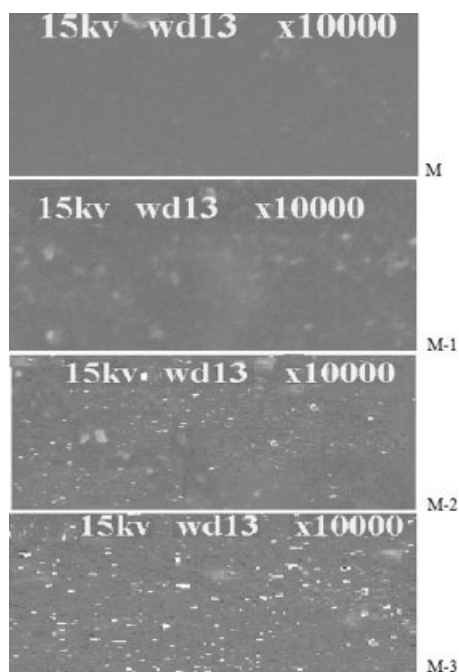
### PV experiments

PV experiments were performed with an in-house designed apparatus reported in our previous articles.<sup>4,36</sup> The effective surface area of the membrane in contact with the feed mixture was 34.23 cm<sup>2</sup>, and the capacity of the feed compartment was about 250 cm<sup>3</sup>. The vacuum in the downstream side of the apparatus was maintained [ $1.33224 \times 10^3$  Pa (10 Torr)] with a two-stage vacuum pump (Toshniwal, Chennai, India). The test membrane was allowed to equilibrate for about 2 h in the feed compartment at the corresponding temperature before the PV experiment was performed with fixed compositions of the feed mixture. After a steady state was attained, the experiments were carried out at 30, 40, and 50°C, and the permeate was collected in a trap immersed in the liquid nitrogen jar on the downstream side at fixed time intervals. The water composition in the feed mixture was varied from 10 to 90 mass %. The flux was calculated by the weighing of the permeate on a digital microbalance. The compositions of water and isopropyl alcohol were estimated by the measurement of the refractive index of the permeate with an accuracy of ±0.0001 units with an Abbe refractometer (Atago-3T, Atago Co., Ltd., Tokyo, Japan) and by comparison with a standard graph that was established with the known compositions of water/isopropyl alcohol mixtures. All the experiments were performed at least three times, and the results were averaged. The results of permeation for water/isopropyl alcohol mixtures during PV were reproducible within an admissible range.

From the PV data, the separation performance of the membranes was assessed in terms of the total flux ( $J$ ), separation selectivity ( $\alpha_{\text{sep}}$ ), and pervaporation separation index (PSI). These were calculated with eqs. (2), (3), and (4), respectively:

$$J = \frac{W}{A \times t} \quad (2)$$

$$\alpha_{\text{sep}} = \frac{P_w/P_{\text{IPA}}}{F_w/F_{\text{IPA}}} \quad (3)$$



**Figure 1** SEM photographs of hybrid membranes with and without zeolite: 0 (M), 5 (M-1), 10 (M-2), and 15 mass % (M-3).

$$PSI = J(\alpha_{sep} - 1) \quad (4)$$

where  $W$  is the mass of the permeate (kg);  $A$  is the effective area of the membrane ( $m^2$ );  $t$  is the permeation time (h);  $P_w$  and  $P_{IPA}$  are the mass percentages of water and isopropyl alcohol in the permeate, respectively; and  $F_w$  and  $F_{IPA}$  are the mass percentages of water and isopropyl alcohol in the feed, respectively.

## RESULTS AND DISCUSSION

### SEM studies

Figure 1 presents SEM photographs of surface views of the hybrid membranes with and without zeolite. The micrographs confirm that the distribution of zeolite increased from membrane M-1 to M-3 with the zeolite loading increasing. The zeolite was distributed evenly throughout the membrane matrix with no apparent clustering. This ensured that the zeolite-incorporated membranes obtained here were free from possible defects.

### Effects of the feed composition and NaY zeolite content on membrane swelling

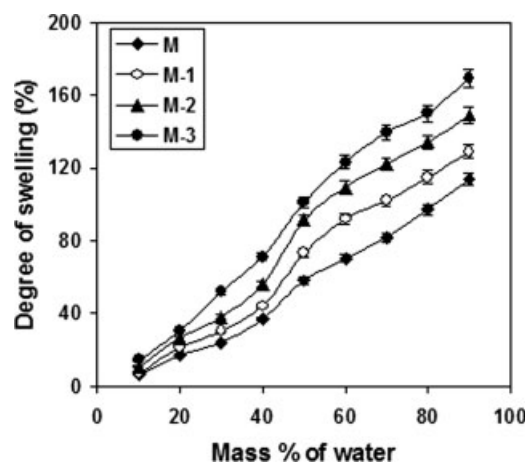
The way in which a membrane swells in certain liquids depends on the chemical composition and microstructure of the polymer (not least the crosslinking density) and the incorporated moiety, which can strongly influence the sorption mechanism.<sup>37</sup>

Thus, the degree of membrane swelling is of course an important factor in the PV process that controls the transport of permeating molecules under the chemical potential gradient.

To study the effects of the feed composition and zeolite loading on the membrane swelling, the degree of swelling (%) of all the membranes was plotted with respect to the mass percentage of water in the feed at 30°C, as shown in Figure 2. The degree of swelling increased for all the membranes as the mass percentage of water increased. This was due to a strong interaction between the water molecules and the membrane, which contained —OH groups and  $Na^+$  ions. The interaction became more marked at a higher concentration of water because water caused a greater degree of swelling than alcohols on account of its higher polarity. When the polymer matrices were filled with NaY zeolite, the degree of swelling increased with respect to the crosslinked PVA; this effect increased with increasing zeolite content. This may be due to the fact that zeolite contains  $Na^+$  ions in its channels, which tend to increase a greater electrostatic force of attraction between water molecules and the membrane. As a result, the adsorption of water molecules increases remarkably, and this in turn becomes responsible for enhanced swelling with an increase in the zeolite content in the membrane.

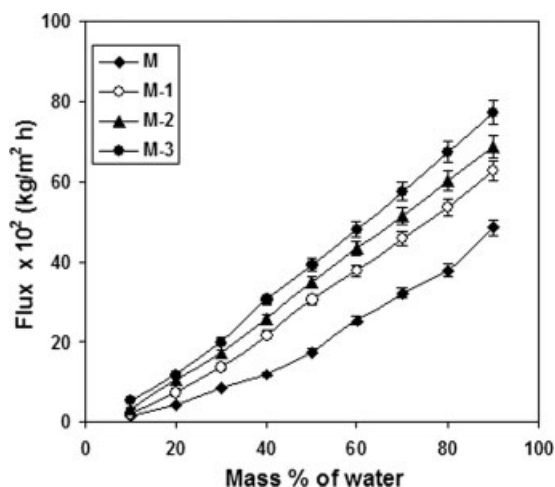
### Effects of the feed composition and NaY zeolite content on the PV properties

Figure 3 demonstrates the effects of the feed composition and zeolite loading on the total permeation flux for all the membranes at 30°C. The permeation flux increased almost linearly for all the membranes with increasing water composition in the feed in



**Figure 2** Variation of the degree of swelling with different mass percentages of water in the feed for hybrid membranes with different mass percentages of NaY zeolite incorporated.

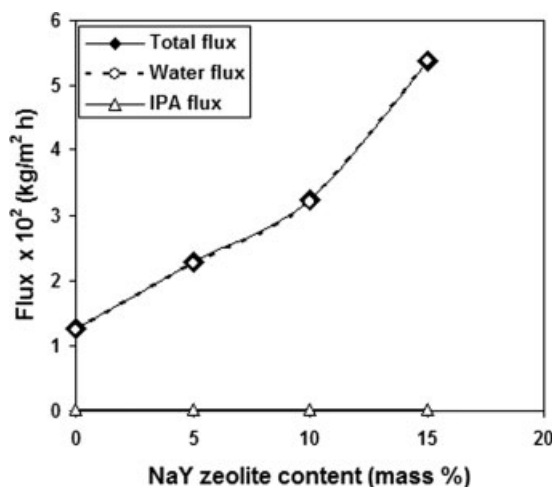




**Figure 3** Variation of the total flux with different mass percentages of water in the feed for hybrid membranes with different mass percentages of NaY zeolite incorporated.

agreement with the results observed in the swelling study. This was due to increased selective interaction between the water molecules and the membrane. However, this situation was more noticeable for the zeolite-incorporated membranes (M-1 to M-3). This was mainly attributed to the combined influence of ionic species ( $\text{Na}^+$ ) present in the zeolite cages and the establishment of pores in the membranes by the incorporation of zeolite, in addition to increased hydrophilicity. The presence of ionic species and hydrophilicity were responsible for the increase in the adsorption process, whereas the creation of pores increased the molecular sieving action, and this made the diffusion process easier.

To assess the extent of permeation of individual components, we plotted the total flux and fluxes of

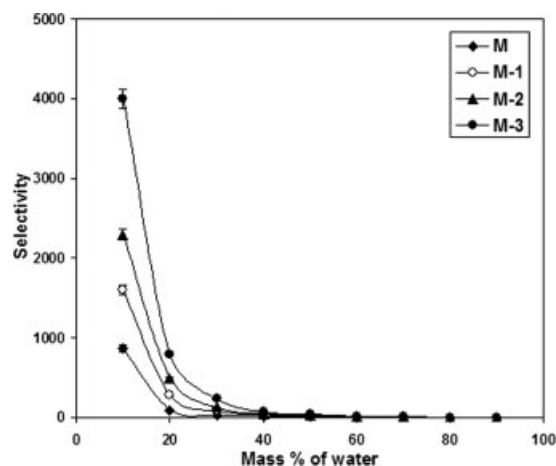


**Figure 4** Variation of the total flux and fluxes of water and isopropyl alcohol (IPA) with different mass percentages of NaY zeolite incorporated into the hybrid membranes with 10 mass % water in the feed.

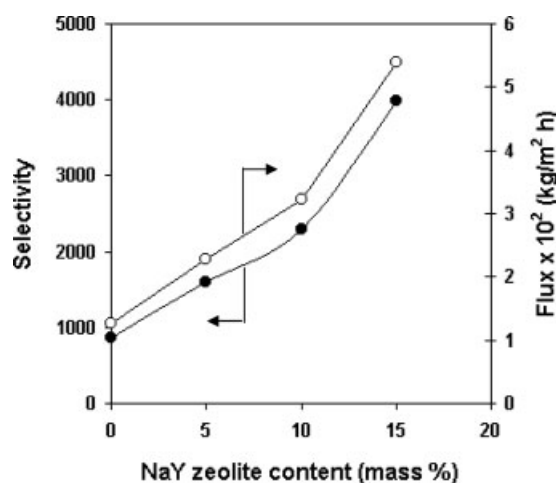
water and isopropyl alcohol as a function of the zeolite content in the membranes for 10 mass % water in the feed, as shown in Figure 4. From the plot, it is clear that the total flux and the flux of water almost overlapped each other for all the membranes, and consequently, the flux of isopropyl alcohol was negligibly small; this indicated that the membranes developed in this study by the incorporation of NaY zeolite were highly selective toward water, with a tremendous improvement in the flux in comparison with the TEOS-crosslinked PVA membrane.

In the PV process, the overall selectivity of a membrane is generally explained on the basis of the interaction between the membrane and the permeating molecules, the molecular size of the permeating species, and the pore diameter of the membrane. Figure 5 displays the effects of both the water composition and zeolite content on the selectivity. The selectivity of all the membranes decreased dramatically from 10 to 20 mass % water in the feed, and then it decreased gradually with the water concentration further increasing. At a higher concentration of water in the feed, the membranes swelled greatly because of the strong interactions between the membrane and the water molecules. This suppressed the interaction within the membrane material (i.e., between NaY zeolite and TEOS-crosslinked PVA). As a result, selectivity decreased drastically at a higher concentration of water in the feed, regardless of the amount of NaY zeolite in the membrane matrix.

In contrast to the observations cited previously, the selectivity increased significantly from membrane M-1 to M-3 with the zeolite content increasing in the membrane matrix. This can be attributed to increased selective interaction between the membrane



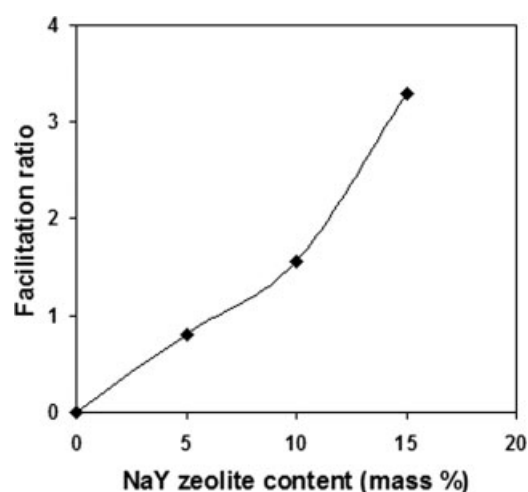
**Figure 5** Variation of the separation selectivity with different mass percentages of water in the feed for hybrid membranes with different mass percentages of NaY zeolite incorporated.



**Figure 6** Variation of the total flux and separation selectivity with different mass percentages of NaY zeolite incorporated into the hybrid membranes with 10 mass % water in the feed.

and water molecules. This can be clearly seen in Figure 6, in which the flux and selectivity are plotted as a function of the zeolite content in the membrane with 10 mass % water in the feed. Generally, as the packing density of the membrane increases, because of either an increase in the crosslinking density or the incorporation of zeolite into the membrane matrix, the permeation flux decreases and the selectivity increases.<sup>38</sup> However, in this study, both the permeation flux and selectivity increased simultaneously with increasing zeolite content in the membrane. Although this was in contrast to a trade-off phenomenon existing between the flux and selectivity in the PV process, a significant enhancement of hydrophilicity, selective adsorption, and the establishment of a molecular sieving action in the membrane matrix overcame the situation.

To understand the molecular sieving effect on the permeabilities for zeolite-incorporated membranes, we have calculated the facilitation ratio with the



**Figure 7** Variation of the facilitation ratio with different mass percentages of zeolite incorporated into the hybrid membranes with 10 mass % water in the feed.

following equation proposed by Jia et al.<sup>24</sup> with 10 mass % water in the feed:

$$(P_{z+p} - P_p)/P_p \quad (5)$$

where  $P_{z+p}$  and  $P_p$  are the permeabilities of zeolite-filled and zeolite-free membranes, respectively. The resulting facilitation ratios are presented in Figure 7. The facilitation ratio increased almost linearly with increasing zeolite content in the membrane matrix, and this indicates that the molecular sieving effect contributed significantly to the permeability. This is in good agreement with the results observed in Figures 3 and 4.

The results for the total flux and selectivity and fluxes of water and isopropyl alcohol measured at 30°C for all the membranes with the investigated feed compositions are presented in Tables II and III, respectively; there was a systematic increase in the total flux with respect to both the water composition and zeolite loading. Similarly, the selectivity

**TABLE II**  
PV Flux and Separation Selectivity Data for Different Membranes Measured at 30°C for Different Mass Percentages of Water in the Feed

Water (mass %)	PV flux ( $\times 10^2$ kg m <sup>-2</sup> h <sup>-1</sup> )				Separation selectivity			
	M	M-1	M-2	M-3	M	M-1	M-2	M-3
10	1.26	2.28	3.23	5.39	865.0	1598.0	2298.0	3991.0
20	4.18	7.54	10.38	11.88	96.0	281.7	496.0	796.0
30	8.54	13.51	17.29	20.11	33.6	81.0	127.3	231.0
40	11.92	21.86	25.85	30.37	18.5	38.0	48.5	73.5
50	17.49	30.42	35.24	39.36	10.8	24.0	28.4	37.5
60	25.42	37.72	43.66	48.14	6.8	12.9	15.2	18.9
70	32.44	45.89	51.69	57.62	4.2	6.7	8.1	9.8
80	37.98	53.74	60.12	67.47	2.3	3.6	4.4	5.1
90	48.69	62.92	68.82	77.36	1.1	1.5	1.7	2.1

**TABLE III**  
**PV Fluxes of Water and Isopropyl Alcohol for Different Mass Percentages of Water in the Feed at 30°C for Different Membranes**

Water (mass %)	PV flux ( $\times 10^2$ kg m <sup>-2</sup> h <sup>-1</sup> )							
	Water				Isopropyl alcohol			
	M	M-1	M-2	M-3	M	M-1	M-2	M-3
10	1.243	2.266	3.221	5.381	0.0129	0.0128	0.0126	0.0121
20	4.02	7.44	10.30	11.82	0.16	0.10	0.08	0.06
30	7.98	13.13	16.98	19.91	0.56	0.38	0.31	0.20
40	11.03	21.03	25.07	29.76	0.89	0.83	0.78	0.61
50	16.01	29.20	34.04	38.34	1.48	1.22	1.20	1.02
60	23.16	35.87	41.83	46.50	2.26	1.85	1.83	1.64
70	29.41	43.14	49.10	55.20	3.03	2.75	2.59	2.42
80	34.26	50.25	56.89	64.30	3.72	3.49	3.23	3.17
90	44.31	58.64	64.69	73.49	4.38	4.28	4.13	3.87

increased systematically with the amount of zeolite increasing throughout the investigated range of water compositions but decreased with respect to the water concentration. With respect to the individual fluxes, the flux of water increased from membrane M to membrane M-3, but the isopropyl alcohol flux was suppressed. This was due to an increase in the hydrophilic property of the membrane by the incorporation of zeolite. On the other hand, the flux of water increased with increasing water concentration in the feed, but the flux of isopropyl alcohol increased instead of decreasing. This presumably reflected greater swelling of the membranes at a higher concentration of water in the feed.

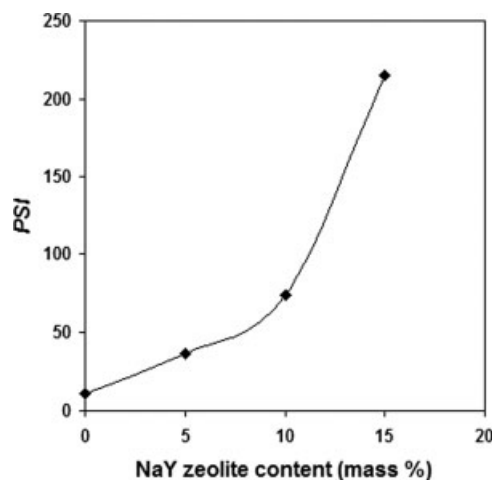
### PSI

PSI is the product of the permeation and separation factor, which characterizes the membrane separation ability. This index can be used as a relative guideline index for the design of a new membrane for PV separation processes and also for the selection of a membrane with an optimal combination of flux and selectivity. Figure 8 shows the effect of the NaY zeolite content on PSI at 30°C for 10 mass % water in the feed. The PSI values increased exponentially with increasing zeolite content, and this signified that the membranes with a higher amount of zeolite incorporated exhibited an excellent performance while separating the water/isopropyl alcohol mixtures. This was attributed to the incorporation of zeolite into the membrane matrix, which changed not only the hydrophilicity of the membranes but also their morphology, which had a significant influence on the diffusion process. Sorption was only the first step; in the second step, namely diffusion, the properties of the zeolite and its significant role in the membrane matrix enhanced the overall performance of the membrane.

On the basis of the significant performance and stability of the membranes shown in this system, we plan to use these membranes for the separation of lower alcohols such as methanol and ethanol, including other organic molecules such as tetrahydrofuran and dioxan in future studies.

### Comparison of the PV performances of the PVA-based membranes

From a thorough literature search, the flux and separation characteristics of water/isopropyl alcohol mixtures measured through PVA-based membranes during PV process are cited.<sup>27,30,38–47</sup> Only the important data are summarized in Table IV along with the data generated from this study. The separation factors of NaY zeolite incorporated, TEOS-crosslinked PVA membranes are much higher than those of other PVA-based membranes, regardless of the membrane thickness and operating temperature. The



**Figure 8** Variation of PSI with different mass percentages of NaY zeolite incorporated into the hybrid membranes with 10 mass % water in the feed.

**TABLE IV**  
**Comparison of the PV Performances of PVA-Based Membranes Reported in the Literature for Water/Isopropyl Alcohol Mixtures**

Membrane	Thickness ( $\mu\text{m}$ )	Temperature ( $^{\circ}\text{C}$ )	Water in the feed (mass %)	Flux ( $\text{kg m}^{-2} \text{h}^{-1}$ )	Separation factor	Reference
PVA/TEOS hybrid (1 : 0.25)	40	30	10	0.0350	63	4
PVA/TEOS hybrid (1 : 0.5)	40	30	10	0.0231	171	4
PVA/TEOS hybrid (1 : 1.0)	40	30	10	0.0119	424	4
PVA/TEOS hybrid (1 : 1.5)	40	30	10	0.0092	900	4
PVA/TEOS hybrid (1 : 2)	40	30	10	0.0375	120	4
Chitosan (5 wt %) incorporated PVA/TEOS hybrid	45	30	10	0.0216	1116	48
Chitosan (10 wt %) incorporated PVA/TEOS hybrid	45	30	10	0.0234	1791	48
Chitosan (15 wt %) incorporated PVA/TEOS hybrid	45	30	10	0.0239	2991	48
NaY zeolite (5 wt %) incorporated PVA/TEOS hybrid	40	30	10	0.0228	1598	This study
NaY zeolite (10 wt %) incorporated PVA/TEOS hybrid	40	30	10	0.0323	2298	This study
NaY zeolite (15 wt %) incorporated PVA/TEOS hybrid	40	30	10	0.0539	3991	This study

permeation flux values obtained from this work are also higher in comparison with most of the membranes reported. Although a few membranes have exhibited higher permeation flux in comparison with the membranes studied here, this has been achieved at the cost of separation factors of meager value.<sup>27,39–43,46</sup> This clearly reveals that the effort made to incorporate NaY zeolite into TEOS-cross-linked PVA membranes is very effective for improving the overall performance of the membranes. This is possible because of the unique properties of zeolite and its morphology. It is hoped that these investigations become a potential route for others to further increase both flux and selectivity.

#### Diffusion coefficient

The mass transport of binary liquid mixtures through a polymer membrane in the PV process is

generally described by the solution–diffusion mechanism, which occurs in three steps: sorption, diffusion, and evaporation.<sup>49</sup> Thus, the permeation rates and selectivity are governed by the solubility and diffusivity of each component of the feed mixture to be separated. In the PV process, because of the establishment of the fast equilibrium distribution between the bulk feed and the upstream surface of a membrane,<sup>11,50</sup> the diffusion step controls the transport of penetrants. Therefore, it is important to estimate the diffusion coefficient of penetrating molecules to understand the mechanism of molecular transport.

From Fick's law of diffusion, the diffusion flux can be expressed as follows<sup>51</sup>:

$$J_i = -D_i \frac{dC_i}{dx} \quad (6)$$

**TABLE V**  
**Diffusion Coefficients of Water and Isopropyl Alcohol Calculated at 30°C from eq. (7) for Different Membranes with Different Mass Percentages of Water in the Feed**

Water (mass %)	Diffusion coefficient ( $\times 10^8 \text{ m}^2/\text{s}$ )							
	Water				Isopropyl alcohol			
	M	M-1	M-2	M-3	M	M-1	M-2	M-3
10	2.50	4.57	6.51	11.0	0.096	0.095	0.094	0.090
20	4.04	7.53	10.5	12.1	1.40	0.88	0.69	0.50
30	5.37	8.89	11.5	13.5	5.29	3.61	2.97	1.92
40	5.54	10.6	12.7	15.1	9.96	9.25	8.63	6.76
50	6.44	11.8	13.8	15.5	19.9	16.3	16.0	13.7
60	7.77	12.1	14.1	15.7	37.8	30.9	30.6	27.3
70	8.46	12.5	14.2	16.0	67.2	61.4	57.6	53.9
80	8.63	12.7	14.4	16.3	125.0	117.0	109.0	106.0
90	9.90	13.1	14.5	16.5	294.0	287.0	277.0	259.0



TABLE VI  
PV Flux and Separation Selectivity at Different Temperatures for Different Membranes  
with 10 Mass % Water in the Feed

Temperature (°C)	PV flux ( $\times 10^2$ kg m $^{-2}$ h $^{-1}$ )				Separation selectivity			
	M	M-1	M-2	M-3	M	M-1	M-2	M-3
30	1.26	2.28	3.23	5.39	865	1598	2299	3991
40	2.14	4.19	5.06	5.85	141	591	891	1277
50	4.41	5.58	6.75	7.33	120	400	634	809

where  $J_i$  is the permeation flux per unit of area (kg/m $^2$  s),  $D_i$  is the diffusion coefficient (m $^2$ /s),  $C_i$  is the concentration of the permeant (kg/m $^3$ ), and  $x$  is the diffusion length (m). Subscript  $i$  stands for water or isopropyl alcohol. For simplicity, it is assumed that the concentration profile along the diffusion length is linear. Thus,  $D_i$  can be calculated with the following equation<sup>52</sup>:

$$D_i = \frac{J_i \delta}{C_i} \quad (7)$$

where  $\delta$  is the membrane thickness. The calculated values of  $D_i$  at 30°C are presented in Table V.

An inspection of Table V shows that just as with the PV study, the diffusion coefficients of water increased significantly from membrane M to membrane M-3, whereas the diffusion coefficients of isopropyl alcohol were suppressed. This further indicates that the membranes developed in this study have a remarkable separation ability with respect to water/isopropyl alcohol mixtures, particularly at the azeotropic concentration of isopropyl alcohol. As discussed previously, this has been attributed to increased hydrophilicity, selective adsorption, and the establishment of molecular sieving action by the incorporation of zeolite into the membrane matrix. However, there was a considerable increase in the diffusion coefficients for all the membranes when the amount of water in the feed was increased. This was expected because of the observed deterioration in membrane selectivity, as discussed in the PV study.

#### Effect of the temperature on membrane performance

The temperature is another important factor affecting the PV process in all the steps (sorption, diffusion, and desorption). Generally, the flux increases as the temperature increases, and the overall temperature effect on the partial flux at a fixed condition can usually be described with an Arrhenius expression. The separation efficiency of the membrane will thus be dependent on the overall activation energy of each permeant.

The effect of the operating temperature on the PV performance was studied for water/isopropyl alcohol mixtures with 10 mass % water in the feed, and

the resulting values are presented in Table VI. The permeation rate increased from 30 to 50°C for all the membranes, whereas the separation factor decreased remarkably. This was due to decreased interaction between the permeants (i.e., water and isopropyl alcohol) and between the permeants and membrane at higher temperatures, and these were the major factors in the plasticizing effect on the membrane. Therefore, the permeation of diffusing molecules and the associated molecules through the membrane became easier, and this resulted in an increase in the total permeation rate, whereas the selectivity was suppressed. Consequently, the transport of water molecules through the membrane was more prominent at a lower temperature.

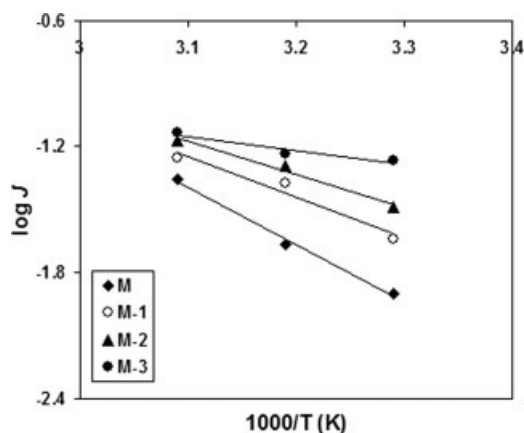
The temperature dependence of permeation and diffusion rates can be expressed with an Arrhenius-type equation<sup>53</sup>:

$$X = X_o \exp\left(\frac{-E_x}{RT}\right) \quad (8)$$

where  $X$  represents permeation ( $J$ ) or diffusion ( $D$ ),  $X_o$  is a constant representing the pre-exponential factor of  $X$ ,  $E_x$  represents the activation energy for permeation or diffusion depending on the transport process under consideration, and  $RT$  is the usual energy term. As the feed temperature increases, the vapor pressure in the feed compartment also increases, but the vapor pressure at the permeate side is not affected. All these result in an increase in the driving force with increasing temperature.

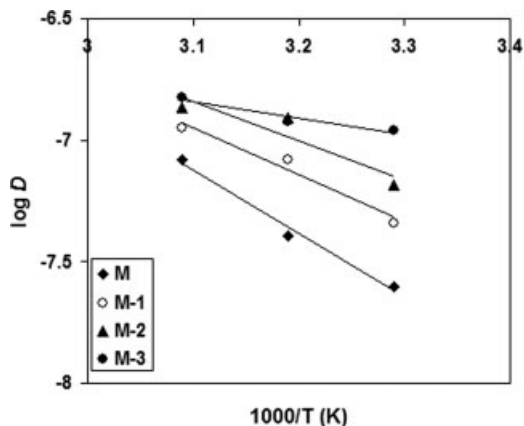
Arrhenius plots of the logarithms of the permeation flux and diffusion versus the reciprocal of the temperature are shown in Figures 9 and 10, respectively. In both cases, linear behavior can be observed, and this suggests that permeability and diffusivity follow an Arrhenius trend. From the least squares fits of these linear plots, the activation energies for permeability ( $E_P$ ) and diffusivity ( $E_D$ ) were estimated. Similarly, we also estimated the activation energies for the diffusion of water ( $E_{Dw}$ ) and isopropyl alcohol ( $E_{DIPA}$ ) and for the permeation of water ( $E_{Pw}$ ), but the plots are not given to avoid crowdedness. The values thus obtained are presented in Table VII.

Table VII shows that the TEOS-crosslinked membrane (M) exhibited higher  $E_P$  and  $E_D$  values than



**Figure 9** Variation of the logarithm of the permeation flux ( $\log J$ ) with the temperature ( $T$ ) for hybrid membranes with different mass percentages of NaY zeolite incorporated with 10 mass % water in the feed.

the zeolite-incorporated membranes (M-1 to M-3). This suggests that both permeation and diffusion processes require more energy for the transport of molecules through a crosslinked membrane (M) because of its dense nature. Obviously, zeolite-incorporated membranes take less energy because of a molecular sieving action attributed to the presence of sodalite cages and supercages in the framework of zeolite.<sup>31</sup> As a result,  $E_P$  and  $E_D$  decreased markedly from membrane M-1 to membrane M-3 with increasing zeolite content. Although the  $E_P$  values were slightly higher than the  $E_D$  values in all the membranes, the difference was insignificant, indicating that both sorption and diffusion contributed equally to the PV process. The same trend was also observed for  $E_{Pw}$  and  $E_{Dw}$  values. On the other hand, a significant difference was noticed between  $E_{Dw}$  and  $E_{DIPA}$  values. However, the difference was more significant, particularly for the membranes



**Figure 10** Variation of the logarithm of the diffusion ( $\log D$ ) with the temperature ( $T$ ) for hybrid membranes with different mass percentages of NaY zeolite incorporated with 10 mass % water in the feed.

**TABLE VII**  
Arrhenius Activation Parameters for Permeation, Diffusion, and Heat of Sorption

Parameter (kJ/mol)	M	M-1	M-2	M-3
$E_P$	51.06	36.60	30.02	12.45
$E_D$	48.61	36.52	29.97	12.42
$E_{Pw}$	48.51	35.92	29.60	12.09
$E_{Dw}$	48.91	36.38	29.86	12.35
$E_{DIPA}$	120.14	92.57	82.32	77.37
$\Delta H_S$	2.45	0.08	0.05	0.03

having a higher loading of zeolite, suggesting that membranes developed with a higher loading of zeolite exhibited remarkable selectivity toward water.

The  $E_P$  and  $E_D$  values ranged from 12.45 to 51.06 kJ/mol and from 12.42 to 48.61 kJ/mol, respectively. Using these values, we have further calculated the heat of sorption ( $\Delta H_S$ ) as follows:

$$\Delta H_S = E_P - E_D \quad (9)$$

The resulting  $\Delta H_S$  values are also included in Table VII. The  $\Delta H_S$  values give additional information about the transport of molecules through the polymer matrix. It is a composite parameter involving contributions from Henry's type of sorption and Langmuir's type of sorption.<sup>54</sup> Henry's mode requires both the formation of a site and the dissolution of chemical species into that site. The formation of a site involves an endothermic contribution to the sorption process. In the case of Langmuir's mode, the site already exists in the polymer matrix, and consequently, sorption occurs by a hole-filling mechanism, making an exothermic contribution. However, the  $\Delta H_S$  values obtained in this study are positive for all the membranes, but the magnitude is quite small for zeolite-incorporated membranes (M-1 to M-3). This indicates that the amount of zeolite incorporated into crosslinked PVA membranes was not enough to create sufficient sites in the membrane matrix, and so Henry's type of sorption still predominated, making an endothermic contribution.

## CONCLUSIONS

NaY zeolite was incorporated into a hybrid membrane that was prepared with PVA and TEOS through hydrolysis followed by a cocondensation reaction. Zeolite-incorporated membranes exhibited a significant improvement in the performance while separating water/isopropyl alcohol mixtures. An increase of zeolite in the membrane matrix resulted in a simultaneous increase of both the permeation flux and selectivity. This was attributed to a significant enhancement of the hydrophilic character, selective adsorption, and the establishment of a molecular

sieving action. While assessing the membrane's efficiency, we found that the total flux and flux of water overlapped each other, and this suggested that the membranes developed in this study by the incorporation of zeolite were particularly selective toward water. The PV separation index data also indicated that the higher the zeolite loading was, the better the membrane performance was. The highest separation selectivity was found to be 3991 with a flux of  $5.39 \times 10^{-2}$  kg/m<sup>2</sup> h for the membrane having the highest loading of zeolite at 30°C for 10 mass % water in the feed. With respect to temperature, the permeation rate increased although the selectivity was suppressed with increasing temperature. This was attributed to decreased interaction between the permeants and between the permeants and membrane at higher temperatures.

The  $E_P$  and  $E_D$  values ranged from 12.45 to 51.06 kJ/mol and from 12.42 to 48.61 kJ/mol, respectively. The zeolite-incorporated membranes exhibited significantly lower activation energies than a hybrid membrane, and this indicated that the permeants consumed less energy during the process; this was a result of a molecular sieving action in the membrane matrix due to the presence of sodalite and supercages in the framework of zeolite. For all the membranes, Henry's mode of sorption apparently dominated the process, making an endothermic contribution.

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