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Pervaporation Separation of Water–Isopropanol Mixtures Using ZSM-5 Zeolite Incorporated Poly(vinyl alcohol) Membranes


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ABSTRACT: A solution technique was employed to prepare ZSM-5 zeolite incorporated poly(vinyl alcohol) (PVA) membranes for the pervaporation separation of water-isopropanol mixtures. The membranes were characterized by Fourier transform infrared spectroscopy and differential scanning calorimeter. Glass transition temperatures of the membranes varied from 102 to 110°C, with increasing zeolite content of the membrane. The effect of zeolite loading and feed composition on pervaporation performance of the membranes was analyzed. The membrane containing 6 mass % of zeolite gave the highest separation selectivity of 216 for 10 mass % of water containing feed mixture at 30°C. Increase in water selectivity of the membrane was explained as due to a reduction in free volume by increasing zeolite content of the membrane. Separation selectivity and permeation flux data are dependent on water composition of the feed mixture, but are comparatively less dependent on temperature. The hindrance of water permeation at higher composition of water in the feed mixture was explained as due to the formation of clusters of water molecules. The overall activation energy and preexponential factors were calculated using Arrhenius equation. Pervaporation data have also been explained on the basis of thermodynamic parameters calculated by using Arrhenius equation as well as relationship proposed by Ping et al. © 2003 Wiley Periodicals, Inc J Appl Polym Sci 90, 2441–2448, 2003

Key words: separation techniques, membranes, zeolites; selectivity, activation energy

INTRODUCTION

Among the many aqueous–organic mixtures, separation of water from its mixture with isopropanol is a challenging task, because the system forms an azeotrope at 14.7 mass % of water; hence, its separation by conventional distillation is not feasible. In contrast, the pervaporation (PV) separation technique, being energy efficient, has been used widely to separate water–isopropanol mixtures. However, flux and selectivity of these membranes were not satisfactory. In an effort to increase the flux and selectivity of the membranes, many studies have been made to incorporate metal complexes and zeolites in the membranes. The zeolite-incorporated polymer membranes have received much attention recently in gas and PV separation studies. The incorporation of zeolite or porous fillers in dense membrane can improve the separation performance of the membranes due to combined effect of molecular sieving action, selective adsorption, and difference in diffusion rates. In addition, zeolites have high mechanical strength, good thermal and chemical stability, and thus, the membranes, when incorporated with these fillers, can be used over the wide range of operating conditions.

Silicalite and ZSM-5 zeolites having the MFI-type structures have been widely studied in membrane applications. Silicalite is a pure silica zeolite having straight channels interconnected by zigzag channels. The straight channels in ZSM-5 zeolite are elliptical, with an opening of 0.51 × 0.37 nm, and the
water and isopropanol mixtures for 24 h at 30°C using an electronically controlled oven (WTB Binder, Germany). The masses of the dry membranes were first determined. The dry membranes were equilibrated by soaking in different composition of the mixture in a sealed vessel, at 30°C for 24 h and then the swollen membranes were weighed immediately after careful blotting on a single pan digital microbalance (Mettler, AE240, Switzerland) having a sensitivity of ±0.01 mg. The % degree of swelling (DS) was calculated as:

$$DS(\%) = \left( \frac{W_s - W_d}{W_d} \right) \times 100$$ (4)

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

Fourier transform infrared (FTIR) spectroscopy
Dispersion of different amounts of ZSM-5 zeolite in the PVA matrix was confirmed by FTIR (Nicolet, Impact 410, USA). Polymer samples were ground well to make KBr pellets under a hydraulic pressure of 600 kg and spectra were recorded in the range of 400–4000 cm\(^{-1}\).

Differential scanning calorimeter
Thermal properties of the membranes were measured using differential scanning calorimeter (Stanton, Rederoff DSC1500) at a heating rate of 10°C/min.

Wide-angle X-ray diffraction (WAXD)
Morphologies of the PVA membranes under different loadings of zeolite were studied at room temperature using a Brucker's D-8 advanced wide-angle X-ray diffractometer. The X-ray source was Ni-filtered Cu-K\(\alpha\) radiation (40 kV, 30 mA). The dried membranes of uniform thickness (~40 \(\mu\)m) were mounted on a sample holder and the X-ray tracings were recorded in the range of 5–45° at a speed of 8° per min.

RESULTS AND DISCUSSION
Membrane characterization

FTIR studies
FTIR spectra of the crosslinked PVA membrane and those of different amounts of ZSM-5 zeolite loaded membranes are given in Figure 1. A characteristic strong and broad band appearing at around 3040 cm\(^{-1}\) corresponds to O–H stretching vibrations of the hydroxyl group of PVA. On the other hand, peak intensity of the zeolite-loaded samples did not change, indicating that hydroxyl groups of PVA are not involved in any chemical reaction with the zeolites. A sharp intense band appearing at around 1100 cm\(^{-1}\) is assigned to Si–O stretching,\(^18\) and the multiple bands appearing between 447 and 1000 cm\(^{-1}\) are assigned to the stretching of Al–O vibrations\(^19\) due to the presence of zeolite. The intensity of these bands increased further with increasing the amount of zeolite in the membranes, which ascertains the complete dispersion of zeolite in the crosslinked PVA membranes.

X-ray diffraction studies
X-ray diffraction patterns of the membranes are presented in Figure 2. The crosslinked PVA membrane (M) exhibits a typical peak that appeared at 2\(\theta\) = 20°, which is almost similar to pure PVA membrane pattern\(^1\) even though the membrane was crosslinked with very small quantity of GA. A small quantity of GA did not influence on the existing state of pure PVA membrane. Thus, it can be assigned to be a mixture of (101) and (200).\(^20\) The X-ray diffraction patterns of the membranes (M-1 to M-3) show that as the loading of zeolite increased, peak intensity of the crosslinked PVA membranes decreased at around 2\(\theta\) = 20°. This revealed that the relative crystallinity of PVA crosslinked membranes decreased with increasing loading of the zeolite. An additional peak has appeared as the zeolite content was increased at around 2\(\theta\) = 23 degree. This is due to the presence of ZSM-5 zeolite in the membranes, whose intensity further increased as the zeolite content increased in the membranes from M-1 to M-3.
Effect of feed composition on pervaporation properties

The effect of water composition on the total permeation flux, flux of water, and isopropanol is shown in Figure 5(A), (B), and (C). It is observed that permeation flux increased with increasing the amount of water in the feed mixture, reaching a maximum at around 30 mass % of water, and then it decreased steeply with further increase of water composition in the feed. A similar behavior is observed for the individual components viz., water and isopropanol, as seen in Figure 5(B) and (C), respectively. Such a decreasing tendency after attaining a maximum value is due to the hindrance in permeating process occurred in the membrane owing to the formation of water clusters. At higher water contents in the feed, clustering of water molecules will be more, and cluster size might continue to increase with increasing amount of water content in the feed.23-25 On the other hand, selectivity as shown in Figure 6 decreased drastically up to 20 mass % of water, and then it remains constant over the entire composition of water in the feed mixture, showing not much variation beyond 20 mass % in the feed with the varying amounts of zeolite in the membranes.

Effect of zeolite loading on membrane swelling

Figure 7 displays the effect of zeolite loading on degree of swelling for 10 mass % of water in the feed mixture. It is found that degree of swelling decreased with increasing the amount of zeolite loading. This decrease may be due to the fact that flexibility of the polymer chains in the zeolite-filled membranes might have decreased with increasing amount of zeolite in the membrane. In addition, the hydrophilic nature of the membranes reduced from M-1 to M-3 due to the presence of zeolite, which is hydrophobic in nature. The results of $T_g$ also indicated that zeolite-filled membranes have a rigid structure due to reduction in free volume upon increasing the zeolite loading.

### Table II

<table>
<thead>
<tr>
<th>Mass % water</th>
<th>$J_{W}$ $10^2$ (kg/m²h)</th>
<th>$J_{IPA}$ $10^2$ (kg/m²h)</th>
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<tbody>
<tr>
<td></td>
<td>M-1</td>
<td>M-2</td>
</tr>
<tr>
<td>10</td>
<td>0.41</td>
<td>0.30</td>
</tr>
<tr>
<td>20</td>
<td>1.47</td>
<td>1.28</td>
</tr>
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<td>30</td>
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<td>40</td>
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</tr>
<tr>
<td>50</td>
<td>1.24</td>
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TABLE IV
Diffusion Coefficients of Water and Isopropanol Calculated at Different Temperatures for 10 Mass % of Water in the Feed Mixture for Different Membranes

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$D_w10^6$ (cm$^2$/s) M-1</th>
<th>$D_w10^6$ (cm$^2$/s) M-2</th>
<th>$D_w10^6$ (cm$^2$/s) M-3</th>
<th>$D_{IPA}10^6$ (cm$^2$/s) M-1</th>
<th>$D_{IPA}10^6$ (cm$^2$/s) M-2</th>
<th>$D_{IPA}10^6$ (cm$^2$/s) M-3</th>
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<tr>
<td>30</td>
<td>0.709</td>
<td>0.500</td>
<td>0.705</td>
<td>0.069</td>
<td>1.667</td>
<td>1.628</td>
</tr>
<tr>
<td>40</td>
<td>1.400</td>
<td>1.000</td>
<td>0.877</td>
<td>0.022</td>
<td>0.182</td>
<td>0.067</td>
</tr>
<tr>
<td>50</td>
<td>1.903</td>
<td>1.755</td>
<td>1.580</td>
<td>0.025</td>
<td>0.258</td>
<td>0.215</td>
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</table>

The temperature dependence of total permeation flux or diffusivity follows the Arrhenius trend. The apparent activation energy values calculated from the slopes of the straight lines of the Arrhenius plots by the least squares method and the

$$D_i = D_0 \exp \left( -\frac{E_0}{RT} \right) \tag{6}$$

Here, $E_0$ is the energy of activation for diffusion, and $i$ stands for water or isopropanol components of the mixture. The least square estimations of $E_0$ values are calculated using the values given in Table IV.

Arrhenius plots of $\log J_p$ vs. $1/T$ and $\log D_i$ vs. $1/T$ are shown in Figures 10 and 11(A) and (B) for temperature dependence of total permeation and diffusion, respectively. In all the cases, linear behavior is observed, signifying that temperature dependence of total permeation flux or diffusivity follows the Arrhenius trend. The apparent activation energy values ($E_p$ and $E_d$ for permeation and diffusion, respectively) calculated from the slopes of the straight lines of the Arrhenius plots by the least squares method and the

$$Y_w = \frac{1}{1 + (J_{IPA}/J_w)\exp(-E_{IPA} - E_w)/RT} \tag{7}$$

where $Y_w$ is water composition in the permeate, $J_w$ and $J_{IPA}$ are the permeating flux of water and isopropanol, respectively, $E_w$ and $E_{IPA}$ are the Arrhenius activation energies for diffusion of water and isopropanol, respectively, at the average energy level. The positive value of $(E_{IPA} - E_w)$ indicates that $\alpha_{sep}$ decreases with an increase in temperature. In the present study, calculated values are positive for all the membranes.

TABLE V
Arrhenius Activation Parameters for Permeation, Diffusion, and Heat of Sorption and Energy Difference Values for Water

<table>
<thead>
<tr>
<th>Parameters</th>
<th>M-1</th>
<th>M-2</th>
<th>M-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_p$ (kJ/mol)</td>
<td>-38.79</td>
<td>-42.77</td>
<td>-42.47</td>
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<td>$E_d$ (kJ/mol)</td>
<td>40.37</td>
<td>47.41</td>
<td>46.44</td>
</tr>
<tr>
<td>$\Delta H$ (kJ/mol)</td>
<td>-79.16</td>
<td>-90.17</td>
<td>-88.91</td>
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<tr>
<td>$E_{IPA} - E_w$ (kJ/mol)</td>
<td>90.20</td>
<td>154.40</td>
<td>145.76</td>
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</table>
Development of novel pervaporation membranes for the separation of water–isopropanol mixtures using sodium alginate and NaY zeolite

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Abstract

Using solution technique, NaY zeolite-incorporated sodium alginate (SA) membranes were prepared and were subjected for the pervaporation separation of water–isopropanol mixtures. The resulting membranes were characterized by Fourier transform infrared spectroscopy, wide-angle X-ray diffraction and differential scanning calorimetry. The effects of zeolite loading and feed composition on the pervaporation performance of the membranes were analyzed. Both flux and selectivity increased simultaneously with an increase of zeolite content in the polymer matrix. This was explained on the basis of enhancement of hydrophilicity, selective adsorption and molecular sieving action including reduction of pore size of the membrane matrix. The membrane containing 30 mass% of zeolite shows the highest separation selectivity of 14.33 with a flux of 1.45 × 10⁻² kg/m² h for 5 mass% of water in the feed mixture at 30 °C. The total flux and flux of water are found to be almost close to each other throughout the investigated range, suggesting that the membranes developed are highly water selective. From the temperature-dependent diffusion and permeation values, the Arrhenius activation parameters have been estimated. The resulting low activation energy values obtained for zeolite-incorporated membranes contribute to the superior performance of the PV process.

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Keywords: Separation techniques, Membranes, Zeolite, Selectivity, Activation energy

Introduction

Pervaporation (PV) is a membrane-based process in which the feed mixture is maintained at the atmospheric pressure on the upstream side of the membrane, while the permeate is collected as a vapor because of a low vapor pressure existing on the downstream side. This low (partial) vapor pressure can be achieved by employing a carrier gas using a vacuum pump. The (partial) downstream pressure must be at least lower than the saturation pressure. The chemical potential gradient across the membrane is the driving force for the molecular transport. The PV process, when compared to distillation techniques with which it often competes industrially, is considered to be a less energy-intensive unit process and, hence, it becomes an emerging technology in chemical process industries, finding applications in the separation of azeotropic mixtures [1,2], close boiling components [3–5] and isomeric mixtures [6].

Isopropanol has been widely used in semiconductor and liquid crystal display industries as a water removing agent, and which forms an azeotrope at 14.7 mass% of water concentration [7]. Hence its separation by conventional distillation other than the PV process is not feasible. The successful performance of PV processes largely depends on the physical and chemical properties of the membrane material. Generally, the membrane material that contains a large number of hydrophilic groups is preferred for the dehydration process. Hydrophilic groups absorb water molecules preferentially, leading to high flux and separation factor. However, the incorporation of hydrophilic groups sometimes swells the membrane significantly due to its plasticizing action, resulting in low selectivity. Among the hydrophilic membranes, sodium alginate, which is one of the polysaccharides extracted from seaweed, is found to have an excellent performance as a membrane material for the pervaporation dehydration [8,9]. However, a very high hydrophilicity of sodium
In the above equations, $W$ is the mass of permeate (kg), $A$ the effective membrane area (m$^2$), $t$ the permeation time (h); $P$ and $F$ the mass percent of the permeate and feed, respectively, subscripts $w$ and IPA denote water and isopropanol, respectively.

2.4. Swelling measurements

The degree of membranes swelling was carried out with different compositions of water–isopropanol mixtures using an electronically controlled oven (WTB Binder, Germany). The masses of the dry membranes were first determined. The dry membranes were equilibrated by soaking in different composition of the feed mixture in a sealed vessel at 30°C for 24 h. The swollen membranes were weighed immediately after careful blotting on digital micro-balance (Mettler, B204-S, Toledo, Switzerland) having a sensitivity of ±0.01 mg. The percent degree of swelling (DS) was calculated as

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

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

2.5. Fourier transform infrared (FTIR) spectroscopy

Incorporation of different amounts of NaY zeolite in sodium alginate matrix was confirmed by FTIR (Nicolet, Impact-410, USA). Membrane samples were ground well to make KBr pellets under a hydraulic pressure of 600 kg and spectra were recorded in the range of 400–4000 cm$^{-1}$.

2.6. Differential scanning calorimetry

Thermal properties of the zeolite-incorporated membranes were measured using differential scanning calorimeter (Stanton, Rederoff DSC 1500). The sample weight ranged from 5 to 8 mg and they were heated from ambient temperature to 200°C at the heating rate of 10°C/min. The intercept point of the slopes was taken as the glass transition temperature ($T_g$).

2.7. Wide-angle X-ray diffraction (WAXD)

Crystallinity of the sodium alginate membranes was studied under different loadings of zeolite at room temperature using a Brucker's D-8 advanced wide-angle X-ray diffractometer. The X-ray source was Ni-filtered Cu Kα radiation (40 kV, 30 mA). The dried membranes of uniform thickness (~40 μm) were mounted on a sample holder and the patterns were recorded in the range of 5–45° at a speed of 8°/min.
in the polymer matrix upon increasing the zeolite loading.

Generally, a decrease in free-volume leads to an increase in selectivity and a decrease in permeation flux. But, in the present study, it is observed that with the increase of the zeolite loading, both selectivity and permeation flux also increased significantly from membrane M-1 to M-3 (see Fig. 10). These observations suggest that after incorporating a large amount of zeolite into the membrane matrix, the packing density of the polymer increased apart from increasing hydrophilicity, selective adsorption and molecular sieving action, which are, in turn, responsible for the enhancement of both separation selectivity and permeation flux simultaneously.

3.2 Effects of feed composition and zeolite loading on membrane swelling

It has been realized since the pioneering work of Flory and Rehner reported in the early 1950s [28,29] that, polymer swelling in an aggressive media depends on the extent of crosslinking, morphology of the polymer and the free-volume available within the polymer matrix. In PV experiments, membrane swelling also controls the transport of permeating molecules under the chemical potential gradient. When the polymer matrixes are filled with highly symmetrical zeolite particles, it is likely that the pores of the membranes might be occupied by the zeolite particles.

In an effort to study the effect of feed composition on the membrane swelling, the percent degree of swelling was plotted as a function of different mass% of water in the feed mixture at 30 °C as shown in Fig. 5. It is observed that the degree of swelling increased almost linearly with increasing mass% of water in the feed. This is due to an increase of strong interaction offered by hydroxyl and COO⁻ groups of SA with the water molecules. The interaction becomes more and more predominant when the water concentration is increased in the feed, since water causes a greater degree of swelling than those of alcohols with the SA membrane.
With increasing zeolite content in the membrane, generally, with increasing packing density of the membrane either by increasing the crosslinking density or incorporating the zeolite in the polymer matrix, the permeation flux decreases and selectivity increases [12,13,30]. But in the present study, both the permeation flux and selectivity increased simultaneously with increasing packing density. Although, it is in contrast to the trade-off phenomenon frequently observed between flux and separation factors in PV experiment, a significant enhancement of hydrophilicity, selective adsorption and molecular sieving action overcome the situation by introducing porous zeolite containing ionic particles in the membrane matrix.

Calculated results of total flux and selectivity, fluxes of water and isopropanol, measured at 30 °C for different compositions of feed with respect to zeolite loading in the membranes are presented in Tables 1 and 2, respectively. It is observed that there is a systematic increase in total flux and fluxes of water and isopropanol with respect to the amount of zeolite as well as the feed composition. However, some deviations were found in case of water flux for pure membrane. Similarly, the selectivity increased systematically by increasing the amount of zeolite, throughout the investigated range of water composition.

The pervaporation separation index is the product of total permeation and selectivity, which characterizes the performance of PV membranes. Fig. 11 shows the variation of pervaporation separation index with different mass% of zeolite-incorporated SA membranes at 10 mass% of water in the feed.

Table 1: Pervaporation flux and separation selectivity of different membranes for different mass% of water in the feed at 30 °C

<table>
<thead>
<tr>
<th>Mass% of water</th>
<th>Flux (×10² kg/m² h)</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M</td>
<td>M-1</td>
</tr>
<tr>
<td>5</td>
<td>5.06</td>
<td>9.32</td>
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<td>10</td>
<td>6.77</td>
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<tr>
<td>15</td>
<td>9.98</td>
<td>15.49</td>
</tr>
<tr>
<td>20</td>
<td>9.59</td>
<td>18.48</td>
</tr>
<tr>
<td>25</td>
<td>10.00</td>
<td>20.56</td>
</tr>
</tbody>
</table>

Fig. 9 Variation of separation selectivity with different mass% of water in the feed for different mass% of zeolite-incorporated SA membranes.

Fig. 10 Variation of total flux and selectivity with different mass% of zeolite-incorporated SA membranes at 10 mass% of water in the feed.
frequency and amplitude of the chain jumping also increase and as a result the free-volume becomes larger. Therefore, permeation of the diffusing and the associated molecules through the membranes becomes easier, resulting in an increase of total permeation rate. In addition, the plasticizing effect of permeates and the interaction between the permeates and membrane can also be used to explain the experimental observation. As the temperature increases, the interaction becomes weaker, so the plasticizing effect becomes more important [33]. However, at a lower temperature, transport of water molecules through the membrane matrix becomes prominent. It is interesting to note that flux and selectivity increase from membrane M to M-3 at all the temperatures studied. The temperature dependence of permeation flux was studied using the Arrhenius type relation:

\[ J_0 = \frac{E_p}{R} \exp \left( \frac{-E_p}{RT} \right) \]

Here, \( J_0 \) and \( E_p \) are, respectively, pre-exponential factor and activation energy for permeation, \( R \) the gas constant, and \( T \) the temperature in kelvin. With increasing temperature, the driving force for mass transport also increases, which represents the concentration gradient resulting from difference in the partial vapor pressure of the permeants between the feed and permeating mixture. As the feed temperature increases, vapor pressure in the feed compartment also increases, but the vapor pressure at the permeate side is not affected. All these results, in an increase of driving force due to increase in temperature. In a similar way, mass transport due to diffusion was calculated using the Arrhenius type equation:

\[ D_0 = \frac{E_d}{R} \exp \left( \frac{-E_d}{RT} \right) \]

where, \( E_d \) is the energy of activation for diffusion and \( \Delta H \) stands for water or isopropanol components of the mixture. Arrhenius plots of \( \log J_w \) versus \( 1/T \) and \( \log D_w \) versus \( 1/T \) are shown in Figs. 12 and 13 for the temperature dependence of permeation flux and diffusion of water, respectively. In both the cases, linear behavior is observed, signifying that permeation flux and diffusivity follows the Arrhenius trend. The activation energies for permeation and diffusion were estimated from the Arrhenius plots using the least squares method, and the values so obtained are presented in Table 5. It is noticed that the pure membrane (M) exhibits much higher \( E_p \) and \( E_d \) values compared to zeolite-incorporated membranes (M-1 to M-3). This suggests that the permeating molecules require more energy to transport through the pure membrane due to its crystalline nature, whereas zeolite-incorporated membranes, molecules obviously take less energy. This is because of the molecular sieving action attributed to the presence of sodalite cages and super cages in the framework of zeolite. Although \( E_{pw} \) values of all the membranes are higher than those of \( E_{pw} \) values, yet the difference is not much, indicating that both diffusion and permeation contribute almost equally to the PV process. The \( E_{pw} \) and \( E_{pw} \) values ranged between 33.07 and 4.62 kJ/mol, and 33.19 and 4.62 kJ/mol, respectively. Using these values, the heats of sorption are calculated as \( \Delta H_s = E_{pw} - E_{dw} \). The resulting values are included in Table 5. The \( \Delta H_s \) values give an additional information about the transport of molecules through the polymer matrix. It is a composite parameter involving contributions from Henry’s and Langmuir’s type of sorption. Henry’s law states that the heats of sorption will be positive for liquid transport leading to the dissolution of chemical species into that site within the membrane, giving an endothermic contribution to the sorption process. However, Langmuir’s sorption requires the pre-existence of a site in which sorption occurs by a hole

![Fig. 13 Variation of logDw with temperature for different mass% of zeolite-incorporated SA membranes at 10 mass% of water in the feed](image)

Table 5

<table>
<thead>
<tr>
<th>Parameters</th>
<th>M</th>
<th>M-1</th>
<th>M-2</th>
<th>M-3</th>
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<td>( E_{pw} ) (kJ/mol)</td>
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<td>33.19</td>
<td>33.19</td>
<td>33.19</td>
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<tr>
<td>( E_{dw} ) (kJ/mol)</td>
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<td>33.19</td>
<td>33.19</td>
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<td>( \Delta H_s ) (kJ/mol)</td>
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<td>-0.56</td>
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</tbody>
</table>

![Fig. 12 Variation of logJw with temperature for different mass% of zeolite-incorporated SA membranes at 10 mass% of water in the feed](image)

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free volume between the molecular chains. Its membrane performance has been improved by modifying alginate with different methods such as blending, grafting, and crosslinking. Alternatively, incorporation of highly selective zeolite into the membrane matrix can also be effective. For instance, Cao et al. and Chen et al. respectively, studied the pervaporation separation of hydrophilic zeolite-filled PVA and chitosan membranes for organic-water systems. The incorporation of such zeolites or porous fillers in dense membranes can improve the separation performance of the membranes as the result of the combined effects of molecular sieving action, selective adsorption, and difference in diffusion rates. In addition, zeolites have high mechanical strength and good thermal and chemical stability; thus, the membranes incorporated with zeolites can be used over a wide range of operating conditions.

In the PV process, the simultaneous enhancement of both selectivity and flux has been a big challenge as a consequence of a trade-off phenomenon, existing between flux and selectivity, although much research effort is being continued to overcome the situation by enhancing the hydrophilicity of the membrane by different methods such as γ-irradiation, chemical grafting, and plasma deposition. Recently, we succeeded in increasing both selectivity and flux by judiciously incorporating different amounts of suitable hydrophilic zeolite into SA membranes for the separation of water–isopropanol mixtures.

In conclusion, the pervaporation study is now extended for the separation of water–acetic acid mixtures at 30, 40, and 50°C. The values of permeation flux, separation selectivity, and diffusion coefficient were evaluated. From the temperature dependency of the permeation flux and diffusion coefficient data, the Arrhenius activation parameters were estimated. These results are discussed in terms of the PV separation ability of the membranes.

EXPERIMENTAL

Materials

Sodium alginate (SA) and acetic acid (HAc) were purchased, respectively, from Luba Chemicals (Mumbai, India) and S. D. Fine Chemicals (Mumbai, India). NaY zeolite was kindly supplied by Indian Petrochemicals Corp (Baroda, India). All the chemicals were of reagent grade and used without further purification. Double-distilled water was used throughout the research work.

Membrane preparation

Sodium alginate (4 g) was dissolved in 100 mL of deionized distilled water with constant stirring for about 24 h at room temperature. It was then filtered and the resulting solution was cast onto a glass plate with the aid of a casting knife. The membrane was allowed to dry at room temperature for 2–3 days. The completely dried membrane was subsequently peeled off and was designated as M.

To prepare zeolite-filled SA membrane, a known amount of NaY zeolite was added to the same amount of SA solution. The solution was stirred for about 2 h and then was kept in an ultrasonic bath for about 30 min to break the aggregated crystals of zeolite and to improve the dispersion in the polymer matrix. The resulting homogeneous solution was poured onto a glass plate and the membrane was dried as mentioned above. The amount of NaY zeolite with respect to SA varied from 5 to 15 to 30 mass %, and the resulting membranes were designated as M-1, M-2, and M-3, respectively. The thickness of these membranes was measured at different points using a Peacock dial thickness gauge (Model G, Ozaki Mfg Co., Japan) with an accuracy of ±0.5 μm and the average thickness (∼40 μm) was considered for calculation. The physical and spectroscopic properties of the derivatized membranes, in relation to their structure variation, were as described earlier.

Pervaporation experiments

PV experiments were performed using an indigenously designed apparatus, illustrated in Figure 1(a) and (b). The effective area of the membrane in contact with the feed mixture was 34.23 cm² and the capacity of the feed compartment was about 250 cm³. The vacuum in the downstream side of the apparatus was maintained using a two-stage vacuum pump (Toshniwal, Chennai, India). The test membrane was allowed to equilibrate for about 1 h while in contact with the feed mixture before performing the experiment. 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. The water composition in the feed varied between 5 and 25 mass %. The flux was calculated by weighing the permeate and its composition was estimated by measuring the refractive index of the mixture with an accuracy of ±0.0001 units using a refractometer (Atago-37, Tokyo, Japan), and by comparing it with a standard graph that was established with the known compositions of water–acetic acid mixtures.

Membrane performance in PV experiments was studied by calculating the total flux (J), separation factor (αp), and pervaporation separation index (PSI). These were calculated, respectively, using the following equations.
Effects of feed composition and zeolite loading on pervaporation

To study the effects of feed composition and zeolite loading on the permeation, the total permeation flux was plotted for all the membranes as a function of different mass % of water in the feed, as shown in Figure 3. It is observed that the total permeation flux increased almost linearly for all the zeolite-incorporated SA membranes with increasing amounts of water in the feed, attributed to an increase of selective interactions between water molecules and zeolite-incorporated SA membrane. However, for the pure SA membrane (M), the permeation flux increased linearly up to 10 mass % of water in the feed and, beyond this, the permeation flux increased exponentially. This may be the result of attaining the saturation of interactive groups (COO⁻ and OH⁻) of sodium alginate with increasing water concentration in the feed. However, this phenomenon does not occur with the zeolite-incorporated SA membranes, wherein the increase of

Figure 2 Variation of degree of swelling with different mass % of water in the feed at 30°C for different membranes

Figure 3 Variation of total flux with different mass % of water in the feed at 30°C for different membranes

Figure 4 Variation of separation selectivity with different mass % of water in the feed at 30°C for different membranes
TABLE II
Pervaporation Fluxes of Water and Acetic Acid at Different Mass % of Water in the Feed at 30°C for Different Membranes

<table>
<thead>
<tr>
<th>Mass % of water</th>
<th>( J_w \times 10^3 ) (kg m(^{-2}) h(^{-1}))</th>
<th>( J_{ac} \times 10^3 ) (kg m(^{-2}) h(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M</td>
<td>M-1</td>
</tr>
<tr>
<td>5</td>
<td>1.34</td>
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<tr>
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<tr>
<td>25</td>
<td>3.53</td>
<td>4.83</td>
</tr>
</tbody>
</table>

Presented in Tables I and II, respectively. It is observed that there is a systematic increase of total flux and fluxes of water and acetic acid with increasing amounts of zeolite and feed composition. Similarly, the selectivity increased systematically with increasing amount of zeolite throughout the investigated range of water composition, indicating that the addition of zeolite increases the selectivity of the membranes.

Pervaporation separation index (PSI)

Pervaporation separation index (PSI), defined as the product of total permeation and separation factor, has been used as a performance-evaluating parameter. Figure 6 shows the variation of PSI as a function of zeolite content in the membrane at 30°C for 10 mass % of water in the feed. It is observed that the PSI values increased almost linearly with increasing zeolite content, signifying that the membranes incorporated with a higher amount of zeolite showed better performance for the separation of acetic acid–water mixtures, attributed to the incorporation of zeolite into a membrane matrix that changes not only the membrane’s hydrophilicity but also its structure, which may have a significant influence on diffusion. Sorption is only the first step but in the second step (diffusion), the different properties of zeolite and their significant role in the membrane improve the overall pervaporation performance.

Diffusion coefficient

Transport of binary liquid molecules in PV experiments is generally explained by the solution–diffusion mechanism, which occurs in three steps: sorption, diffusion, and evaporation. 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 process, because of establishing the fast equilibrium distribution between the bulk feed and the upstream surface of a membrane, the diffusion step controls the migration of penetrants. Therefore, it is important to estimate the diffusion coefficient \( D_i \) of penetrating molecules to understand the transport mechanism.

From Fick’s law of diffusion, the diffusion flux can be expressed as:

\[
J_i = -D_i \frac{dC_i}{dx}
\]

where \( J_i \) is the permeation flux per unit area (kg m\(^{-2}\) s\(^{-1}\)), \( D_i \) is the diffusion coefficient (m\(^2\)/s), \( C_i \) is the concentration of the permeate (kg/m\(^3\)), subscript \( i \) stands for water or acetic acid, and \( x \) is the diffusion length (m). For simplicity, it is assumed that the concentration profile along the diffusion length is linear. Therefore, the diffusion coefficient can be calculated using the following equation:

\[
D_i = \frac{J_i \delta}{C_i}
\]

where \( \delta \) is the membrane thickness. The calculated values of \( D_i \) at 30°C are presented in Table III.
both permeating and diffusing molecules require more energy for transport through the pure 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 super cages in the framework of zeolite. As a result, activation energies for permeation and diffusion decreased systematically from membrane M to M-3 with increasing zeolite content.

Although $E_p$ values are higher than those of $E_D$ values in all the membranes, the difference is not significant, indicating that both permeation and diffusion almost equally contribute to the PV process. The $E_p$ and $E_D$ values ranged between 72.28 and 78.16, and 70.95 and 77.38 kJ/mol, respectively. Using these values, we calculated the heat of sorption as

$$\Delta H_s = E_p - E_D \quad (8)$$

The resulting $\Delta H_s$ values are included in Table V. The $\Delta H_s$ values give the additional information about the transport of molecules through the polymer matrix. It is a composite parameter involving contributions of both Henry-type and Langmuir-type of sorption. Henry’s law states that the heat of sorption will be positive for liquid transport, leading to the dissolution of chemical species into the site within the membrane, giving an endothermic contribution to the sorption process. However, Langmuir’s sorption requires the preexistence of a site in which sorption occurs by a hole-filling mechanism, giving an exothermic contribution. In the present study, the $\Delta H_s$ values obtained are slightly positive for all the membranes, suggesting that Henry’s sorption is still predominant, giving an endothermic contribution.

### CONCLUSION

Sodium alginate membranes, incorporated with higher amounts of NaY zeolite, showed better performance while separating water-acetic acid mixtures. An increase of zeolite content in the membrane results in a simultaneous increase of both permeation flux and selectivity, attributed to a significant enhancement of hydrophilic character, selective adsorption, and molecular sieving action, including a reduction of pore size of the polymer matrix. The PV separation index data also indicated that the higher the loading of zeolite, the better the membrane performance. The highest separation selectivity was found to be 42.29 with a flux of $3.80 \times 10^{-2}$ kg m$^{-2}$ h$^{-1}$ for the membrane with the highest loading of zeolite at $30^\circ$C for 5 mass % of water composition in the feed. With respect to the temperature effect, the permeation rate increased, while suppressing the selectivity when the temperature was increased, a phenomenon attributed to increasing the predominance of the plasticizing effect on the membrane when the interaction becomes weaker between permeating molecules, permeants, and membrane at higher temperature.

The $E_p$ and $E_D$ values ranged between 72.28 and 78.16, and 70.95 and 77.38 kJ/mol, respectively. The zeolite-incorporated membranes exhibited lower activation energy compared to that of a pure membrane, indicating that the permeants require less energy dur-
Preparation and characterization of novel pervaporation membranes for the separation of water–isopropanol mixtures using chitosan and NaY zeolite

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Abstract

Novel polymeric membranes were prepared by incorporating the NaY zeolite into chitosan. The resulting composite membranes were characterized by Fourier transform infrared spectroscopy and wide-angle X-ray diffraction. The effect of membrane swelling on the separation performance was studied by varying the water concentration in the feed. The membranes were tested for the pervaporation separation of water–isopropanol mixtures in a temperature range of 30–50 °C. The experimental results showed that both flux and selectivity increased simultaneously with increasing zeolite content in the membrane. This was explained on the basis of enhancement of hydrophilicity, selective adsorption and molecular sieving action by the creation of pores in the membrane matrix. The membrane containing 30 mass% of zeolite shows the highest separation selectivity of 2620 with a substantial flux of 1350 kg/m²h at 30 °C for 5 mass% of water in the feed. The total flux and flux of water are found to be almost close to each other for all the membranes studied, suggesting that the membranes could be used effectively to break the azeotropic point of water–isopropanol mixture, so as to remove a small amount of water from isopropanol. From the temperature-dependent diffusion and permeation values, the Arrhenius activation parameters were estimated. The activation energy values obtained for water permeation (€w) are significantly lower than those of isopropanol permeation (€ipa) values, suggesting that the developed membranes have a higher separation efficiency in water–isopropanol system. The activation energy values for total permeation and water permeation are found to be almost same for all the membranes, signifying that coupled-transport is minimal due to a higher selective nature of membranes. The negative heat of sorption (ΔHs) observed for water sorption in all the membranes suggests the Langmuir’s mode of sorption.

Keywords: Pervaporation, Membranes, Zeolite, Selectivity, Activation energy

1. Introduction

Chemical separation by pervaporation (PV) technique is one of the most popular areas of current membrane research [1]. PV is a combination of preferential permeation followed by evaporation. On one side of the membrane the preferentially sorbed fluid is in the liquid state, and is withdrawn through the membrane as preferentially evaporated vapor by applying a vacuum on the other side of the membrane [2]. The possible application areas for PV separation in industry are numerous, including separation of azeotropic mixtures [3,4], separation of mixtures of organic liquids [5,6], dehydration of organic solvents [7,8] and continuous removal of one of the products of reaction from a bioreactor [9] Separation of the liquids is governed by the chemical nature of the permeating species as well as that of the membrane material, and the morphology of the membrane itself together with the experimental conditions of process operation [10,11]. Purification of organic solvents such as isopropanol (IPA), containing a small amount of water is of vital significance in the area of organic synthesis. Isopropanol is one of the
prove the dispersion of zeolite in the polymer matrix. It was then filtered and left overnight to get a homogeneous solution. The resulting solution was poured onto a glass plate and the membrane was dried as mentioned above. The amount of NaY zeolite with respect to chitosan was varied from 10, 20, 30, and 40 mass%, and the membranes thus obtained were designated as M-2, M-3, M-4, and M-5, respectively. The thickness of these membranes was measured at different points using Peacock dial thickness gauge (Model G, Ozaki MFG Co Ltd, 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.

2.3 Fourier transform infrared (FTIR) spectroscopy

The incorporation of different amounts of NaY zeolite in chitosan was confirmed by FTIR spectroscopy (Nicolet, Impact-410, USA). Membrane samples were ground well to make KBr pellets under a hydraulic pressure of 600 kg/cm² and spectra were recorded in the range of 400–4000 cm⁻¹. In each scan, the amount of membrane sample and KBr were kept constant in order to estimate the changes in the intensities of characteristic peaks with respect to the amount of zeolite loading.

2.4 Wide-angle X-ray diffraction (WAXD)

The morphology of the pure chitosan and its zeolite-incorporated membranes was studied at room temperature using a Bruker’s D-8 advanced wide-angle X-ray diffractometer. The X-ray source was N-filtered Cu Ka radiation (40 kV, 30 mA). The dried membranes of uniform thickness (40 ± 2 μm) were mounted on a sample holder and the patterns were recorded in the reflection mode at an angle 2θ over a range of 5–45° at a speed of 8°/min.

2.5 Swelling measurements

The equilibrium sorption experiments were performed in different compositions of water–isopropanol mixtures using an electronically controlled oven (WTB Binder, Germany). The masses of the dry membranes were first determined and these were equilibrated by immersing 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, Toledo, Switzerland) within an accuracy of ±0.01 mg. The percent degree of swelling (DS) was calculated as:

\[
DS(\%) = \left( \frac{W_s - W_d}{W_d} \right) \times 100
\]

where \( W_s \) and \( W_d \) are the mass of the swollen and dry membranes, respectively.

2.6 Pervaporation experiments

PV experiments were performed using an indigenously designed apparatus reported in previous articles [14,32]. The effective area of the membrane in contact with the feed stream was 24.23 cm² and the capacity of the feed compartment was about 230 cm³. The vacuum in the downstream side of the apparatus was maintained (1333224 × 10⁻³ Pa [10 Torr]) using a two-stage vacuum pump (Toshniwal, Chennai, India). The test membrane was allowed to equilibrate for about an hour while in contact with the feed mixture before performing the PV experiment. After a steady state was attained, the permeate was collected in trap immersed in liquid nitrogen on the downstream side at a fixed time of intervals. The experiments were carried out at 30, 40, and 50 °C. The water composition in the feed mixture was varied from 5 to 30 mass%. The flux was calculated by weighing the permeate on a digital microbalance (Mettler, B204-S, Toledo, Switzerland) within an accuracy of ±0.0001 units, using Abbe’s refractometer (Atago-3T, Japan) and by comparing it with a standard graph of refractive index versus percent composition of water–isopropanol mixture. All the experiments were performed at least three times, and the results were averaged. The results of permeation for water–isopropanol mixtures during the pervaporation were reproducible within an admissible range.

Membrane performance in PV experiments was studied by calculating the total flux (J), separation factor (αsep) and pervaporation separation index (PSI). These were calculated, respectively, using the following equations:

\[
J = \frac{W}{At}
\]

\[
\alpha_{sep} = \frac{P_w/P_{wA}}{P_f/P_{wA}}
\]

\[
PSI = J(\alpha_{sep} - 1)
\]

where \( W \) is the mass of permeate (kg), \( A \) is the effective membrane area (m²), \( t \) is the permeation time (h), \( P_f \) and \( P_w \) are the mass percent of the feed and permeate, respectively, \( \alpha_{sep} \) is the separation factor, and \( \text{PSI} \) is the pervaporation separation index.

3. Results and discussion

3.1 Membrane characterization

3.1.1 FTIR studies

Fig. 1 shows the FTIR spectra of pure chitosan and its NaY zeolite-incorporated membranes. A characteristic strong and broad band exhibited at around 3440 cm⁻¹ in the membrane M-1 corresponds to O–H stretching vibrations of the hydroxyl groups. The bands appeared at around 1630 and 1570 are, respectively, assigned to amine I and amine II functional groups.
port of permeating molecules under the chemical potential gradient.

To study the effect of feed composition and zeolite loading on the membrane swelling, the percent degree of swelling of all the membranes was plotted with respect to different mass% of water in the feed as shown in Fig. 3. It is observed that the degree of swelling increased for all the zeolite incorporated membranes with increasing mass% of water in the feed. This is due to strong interaction occurring between water molecules and membrane containing $\text{NH}_2$, $\text{NH}_3^+$, $\text{OH}$ groups and $\text{Na}^+$ ions. The interaction becomes more predominant when the water concentration is increased further, since water causes a greater degree of swelling than that of alcohols with the zeolite-incorporated chitosan membranes. However, in case of pure membrane, the degree of swelling appears to be constant at higher concentration of water. This is indicative of decrease in solubility of penetrants in the membrane due to an attainment of saturation of hydrophilic groups present in the membrane matrix. This situation is not with zeolite-incorporated membranes, wherein incorporated zeolite increases the hydrophilic property of the membranes. Thus, the degree of swelling shows a steep increase at higher concentration of water in the feed.

When the polymer matrices are filled with NaY zeolite, the degree of swelling increased more than that of a virgin membrane. This effect becomes almost linear when the zeolite content in the membrane is increased and is clearly seen from Fig. 4. This may be due to the fact that zeolite has cationic particles in its cages, which tend to increase a greater electrostatic force of attraction between the water molecules and membranes. As a consequence, adsorption of water molecules increases remarkably and this, in turn, becomes responsible for the enhanced swelling with an increase of zeolite content in the membrane.

### 3.3 Effects of feed composition and zeolite loading on pervaporation properties

Fig. 5 shows the effect of feed composition on the total permeation flux for all the membranes. It is found that the total permeation flux increases almost exponentially-type for all the zeolite-incorporated membranes with increasing the amount of water in the feed and this is in accordance with the results observed in the swelling study. However, for pure chitosan membrane, the permeation flux was increased linearly up to 25 mass% of water in the feed and beyond this, the permeation flux appeared to be constant. This suggests that the interactive group of chitosan attains saturation at higher concentration of water in the feed. But, this trend was not observed in case of zeolite-incorporated chitosan membranes, wherein an increase of NaY zeolite content in the membranes enhances the selective interaction between the water molecules and membrane. This is mainly attributed to a combined influence of ionic species ($\text{Na}^+$) present in the zeolite cages and porous nature of zeolite apart from hydrophilic nature of the membrane.

![Figure 3](image1.png)

**Fig. 3** Variation of degree of swelling with different mass% of water in the feed for different mass% of zeolite incorporated chitosan membranes.

![Figure 4](image2.png)

**Fig. 4** Variation of degree of swelling with different mass% of zeolite incorporated chitosan membranes for 10 mass% of water in feed.

![Figure 5](image3.png)

**Fig. 5** Variation of total flux with different mass% of water in the feed for different mass% of zeolite incorporated chitosan membranes.
tive zeolite-incorporated membranes, the transport of water molecules through the membrane takes place in a straight path through the zeolite pores with subsequent adsorption at the feed side followed by desorption at the permeate side, which in turn is responsible for higher water flux. If enough water is present inside the membrane, the higher pores will be largely occupied by water molecules, prohibiting the isopropanol molecules from entering the pores of zeolite. Thus, on its way through the membrane the isopropanol molecules have to travel around the zeolite pores. The higher water concentration inside the polymer close to the permeate side of the membrane and the fact that water can travel along the straight path while isopropanol has to follow a more tortuous path act together in explaining the way in which membrane performance is enhanced both in selectivity and flux when zeolite is added to the polyester matrix [29].

Calculated results of water and isopropanol fluxes, measured at 30 °C for different compositions of feed with respect to zeolite loading in the membranes are presented in Table 2. It is observed that there is a systematic increase of water flux with increasing zeolite loading and water composition in the feed. Although, the flux of isopropanol is increased with increasing water composition in the feed, but with respect to zeolite loading it is decreased.

### 3.4 Effect of zeolite loading on pervaporation separation index

The pervaporation separation index is the product of total permeation and separation factor, which characterizes the membrane separation ability. This index can be used as a relative guideline for the design of pervaporation membrane separation processes and to select a membrane with an optimum flux and selectivity. Fig. 9 shows the variation of PSI as a function of zeolite content in the membrane for 10 mass% of water in the feed at 30 °C. It is observed that the PSI values increased exponentially with increasing zeolite content in the membrane, signifying that the membranes incorporated with higher amount of zeolite showed better performance for the separation of isopropanol-water mixtures. This is because the incorporation of zeolite into a membrane matrix changes not only the membrane's hydrophilicity but also its structure, which may have a significant influence on diffusional transport, unique properties of zeolite and their significant role in the membrane matrix improve the overall permeation performance of the membranes

### 3.5 Comparison of PV performance of chitosan-based membranes

Table 3 summarizes the flux and separation characteristics of chitosan-based membranes for water-isopropanol mixtures. The separation factors of zeolite-incorporated membranes are reasonably higher than those of composite and pure chitosan membranes [18]. However, the chitosan membranes cross-linked with sulfosuccinic acid [27] and glutaraldehyde [10] have significantly higher selectivity even the measured temperatures are high. Thus it may be because of lower thickness obtained in membrane preparation, which might have played a decisive role in achieving higher selectivity in addition to membrane property. Among the membranes developed in the present study, the highest zeolite loaded membrane (M-5) showed better permeation flux, which is comparable to the membranes reported by others. Based on the comparison, it clearly reveals that the mass of zeolite loaded and membrane thickness play a key role in achieving higher permeation flux and separation factor. Hence, in future we intend to prepare ultra-thin membranes by adopting a suitable method to improve both permeation flux and separation factor.

### Table 2

Pervaporation fluxes of water and isopropanol for different mass% of water in the feed at 30 °C for different membranes

<table>
<thead>
<tr>
<th>Mass% of water</th>
<th>(J_w \times 10^3 ) (kg/m²h)</th>
<th>(J_{ip} \times 10^3 ) (kg/m²h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M-1</td>
<td>M-2</td>
</tr>
<tr>
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<td>3.65</td>
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