CHAPTER-III

Development of Novel Pervaporation Membranes for the Separation of Water-Isopropanol Mixtures Using Sodium Alginate and NaY Zeolite

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 creation of pores in the membrane matrix. The membrane containing 30 mass % of zeolite shows the highest separation selectivity of 614 with a flux of $14.59 \times 10^{-2}$ kg/m$^2$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 here 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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### III.1. INTRODUCTION

Pervaporation 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 vapour because of a low vapour pressure existing on the downstream side. This low (partial) vapour 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 operation 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 process 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 alginate resulting from both of its carboxyl and hydroxyl groups, leads to a significant swelling of membrane in aqueous solution, followed by a remarkable decline of selectivity and mechanical strength. To overcome these drawbacks, several researchers have modified the alginate membranes for the effective dehydration performance. Yeom and Lee [10] crosslinked the sodium alginate membrane with glutaraldehyde for the separation of water-isopropanol mixture. Haung and co-workers [11] prepared a novel two-ply dense composite membranes using successive casting of sodium alginate and chitosan for the dehydration of isopropanol and ethanol. Recently, Aminabhavi and co-workers [12,13] prepared the blend membranes of sodium alginate with poly(vinyl alcohol) and were employed to separate water-isopropanol mixtures. Although these membranes improved their physical properties, none of them was found to increase either permeation flux or separation factor very significantly. In the PV process, the simultaneous
enhancement of both parameters is a big challenge due to a trade-off phenomenon, which exists between flux and separation factor. But the efforts in this direction are being continued to overcome the situation by improving the membrane performance with different methods by elevating the hydrophilicity of the membrane, viz., $\gamma$-irradiation, chemical grafting and plasma deposition [14-16].

Another efficient method to improve the PV performance is to incorporate hydrophilic zeolite into a polymer solution. As a result of this, polymeric membranes have received much attention recently in gas and PV separation studies [17,18]. The incorporation of zeolite or porous fillers into dense membrane can improve the separation performance of the membranes [17-19] due to combined effects of molecular sieving action, selective adsorption and difference in diffusion rates. In addition, zeolites have a high mechanical strength, good thermal and chemical stability, and the membranes incorporated with these fillers can be used over a wide range of operating conditions. Hence, we have chosen NaY zeolite, as a filler which is hydrophilic in nature and its structure is isomorphous to the mineral faujasite, as determined by X-ray [20,21] and neutron powder diffraction [22]. The framework is composed of cubo-octahedral sodalite cages linked together in a tetrahedral arrangement by six membered rings of oxygen atoms to form large cavities, called supercages. The supercages are interconnected by 12-ring windows consisting of 12 Si/Al and 12 oxygen atoms. A single unit cell contains eight sodalite cages and eight supercages [23].
In the present study, an attempt has been made to enhance both permeation flux and separation factor simultaneously by suitably modifying the sodium alginate membrane with the incorporation of NaY zeolite using a solution technique. The PV characteristic as well as temperature dependence of the membrane were explored for the separation of water-isopropanol mixture.

III.2. EXPERIMENTAL

III.2.1. Materials

Sodium alginate (SA) was purchased from Luba Chemicals, Mumbai, India. Isopropanol (IPA) was obtained from s. d. fine Chemicals, Mumbai, India. NaY zeolite was kindly supplied by Indian Petrochemicals Corporation Ltd., Baroda, India. These are of reagent grade samples and were used as received. Double distilled water was used throughout the research work. The characteristic properties of NaY zeolite are given in Table III.1.

Table III.1. Physicochemical properties of hydrophilic NaY zeolite\textsuperscript{22,23}.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Counter ion</td>
<td>Na\textsuperscript{+}</td>
</tr>
<tr>
<td>SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>2.6</td>
</tr>
<tr>
<td>Density</td>
<td>1.27 g/ml</td>
</tr>
<tr>
<td>Pore size</td>
<td>0.5-2.0 μm</td>
</tr>
<tr>
<td>Pore volume</td>
<td>0.47 ml/g</td>
</tr>
<tr>
<td>Topology</td>
<td>FAU</td>
</tr>
<tr>
<td>Nature</td>
<td>Hydrophilic</td>
</tr>
</tbody>
</table>

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III.2.2. Membrane Preparation

Sodium alginate (4 g) was dissolved in 100 ml of deaerated-distilled water with a constant stirring for about 24 h at room temperature. It was then filtered and the resulting homogeneous solution was cast onto a glass plate with the aid of a casting knife. It 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 into the SA solution. The amount of SA solution was kept constant each time. The solution was stirred for about 2 h and then, it was kept in an ultrasonic bath at a fixed frequency of 38 kHz (Grant XB6, UK) for 30 min to break the aggregated crystals of zeolite so as to improve the dispersion in the polymer matrix. 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 SA varied as 5, 15 and 30 mass %, and the membranes thus obtained were designated as M-1, M-2 and M-3, 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 (~ 40 μm) was considered for calculation.
III.2.3. Pervaporation Experiments

Pervaporation experiments have been carried out using an indigenously designed apparatus given in Fig. II.3. The water composition of the feed mixture varied between 5 and 25 mass %. The rest of the procedure was followed as described in Section II.2.3.

Membrane performance was studied by calculating the total flux \((J)\), separation factor \((a_{sep})\) and pervaporation separation index \((PSI)\). These were calculated, respectively, using the equations (II.8-II.10). The resulting values of flux and selectivity are presented in Table III.2.

III.2.4. Swelling Measurements

The degree of swelling of membranes was carried out by soaking in different compositions of water and isopropanol mixtures for 24 h at 30°C. The further procedure including the calculation of degree of swelling was followed as discussed in Section II.2.2.

III.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 with KBr to make pellets under a hydraulic pressure of 600 kg 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 characteristics peaks with respect to the amount of zeolite loading.

**III.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 ($T_g$). A repeat run, following cooling at 10°C/min exhibited reproducibility within ±1.5 for $T_g$ values.

**III.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 reflection mode at an angle 2θ over a range of 5 - 45° at a speed of 8° per min.

**III.3. RESULTS AND DISCUSSION**

**III.3.1. Membrane Characterization**

**III.3.1.1. FTIR studies**

FTIR spectra of pure sodium alginate membrane and those of different amounts of NaY zeolite loaded membranes are presented in Fig. III.1.
A characteristic strong and broad band appeared at around 3440 cm⁻¹ in membrane M, corresponding to O-H stretching vibrations of the hydroxyl group. The strong bands appeared at around 1620 and 1416 cm⁻¹ are assigned, respectively to antisymmetric and symmetric COO⁻ stretching vibrations of the
carboxyl group of sodium alginate [24]. The intensity of these bands did not change upon loading different amounts of zeolite in polymer matrix, indicating that OH and COO' groups of SA are not involved in bond formation with the zeolite. In addition, a strong peak appeared at around 1100 cm\(^{-1}\) is assigned to C-O stretching of SA. The Si-O band [25] also appeared at the same wavelength upon loading zeolite in the polymer matrix and hence, C-O and Si-O bands are almost overlapping in the spectra. Upon increasing the zeolite loading, the intensity of Si-O band was increased in the spectra from M-1 to M-3. On the other hand, the multiple bands appearing between 447 and 1000 cm\(^{-1}\) are assigned to Al-O stretching vibrations [26]. The intensity of these bands was also increased further by increasing the amount of zeolite in the polymer matrix and both of them ascertain the complete dispersion of zeolite in the SA membranes.

**III.3.1.2. X-ray diffraction studies**

The WAXD patterns of all the membranes including pure zeolite are presented in Fig. III.2. All the peaks match with those reported by Kita et al. [27] and Yeom and Lee [10] for X-type crystals of NaY zeolite and SA, respectively, with respect to the positions and intensities of the observed reflections, and no additional peaks were observed. From the pattern, it is observed that after incorporating 5 and 15 mass % of NaY zeolite into SA, the resulting membranes (M-1 and M-2) show the characteristic peaks of both the zeolite and SA. However, when the zeolite content increased to 30 mass % (M-3), almost no characteristic peak of SA was
noticed in the WAXD pattern, indicating that SA no longer retains its crystallinity when the NaY zeolite content reaches or exceeds beyond 30 mass %. On the contrary, the resulting membranes tend to have a more rigid structure owing to the restriction of polymer chain mobility with increasing the zeolite loading in membrane matrix.

![Wide-angle X-ray diffraction patterns for pure NaY zeolite and SA membranes with and without zeolite: (M) 0 mass %; (M-1) 5 mass %; (M-2) 15 mass %; (M-3) 30 mass %.

Fig. III.2. Wide-angle X-ray diffraction patterns for pure NaY zeolite and SA membranes with and without zeolite: (M) 0 mass %; (M-1) 5 mass %; (M-2) 15 mass %; (M-3) 30 mass %.

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III.3.1.3. Glass transition temperature ($T_g$)

In an effort to study the effect of zeolite loading on the membrane matrix, the glass transitions were measured for different membranes and are shown in Fig. III.3.

![Graph showing the effect of zeolite content on glass transition temperature of SA membrane.](image)

**Fig. III.3.** Effect of zeolite content on glass transition temperature of SA membrane.

The $T_g$ of the SA membrane decreased systematically as the zeolite loading increased. It manifests that the incorporation of zeolite decreases the crystallinity of the polymer as evidenced from X-ray patterns, even though the segmental motions of the polymer chains are restricted due to reduction of free-volume 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. III.9). These observations suggest that after incorporating a large amounts 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.

**III.3.2. Swelling Study**

**III.3.2.1. 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 matrices 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. III.4. 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. When the polymer matrices are filled with NaY zeolite, the degree of swelling increases more than that of a pure sodium alginate membrane. This effect becomes more prominent when the zeolite content in the membrane is increased, which is clearly viewed in Fig. III.5. This may be due to the fact that zeolite has cationic particles, which tend to increase a greater electrostatic force of attraction between water molecules and membrane. As a consequence, adsorption of water molecules increases remarkably and this, in turn becomes responsible for an enhanced swelling with an increase of zeolite content in the membrane.

Fig. III.4. Variation of degree of swelling with different mass % of water in the feed for different mass % of zeolite incorporated SA membranes.
Fig. III.5. Variation of degree of swelling with different mass % of zeolite incorporated SA membranes for 10 mass % of water in feed.

**III.3.3. Pervaporation Performance**

**III.3.2.1. Effects of feed composition and zeolite loading on pervaporation**

Figure III.6 shows the effect of feed composition on the total permeation flux for all the membranes. It is observed that the total permeation flux increased almost linearly for all the zeolite incorporated SA membranes with increasing amount of water in the feed. This is due to an increase of selective interactions between water molecules and zeolite incorporated SA membrane. However, for pure sodium alginate membrane (M), the permeation flux increased up to 15 mass % of water in the feed and beyond this, the permeation flux becomes almost constant.
Fig. III.6. Variation of total flux with different mass % of water in the feed for different mass % of zeolite incorporated SA membranes.

This may be due to the saturation of interactive groups (COO' and OH) of sodium alginate at higher concentration of water in the feed. But, this is not the case with zeolite incorporated SA membranes, wherein an increase of NaY zeolite content in the membranes enhances the selective interaction between the water molecules and membrane. This property is mainly attributed to a combined influence of ionic species (Na+) present in the zeolite cages and porous nature of zeolite, which together lead to an increase of water adsorption as evidenced in the swelling study. These, in turn become responsible for a higher permeation flux with increasing water concentration in the feed. In order to see the extent of permeation of individual components, we have plotted the total flux and fluxes of water and isopropanol as a function of zeolite content in the membrane for 10 mass % of water in the feed as shown in Fig. III.7.
Fig. III.7. Variation of total flux, fluxes of water and \textit{IPA} with different mass % of zeolite incorporated SA membranes at 10 mass % of water in the feed.

From the plot, it is clearly observed that, the total flux and flux of water are almost close to each other and further the trend remained the same for all the membranes. However, the flux of isopropanol is negligibly small and remained constant for all the membranes, indicating that the membranes developed in the present study are highly water selective.

The overall selectivity of a membrane in the PV process is generally determined on the basis of interaction between the membrane and permeating molecules, molecular size of the permeating species and pore diameter of the membrane. Figure III.8 displays the effect of water composition on the selectivity for all the membranes. It is observed that the selectivity decreased exponentially...
for all the membranes with increasing water concentration in the feed. This is due to a greater swelling with increasing water concentration in the feed, owing to an increase of selective interaction between the membrane and water molecules.

On the contrary, the selectivity increased from membrane M-1 to M-3 upon increasing the NaY zeolite content in the membrane. Further, it can be clearly observed from the Fig. III.9 showing the variation of flux and selectivity as a function of zeolite content in the membrane at 10 mass % of water in the feed. It clearly indicates that both the permeation flux and selectivity increased 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

Fig. III.8. Variation of separation selectivity with different mass % of water in the feed for different mass % of zeolite incorporated SA membranes.

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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 factor 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.

Fig. III.9. Variation of total flux and selectivity with different mass % of zeolite incorporated SA membranes at 10 mass % of water in the feed.

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 III.2 and III.3, 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.

Table III.2. 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>$J \times 10^2$ (kg/m²h)</th>
<th>$\alpha_{sep}$</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>
</tr>
<tr>
<td>10</td>
<td>6.77</td>
<td>14.19</td>
</tr>
<tr>
<td>15</td>
<td>9.98</td>
<td>15.49</td>
</tr>
<tr>
<td>20</td>
<td>9.99</td>
<td>18.48</td>
</tr>
<tr>
<td>25</td>
<td>10.00</td>
<td>20.56</td>
</tr>
</tbody>
</table>

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Table III.3. Pervaporation flux of water and isopropanol for different membranes at different mass % of water in the feed at 30°C.

<table>
<thead>
<tr>
<th>Mass % of water</th>
<th>( J_w \times 10^2 \text{(kg/m}^2\text{h)} )</th>
<th>( J_{IPA} \times 10^2 \text{(kg/m}^2\text{h)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M</td>
<td>M-1</td>
</tr>
<tr>
<td>5</td>
<td>4.82</td>
<td>8.95</td>
</tr>
<tr>
<td>10</td>
<td>6.43</td>
<td>13.55</td>
</tr>
<tr>
<td>15</td>
<td>9.46</td>
<td>14.72</td>
</tr>
<tr>
<td>20</td>
<td>9.39</td>
<td>17.47</td>
</tr>
<tr>
<td>25</td>
<td>9.00</td>
<td>19.16</td>
</tr>
</tbody>
</table>

The pervaporation separation index (PSI) is the product of total permeation and selectivity, which characterizes the performance of PV membranes. Figure III.10. 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 linearly with increasing the zeolite content. This indicates that the sorption data not always necessarily correspond to the permeation data, because the diffusion through the membrane also contributes to the permeation. The incorporation of zeolite into membrane matrix changes not only the membrane’s hydrophilicity but also its structure, which may have a significant influence on the diffusion. Sorption is only the first step and in the second step (diffusion), the

\[ \text{Chapter-III} \quad 96 \]
different properties of zeolite improve the overall permeation performance of the membranes. As a result, membranes of the present study showed a better performance at a higher loading of zeolite.

![Graph showing variation of pervaporation separation index with NaY zeolite content](image)

**Fig. III.10.** Variation of pervaporation separation index with different mass % of zeolite incorporated SA membranes at 10 mass % of water in the feed.

**III.3.4. 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 [30]. 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 [4,31], diffusion step controls the migration of penetrants. Therefore, it is important to estimate the
diffusion coefficient, $D_t$ of penetrating molecules to understand the transport mechanism.

From the Fick’s law of diffusion, the diffusion flux can be expressed as [33]:

$$J_i = -D_i \frac{dC_i}{dx} \quad (III.1)$$

where $J$ is the permeation flux per unit area (kg/m$^2$/s), $D$ is the diffusion coefficient (m$^2$/s), $C$ is the concentration of the permeate (kg/m$^3$), subscript $i$ stands for water or organic liquid, 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 equation [34]:

$$J_i = \frac{D_i}{\delta} C_i \quad (III.2)$$

where $\delta$ is the membrane thickness. The computed values of $D_t$ at 30°C are presented in Table III.4. As evidenced in pervaporation study, the diffusion coefficients of water as well as IPA increase from membrane M to M-3. But, the magnitude of IPA is small as compared to water, indicating that membranes are highly selective towards water. However, there is a considerable decrease in diffusion coefficient of water for all the membranes with increasing amount of water in the feed. Such a decrease is quite dramatic at higher composition of
water in the feed due to an enhanced swelling behaviour of the membrane. On the contrary, diffusion coefficient of IPA increases for all the membranes with increasing water composition in feed. This is expected due to decrease in membrane selectivity towards water.

**Table III.4.** Diffusion coefficients of water and isopropanol for different membranes calculated at 30°C from Eq. III.2 for different mass % of water in the feed.

<table>
<thead>
<tr>
<th>Mass % of water</th>
<th>$D_w \times 10^7$ (m²/s)</th>
<th>$D_{IPA} \times 10^9$ (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M</td>
<td>M-1</td>
</tr>
<tr>
<td>5</td>
<td>1.99</td>
<td>3.81</td>
</tr>
<tr>
<td>10</td>
<td>1.32</td>
<td>2.84</td>
</tr>
<tr>
<td>15</td>
<td>1.29</td>
<td>2.03</td>
</tr>
<tr>
<td>20</td>
<td>0.95</td>
<td>1.80</td>
</tr>
<tr>
<td>25</td>
<td>0.73</td>
<td>1.57</td>
</tr>
</tbody>
</table>

**III.3.5. Effect of Temperature**

Effect of temperature on PV performance of water-isopropanol mixture for zeolite filled membranes has been studied for the feed mixture containing 10 mass % of water. The results of PV flux and separation selectivity data at 30, 40 and 50°C are presented in Table III.5.
Table III.5. Pervaporation flux and separation selectivity for different membranes at different temperatures for 10 mass % of water in the feed.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>$J \times 10^2$ (kg/m²h)</th>
<th>$\alpha_{sep}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M</td>
<td>M-1</td>
</tr>
<tr>
<td>30</td>
<td>6.77</td>
<td>14.19</td>
</tr>
<tr>
<td>40</td>
<td>7.53</td>
<td>15.49</td>
</tr>
<tr>
<td>50</td>
<td>15.70</td>
<td>16.3</td>
</tr>
</tbody>
</table>

It is observed that for all the membranes the flux values increased systematically with increasing temperature, whereas separation selectivity values decreased. This is due to the expansion of free-volume as explained in the free-volume theory [35]. According to this theory, as the temperature increases, the 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 [36]. 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:

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

(III.3)

where, \( J_0 \), and \( E_p \) are respectively, pre-exponential factor and activation energy for permeation; \( R \) is gas constant and \( T \) is temperature in kelvin. With increasing temperature, the driving force for mass transport also increases, which represents the concentration gradient resulting from a difference in the partial vapour pressure of the permeates between the feed and permeating mixture. As the feed temperature increases, vapour pressure in the feed compartment also increases, but the vapour 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:

\[ D_i = D_{i0} \exp \left( -\frac{E_{Di}}{RT} \right) \]  

(III.4)

where, \( E_D \) is the energy of activation for diffusion and \( i \) 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. III.11 and III.12 for the temperature dependence of permeation flux and diffusion of water, respectively. In both the cases, linear behaviour 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 III.6. It is noticed that the pure membrane (M) exhibits much higher $E_{pw}$ and $E_{Dw}$ 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 and obviously molecules take less energy for zeolite-incorporated membranes. This is because of the molecular sieving action attributed to the presence of sodalite cages and super cages in the framework of zeolite. Although $E_{Dw}$ 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 contributes almost equally to the PV process.

Table III.6. Arrhenius activation parameters for permeation and diffusion of water, and heat of sorption for water.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>M</th>
<th>M-1</th>
<th>M-2</th>
<th>M-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>($kJ/mol$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_{pw}$</td>
<td>33.07</td>
<td>8.87</td>
<td>7.32</td>
<td>4.06</td>
</tr>
<tr>
<td>$E_{Dw}$</td>
<td>33.19</td>
<td>9.08</td>
<td>7.76</td>
<td>4.62</td>
</tr>
<tr>
<td>$\Delta H_s$</td>
<td>-0.12</td>
<td>-0.21</td>
<td>-0.44</td>
<td>-0.56</td>
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</table>
Fig. III.11. Variation of $\log J_w$ with temperature for different mass % of zeolite incorporated SA membranes at 10 mass % of water in the feed.

Fig. III.12. Variation of $\log D_w$ with temperature for different mass % of zeolite incorporated SA membranes at 10 mass % of water in the feed.
The $E_{pw}$ and $E_{Dw}$ values ranged between 33.07 and 4.06, and 33.19 and 4.62 kJ/mol, respectively. Using these values, we have calculated the heat of sorption as:

$$\Delta H_s = E_{pw} - E_{Dw}.$$  \hspace{1cm} (III.5)

The resulting values are included in Table III.6. 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 and Langmuir’s 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 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 filling mechanism, giving an exothermic contribution. The $\Delta H_s$ values obtained in the present study are negative for all the membranes, suggesting that Langmuir’s sorption is predominant due to the presence of porous nature of zeolite in the membrane matrix, giving an exothermic contribution.

III.4. CONCLUSIONS

Incorporation of NaY zeolite in sodium alginate has shown a significant improvement in the membrane performance while separating water-isopropanol mixtures. An increase of zeolite content in the membrane results in simultaneous

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increase of both permeation flux and selectivity. This was explained on the basis of a significant increase in hydrophilic character, selective adsorption and molecular sieving action including creation of pores in the polymer matrix as evidenced by $T_g$, X-ray pattern and swelling study. The PV separation index data also indicate that higher the degree of zeolite loading better is the membrane performance. The highest separation selectivity was found to be 614 with a flux of $14.59 \times 10^{-2}$ kg/m$^2$h for a higher loading of zeolite in the membrane at 30°C for 5 mass % of water composition in feed. Experimental data also reveal that the total flux and flux of water are almost close to each other throughout the investigated range, indicating that the NaY zeolite loaded membranes are highly water selective, and this is also in accordance with the diffusion study. Temperature effect study shows the increase in permeation flux and decrease in selectivity when the temperature was increased. This was discussed on the basis of free-volume theory and plasticizing effect. The estimated $E_{pw}$ and $E_{Dw}$ values using the Arrhenius plot ranged between 33.07 and 4.06, and 33.19 and 4.62 kJ/mol, respectively. The pure membrane exhibits higher activation energy due to its crystalline nature. However, the much lower activation energy values obtained for zeolite incorporated membranes indicate that molecules take less energy during the process due to molecular sieving action attributed to the presence of sodalite cages and super cages in the framework of zeolite. The small difference occurred between $E_{pw}$ and $E_{Dw}$ values indicate that both diffusion and permeation contribute almost equally to the PV process. All the membranes exhibit negative $\Delta H_s$ values,
suggesting that sorption is mainly dominated by Langmuir’s mode of sorption, giving an exothermic contribution due to the presence of porous zeolite in the membrane matrix.

III.5. REFERENCES


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