Blend Membranes of Sodium Alginate/Poly(Styrene Sulfonic Acid) for Isopropanol Dehydration

ABSTRACT

This chapter addresses the preparation of blend membranes of sodium alginate (NaAlg) with 5 and 10 wt. % of poly(styrene sulfonic acid) (PSSA) that are crosslinked with glutaraldehyde to investigate pervaporation (PV) dehydration of isopropanol at different temperatures and membrane thicknesses. These blend membranes were designated as NaAlg-PSSA(5) and NaAlg-PSSA(10), respectively and neat NaAlg membrane was designated as NaAlg. NaAlg-PSSA(10) membrane offered higher values of flux and selectivity than pristine NaAlg membrane. Activation parameters were computed to explain the transport results. Membrane selectivity increased, but flux decreased with increasing membrane thickness; however, a reverse trend was observed at increasing temperature.

Results of this chapter are communicated to Separation and Purification Technology
V.1. INTRODUCTION

Pervaporation (PV) is an attractive membrane-based technique that has been used to separate azeotropic, closely-boiling, isomeric or temperature-sensitive liquid mixtures [1-3]. The technique is environmentally benign unlike distillation [4]. Transport across the PV membrane occurs due to sorption and diffusion of liquids; however, evaporation occurs from the downstream side [5]. Among the many polymers used as membranes, polymer blends are attractive, since these could offer increased flux and selectivity over the homopolymeric membranes [6-8]. Even though NaAlg has been widely used as a PV membrane, but due to its drawbacks like water-soluble property and mechanical weakness [9], blends, grafts and filled composite membranes of NaAlg have been attempted [10-14]. In this communication, we report the development of blend membranes of NaAlg with poly(styrene sulfonic acid), PSSA in PV dehydration of isopropanol, since it is a widely used solvent in pharmaceutical industry; it forms an azeotrope at 12.5 wt. % of water. In this research, membrane performance was tested at different temperatures and thicknesses.

V.2. RESULTS AND DISCUSSION

V.2.1. Scanning Electron Microscopy

According to Fig.V.1, surface SEM of NaAlg-PSSA(10) suggests the uniform distribution of PSSA segments in the blend matrix of NaAlg.

V.2.2. Universal Testing Machine

Pristine NaAlg exhibited % elongation of 210 with a maximum tensile strength of 20 N/mm², whereas NaAlg-PSSA(5) and NaAlg-PSSA(10) blend membranes exhibited % elongations of 180 and 170, respectively with the tensile strengths of 23 and 25 N/mm², suggesting the improved tensile strength properties of the blend membranes over that of pristine NaAlg membrane.
Figure V.1 displays the % sorption data of all the membranes at 30°C for 10, 15, 20, 25 and 30 wt. % water-containing feed mixtures. Sorption results of both the blend membranes are higher than the pristine NaAlg membrane, suggesting their increased hydrophilicity due to the presence of PSSA. Increased flux of the blend membranes compared to pristine NaAlg membrane and as well as increased sorption with increasing water content of the feed mixture of the membranes is due to increased hydrophilicity of the membranes due to the presence of PSSA segments, which would increase the hydrogen-bonding interactions between membranes and water. Such hydrophilic interactions would result in a further increase with increasing
temperature as shown typically in Fig.V.3 at 30°, 40° and 50°C for 10 wt % water-containing feed mixture.

Fig.V.2. % Sorption curves of pristine NaAlg (●), NaAlg-PSSA(5) (■) and NaAlg-PSSA(10) (▲) blend membranes at 30°C.

Fig.V.3. Bar graph of % sorption of pristine NaAlg, NaAlg-PSSA(5) and NaAlg-PSSA(10) blend membranes at 30°, 40° and 50°C.
V.2.4 Membrane Performance

Separation ability of the membranes was studied in terms of $J$, $\alpha$, PSI and $\beta$ values. Figure V.4 shows the variation of $J$ and $\alpha$ with water content of the feed mixture. The $\alpha$ values of the blend membranes are higher for 10 wt % water-containing feed mixture than pristine NaAlg membrane. Flux of all the membranes increased with increasing water content of the feed mixture giving a sacrifice in $\alpha$. At high water content (30 wt %) of the feed mixture, pristine NaAlg membrane exhibited a very small $\alpha$ value of 96 with a flux of 0.104 kg/m²h. For the same mixture, NaAlg-PSSA(5) and NaAlg-PSSA(10) blend membranes exhibited $\alpha$ values of 129 and 266 with fluxes of 0.129 and 0.153 kg/m²h, respectively. Pristine NaAlg had $\alpha$ and $J$ values of 678 and 0.047 kg/m²h, respectively, which increased to 959, 0.064 kg/m²h and 3904, 0.079 kg/m²h for NaAlg-PSSA(5) and NaAlg-PSSA(10) blend membranes when tested for 10 wt % water-containing feed mixture. This clearly suggests that the performance of the pristine NaAlg membrane was improved after blending with PSSA. It is observed that $J$ and $\alpha$ values of the membranes increased considerably with increasing amount of PSSA of the blend membranes (see Fig. V.5.)
Fig. V.4. Water flux and selectivity vs wt % water in feed for (a) pristine NaAlg, (b) NaAlg-PSSA(5) and (c) NaAlg-PSSA(10) blend membranes at 30°C. Symbols flux (▲) and separation factor (Δ).
Fig. V.5. Water flux and selectivity vs wt % of PSSA in the blend membrane for 10 wt % water-containing isopropanol feed at 30°C. Symbols: flux (○) and selectivity (●).

V.2.5. Effect of Membrane Thickness

Effect of membrane thickness on PV performance was studied typically for NaAlg-PSSA(10) membrane with 10 wt % water-containing feed, which exhibited the highest α. Variation of α and J values for different thicknesses of the membranes (30, 40 and 50 µm) are displayed in Fig. V.6. The α and J values of 30 µm thick NaAlg-PSSA(10) membrane are, respectively 1627 and 0.117 kg/m²·h. However, with increasing membrane thickness, i.e., up to 40 and 50 µm, the α values increased to 2423 and 3904, while the flux values declined from 0.101 to 0.078 kg/m²·h. This is quite expected [15].
Fig. V.6. Water flux and selectivity vs wt % water in the feed for NaAlg-PSSA(10) blend membranes of 30, 40 and 50 μm thicknesses

V.2.6. Effect of Feed Water Composition

Results of $PSI$ and $\beta$ of the membranes displayed, respectively in Fig. V.7(a) and (b), display a systematic decrease with increasing water composition of the feed mixture. $PSI$ and $\beta$ values of the blend membranes are higher than the pristine NaAlg membrane, but the initial large difference between $PSI$ values is due to larger differences in their $\alpha$ values. The $\beta$ values of all the membranes are quite identical for all the membranes due to small differences in the wt % of water obtained on the permeate side.
V.7. PSI (a) and β (b) vs wt % water in the feed for pristine NaAlg (●), NaAlg-PSSA(5) (■) and NaAlg-PSSA(10) (▲) blend membranes at 30°C

V.2.7. Effect of Temperature

The PV performance was investigated at 40°C and 50°C for 10 wt % water-containing feed, these data are also included in Table V.1. Analysis of flux data was done using the Arrhenius equation

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

where \( J \) is permeation flux of water, \( J_0 \) is permeation rate constant, \( E_p \) is activation energy for permeation, \( R \) is molar gas constant and \( T \) is temperature in Kelvin. Arrhenius plots are displayed in Fig.V.8. We find that \( E_p \) values are positive in all the...
cases The $E_p$ values decreased with increasing amount of PSSA of the blend membranes, for e.g., $E_p$ values of 27 08, 22 40 and 19 97 kJ/mol were observed for NaAlg, NaAlg-PSSA(5) and NaAlg-PSSA(10) membranes, respectively suggesting the reduced energy values required to cross Eyring's energy barrier, thereby allowing water molecules to move faster through the blend membranes than the pristine NaAlg membrane.

Table V.1. Pervaporation Data of 10 wt. % Water-Containing Feeds at 30$^0$, 40$^0$ and 50$^0$C

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Wt. % of water in permeate</th>
<th>flux ($J$) (kg/m$^2$ h)</th>
<th>Selectivity ($\alpha$)</th>
<th>PSI</th>
<th>$\beta$</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>30$^0$C</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>NaAlg</td>
<td>98.69</td>
<td>0.047</td>
<td>678</td>
<td>31.90</td>
<td>14.10</td>
</tr>
<tr>
<td>NaAlg-PSSA(5)</td>
<td>99.07</td>
<td>0.064</td>
<td>959</td>
<td>61.41</td>
<td>14.15</td>
</tr>
<tr>
<td>NaAlg-PSSA(10)</td>
<td>99.77</td>
<td>0.079</td>
<td>3904</td>
<td>307.13</td>
<td>14.25</td>
</tr>
<tr>
<td>40$^0$C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaAlg</td>
<td>97.33</td>
<td>0.072</td>
<td>328</td>
<td>23.53</td>
<td>13.90</td>
</tr>
<tr>
<td>NaAlg-PSSA(5)</td>
<td>98.15</td>
<td>0.095</td>
<td>477</td>
<td>45.48</td>
<td>14.02</td>
</tr>
<tr>
<td>NaAlg-PSSA(10)</td>
<td>98.86</td>
<td>0.114</td>
<td>780</td>
<td>89.12</td>
<td>14.12</td>
</tr>
<tr>
<td>50$^0$C</td>
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<tr>
<td>NaAlg</td>
<td>96.82</td>
<td>0.109</td>
<td>274</td>
<td>29.64</td>
<td>13.83</td>
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<tr>
<td>NaAlg-PSSA(5)</td>
<td>97.43</td>
<td>0.127</td>
<td>341</td>
<td>43.14</td>
<td>13.92</td>
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<tr>
<td>NaAlg-PSSA(10)</td>
<td>97.89</td>
<td>0.145</td>
<td>418</td>
<td>60.43</td>
<td>13.98</td>
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</tbody>
</table>
Fig. V.8. Arrhenius plots of $\ln J$ vs $1/T$ for pristine NaAlg ($\bullet$), NaAlg-PSSA(5) ($\blacksquare$) and NaAlg-PSSA(10) ($\triangle$) blend membranes taken with 10 wt % water in feed.

V.2.8. Literature Comparison

Table V.2 compares the present PV data with some of the reported data on flux and selectivity. The present results of NaAlg-PSSA(10) membrane are better than those of the published reports [16-20].
Table V.2. Comparison of PV Data of the Present Membranes with Literature at 30°C

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>Flux $J$ (kg/m²·h)</th>
<th>Selectivity $\alpha$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaAlg-PSSA(5)</td>
<td>0.064</td>
<td>959</td>
<td>Present work</td>
</tr>
<tr>
<td>NaAlg-PSSA(10)</td>
<td>0.079</td>
<td>3904</td>
<td>-do-</td>
</tr>
<tr>
<td>Two-ply NaAlg/CS</td>
<td>0.554</td>
<td>2,010</td>
<td>16</td>
</tr>
<tr>
<td>pAAm-g-NaAlg</td>
<td>0.088</td>
<td>96</td>
<td>17</td>
</tr>
<tr>
<td>NaAlg/PVA blend</td>
<td>0.041</td>
<td>579</td>
<td>18</td>
</tr>
<tr>
<td>NaAlg/pAAm-g-GG blend</td>
<td>0.026</td>
<td>891</td>
<td>19</td>
</tr>
<tr>
<td>NaAlg + 5 wt. % PVA + 10 wt. % PEG</td>
<td>0.030</td>
<td>3,591</td>
<td>20</td>
</tr>
</tbody>
</table>

NaAlg-Sodium alginate; CS-Chitosan; pAAm-Poly(acrylamide); PVA-Poly(vinyl alchol); GG-Guar gum; PEG-Poly(ethylene glycol)

V.3. CONCLUSIONS

The present study is an attempt to improve the PV performance of the pristine NaAlg membrane by blending it with 5 and 10 wt. % PSSA. Indeed, the $\alpha$ and $J$ values were better than those of the previously published data for the PV dehydration of isopropanol. Selectivity decreased, but flux increased with increasing water composition of the feed, following the trends of sorption data. As regards the effect of membrane thickness, selectivity increased, but flux decreased with increasing membrane thickness. Temperature dependency of PV showed a linear relationship of flux with temperature as per the Arrhenius equation. An increase in flux with a decrease in selectivity was observed at higher temperatures. Blend membranes of NaAlg/PSSA at higher composition (>10 wt. %) could not be developed due to phase separation. Permeation separation index and enrichment factor data exhibited decreasing trends with increasing amount of water in the feed mixtures.
V.4. REFERENCES