Chapter 6

Separation of Organic-Organic Liquid
Mixtures by Pervaporation

Summary

Poly (ethylene-co-vinyl acetate) (EVA) films can be used for the selective separation of aromatic hydrocarbons from alcohol-hydrocarbon mixtures. Membranes showed hydrocarbon selectivity only when they were modified with benzoyl peroxide (BP) or dicumyl peroxide (DCP). It was found that the selectivity and flux were strongly influenced by the feed composition. The component fluxes were calculated to account for the high selectivity of DCP modified membranes. The influence of crosslinking density of the membranes on pervaporation was also analysed. The maximum separation and flux were found to be associated with an optimum amount of crosslinking agent. It is observed that selectivity was independent of the thickness of membranes. The influence of the molecular size of predominately permeating species and cure time on the permeation flux and selectively were also investigated. A comparison of the pervaporation characteristics of methanol/toluene mixtures with ethanol/toluene mixtures was also done. The second part deals with pervaporation of chlorinated hydrocarbon-acetone mixtures. The permeation characteristics in the pervaporation process were examined using carbon tetrachloride/acetone mixtures. Modified membranes exhibited carbon tetrachloride permselectivity, but unmodified membranes did not display the permselectivity of crosslinked polymer. A mixture of chloroform and acetone having a composition near the azeotrope region was separated.

A part of the results of this chapter has been published in the Journal of Applied Science, Vol. 60, 735 (1996) and the other part has been communicated to Separation Science and Technology.
6.1. Introduction

In 1970’s and 80’s membrane assisted separation of liquids and gases became an exceedingly important field of research. Even today, the membrane separation processes are gaining more and more importance in the chemical industries because of low cost, easy maintenance, stability in hostile environments, low energy and material consumption, the continuous nature of the process, simplicity and flexibility of control [1-3]. The ability of polymers to selectively solubilise and transport the molecules of gas, vapour, liquid and sometimes solute through its solid phase has made them, the most preferable material for membrane separation process.

Currently pervaporation is the most developed membrane separation method used widely. This method attracts the attention of specialists in chemical and related fields like biochemical and petrochemical industries as energy saving and environment friendly technology. The main advantage that makes this method an outstanding one is that it can be used to separate any liquid mixture in all concentration ranges [2-5]. The driving force for the transport is the concentration difference across the membrane due to pressure difference. When in contact with the feed mixture, the membrane works as a pseudo liquid immobilized layer. At first, the component molecules get absorbed on the upper side of the membrane and then diffuse to the other side. On the other side, utilizing a minimum energy of enthalpy of vaporization, a phase change occurs and the vapour is removed and then condensed. The permeate composition is
mainly determined by relative affinities of the feed components for the membrane and their unequal mobilities within the membrane. Hence permeate composition will vary from that of the feed.

The separation basis of pervaporation is a solution diffusion mechanism i.e., flux is a function of solubility and diffusivity. Solubility is a thermodynamic property whereas diffusivity is a kinetic property and both affects selectivity as well as the flux. If permeate rapidly evolves under a low pressure, then diffusion is the rate limiting step. If the downstream pressure is allowed to increase, a transition occurs, i.e. desorption slows down and it will turn out to be the rate determining step.

Pervaporation can be used for dehydration of organic solvents [6,7] and removal of organics from aqueous streams [8,9]. Additionally, pervaporation has emerged as a good choice for the separation of heat sensitive products.

membranes for the pervaporation of toluene-water system. Kurkuri and Aminabhavi (14) investigated the pervaporation (PV) separation of 1,4 – dioxane – water mixture at 30 and 50°C for 10 wt% of water using the blend membrane of acrylamide of sodium alginate. Wang et al. (15) reported the flux values of 0.318 and 0.417 kg/m²h with selectivities of 419 and 663 respectively for the alginate composite membrane in separating 1,4–dioxane – water mixture. A novel polymer membrane system consisting of interpenetrating network of hydroxyl terminated polybutadiene based poly urethane urea – poly (methyl methacrylate) was prepared and used for the pervaporation of toxic p-chlorophenol and 2,4 – dichlorophenol from their dilute aqueous solutions [16]. Kariduraganavar [17] separated water-isopropanol mixtures using sodium alginate and NaY zeolite membranes. The effects of zeolite loading and feed composition on pervaporation were analysed. Industrial scale applications of pervaporation, particularly for hydrophobic mixtures, have been limited in part by inadequate membrane performance and high membrane cost. Good membrane performance requires high selectivity and acceptable permeability. Thus economical polymeric membrane material development is a key issue for eventual implementation of this technology. Therefore, the present work is to develop a new polymer membrane based on differently crosslinked polymer poly (ethylene-co-vinyl acetate) (EVA) for the selective separation of organic-organic mixtures by pervaporation.
This chapter deals with pervaporation of aromatic hydrocarbon / alcohol and chlorinated hydrocarbon – acetone mixtures. Special attention is being given to the effect of feed composition on permeation flux and selectivity. The effects of cure time of the membranes, film thickness and the molecular size of permeate on the separation process were also examined. Chloroform and acetone form an azeotropic composition. A composition near azeotropic region has been analysed.

6.2. Result and Discussion
6.2.1. Pervaporation of aromatic hydrocarbon / alcohol mixtures
6.2.1.1. Swelling characteristics

Initially a piece of a dry membrane was weighed and swelled in the solution mixture of carbon tetrachloride and acetone of known composition for 24 h at 30°C. The swollen membrane was taken out and wiped with tissue paper to remove adherent solvent and then weighed. Difference between the weights gave the amount of solvent absorbed by the polymer. The swelling ratio was calculated using the equation 2.4 (Chapter 2).

The degree of swelling of uncrosslinked membrane (D₀), DCP modified (D₁) and BP modified membranes (B₁) are represented in Figure 6.1. B.P modified membranes showed a higher swelling while uncrosslinked membranes exhibited a lower swelling. The lower swelling ratio of uncrosslinked membranes is due to the crystalline nature. The crystalline nature was evident from the X-ray diffraction patterns given in Figure 3.4 (Chapter 3). Since the degree of crosslinking and swelling ratio are
inversely related, the differences in the swelling behaviour of DCP and BP modified membranes can be attributed to the different degrees of crosslinking. In all cases, as the concentration of toluene in the feed increases the swelling ratio also increases.

![Swelling ratio vs Toluene in the feed (wt%)](image)

**Figure 6.1.** Effect of feed composition on swelling ratio

### 6.2.1.2. Pervaporation of ethanol / toluene mixtures through EVA membranes

The toluene concentration in the permeate for various toluene – ethanol mixtures through unmodified, DCP and BP modified membranes is presented in Figure 6.2. The operating temperature was 30°C. EVA shows good affinity towards aromatic hydrocarbons and is highly swollen in aromatic hydrocarbons.
Since solubility parameter of EVA and toluene are close, ($\delta$ of EVA and toluene are 18.8 & 18.2 (MPa)$^{1/2}$, respectively) it is expected that EVA will preferentially permeate toluene from ethanol-toluene mixtures and hence will be more selective towards toluene. But unmodified membranes did not show any toluene selectivity and showed a selectivity less than unity for all concentrations. The crystalline domains generate a compact structure and this slows down the diffusion of bigger hydrocarbon molecules. Long range order is responsible for the non-selectivity of unmodified membranes.

Membranes modified with DCP and BP were more selective towards hydrocarbons than alcohol molecules. The modification of membranes by the inclusion of BP and DCP reduces the crystallinity, as a result of crosslinking. Also these molecules probably increase the hydrophobic nature to such an

**Figure 6.2:** Pervaporation characteristics of EVA membranes.
extent that the membrane becomes more selective towards hydrophobic molecules.

For modified membranes, hydrocarbon selectivity is highest for DCP modified membranes. This is due to the presence of more crosslinks in DCP modified membranes and this significantly increases the selectivity of membranes.

6.2.1.3. Influence of feed composition

According to solution-diffusion mechanism permselective properties of pervaporation membranes are determined by solubility and diffusivity of the permeating components in the membrane. Since both sorption and diffusion phenomena are dependent on the composition of liquid mixture, the permeation properties are strongly influenced by the feed composition.

The effect of feed composition on the permeation rate and separation factors were investigated for different mixtures. Figure 6.3 represents the effect of feed composition on the permeation fluxes. Low fluxes are obtained when the toluene concentration in the feed is less for all the three membranes and the fluxes increase strongly when hydrocarbon content in the feed increases. With the increase in hydrocarbon content, free volume of the membrane increases due to plasticization and this leads to higher flux. Figure 6.4 gives the effect of feed composition on selectivity. The selectivity also increases with the increase in toluene concentration in the feed. As the concentration of toluene in the feed increases, the solubility of toluene in the membrane increases owing to closer solubility parameter
values. The diffusivity also increases along with solubility and hence they exhibit a high selectivity.

**Figure 6.3**: Effect of feed composition on permeation fluxes

**Figure 6.4**: Effect of feed composition on selectivity
The total flux \( J \) can be divided into the component flux of toluene (\( J_{\text{toluene}} \)) and that of ethanol (\( J_{\text{ethanol}} \)) by using the permeate composition data.

\[
J_{\text{toluene}} = J \times Y_{\text{toluene}} \quad (6.1)
\]
\[
J_{\text{ethanol}} = J \times Y_{\text{ethanol}} \quad (6.2)
\]

where \( Y_{\text{toluene}} \) and \( Y_{\text{ethanol}} \) are the concentration of toluene and ethanol in the permeate respectively. The component fluxes of toluene / ethanol mixtures were calculated from the above equations and are shown in Figure 6.5 as a function of feed composition for D1 membrane.

\[\text{Figure : 6.5 : Effect of feed composition on component fluxes}\]

With the increase in feed composition, toluene flux increases and ethanol flux decreases. The increase in selectivity with increase in feed
composition is due to the increase of toluene flux compared to ethanol flux. The high selectivity of DCP modified membranes can also be explained on the basis of the high percentage of toluene flux compared to other systems. The percentage of component fluxes is given in Table 6.1.

**Table 6.1**: Component Flux (Percentage) (70/30 composition)

<table>
<thead>
<tr>
<th>Systems</th>
<th>Toluene Flux</th>
<th>Ethanol Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>D₁</td>
<td>60.4</td>
<td>6.56</td>
</tr>
<tr>
<td>B₁</td>
<td>52</td>
<td>9.2</td>
</tr>
<tr>
<td>D₀</td>
<td>36</td>
<td>23.04</td>
</tr>
</tbody>
</table>

The high percentage of toluene flux and low percentage of ethanol flux contribute significantly towards the high selectivity of DCP modified membranes. The percentage of toluene flux is least for the unmodified membranes. Thus selectivity towards aromatic hydrocarbon decreases in the order DCP > BP > unmodified EVA membranes.

**6.2.1.4. Effect of crosslinks on pervaporation**

The effect of the number of moles of DCP in the membrane on the pervaporation performance of 50 weight percentage of toluene-alcohol mixture is given in Figure 6.6. With increase in the number of moles of DCP in the membrane, toluene concentration in the permeate and the permeation rate decreases. Consequently a minimum amount of DCP should be included.
The low permeation rate and the absence of toluene selectivity for the unmodified EVA are due to the crystalline nature, which generates a compact structure and hence lower porosity. The porosity and selectivity are increased upon the addition of moderate amounts of DCP because these molecules introduce some disorder by forming random C-C networks. Crystallinity is substantially reduced in the crosslinked sample. For crosslinked samples, the permeation rate and selectivity vary in the order $D_1 > D_2 > D_4 > D_6 > D_8$. When the amount of DCP used for crosslinking is increased, the extent of crosslinking goes up. When the amount of DCP becomes too large, the polymer chains become very rigid due to crosslinking and this prevents the sorption of molecules into the network.
6.2.1.5. Effect of film thickness

Pervaporation of 50-weight percentage of alcohol-toluene mixture was carried out through DCP modified membranes with different film thickness. The weight percentage of toluene in the permeate and permeation fluxes are given in Figure 6.7. It is found that, the separation efficiency of the membrane is independent of the thickness of membrane. However, the permeation flux decreases with increasing thickness of the membrane.

![Graph: Dependence of film thickness on pervaporation.](image)

Figure 6.7 : Dependence of film thickness on pervaporation.

6.2.1.6. Influence of cure time

Another significant parameter controlling the separation process was found to be the cure time of the membranes. The toluene weight percentage in the permeate and the permeation fluxes of 50 weight percentage of toluene-ethanol mixtures through DCP membranes with different cure times are presented in Figure 6.8. It shows that as the cure time of the
membrane increases the permeation flux decreases. The increase in cure time increases the number of crosslinks between the polymeric chains, thereby enhancing the rigidity of the macro molecular network. This in turn reduces the flux but enhances the separation efficiency.

![Graph](image.png)

**Figure : 6.8 :** Effect of cure time on the separation efficiency and permeation flux

### 6.2.1.7. Pervaporation of benzene-ethanol mixtures

The influence of the molecular weight of the predominantly permeating species on separation process was investigated by carrying out the pervaporation of benzene-ethanol mixtures through DCP modified membranes. The trend of the dependence of flux and selectivity on the feed composition is almost the same as that for toluene-ethanol mixtures. With the increase in benzene concentration in the feed, the permeation flux and selectivity increases. It is found that for the same feed composition, the separation factor and fluxes are much higher for
benzene-ethanol mixtures. This is in agreement with the fact that low molecular weight molecule diffuses more easily through a compatible medium. Figure 6.9 presents the weight percentage of benzene in the permeate and permeation fluxes for different mixtures through DCP modified membranes.

![Graph showing pervaporation characteristics of benzene-alcohol mixtures](image)

**Figure 6.9**: Pervaporation characteristics of benzene-alcohol mixtures

**6.2.1.8. Pervaporation of methanol-toluene mixtures**

The pervaporation results for the methanol-toluene mixtures are given in Figure 6.10. Here again the trend of the dependence of flux and selectivity on the feed composition is the same as that of ethanol-toluene mixture. With increase of toluene concentration in the feed, the flux and selectivity increases.
From the comparison of pervaporation properties of methanol-toluene versus ethanol-toluene mixture, it can be seen that selectivity is higher in ethanol-toluene, than methanol-toluene for the same feed composition. But the pervaporation fluxes are higher for methanol-toluene mixture. This is due to the different degrees of interaction. Methanol shows a stronger affinity towards EVA since methanol is more polar. EVA is slightly polar in nature and hence there may be dipole-dipole interaction. This results in the reduction of selectivity of EVA membranes towards methanol-toluene mixtures. In addition, the smaller methanol molecules can penetrate more easily than the ethanol molecules. The molar volume of methanol is about two third of ethanol, which implies that methanol, the smaller molecule will permeate faster through a membrane than ethanol. Thus stronger interaction of methanol towards EVA membrane reduces its hydrocarbon selectivity but increases the permeation flux.
6.2.2. **Pervaporation characteristics of EVA membranes towards carbon tetrachloride-acetone mixtures**

Pervaporation of a binary mixture of carbon tetrachloride and acetone containing 50 weight % of each was carried out through unmodified and DCP modified membranes. The selectivity of unmodified and DCP modified membranes (D₁₁) for the above mixture is 0.85 and 4.38 respectively. Since the solubility parameters of carbon tetrachloride and EVA are close, it is expected that carbon tetrachloride would preferentially permeate and hence would be more selective towards carbon tetrachloride. However, experiments show that unmodified membranes do not exhibit any carbon tetrachloride selectivity and the selectivity is close to unity. This is due to the long range order persisting in unmodified membranes; even though sorption of carbon tetrachloride in the membrane is high; its diffusion is lower than that of acetone. The compact crystalline regions form a tortuous path for the diffusion of bigger carbon tetrachloride molecules. Thus both molecules can permeate with equal probability. The above results are complementary to the results using aromatic hydrocarbon/ethanol mixtures.

Modified membranes exhibited a higher selectivity and were more selective towards CCl₄. As a result of crosslinking, there is a reduction in crystallinity. Thus CCl₄ can permeate more easily through the modified membranes.
Permeation rate for the unmodified and DCP modified membranes for the binary mixture of CCl$_4$ and acetone containing 50 weight % is 0.28 and 0.57 kg/m$^2$h respectively. The compact crystalline regions of unmodified EVA, prevents the diffusion of molecules and this accounts for its low flux. When EVA was crosslinked, the crosslinking introduced C-C networks, thereby reducing the crystallinity and increasing the porosity.

**6.2.2.1. Influence of feed composition**

The permeation properties of the membrane are strongly influenced by the feed composition. Figures 6.11 and 6.12 shows the effect of feed composition on the selectivity and the permeation rate for various CCl$_4$ /acetone mixtures. It is very clear from the figures that, with the increase of CCl$_4$ concentration in the feed, the permeation rate and selectivity of chlorinated hydrocarbons increase.

![Figure 6.11: Effect of feed composition on selectivity](image-url)
As the concentration of CCl₄ in the feed increases, the solubility of CCl₄ in the membrane increases owing to closer solubility parameter values. The diffusivity also increases along with solubility. With the increase in CCl₄ concentration, free volume of the membrane increases due to plasticization and hence the rate increases. The high flux values are quite reproducible.

6.2.2.2. Calculation of pervaporation separation index (PSI)

The pervaporation separation index (PSI) is calculated using the equation.

\[
\text{PSI} = J (\alpha - 1)
\]

(6.3)

where \( J \) is the total flux and \( \alpha \) is the selectivity. The pervaporation separation index is plotted as a function of feed composition in Figure 6.13.
for CCl₄ – acetone mixtures. PSI increases with increase in feed composition for all the systems under examination. PSI is maximum for DCP modified EVA membranes.

![Figure 6.13: Effect of feed composition on pervaporation performance](image)

**Figure 6.13:** Effect of feed composition on pervaporation performance

### 6.2.2.3. Separation of azeotropic mixture

Chloroform and acetone form a high boiling azeotrope at 78.5 wt% of chloroform. The modified EVA membranes showed chloroform selectivity from chloroform – acetone mixtures. A composition of chloroform and acetone near the azeotropic region was examined by pervaporation. A high selectivity and flux were observed. The results are given in Table 6.2. Thus modified membranes are effective for the separation of azeotropic mixtures.
Table 6.2: Separation of Chloroform-Acetone Mixture

<table>
<thead>
<tr>
<th>Wt% of CHCl₃ in the feed</th>
<th>Wt % CHCl₃ in the permeate</th>
<th>Selectivity ($\alpha_{ij}$)</th>
<th>Permeation rate (Kg/m².h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>81.2</td>
<td>97.6</td>
<td>9.42</td>
<td>8.47</td>
</tr>
</tbody>
</table>

6.3. Conclusion

Aromatic hydrocarbon selective membranes were prepared from poly (ethylene-co-vinyl acetate) (EVA). Dicumyl peroxide (DCP) and benzoyl peroxide (BP) were used for crosslinking. Virgin EVA membranes were prepared. Their pervaporation properties were investigated using toluene-ethanol mixtures. DCP and BP modified membranes showed hydrocarbon permselectivity. BP modified membranes showed a higher flux than DCP modified membranes for all the concentrations. However, the unmodified membranes did not show any hydrocarbon selectivity. Different membranes with different loading of DCP were prepared. It was observed that as the amount of DCP increased, the selectivity and permeation flux decreased. Thus maximum flux and separation factor were observed for membranes with minimum amount of DCP ($D_1$).

It is also observed that the membrane performance was strongly influenced by the feed mixture composition. For all the mixtures both flux and weight percentage of hydrocarbon in the permeate increased with increase in hydrocarbon content in the feed.
Toluene/methanol mixtures showed higher fluxes than toluene-ethanol mixtures. Benzene-alcohol mixtures showed higher flux and separation factor than toluene-alcohol mixtures. The difference in the molecular size between benzene and toluene favours the permeability of the smaller molecule. The separation factor of the membranes appear to be independent of their thickness while the flux decreases with increase in membrane thickness. The cure time of the membranes and the separation efficiency were directly related.

DCP modified EVA membranes exhibited CCl₄ selectivity from CCl₄ – acetone mixtures. However unmodified membranes did not show CCl₄ selectivity. The performance of the membranes was strongly influenced by the feed composition. Pervaporation of chloroform-acetone mixture having composition near the azeotropic region showed higher flux and selectivity. The high values for flux and selectivity assure the effectiveness of DCP modified EVA membranes in pervaporation studies.
References


