CHAPTER - 5

Separation of isopropyl alcohol – water mixtures by pervaporation using copolymer membrane: Analysis of sorption and permeation
5.1 INTRODUCTION:

As one of the most important organic intermediates isopropanol (IPA) is used in many chemical processes. Concentrated IPA solution is widely used as cleaning agent in chemical and semi conductor industries [1]. However, IPA-water mixtures form azeotrope (87.7 wt% IPA in water) with an azeotropic boiling point of 80.3°C. Thus, industrially IPA is concentrated up to azeotropic point by normal distillation [1]. Azeotropic distillation is employed for concentration of IPA from 87.7 to 99.5%. This azeotropic distillation needs very high energy because of large reflux ratio. Further, water is collected as vapor from the top of the column. Thus, a low energy separation process like pervaporation (PV) is being tried as an alternative candidate for dehydration of IPA at and above azeotrope point [2]. Over the last few decades PV is being extensively used for solvent dehydration with setting up of more than 100 membrane units operating worldwide [3]. A stable hydrophilic membrane having high permeability and water selectivity is required for effective PV dehydration. Most of the commercially available membranes used for solvent dehydration are made by crosslinking polyvinyl alcohol (PVOH) with glutaraldehyde [4]. However, PVOH membranes show extensive swelling in diluted feed with loss of selectivity. Thus, in recent times PVOH membrane has been physically and chemically modified to improve its separation potential. Acrylic acid and hydroxyethylmethacrylate was copolymerized in the matrix of PVOH followed by crosslinking with glutaraldehyde to form crosslinked interpenetrating network (IPN) type polymer. These crosslinked IPN membranes showed higher flux and selectivity than pristine PVOH membranes [5]. Filled PVOH membrane was made by incorporating micro size aluminosilicate filler in the matrix of PVOH. This filled membrane was reported to show high flux
and selectivity even for diluted feed [6]. Apart from PVOH other membranes were also tried for pervaporative dehydration of IPA. Inorganic membrane made from silica [4] was also used for dehydration of IPA. This inorganic membrane gave higher flux but much lower selectivity than glutaraldehyde crosslinked PVOH membrane. To improve separation potential of inorganic membrane, organic-inorganic hybrid membrane was synthesized from 1, 2-bis(triethoxysilyl) ethane (BTESE) by a sol-gel technique [7]. Accordingly, BTESE100 membrane produced by firing BTESE at 100°C gave flux of 2.51 kg/m²hr and water selectivity of 130 for 90 wt% IPA. Shi et al [8] incorporated nano sized zeolitic imidazolate framework (ZIF) into the matrix of polybenzimidazole to produce mixed matrix membrane. This mixed matrix membrane showed much higher water permeability than unfilled polybenzimidazole membrane. PV membrane was also synthesized from engineering plastics like polyphenylsulfone (PPS) and sulfonated polyphenylsulfone (SPPS). SPPS membrane showed higher flux and selectivity than PPS membrane for dehydration of C1-C4 alcohols [9]. High performance hollow fiber membrane consisting of thin film composite (TFC) polyamide membrane gave high flux of 1.2 kg/m²hr and selectivity of 624 for 85 wt% IPA at 50°C [10]. Polyelectrolyte composite membranes were prepared by electrostatic self assembly of oppositely charged polyethyleneimine and polyacrylic acid on polyacrylonitrile support. This polyelectrolyte membrane with two bilayers concentrated 9 wt% IPA in feed to 98 wt% in permeates at 70°C [11]. Hydrophobic inert polymer having high free volume was also used for pervaporative dehydration of IPA. Thus, perfluorinated membrane [12] yielded a flux of 0.05 kg/m²hr and water selectivity of 500 for 98 wt% IPA at 20°C.
From the above discussion it appears that in recent times membranes made from crosslinked, filled and chemically modified hydrophilic polymers and engineering plastics, silica and zeolyte based inorganic membranes, mixed matrix membranes, thin film composite membranes, polyelectrolyte membranes, etc. were tried for separation of water-IPA mixtures. Crosslinked hydrophilic membranes show extensive swelling and hence poor selectivity for diluted feed. The membranes made from engineering plastics like polyethersulfone or polyamide is mechanically very stable. However, these polymers are difficult to process into a membrane because of its limited solubility. Inorganic membranes are resistant to most of the solvents and mechanically durable but show lower selectivity than polymeric membranes [4]. The requirement of polymer-polymer compatibility factor of a blend membrane or polymer-filler compatibility of a mixed matrix membrane limits its applications. Network type structure of an IPN membrane gives high selectivity at the cost of flux. Polyelectrolyte membranes are not chemically stable under various process conditions. In contrast, in a binary copolymer membrane properties of two different polymers are combined. Unlike most of the water soluble polymers, crosslinker is not needed for a copolymer for resisting swelling if homopolymer of one of its constituent monomer is resistant to the permeant mixtures. Thus, in absence of any crosslinker no network structure is formed within the membrane matrix which gives increased permeability. These membranes are also mechanically stable. Thus, membranes made from acrylic copolymers have also been used for solvent dehydration. Poly(acrylonitrile –co-methyl acrylate), a copolymer of acrylonitrile and methyl acrylate has been used for organic-organic separation as well as for solvent dehydration [13,14]. In the present work poly(acrylonitrile –co-methyl acrylate) copolymer
designated as PANMA was used for pervaporative dehydration of IPA over the concentration range of 75 to 100 wt% IPA in water.

5.2. THEORY:

5.2.1 Sorption, Membrane phase composition and preferential sorption:

If $M_1$ and $x_{im}$ are molecular weight and mole fraction of preferentially sorbed component 1, number of moles $N_m$ absorbed per gm dry membrane for binary mixtures of component i and j is given by

$$\frac{S}{M_{avg.}} = \frac{N_m}{x_{im}M_i + (1-x_{im})M_j} = \frac{S}{x_{im}M_i + (1-x_{im})M_j} \tag{5.1}$$

Here $S$ is total sorption of binary liquid mixtures per gm of dry membrane. Since component i is sorbed more than component j in the membrane, the excess of number of moles of preferentially sorbed i in comparison to its feed concentration per gm of dry membrane may be expressed in terms of a parameter called preferential sorption ($\Omega$) [15, 16]

$$\Omega_i = N_m(x_{im} - x_{ib}) \tag{5.2}$$

Where, $x_{im}$ and $x_{ib}$ are mole fraction of preferentially sorbed component i (i.e. water in the present system) in membrane and bulk feed, respectively which may be obtained experimentally. From Eq. 5.1 and 5.2

$$\Omega_i = \frac{S}{x_{im}M_i + (1-x_{im})M_j}(x_{im} - x_{ib}) \tag{5.3}$$
5.2.2 Solvent cluster or mean cluster size (MCS) :

Solvent cluster or mean cluster size (MCS) is obtained from modified Zimm–Lundberg equation [17] i.e.

\[
\text{MCS} = \frac{(1 - \Phi_1)(1 + k_2 \Phi_1) \ln(1 + k_2 \Phi_1)}{k_2 \Phi_1} + \Phi_1 
\]  

(5.4)

Where  \( k_2 = \frac{k_s - k_p}{k_p} \)  

(5.5)

Here  \( k_s \) and \( k_p \) are ENSIC parameters obtained from Eq. 3.4 given in chapter-3 page-146.

Interaction parameter between membrane and solvent based on Flory-Huggins thermodynamics at infinite dilution (\( \lambda_{ip}^{\mu} \)) may be obtained from ENSIC parameter using the following Eq.5.6 [17]

\[
\lambda_{ip}^{\mu} = \ln \left( \frac{1}{k_p} \right) - 1 
\]  

(5.6)

5.2.3 Determination of Diffusion coefficient :

Diffusion of permeants through dense pervaporation membrane may be more accurately expressed in terms of solvent volume fraction in stead of solvent molarity based on transfer solution volume fraction model (TSVF) as described in chapter-4 page-199,

As per this model flux ratio of component i and j (\( J_i/J_j \)) may be expressed in terms of diffusion coefficients as
\[ \frac{J_i}{J_j} = \frac{D_{ij} V_j \phi_{iu}}{D_{ji} V_i \phi_{ju}} \]  \hspace{1cm} (5.7)

Further, partial flux of component \( i \) (\( J_i \)) may be expressed in terms of volume fraction on up stream (\( \phi_{iu} \)) and downstream (\( \phi_{id} \)) side as

\[ J_i = \frac{D_{im}}{V_i L} (\phi_{iu} - \phi_{id}) \]  \hspace{1cm} (5.8)

Average diffusivity, \( D_{im} \) may be expressed as

\[ D_{im} = D_{i0} \int_{\phi_u}^{\phi_d} \frac{f(\phi)}{\phi_u - \phi_d} \, d\phi \]  \hspace{1cm} (5.9)

Where \( L \) is membrane thickness and \( V_i \) is molar volume of component \( i \). Assuming Greenlaw’s law of linear dependency of diffusion coefficient

\[ f(\phi) = 1 + \lambda \phi \]  \hspace{1cm} (5.10)

where \( \lambda \) is plasticization coefficient

Thus, \( J_i = \frac{1}{V_i L} D_{i0} \left[ 1 + \frac{1}{2} \lambda \left( \phi_{iu} + \phi_{id} \right) \right] (\phi_{iu} - \phi_{id}) \)  \hspace{1cm} (5.11)

For low downstream pressure, \( \phi_{id} = 0 \)

Therefore, \( J_i = \frac{1}{V_i L} D_{i0} \left[ 1 + \frac{1}{2} \lambda \phi_{iu} \right] (\phi_{iu}) \)  \hspace{1cm} (5.12)

Where, \( \phi_{iu} \) = total water (solvent) volume fraction on upstream side of membrane.

Diffusion coefficient at infinite dilution and plasticization coefficient may be obtained using Eq. 5.7 and 5.12.

**5.3. EXPERIMENTAL :**
5.3.1 Materials and Membrane:

Pervaporation membrane was prepared from commercially available copolymer poly(acrylonitrile-co-methyl acrylate) designated as PANMA. Availability and properties of the polymer is given in detail in chapter-4 page 188. Membrane was cast on a clean and smooth glass plate from solution of the copolymer in DMF (5 wt%) by similar experiment as described in chapter-4, page. The membrane thickness was maintained at ~50 microns. The thickness was measured by Test Method ASTM D 374 using a standard dead mass thickness gauge (Baker, Type J17).

5.3.2 Sorption and Permeation study:

5.3.2.1 Total sorption, sorption selectivity and preferential sorption:

Total Sorption of IPA-water mixtures and sorption selectivity for water was obtained by similar experiment as described in chapter-1, page 50. Interaction parameters of IPA-water mixtures (\(\chi_{ij}\)) as well as solvent-polymer (IPA-polymer, \(\chi_{ip}\) or water-polymer, \(\chi_{jp}\)) were determined by similar methods as described in chapter-2 page 95-96 using Eq. 2.1 and Eq. 2.7. The preferential sorption of the membrane was also obtained from the change in feed concentration by sorption using Eq. 5.3

5.3.2.2 Permeation study:
Permeation experiments with this membrane was also carried out at different feed concentrations and feed temperatures in a stirred batch pervaporation cell as reported in detail in chapter-1 page-51. Separation factor for water was determined from feed and permeate composition by similar experiments as described in chapter-1, page-53 using Eq. 1.19. Each experiment was repeated three times and the results were averaged to minimize error. The results were reproducible, and the errors inherent in the pervaporation measurements were less than ±5%. The feed, membrane (for sorption experiment) and permeate (for pervaporation experiment) were analyzed by similar experiments as described in chapter-1, page-51-53.

5.4. RESULTS AND DISCUSSION:

5.4.1 Swelling Studies:

5.4.1.1 Effect of feed concentration on sorption isotherms:

Sorption isotherms at four different temperatures (30°C, 40°C, 50°C and 60°C) along with sorption selectivity are shown in Fig.5.1. From Fig.5.1 it is observed that total sorption of water and IPA mixtures increases almost linearly with feed water concentration. Sorption selectivity is observed to decrease exponentially with feed concentration. The effect of temperature on sorption and sorption selectivity is also shown in the same Fig.5.1. It is observed that increase in temperature results in increase in sorption but decrease in sorption selectivity. The increase in sorption with feed concentration may be ascribed to increased interaction of water with the
hydrophilic membrane. At higher feed water concentration swelling of the membrane also increases due to this increased interaction. Increased swelling leads to increase in free volume in the membrane resulting in decrease in water selectivity. At higher temperature mobility of the copolymer chain increases with increased free volume which results in increased sorption but decrease in sorption selectivity. Preferential sorption of water is also observed to increase initially with feed concentration of water as shown in Fig. 5.2. However, the change of preferential sorption of water is marginal from 2.5 to 18.5 wt% water in feed. Thereafter it decreases sharply signifying plasticization of the membrane. Preferential sorption is found to increase with temperature as observed in Fig. 5.2. Similar results were also reported elsewhere [15, 18].

5.4.1.2 Thermodynamic parameters based on Flory Huggins model:

The interaction parameter (IP) between solvents i.e. water and IPA in feed ($\chi^{f}_{ij}$) was determined by Eq. 2.1 (Chapter-2, page-95). Interaction parameter between solvents in membrane membrane ($\chi^{m}_{ij}$) was determined using similar regressed Eq. 3.1 and Eq.3.2 (chapter-3, page-146). IP between solvent and polymer (membrane) was determined by using Eq. 2.7 (chapter-2, page-96). The variation of IP of solvents with feed activity of water in feed and in membrane is shown in Fig.5.3. From this figure it is observed that $\chi^{f}_{ij}$ is much higher than $\chi^{m}_{ij}$ for any feed concentration at 30°C. The greater the value of IP, the lower will be the interaction. Thus, water-IPA interaction in membrane is much higher than their interaction in feed. It explains sorption of water-IPA mixtures by the membrane. It is also observed from Fig.5.3 that with increase in feed water concentration $\chi^{f}_{ij}$ decreases while $\chi^{m}_{ij}$ increases. Water and IPA
are both polar solvents. As water concentration in feed increases, interaction between water and IPA increases because of cluster formation by hydrogen bonding [18]. Thus, $\chi_{ij}$ decreases indicating increased interaction of water and alcohol at higher feed water concentration. However, in membrane opposite phenomena occurs since membrane-water interaction increases at higher feed concentration resulting in decreased interaction between water and alcohol in membrane and hence increase in $\chi_{ij}^m$ values. It is observed from Fig.5.3 that $\chi_{ij}^m$ increases at higher temperatures i.e. at higher temperature water-IPA mutual interaction in membrane decreases. From Fig.5.4 IP of membrane-water ($\chi_{im}$) is observed to be much lower than IP of membrane-IPA ($\chi_{jm}$) signifying preferential water sorption by the membrane. It is also observed that $\chi_{jm}$ decreases with temperature though change of $\chi_{im}$ with temperature is not significant. Thus, due to increased interaction of membrane and IPA sorption selectivity of water decreases at higher temperature.

5.4.1.3 Coupling effect in sorption based on Flory Huggins model:

Coupling in sorption i.e. mutual interaction of water and IPA in membrane during sorption may be evaluated in terms of activity coefficient of water and IPA. Activity coefficient of water and IPA for state-I (single pure component), state-II (binary components without coupling) and state-III condition (binary components with coupling) is obtained using Eq.4.2-4.5 based on Flory Huggins model as mentioned in chapter-4, page-186. From Fig.5.5 it is observed that state-II activity coefficient of water in membrane is much higher than its state-I activity coefficient. This positive deviation of membrane phase activity coefficient implies that the interaction between
water and membrane dominates water activity in the membrane. However, due to coupling effect between water and IPA in the membrane [18] state-III activity coefficient of water is found to be lower than its state-II activity. Similar trend is also observed for IPA. However, in this case coupling effect is more pronounced and state-III activity of IPA at higher feed water concentration is observed to be lower than its state-I activity. Similar results were reported by Ren and Jiang [19] for ethanol-water system with crosslinked chitosan membrane.

5.4.1.4 Thermodynamic parameters based on ENSIC model:

Solvent clustering in membrane was explained using ENSIC model. The exponential regression of experimental volume fraction of water against its feed activity is shown in Fig.5.6. The ENSIC parameters i.e. $k_s$ and $k_p$ along with standard errors and regression coefficients $r^2$ are given in table-5.1. The much higher values of $k_s$ than $k_p$ as shown in table-5.1 confirms solvent clustering in the membrane [17]. Mean cluster size (MCS) as obtained using ENSIC parameters (Eq. 5.4) is observed to increase with increase in feed water concentration and temperature as shown in Fig.5.7.

5.4.1.5 Coupling effect in sorption based on ENSIC model:

The coupling effect ($C_F^{ENSIC}$) in sorption was also quantitatively evaluated using Eq. 4.6 based on ENSIC model as mentioned in chapter-4, page-187. From Fig.5.7 it is observed that at low feed activity of water $C_F^{ENSIC}$ of both IPA and water exceeds
unity signifying positive coupling effect in sorption. It is also observed that at lower feed water concentration $C_{F\text{ENSIC}}$ of IPA is much higher than $C_{F\text{ENSIC}}$ of water signifying strong influence of water on IPA sorption. CF of IPA and water is observed to decrease at higher temperature which may be due to decrease in interaction between water and IPA at higher temperature (Fig.5.3). Similar $C_{F\text{ENSIC}}$ values were also reported elsewhere [20, 21].

5.4.2 Pervaporation(PV) Studies:

5.4.2.1. Effect of feed concentration :

Flux and separation factor :

The effect of feed water concentration on partial molar flux of water and IPA at four different PV temperatures ($30^\circ\text{C}$, $40^\circ\text{C}$, $50^\circ\text{C}$ and $60^\circ\text{C}$) is shown in Fig.5.8. It is observed that both water and IPA flux increases almost linearly with feed concentration. It is also observed that over the feed concentration range water flux is much higher than IPA flux which signifies water selectivity of the membrane. The increase in molar water flux with concentration may be ascribed to increased interaction of water with membrane at higher feed water concentration. Further, at higher feed concentration swelling of the membrane increases which results in increase in IPA flux. Thus, separation factor for water is observed to decrease almost exponentially with feed concentration as shown in Fig.5.9. It is also observed that with increase in feed temperature both water and IPA flux increases. With increase in temperature vapour pressure of water and IPA increases. Further, segmental motion of
the copolymer membrane also increases with temperature. Thus, both water and IPA flux increases at higher temperature.

Permeability and membrane selectivity:

Effect of feed concentration on partial permeability and intrinsic membrane selectivity at four different feed temperatures i.e. 30, 45, 50 and 60°C is shown in Fig.5.10 and Fig.5.11, respectively. Like partial flux partial permeability of water is also observed to be much higher than permeability of IPA over the entire feed concentration range. However, unlike flux, permeability of water is observed to decrease with feed concentration though at higher feed concentration (~15 mass% water in feed) permeability increases with feed concentration at 30 and 45°C. At higher temperature i.e. at 50°C and 60°C change of partial permeability of water with feed concentration is marginal as observed in Fig.5.10. In contrast permeability of IPA is observed to increase almost linearly with concentration like flux. It is also observed that at higher temperature both water and IPA permeability decreases. Driving force normalized permeability is the ratio of partial flux and partial pressure difference across the membrane (Eq.-2.12a, chapter-2, page-99). Initially, with increase in feed concentration increase in partial pressure difference (denominator of permeability Eq.-2.12a, page-99) more than offset increase in flux (numerator of Eq.2.12a) and thus permeability decreases almost exponentially with concentration. However, at higher feed concentration increase in flux and thickness of the membrane (due to increased swelling) more than counteracts increase in partial pressure difference and thus permeability increases with concentration. Partial pressure difference across
the membrane also increases with temperature due to increased vapour pressure of solvents at higher temperatures. Thus, permeability decreases with temperatures for both water and IPA. Similar kind of results of permeability vs. feed concentration was also reported elsewhere [22, 23, 6]. Intrinsic membrane selectivity which is the ratio of partial permeability of water and IPA is observed (Fig.5.11) to decrease almost exponentially with feed concentration. This may be due to increase in IPA permeability at a much higher rate than water permeability with concentration. Membrane selectivity also decreases with temperature since at higher temperature both water and IPA permeability decreases.

5.4.2.2 Determination of Diffusion coefficient:

For determination of diffusion coefficient of water and IPA flux ratio of water and IPA (Ji/Jj) was plotted against ratio of volume fraction of water and IPA on membrane upstream side based on Eq. 5.7. This is shown in Fig.5.12 for flux data at 30°C. Similar trendlines were obtained at other feed temperatures. From the linear trendline (Fig.5.12) ratio of diffusion coefficients at infinite dilution (D_i0/D_j0) was obtained by dividing slope of the line with ratio of molar volumes (V_i/V_j) of component i and j. Polynomial fitting (degree of freedom 2 with zero intercept) of experimental water flux data (J_i) against its volume fraction (φ_i) on membrane upstream side (Fig.5.13) yielded the values of diffusion coefficient of water at infinite dilution (D_i0) and plasticization coefficient λ by comparing this regressed equation with Eq.-5.12. The values of D_i0, D_j0 and λ at different feed temperatures are shown in Table 5.2. From table-5.2 negative λ value is observed at lower feed temperatures.
i.e. at 30 and 45°C. The negative value of plasticization coefficient i.e. \( \lambda \) was also reported elsewhere [24]. At higher temperature i.e. at 50 and 60°C positive \( \lambda \) value is obtained as shown in table-5.2. At lower temperature bigger IPA molecule restricts the movement of smaller water molecules through the membrane resulting in negative \( \lambda \) value [24]. It is also observed from Table-5.2 that \( D_{i0} \) is higher than \( D_{j0} \). The higher diffusion coefficient of water than IPA may be ascribed to smaller kinetic diameter of water (0.296 nm) than IPA (0.450) [25]. These values of diffusion coefficients are also comparable to those reported for pervaporative transport of some of the organics and water through dense polymeric membranes. [26, 27]

5.4.2.3 Activation Energy:

Activation energy for permeation of water (\( E_{p\text{water}} \)) and IPA (\( E_{p\text{IPA}} \)) was obtained from slope of linear plotting of \( \ln P_{\text{water}} \) and \( \ln P_{\text{IPA}} \) against inverse of absolute temperature (1/T) at various feed concentrations as shown in Fig.5.14. In each of these linear regressions the values of regression coefficients (\( r^2 \)) was much above 0.9. The variation of activation energy of permeation for water and IPA with feed concentration is shown in Fig.5.15. From this figure it is observed that \( E_{p\text{water}} \) is much lower than \( E_{p\text{IPA}} \) over the entire feed concentration range. The hydrophilic copolymer membrane causes much easier permeation of water molecules than IPA molecules resulting in lower \( E_{p\text{water}} \). At higher feed water concentration both \( E_{p\text{water}} \) and \( E_{p\text{IPA}} \) decreases due to plasticization of the membrane.

5.4.2.4. Comparison of present work with reported data:
Driving force normalized water permeability and intrinsic membrane selectivity of various reported membranes and the present copolymer membrane for IPA-water system is compared is shown in Table 5.3. Permeability and selectivity data of various reported membranes were calculated from available flux and separation factor data using equation-2.12a, 2.16, respectively as given in chapter-2 page – 99-100. For composite membrane thickness of active layer was assumed to be 1 micron[28]. It is observed that some of the membranes show very high selectivity but low permeability while other reported membranes show high permeability at the cost of low selectivity. In contrast, the present copolymer membrane shows a good balance of permeability and selectivity under identical condition.

5.5. CONCLUSION:

Sorption and permeation of water-IPA mixture through copolymer PANMA membrane at different feed concentration and temperatures were studied. Flory-Huggins thermodynamics and ENSIC model were found to explain well the sorption of the membrane at various feed concentrations and temperatures in terms of interaction parameters. Solvent clustering was also explained by ENSIC model. Flux, separation factor, permeability and intrinsic membrane selectivity of the membrane at different feed concentrations and temperatures were also determined. Diffusion coefficient of solvents through the membranes was determined using modified solution diffusion model. The membrane was found to show good flux and separation
factor for water over a wide range of feed concentration. This copolymer membrane may also be suitably used for pervaporative dehydration of other similar organics.

List of symbols:

A  area (m²)

a  activity (-)

D  Diffusion coefficient (m²/s)

E  activation energy (kJ/deg mol)

ΔG°  Excess free energy

J  Flux (g/m²·hr)

k  ENSIC interaction parameter (-)

L  thickness of membrane (cm)

M  Molecular weight (g/mol)

Nₘ  Number of mol (-)

S  Total sorption (g/g membrane)

t  time (s)

T  absolute temperature (K)

v  volume fraction in feed (-)

V  molar volume (cm³/mol)

W  mass of permeate (g)

w  mass of membrane (g)

x  mol fraction (-)

Y  membrane phase/permeate concentration (wt%)

X  membrane phase/ feed concentration (wt%)
Greek letters:

\( \lambda \) plasticization coefficient (-)

\( \Omega \) Preferential sorption (-)

\( \chi \) interaction parameter (-)

\( \gamma \) activity coefficient (-)

\( \phi \) volume fraction (-)

Subscript:

b bulk

d downstream

f feed

i component i (water)

j component j (IPA)

m membrane phase

s saturated

u upstream
REFERENCES:


[33] S.B. Teli, G.S. Gokavi, M. Sairam, T.M. Aminabhavi, Mixed matrix membranes of poly(vinyl alcohol) loaded with phosphomolybdic heteropolyacid for the


Table 5.1 Values of ENSIC parameters

<table>
<thead>
<tr>
<th>K_p x 10^2</th>
<th>K_s x 10^2</th>
<th>Standard error for K_s-K_p</th>
<th>Standard error for K_s-K_p/K_p</th>
<th>r^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001822</td>
<td>7.771482</td>
<td>1.89441</td>
<td>5.75E-04</td>
<td>0.8890</td>
</tr>
<tr>
<td>0.019443</td>
<td>4.349783</td>
<td>1.86273</td>
<td>0.0072</td>
<td>0.8897</td>
</tr>
<tr>
<td>0.071407</td>
<td>2.286937</td>
<td>1.25358</td>
<td>0.03978</td>
<td>0.8864</td>
</tr>
<tr>
<td>0.09663</td>
<td>1.89273</td>
<td>1.15257</td>
<td>0.06616</td>
<td>0.8988</td>
</tr>
</tbody>
</table>

Table 5.2 Diffusion coefficient at infinite dilution for water (D_{i0}) and IPA (D_{j0})

<table>
<thead>
<tr>
<th>Temperatur(°C)</th>
<th>D_{i0} x 10^7 m^2/sec</th>
<th>D_{j0} x 10^7 M^2/sec</th>
<th>K (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>9.11</td>
<td>1.81</td>
<td>-1.45</td>
</tr>
<tr>
<td>40</td>
<td>12.32</td>
<td>2.04</td>
<td>-1.15</td>
</tr>
<tr>
<td>50</td>
<td>15.42</td>
<td>2.81</td>
<td>0.177</td>
</tr>
<tr>
<td>60</td>
<td>18.67</td>
<td>3.12</td>
<td>1.28</td>
</tr>
</tbody>
</table>
## Table 5.3 Comparison of performances of membranes reported for pervaporative dehydration of IPA

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Feed water concentration (wt%)</th>
<th>Temperature °C</th>
<th>Water permeability x $10^{11}$ molm$^{-1}$s$^{-1}$kPa$^{-1}$</th>
<th>Membrane selectivity (-)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PER VAP 25 IO</td>
<td>12.5</td>
<td>70</td>
<td>347.5</td>
<td>76.68</td>
<td>[4]</td>
</tr>
<tr>
<td>PERVAP SMS</td>
<td>12.5</td>
<td>70</td>
<td>694.98</td>
<td>24.54</td>
<td>[4]</td>
</tr>
<tr>
<td>PVA/PAA:85/15 (%mass)</td>
<td>10</td>
<td>40°C</td>
<td>1.38</td>
<td>2.25</td>
<td>[29]</td>
</tr>
<tr>
<td>PVA–PANI-III</td>
<td>10</td>
<td>30</td>
<td>28.77</td>
<td>172.81</td>
<td>[30]</td>
</tr>
<tr>
<td>Chitosan/TDI</td>
<td>8.4</td>
<td>30</td>
<td>1639.71</td>
<td>123.32</td>
<td>[31]</td>
</tr>
<tr>
<td>P84 co-polyimide</td>
<td>15</td>
<td>60</td>
<td>390.7</td>
<td>1948</td>
<td>[32]</td>
</tr>
<tr>
<td>PVA/HPA-7</td>
<td>10</td>
<td>30</td>
<td>616.26</td>
<td>27.53</td>
<td>[33]</td>
</tr>
<tr>
<td>PVA-TMC</td>
<td>11</td>
<td>60</td>
<td>372</td>
<td>9.07</td>
<td>[34]</td>
</tr>
<tr>
<td>PVAHI</td>
<td>5.3</td>
<td>33</td>
<td>1704.25</td>
<td>129.46</td>
<td>[35]</td>
</tr>
<tr>
<td>PVGLU2</td>
<td>12.265</td>
<td>30</td>
<td>2158.53</td>
<td>16.7</td>
<td>[6]</td>
</tr>
<tr>
<td>SPPSU</td>
<td>15</td>
<td>60</td>
<td>12.7</td>
<td>10000</td>
<td>[9]</td>
</tr>
<tr>
<td>BTESE100</td>
<td>10</td>
<td>75</td>
<td>100</td>
<td>100</td>
<td>[7]</td>
</tr>
<tr>
<td>PAI-polyamide TFC</td>
<td>15</td>
<td>50</td>
<td>14277</td>
<td>177</td>
<td>[10]</td>
</tr>
<tr>
<td>PANMA</td>
<td>12.4</td>
<td>30</td>
<td>1915.88</td>
<td>63.5</td>
<td>Present work</td>
</tr>
<tr>
<td>PANMA</td>
<td>12.4</td>
<td>60</td>
<td>478.16</td>
<td>38</td>
<td>Present work</td>
</tr>
</tbody>
</table>

PVA – polyvinyl alcohol, PERVAP 25 IO – cross-linked polyvinyl alcohol (PVA), PERVAP SMS – microporous silica membrane PAA – polyacrylic acid PANI – polyaniline HPA – phosphomolybdic heteropolyacid PVA-TMC – trimesoyl chloride crosslinked PVA PVAHI – Semi IPN of copolymer of acrylic acid (AA) and hydroxyethylmethacrylate (HEMA) in PVOH TDI – toluene-2,4-diisocyanate P84 – BTDA-TDI/MDI co-polyimide of 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 80% methylphenylene-diamine + 20% methylene diamine, Sppsu-sulfonated polyphenylsulfone, BTESE100-1,2-bis(trithoxysilyl) ethane, PAI-polyamide TFC-polyamideimide thin film composite
Fig. 5.1 Variation of total sorption and sorption selectivity for water at different temperatures

Fig. 5.2 Variation of preferential sorption with feed concentration at different temperatures
Fig. 5.3 Variation of interaction parameter between water and IPA in feed and membrane

- $\chi_{ij}$:
  - $\chi_{ijf}$: Interaction parameter in feed.
  - $\chi_{ijm30}$, $\chi_{ijm40}$, $\chi_{ijm50}$, and $\chi_{ijm60}$: Interaction parameter in membrane.

Fig. 5.4 Variation of $\chi_{im}$ and $\chi_{jm}$ with temperature

- $\chi_{im}$ and $\chi_{jm}$: Interaction parameters.
Fig. 5.5 Variation of State-I, State-II and State-III activity coefficient with feed concentration at 30 °C

Fig. 5.6 Exponential regression for ENSIC parameters of solvents
Fig. 5.7 Variation of coupling factor (CF) and mean cluster size (MCS) with feed activity of water

Fig. 5.8 Variation of partial molar flux with feed concentration at different temperatures
Fig. 5.9 Variation of separation factor (SF) of water with feed concentration at different temperatures (30° C, 45° C, 60° C and 70° C)

Fig. 5.10 Variation of partial permeability with feed concentration of water
Fig. 5.11 Variation of membrane selectivity (MS) with feed concentration of water

Fig. 5.12 variation of flux ratio with feed side volume fraction ratio at 30°C

\[ \frac{J_i}{J_j} = a \left( \frac{\Phi_i}{\Phi_j} \right) \]

\[ a = 6.933, r^2 = 0.93436, \quad \text{std error} = 0.36025 \]
Fig. 5.14 Arrhenius plot based on partial permeability at different feed concentration
Fig. 5.15 Variation of activation energy for permeation with feed concentration

Activation energy for permeation (kJule/degmolK)

Feed concentration of water (wt%)

Ewater
EIPA