CHAPTER - 4

Sorption and Permeation of acetic acid-water mixtures by

Pervaporation using Copolymer membrane
4.1. INTRODUCTION

As also mentioned in chapter-2, acetic acid is considered as one of the most important organic intermediates in chemical industries and pervaporative dehydration of acetic acid is a promising candidate in separation science and technology[1]. Hydrophilic membranes based on various polymers like polyvinyl alcohols[2-6], unfilled and filled sodium alginates [7,8], interpenetrating network (IPN) polymers [9], polyphenyl sulfone [10], blend of two or more polymers[11], copolymers [ 12,13], etc., were reported for pervaporative dehydration of acetic acid. The performance of a filled or crosslinked membrane depends on type and amount of a filler or a crosslinker [14]. In contrast, a copolymer membrane without any crosslinker or filler makes the separation process simple but more effective.

Thus, in recent years copolymer membranes are being extensively used in various membrane processes like fuel cell [15], ultrafiltration [16], gas separation [17] and pervaporation[12, 13, 18]. In copolymer membrane properties of two different polymers are combined in one copolymer. Further, a crosslinker is not needed for a copolymer for resisting swelling if homopolymer of one of its constituent monomer is resistant to the solvent mixtures. Thus, in absence of any crosslinker no network structure is formed within the matrix of a copolymer membrane which gives increased permeability. Considering all of these advantages, in the present work poly ( acrylonitrile –co-methyl acrylate) copolymer designated as PANMA was used as the membrane material. This low cost PANMA copolymer is extensively used for making PAN fiber. In this copolymer the
major comonomer moiety is acrylonitrile which has limited affinity for water. However, it gives the mechanical integrity of the membrane. The other commoner moiety i.e. methyl acrylate gives water permeability of PANMA membrane because of its hydrophilic acrylate ester functional group. Earlier, this copolymer was reported to give high flux and water selectivity for pervaporative dehydration of tetrahydrofuran[19]. Thus, in the present work, membrane made from PANMA copolymer was used for pervaporative separation of water-acetic mixtures over the entire concentration range of 99.5 to 80 wt% acids in water including 100 wt% acid and water.

4.2. THEORY

4.2.1 Activity coefficient and coupling effect based on Flory-Huggins Thermodynamics :

The activity of solvent 1 i.e. \(a_1\) is expressed as product of its activity coefficient (\(\gamma_1\)) and mole fraction (\(x_1\)). However, within the membrane the mole fraction of component 1 is difficult to measure since a polymer has a molecular weight distribution in stead of a single molecular weight. Assuming constant density of solvents and polymer within the membrane, the mole fraction term may be replaced with volume fraction. Accordingly, activity of component 1 within the membrane may be assumed as [20,21]

\[
a_{1m} = \varphi_{1m} \gamma_{1m} \quad (4.1)
\]
However, for a single component sorption by membrane i.e. for pure water or pure acetic acid sorption, $a_{1m} = 1$ and activity coefficient for single component in membrane (state I) is

$$\gamma_1^m = \frac{1}{\varrho_1^m} \quad (4.2)$$

Similarly, activity coefficient of component i or j in binary mixtures of i and j without considering the coupling effect between i and j (state II) is obtained using Flory Huggins thermodynamics i.e.

$$\ln \gamma_i^m = \varphi_p + \chi_{ip} \varphi_p^2 = (1 - \varphi_i) + \chi_{ip}(1 - \varphi_i)^2 \quad (4.3)$$

Where $\gamma_i$ is activity coefficient of component 1, $\varphi_p$ is volume fraction of membrane polymer and $\chi_{ip}$ is interaction parameter between component 1 and membrane.

Considering coupling effect the activity coefficient of components i or j (state-III) may be obtained using the following Eq.-4.4 and 4.5 [20,21]

$$\ln \gamma_i^m = \varphi_p + \chi_{ip} \varphi_p^2 + (1 - \frac{V_i}{V_j})\varphi_j + \chi_{ij} \varphi_j^2 + (\chi_{ij} + \chi_{ip} - \frac{V_i}{V_j} \chi_{jp}) \varphi_j \varphi_p - u_i \varphi_i \varphi_j \frac{\partial \gamma_{ij}}{\partial \varphi_i} \quad (4.4)$$

$$\ln \gamma_j^m = \varphi_p + \chi_{jp} \varphi_p^2 + (1 - \frac{V_i}{V_j})\varphi_i + \chi_{ij} \varphi_i^2 + \frac{V_i}{V_j} (\chi_{ij} - \chi_{ip} + \frac{V_i}{V_j} \chi_{jp}) \varphi_i \varphi_p + u_j \varphi_j \frac{\partial \gamma_{ij}}{\partial \varphi_j} \quad (4.5)$$

Here $V_i$ is molar volume of solvent 1.

4.2.2 Coupling factor (CF) based on ENSIC model:
Based on ENSIC model solvent coupling may be defined in terms of coupling factor (CF) i.e.

\[ CF_1 = \frac{\varphi_{1\text{expt}}}{\varphi_{1\text{binary}}} \]  

(4.6)

Where, \( CF_1 \) is coupling factor of component 1, \( \varphi_{1\text{expt}} \) is experimental volume fraction of solvent 1 in ternary solvent1-solvent 2-membrane system and \( \varphi_{1\text{binary}} \) is volume fraction of the same solvent in solvent-membrane binary system theoretically interpolated from ENSIC model [22]

4.2.3 Thermodynamic sorption selectivity :

Sorption selectivity of thermodynamic swelling process may be defined as [23]

\[ \beta = \frac{\varphi_i^m/\varphi_j^m}{x_i/x_j} = \frac{\gamma_i^f/\gamma_j^m}{\gamma_j^f/\gamma_j^m} = \frac{k_i^f}{k_j^m} \]  

(4.7)

Where, \( k_i^f \) and \( k_j^m \) are distribution coefficient of component i and j in feed and membrane, respectively. However, sorption selectivity in terms of mole fraction may be written as

\[ \alpha_{\text{sorp}} = \frac{x_i^m/x_j^m}{x_i^f/x_j^f} = \beta \frac{V_j}{V_i} \]  

(4.8)
4.2.4 Coupling in Pervaporation:

Phenomenological deviation coefficient ($\varepsilon$):

Coupling in pervaporation was defined as deviation of actual flux ($J_1$) from its ideal flux ($J_{1\text{ideal}}$). It was expressed in terms of phenomenological deviation coefficient [24],

$$\varepsilon_1 = \frac{J_1}{J_{1\text{ideal}}} = \frac{J_1}{J_0^\text{n}_{1\text{x}_1}} = \frac{J_1^n}{J_1^0} \quad (4.9)$$

Where $\varepsilon_1$, $J_1^n$ and $J_1^0$ are phenomenological deviation coefficient, molar normalized permeation flux and local permeation flux, respectively, of component 1.

4.3. EXPERIMENTAL

4.3.1 Materials:

Pervaporation membrane was prepared from commercially available PANMA copolymer. This PANMA copolymer was kindly supplied by Consolidated Fiber India Limited, Haldia, West Bengal. The detailed specification of the copolymer is given in Table-4.1. High purity analytical grade acetic acid purchased from E.Marc, Mumbai, and double distilled water was used for making acetic acid-water feed mixtures of varied compositions.
4.3.2 Casting of membrane from copolymer:

The copolymer was dissolved in dimethyl formamide (5 wt% polymer in solvent) by stirring on a magnetic plate for around three hours till a clear viscous polymer solution was obtained. This clear polymer solution was then cast on a clean and smooth glass plate and the cast membrane was dried overnight at ambient condition. It was then taken in a vacuum oven and annealed for another three hours at 70°C to eliminate any residual solvent. The membrane thickness was maintained at ~50 micron. The thickness was measured by Test Method ASTM D 374 using a standard dead mass thickness gauge (Baker, Type J17).

4.3.3 Sorption and Pervaporation study:

Sorption and pervaporation study with acetic acid–water mixtures (0.01 to 0.5 mole fraction of water) at different temperatures (30°C to 60°C) were carried out by similar method as described in chapter-1, page-50 - 53.

4.4. RESULT AND DISCUSSION
4.4.1 Swelling Studies:

Effect of feed concentration on sorption isotherms:

Total sorption and sorption selectivity at three different temperatures are shown in Fig.4.1. From Fig.4.1 it is observed that with increase in feed concentration of water degree of swelling or total sorption of water and acetic acid mixtures by the membrane increases. It may be conceived that due to hydrophilic nature of the copolymer membrane total sorption increases with feed water concentration. From this figure it is also observed that sorption selectivity of water decreases almost exponentially with feed concentration. As water content in feed increases, the swelling of the membrane also increases because of increased interaction of water with the hydrophilic membrane. Increased swelling leads to increased free volume in the membrane resulting in decreased water selectivity. Further, at higher feed water concentration, size of the water cluster in the membrane also grows in size which prevents electrostatic interaction of water with polar nitrile or ester group of the copolymer. In this case water-acetic acid interaction increases in the solvent cluster through hydrogen bonding which influence the sorption behavior. The effect of temperature on total sorption and sorption selectivity is also observed from Fig.4.1. For the same feed concentration, sorption is found to increase at higher temperature while water selectivity for sorption decreases with temperature. 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 mole fraction of water as shown in Fig.4.2. At around 0.35 to 0.4 mole fraction of feed water concentration preferential sorption reaches its maximum value and then it goes down with further increase in feed concentration of water. In fact, at higher feed water concentration, acid sorption also increases with decrease in preferential sorption.

4.4.2 Thermodynamic parameters:

The variation of $\chi_{ij}^f$ and $\chi_{ij}^m$ with feed activity of water is shown in Fig.4.3. The values of $\chi_{ij}^f$ and $\chi_{ij}^m$ are shown in Table 4.2. These values are in close agreement with those reported for similar systems [13, 25]. The greater the values of interaction parameter between two components, the lower will be their mutual interaction. Thus, total sorption and sorption selectivity may be explained by comparing relative values of interaction parameters. Accordingly, the sorption of water-acid mixture by the membrane was due to much lower interaction parameter of water-membrane or acid-membrane (Table 4.2) than interaction parameter of water-acid in feed or membrane (Fig.4.3). From Table 4.2 it is also observed that interaction parameter of polymer-water is much smaller than interaction parameter of polymer-acid. Thus, the membrane showed preferential water sorption. From Fig.4.3 it is also observed that interaction parameter between water and acid is much higher in feed than in membrane for any feed concentration. This indicates higher water-acid interaction in membrane which may be due to clustering of two polar solvents i.e. water and acid through hydrogen bonding [26, 27] in membrane.
4.4.3 Coupling effect in sorption based on Flory-Huggins model:

In thermodynamics of swelling process activity coefficient of a component in the membrane is not only influenced by interaction between that component and the membrane polymer (i.e. water-membrane or acid-membrane) but also by their mutual interaction in the membrane (i.e. water and acid) which is termed as coupling [23]. To understand the mutual interaction of the solvent-membrane and also coupling effect in sorption, activity coefficient of water and acid in membrane (obtained using Eq 4.2 to 4.5) is plotted against feed concentration of water (in mole fraction) for state-I, state-II and state-III in Fig. 4.4a and 4.4b. For state-I condition activity coefficient of pure component i.e. water or acid is obtained using Eq.4.2 without considering any interaction or coupling. In state-II condition activity coefficient of i or j in membrane is obtained using Eq.4.3 where interaction of component i or j with membrane is considered. In this case activity of component i in membrane is equal to its activity in feed. For state-III condition membrane phase activity coefficient of both i and j is calculated using Eq.4.4 and 4.5 where mutual interaction of i and j as well as interaction of i or j with membrane is considered. In this case activity of component i or j in membrane is equal to its activity in feed in a thermodynamic swelling equilibrium condition. From Fig.4.4a 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 each component in the membrane
state-III activity is found to be lower than state-II activity [23]. The negative deviation of membrane phase activity coefficient of acid in state-III is observed in Fig.4.4b. With increase in water content in feed, the interaction between water and acid increases and hence, coupling effect becomes more extensive at higher feed water concentration.

4.4.4 Coupling effect in sorption based on ENSIC model:

ENSIC model:

For a polar-polar solvents system like water and acetic acid clustering of solvents in membrane may be obtained more accurately ENSIC model (Eq. 3.4, chapter-3, page-146). Accordingly, membrane phase concentration of water and acid were calculated by fitting experimental data to this equation as shown in Fig.4.5. The values of regression coefficients, and standard errors as shown in Table 4.2 indicates good fitting of experimental data for water while for acid error is much higher though regression coefficient for both components are > 0.9. The $K_p$ and $K_s$ values based on ENSIC model is also given in Table 4.2. $K_s$ values for both water and acid are observed to be much higher than its $K_p$ values which also signifies solvent clustering in the membrane matrix. Further, the $K_p$ value of water-membrane is observed to be much higher than $K_p$ value of acid which implies more water-membrane interaction than acid-membrane interaction. The Flory-Huggins and ENSIC parameter values as given in Table 4.2 are also close to
those reported for similar polymer-solvent system [13, 28]. The coupling coefficient for water and acid as obtained using Eq.4.5 based on ENSIC model is plotted against feed water concentration in Fig.4.6. From this figure no definite trend lines are observed for variation of coupling factor with feed concentration though at higher feed water concentration coupling factor of both water and acid exceeds its ideal values signifying positive coupling effect in sorption. This kind of CF values were also reported by Drioli et al [29] and Jonquières et al[22].

4.4.5 Pervaporation(PV) Studies :

4.4.5.1. Effect of feed concentration on Permeate concentration, Flux and selectivity:

Permeate concentration :

From Fig.4.7 it is observed that over the entire feed concentration range the PANMA copolymer membrane shows much higher permeate concentration of water than its corresponding feed concentration signifying good separation characteristic of the membrane. It is also observed from the same figure that pervaporation separation characteristic is much better than separation characteristic based on sorption or its vapor-liquid equilibrium data.

Flux and Selectivity :
Variation of total molar flux and selectivity with feed concentration at various PV
 temperatures is shown in Fig.4.8a while variation of partial flux with feed concentration
 is shown in Fig.4.8b. Total molar flux was obtained from the following Eq.4.10
\[
J_n = \frac{W}{MAt} = \frac{W}{M_i x_i + M_j (1 - x_j)} \overline{At}
\]
4.10

Where, \( W \) is the amount of total permeate coming out from the membrane during PV in
time \( t \), \( A \) is the area of the membrane, \( x_i \) is mole fraction of component \( i \) in permeate, \( M_i \)
and \( M_j \) are molecular weight of component \( i \) (i.e. water, \( M_i=18 \)) and \( j \) (i.e. acid, \( M_j=60 \))
and \( \overline{M} \) is average molecular weight of permeate.

From Fig.4.8a and Fig.4.8b it is observed that flux increases almost linearly with feed
concentration. As water concentration in feed increases, both total and partial flux
increases due to increased interaction of water with membrane. It is also observed that
partial acid flux is much lower than water flux which also confirms hydrophilic
characteristic of the membrane. At higher feed water concentration due to increased
sorption free volume of the membrane also increases with increase in acid flux. Thus,
water selectivity of the membrane is observed to fall almost exponentially with feed
concentration as shown in Fig.4.8a. It is observed from Fig.4.8b that with increase in feed
temperature both water and acid flux increases. The mobility of the solvents and
segmental motion of the polymer chain of the membrane increases with temperature.
Further, with increase in temperature vapour pressure of the solvent in feed side also
increases whereas pressure at the permeate side is retained. These factors result in
increase in flux with temperature.
4.4.5.2. Effect of feed concentration on pervaporation separation index (PSI), enrichment factor (EF) and phenomenological deviation coefficient ($\varepsilon$):

**PSI & EF:**

The optimum PV performance of a membrane is evaluated in terms of PSI which is a product of total flux and selectivity. From Fig.4.9 it is observed that initially at low feed water concentration the membrane shows very high PSI which decreases almost exponentially with increase in feed concentration. At higher feed water concentration the decrease in selectivity is much higher than increase of flux. Thus, at higher feed concentration PSI decreases. The variation of enrichment factor (EF) with concentration shows a similar trend.

**Phenomenological deviation coefficient ($\varepsilon$):**

At very low feed concentration of water i.e. at very high acid concentration acid-water interaction is much higher than water-membrane interaction. Thus, from Fig.4.9 $\varepsilon_{\text{water}}$ is observed to be higher than $\varepsilon_{\text{acid}}$. Both of these $\varepsilon$ coefficients are observed to decrease with increase in feed concentration. Because of close association of polar-polar solvent pair water and acetic acid, $\varepsilon$ is observed to be above unity for water and acid over the entire...
feed concentration signifying positive coupling effect of water and acid on their respective flux.

Flow coupling and plasticization:

Because of mutual interaction partial flux of one component is influenced by presence of the other component. This is defined as flow coupling while plasticization is swelling of a membrane by one of the solvents. If the plot of partial flux against feed to permeate side pressure differential at a constant temperature and fixed downstream pressure is linear, flow coupling and plasticization may be considered to be negligible. In this case each component permeates for its own driving force [30]. In Fig.4.10 variation of partial molar flux of water and acid is plotted against difference of partial pressure on feed and permeate side for both water and acid. Partial pressure of a component on feed side was obtained by multiplying its activity coefficient with mol fraction and saturated vapor pressure while partial pressure on permeate (downstream) side was obtained by multiplying downstream pressure (~1 mm Hg) with mole fraction of the permeate (Eq.,2.11 chapter-2, page-99). Variation of partial molar flux of water and acid is not linear as observed in Fig.4.10 which confirms influence of one component on partial flux of the other component through plasticization and flow coupling.

4.4.5.3. Effect of feed concentration on partial permeability and membrane selectivity:
The variation of driving force normalized partial flux and selectivity i.e. partial permeability and membrane selectivity for the copolymer membrane at different feed temperatures i.e. at 30, 40, 50 and 60°C are shown in Fig.4.11. It is observed that over the entire feed concentration range water permeability of the membrane is much higher than acid permeability signifying water selectivity of the membrane. It is also observed that unlike flux (Fig.4.8), permeability decreases with feed concentration though the change in permeability above around 5 wt% feed water concentration is marginal. In fact, increase of flux of a component with concentration is more than offset by increase of its partial pressure difference across the membrane (denominator of permeability Eq. 2.12a, chapter-2, page-99). Thus, permeability decreases almost exponentially with feed concentration. However, as the feed water concentration increases, swelling and hence membrane thickness (numerator of permeability Eq.2.12a, chapter-2, page-99) also increases. Thus, at higher feed water concentration increase in flux and membrane thickness counteracts the increase in partial pressure difference and thus permeability changes little with further increase of feed concentration. Similar kind of results of permeability vs. feed concentration was also reported elsewhere [9, 13, 14]. It is also observed from the same figure that intrinsic membrane selectivity also decreases with feed concentration like PV selectivity. Temperature has a negative effect on both permeability and selectivity in that with temperature both permeability and membrane selectivity decreases. In this case also increase in flux with temperature (Fig.4.8) is more than offset by increase of vapor pressure and hence partial pressure differential at higher temperatures.
4.4.5.4 Diffusion coefficient:

Diffusion of solvents through dense pervaporation membrane may be more accurately expressed in terms of solvent volume fraction in stead of solvent molarity. As per transfer solution volume fraction model (TSVF), the ratio of partial flux of component i and j through a PV membrane may be expressed as [31]

\[
\frac{J_i}{J_j} = \frac{D_{i0} V_j d\phi_i}{D_{j0} V_i d\phi_j} \tag{4.10a}
\]

Where, \(J_i, D_{i0}, V_1\) and \(\phi_1\) are partial flux, diffusion coefficient at infinite dilution, molar volume and membrane phase volume fraction, respectively, of component 1.

Integrating the above equation from upstream side to downstream side of the membrane results in

\[
\frac{J_i}{J_j} = \frac{D_{i0} V_j \phi_{iu} - \phi_{id}}{D_{j0} V_i \phi_{ju} - \phi_{jd}} \tag{4.11}
\]

Due to low pressure, concentration on the downstream side of the membrane is too low to be considered, i.e. \(\phi_{id}=\phi_{jd}=0\) Thus, the above Eq.4.11 reduces to

\[
\frac{J_i}{J_j} = \frac{D_{i0} V_j \phi_{iu}}{D_{j0} V_i \phi_{ju}} \tag{4.12}
\]

Plotting of flux ratio of component i and j against ratio of membrane phase upstream concentration of component i and j was not linear without intercept to make it comparable to equation-21. Thus, \(J_i\) was plotted against \(J_j\) (fig.4.12a) and \(\phi_{ju}\) was plotted.
against \( \phi_{iu} \) (fig. 4.12b) setting intercept zero to yield the following relation with fairly good fitting of experimental data.

\[
\frac{J_i}{J_j} = 14.306 \quad (4.12a) \quad \text{and} \quad \frac{\phi_{iu}}{\phi_{ju}} = 1.009 \quad (4.12b)
\]

The ratio of molar volume of \( j \) (acetic acid) and \( i \) (water) i.e. \( V_j/V_i \) is 0.3164. Thus, ratio of diffusion coefficient of component \( i \) and \( j \) is obtained from Eq. 4.12, 4.12a and 4.12b i.e. \( D_{i0}/D_{j0} = 44.81 \quad (4.12c) \)

Further, Partial flux of component \( i \) may be written as

\[
J_i = \frac{D_{i0}}{V_i L} (\phi_{iu} - \phi_{id}) \int_{\phi_d}^{\phi_u} \gamma \phi d \phi \quad (4.13)
\]

Or, \( J_i = \frac{D_{im}}{V_i L} (\phi_{iu} - \phi_{id}) \quad (4.14) \)

Here \( L \) is membrane thickness (m) during experiment.

\[
D_{im} = D_{i0} \int_{\phi_d}^{\phi_u} \gamma \phi_i d \phi_i \quad (4.15)
\]

Or,

\[
D_{im} = D_{i0} \frac{\exp(\gamma x_u - \gamma \phi_d)}{\gamma (\phi_u - \phi_d)} \quad (4.16)
\]

Thus, \( J_i = \frac{1}{V_i L} D_{i0} \exp(\gamma \phi_i - \gamma \phi_d) (\phi_{iu} - \phi_{id}) \quad (4.17) \)

For low downstream pressure, \( \phi_d = 0, \exp(\phi_d) = 1 \)

Therefore, \( J_i = \frac{D_{i0}}{V_i L} \frac{\exp(\gamma \phi_i) - 1}{\gamma_j \phi_i + \phi_j} \quad (4.18) \)

Where, \( \phi_u = \text{total solution volume fraction on upstream side of membrane} = \phi_{iu} + \phi_{ju} \)

200
Plotting of partial flux of i component i.e. water (J_i) against total sorbed volume fraction (\( \varphi_u \)) gave the following regressed exponential Eq. 4.19 with fairly good fitting of experimental data as shown in fig.4.12c.

\[
J_i = 1.51346 \times 10^{-5} \times \frac{[\exp(7.876 \times \varphi_u) - 1]}{1 + \varphi_u / \varphi_{iu}}
\]  

Comparing Eq. 4.18 and 4.19 and using Eq. 4.12a, plasticization coefficient \( \gamma \) is obtained as 7.876, diffusion coefficient of water and acid at infinite dilution i.e. \( D_{i0} \) and \( D_{j0} \) are obtained as \( 2.15 \times 10^{-7} \) m\(^2\)/s and \( 4.9 \times 10^{-9} \) m\(^2\)/s, respectively. Higher diffusion coefficient of water may be attributed to its smaller kinetic diameter (0.296 nm) in comparison to acid (0.436) [32]. The small water molecules move much faster than acid molecules through the highly hydrophilic copolymer membrane. 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. [33, 34].

4.4.5.5 Activation Energy :

Driving force for PV process is normalized for permeability. Hence, activation energy for permeation (\( E_{pi} \)) based on permeability data at different temperatures is more reliable than apparent activation energy obtained with flux data at different temperatures [35]. Activation energy for permeation (\( E_{pi} \)) is obtained from the slope of the Arrhenius type
linear plot of logarithmic of partial permeability ($\ln P_i$) against inverse of absolute temperature (1/T) using the following Eq. 4.20

$$\ln P_i = \ln P_{0i} - \frac{E_{pi}}{RT}$$  \hspace{1cm} (4.20)

Where, $P_{0i}$ is pre exponential factor of component i for permeability, R and T are universal gas constant and absolute temperature, respectively. Activation energy for permeation at various feed concentrations along with preexponential factors and regression coefficients ($r^2$) for each of these calculations are shown in Table 4.3a for water and Table 4.3b for acid. From the values of regression coefficients given in Table 4.3a and 4.3b, it appears that the linear fitting of the permeability data in Arrhenius equation was good. It is observed that activation energy for permeation of water ($E_{pw}$) is lower than acid ($E_{pa}$) over the entire feed concentration which implies easier permeation of water than acid through the hydrophilic membrane.

4.4.5.6. Comparison of present work with reported data :

The performance of the copolymer membrane used in the present work was compared with other reported membranes used for pervaporative separation of acid-water mixtures. This is shown in Table 4.4. From the data given in Table 4.4 it appears that the flux and selectivity of the present copolymer membrane is comparable to those reported for similar operating condition.
4.5. CONCLUSION:

Hydrophilic acid resistant pervaporation membrane was cast from poly (acrylonitrile-co-methyl acrylate) copolymer which is commercially used for making PAN fiber. Sorption and permeation of water-acid mixtures through this membrane were studied. Various thermodynamic parameters based on Flory-Huggins and ENSIC model was evaluated. Total solution volume fraction was considered for determining diffusion coefficient of solvents through the membrane. Coupling and plasticization during transport was also studied. Partial permeability was determined from vapour pressure data while activation energy for permeation was obtained by fitting permeability data at different temperatures to an Arrhenius type equation. The hydrophilic membrane was found to show very high water selectivity for a highly concentrated acid–water mixtures with acceptable flux. This copolymer membrane may also be suitably used for pervaporative dehydration of other similar organics.

REFERENCES


Table 4.1 Specification of the PANMA copolymer

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Poly (acrylonitrile-co-methyl acrylate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>(-(CH_2CHCN)_m-(CH_2-CHCO_2CH_3)_n, m:n=91.4:8.6</td>
</tr>
<tr>
<td>Method of Polymerization</td>
<td>Slurry Polymerization</td>
</tr>
<tr>
<td>Molecular weight (no. avg)</td>
<td>55500</td>
</tr>
<tr>
<td>Intrinsic viscosity (dl/g)</td>
<td>1.37</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>79.8 MPa</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>3.5%</td>
</tr>
<tr>
<td>Glass transition temperature</td>
<td>85°C</td>
</tr>
</tbody>
</table>

Table 4.2 : Flory Huggin (FH) Interaction parameter (χ) and ENSIC solvent-solvent affinity (K_s) and solvent-polymer affinity (K_p) with the copolymer membrane

<table>
<thead>
<tr>
<th>Solvent</th>
<th>χ</th>
<th>(K_s-K_p)/std.error</th>
<th>[K_p/(K_s-K_p)]/std.error</th>
<th>Adjusted r²</th>
<th>K_s</th>
<th>K_p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.681</td>
<td>1.446/0.542</td>
<td>0.280/0.140</td>
<td>0.989</td>
<td>1.852</td>
<td>0.405</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>1.523</td>
<td>47.468/11.336</td>
<td>1.2 x 10⁻⁶/3 x 10⁻⁶</td>
<td>0.908</td>
<td>47.5</td>
<td>0.000056</td>
</tr>
</tbody>
</table>

Table 4.3a : Activation energy for permeation (E_{pw}) and pre exponential factor (P_{ow}) of water

<table>
<thead>
<tr>
<th>Feed concentration (wt% water)</th>
<th>Slope</th>
<th>Intercept</th>
<th>r²</th>
<th>P_{ow} x 10^{10} (molm⁻²s⁻¹Pa⁻¹)</th>
<th>E_{pw} (kJ/deg.mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.95</td>
<td>4586.6</td>
<td>-22.256</td>
<td>0.9954</td>
<td>2.15</td>
<td>38.13</td>
</tr>
<tr>
<td>2.86</td>
<td>2991.8</td>
<td>-18.051</td>
<td>0.9476</td>
<td>144</td>
<td>24.87</td>
</tr>
<tr>
<td>4.77</td>
<td>3308.5</td>
<td>-19.206</td>
<td>0.9143</td>
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<td>9.56</td>
<td>4475.2</td>
<td>-22.946</td>
<td>0.9965</td>
<td>1.08</td>
<td>37.20</td>
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<tr>
<td>19.23</td>
<td>4271.4</td>
<td>-22.555</td>
<td>0.9973</td>
<td>1.60</td>
<td>35.51</td>
</tr>
</tbody>
</table>
Table 4.3: Activation energy for permeation ($E_{pa}$) and pre exponential factor ($P_{oa}$) of acid

<table>
<thead>
<tr>
<th>Feed concentration (wt% water)</th>
<th>Slope</th>
<th>Intercept</th>
<th>$r^2$</th>
<th>$P_{ow}$ x 10$^8$ (molm$^{-2}$ s$^{-1}$Pa$^{-1}$)</th>
<th>$E_{pw}$ (kJ/deg.mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.95</td>
<td>2757.3</td>
<td>-20.07</td>
<td>0.9886</td>
<td>0.19</td>
<td>22.92</td>
</tr>
<tr>
<td>2.86</td>
<td>2375.3</td>
<td>-18.569</td>
<td>0.9595</td>
<td>0.86</td>
<td>19.74</td>
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<tr>
<td>4.77</td>
<td>1299.2</td>
<td>-15.184</td>
<td>0.9748</td>
<td>25.44</td>
<td>10.80</td>
</tr>
<tr>
<td>9.56</td>
<td>2256</td>
<td>-17.837</td>
<td>0.9132</td>
<td>1.79</td>
<td>18.75</td>
</tr>
<tr>
<td>19.23</td>
<td>2341.3</td>
<td>-17.793</td>
<td>0.9204</td>
<td>1.87</td>
<td>19.46</td>
</tr>
</tbody>
</table>

Table 4.4: Comparison of performances of membranes reported for pervaporative dehydration of acetic acid

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Feed water concentration (wt%)</th>
<th>Temperature ($^0$C)</th>
<th>Normalized Flux, (kg/m$^2$ h)</th>
<th>Water selectivity (-)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVOH-GLU (Pervap 2201, Sulzer)</td>
<td>10</td>
<td>25</td>
<td>12</td>
<td>20</td>
<td>[2]</td>
</tr>
<tr>
<td>PVOH-g-AN membrane</td>
<td>10</td>
<td>30</td>
<td>1.75</td>
<td>14</td>
<td>[4]</td>
</tr>
<tr>
<td>PVOH-TEOS</td>
<td>10</td>
<td>30</td>
<td>3.32</td>
<td>2423</td>
<td>[5]</td>
</tr>
<tr>
<td>PVOH-Na-Alg blend</td>
<td>10</td>
<td>30</td>
<td>0.717</td>
<td>40.3</td>
<td>[6]</td>
</tr>
<tr>
<td>Na-Alg-HAD</td>
<td>15</td>
<td>70</td>
<td>0.262</td>
<td>161</td>
<td>[7]</td>
</tr>
<tr>
<td>Na-Alg silicotungstic acid hybrid membrane</td>
<td>10</td>
<td>30</td>
<td>9.7</td>
<td>22,491</td>
<td>[8]</td>
</tr>
<tr>
<td>FIPN502</td>
<td>0.95</td>
<td>30</td>
<td>4.242</td>
<td>168.72</td>
<td>[9, SECTION-II]</td>
</tr>
<tr>
<td>PANBA0.5</td>
<td>28.3</td>
<td>30</td>
<td>8.67</td>
<td>101.67</td>
<td>[12]</td>
</tr>
<tr>
<td>PANMA</td>
<td>0.95</td>
<td>30</td>
<td>1.709</td>
<td>408.91</td>
<td>Present work</td>
</tr>
<tr>
<td>PANMA</td>
<td>9.5</td>
<td>30</td>
<td>4.375</td>
<td>35.98</td>
<td>Present work</td>
</tr>
</tbody>
</table>

PVOH-polyvinyl alcohol, GLU-PVOH-glutaraldehyde crosslinked PVOH, PVOH-g-AN-acrylonitrile grafted PVOH, PVOH-TEOS-tetraethyl orthosilicate croslinked PVOH, PVOH-Na-Alg blend-Sodium alginate-PVOH blend, FIPN-FILLED ipn membrane, PANBA0.5-poly (acrylonitrile-co-butyl acrylate) copolymer filled with 0.5 wt% filler, PANMA-poly (acrylonitrile-co-methyl acrylate) polymer
Fig. 4.1 Variation of total sorption and water selectivity with feed concentration of water at 30°C, 45°C and 60°C temperatures

Fig. 4.2 Variation of preferential sorption of water with feed water concentration at 30°C, 45°C and 60°C temperatures
Fig. 4.3 Variation of interaction parameter between water and acid with feed concentration of water

Fig. 4.4a Variation of membrane phase activity coefficient of water with feed mole fraction for single component (state-I), binary mixtures without interaction (state-II) and binary mixture with interaction (state-III) sorption
Fig. 4.4b Variation of membrane phase activity coefficient of acid with feed mole fraction for single component (state-I), binary mixtures without interaction (state-II) and binary mixture with interaction (state-III) sorption.

Fig. 4.5 Fitting of experimental data to ENSIC model.

Equation: $y = a(1 - \exp(-b \times x))$

<table>
<thead>
<tr>
<th>Adj. R-Square</th>
<th>Value</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.98927</td>
<td>0.90853</td>
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</tbody>
</table>

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>a</td>
<td>-0.28046</td>
<td>0.14079</td>
</tr>
<tr>
<td>B</td>
<td>b</td>
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<tr>
<td>C</td>
<td>a</td>
<td>-1.24E-6</td>
<td>3.16E-6</td>
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<tr>
<td>C</td>
<td>b</td>
<td>-47.46809</td>
<td>11.33654</td>
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</tbody>
</table>
Fig. 4.6 Variation of coupling factor (CF) of water and acid with feed activity of water

Fig. 4.7 Variation of permeate concentration of water with its feed concentration at 30 °C
Fig. 4.8a Variation of total flux and separation factor (SF) for water with feed concentration

Fig. 4.8b Variation of partial flux with feed concentration
Fig. 4.9 Variation of PSI, EF and $\varepsilon$ with feed concentration of water at 30°C

Fig. 4.10 Variation of partial molar flux with partial pressure difference across the membrane at 30°C.
Fig. 4.11 Variation of partial permeability and intrinsic membrane selectivity with feed concentration of water at different feed temperature

Fig. 4.12a Variation of $\phi_{iu}$ with $\phi_{ju}$

$\phi_{ju} = 0.9914 \phi_{iu}$

$R^2 = 0.9857$
Fig. 4.12b Variation of $J_j$ with $J_i$

$J_j = 0.0699J_i$

$R^2 = 0.9642$

Fig. 4.12c Water flux vs. total volume fraction (V.F.) of solvents

Equation: $y = a(1 - \exp(-b^x))$

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
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<td>1.95352E-5</td>
</tr>
<tr>
<td>B</td>
<td>-7.87653</td>
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Adj. R-Square: 0.90007