Pervaporation dehydration of ethanol using the blend nanocomposite membranes of sodium alginate-poly(vinyl pyrrolidone) incorporated with phosphotungstic acid

ABSTRACT

Nanocomposite membranes (NCMs), prepared by incorporating phosphotungstic acid, $H_3PW_{12}O_{40}$, nanoparticles within the host sodium alginate/poly(vinyl pyrrolidone) blend polymer membranes exhibit pervaporation separation properties that differ significantly from those of the host, even with small amounts of nanoparticles. A significant challenge is how to tailor the properties of these materials for pervaporation dehydration of ethanol, because NCMs derive their properties from a collective and complex range of enthalpic and entropic interactions. In this work, we showed the improved thermal stability and separation characteristics of the blend nanocomposite membranes of sodium alginate and poly(vinyl pyrrolidone) prepared by solution casting method. Increase of feed water composition and temperature on the pervaporative dehydration of ethanol resulted in a drastic reduction of membrane performance; while the membrane performance was optimum for 15 wt % $H_3PW_{12}O_{40}$ incorporated NCMs at 10 wt. % of water in the feed. Diffusion behavior of water and ethanol through these membranes was analyzed by Fick’s equation. The pervaporation performance was analyzed by the principles of sorption-diffusion model as well as Flory-Huggins theory.
VI.1. INTRODUCTION

Ethanol, a much needed bio-fuel, is produced from the biomass and it can be mixed with petrol in view of its high octane number and heat of vaporization [1] to reduce the cost and alleviate the environmental pollution. Ethanol being used widely in pharmaceutical, chemical, and beverage industries forms an azeotrope at 4 wt. % water. Purification of ethanol from the aqueous broth mixture using conventional distillation is costly and it requires benzene as an entrainer, a deadly carcinogen. Alternatively, the membrane-based pervaporation (PV) separation is an attractive approach to separate azeotropic mixtures [2, 3]. Apart from these efforts, developments of novel composite membranes (NCMs) by the physical mixing nanoparticles as inorganic fillers [4, 5] has led to the maximum performance of the membrane at a certain concentration of the filler. This has prompted research developments in novel type of nanocomposite membranes (NCMs) for PV separation application [6-9].

Among the many polymeric membranes, NaAlg has been widely used in PV dehydration of organics [10-12] due to its good membrane forming ability; but its excessive swelling in aqueous media lowers its selectivity to water. In order to achieve an improved membrane stability and selectivity to water, efforts were concentrated on the use of blend membranes of NaAlg with other polymers such as hydroxyethyl cellulose, poly(vinyl alcohol) and guar gum-grafted polyacrylamide [13-17]. Poly(vinyl pyrrolidone) (PVP) is also a widely studied biopolymer that finds applications in pharmaceutical area [2] as well as in PV dehydration studies [4,18].

Polymer blends have received a great deal of attention due to the diversity of materials prepared from various pristine polymeric components. Blend properties can be tailored from carefully selected polymer components with the desired characteristics. Thus, blending of polymer films has the potential to improve the material strength and to modulate hydrophilic hydrophobic characteristics as well as barrier properties to liquids [13]. In order to achieve the
improved separation of water-ethanol mixtures by the PV dehydration process, blending of NaAlg with PVP is considered to limit the excessive swelling of NaAlg. Since NaAlg and PVP polymers are completely miscible in all proportions, due to the hydrogen-bond formation between the donor groups of NaAlg and the acceptor groups of PVP, therefore, in the blend system, it is thought that selectivity of NaAlg to water might be enhanced thus, favoring the dehydration of ethanol [19].

Phosphotungstic acid (PWA) has been the rarely studied filler [20, 21] in developing NCMs. However the potential interactions between PWA and the host polymer would be responsible to achieve extraordinary separation performance of membrane. The PWA consists of Keggin unit as a primary structure, i.e., the polyanion [PW_{12}O_{40}]^{3-}, and a secondary structure, i.e., a regular three-dimensional assembly of the heteropolyanions with counter cations (protons) and additional water molecules [22]. This Keggin unit consists of a central PO4 tetrahedron surrounded by four W_{12}O_{36} sets, linked together through oxygen atoms of which, four types can be distinguished; the central oxygen atom belonging to PO4 tetrahedron is shared by three tungsten atoms, while the edge-sharing oxygen atoms bridge two tungsten atoms of the same set. The corner-sharing oxygen atoms bridge two tungsten atoms of different sets and terminal oxygen atoms are associated with a single tungsten atom. The bridging and terminal oxygen atoms are on the periphery of the structure, which are available to associate with protons or water molecules to form hydrates that are thought to enhance selectivity to water. Also, hydrogen-bonding is likely to be established between PWA and the NaAlg/PVP blend system. Due to these advantages, PWA-loaded NaAlg/PVP blend nanocomposite membrane is selected to investigate the PV separation of ethanol. Four membranes were fabricated unfilled blend membrane and three NCMs incorporated with 5, 10 and 15 wt. % of PWA nanoparticles. All the membranes were characterized by a variety of techniques and their PV performances were evaluated for ethanol dehydration.
VI. 2. RESULTS AND DISCUSSION

VI.2.1. X-RD

The microstructure of NaAlg/PVP blend membrane along with their respective NCMs was studied by X-RD. Figure VI.1 displays the X-RD patterns of the samples of NaAlg/PVP, NCM-5, NCM-10 and NCM-15 membranes. From the spectra, a moderately sharp peak is observed for NaAlg/PVP at 120 of 2θ, indicating its semi-crystalline nature, whereas the XRD curves for NCMs exhibit broad peaks, indicating the average intermolecular distance of the amorphous regions of the matrix at 120 of 2θ. On the other hand, relatively sharp intensity peaks observed at 2θ of 22.5° indicate the existence of higher free volume in the unfilled blend membrane, which reduces the selectivity due to increase of flux. Thus, the interactions of PWA nanoparticles with polymer blend would hinder the ordered packing of polymeric chains, resulting in a reduced crystallinity of the blend. However, the loss of crystallinity due to the addition of PWA is evident in Fig. VI.1, wherein a decrease in peak intensity is observed; this supports the observed improvement in selectivity with increased loading of PWA.

Fig. VI.1. X-RD curves of NaAlg/PVP, NCM-5, NCM-10 and NCM-15.
VI.2.2. SEM analysis

The distribution of PWA nanoparticles in the unfilled blend matrix of NaAlg/PVP exerts an influence on its transport properties. Typical SEM images of NaAlg/PVP and NCMs displayed in Fig. VI.2 suggest smooth surfaces for all membranes with no phase separation, suggesting a homogenous distribution of filler nanoparticles with no visual agglomerations and no cracks on the surface of NCMs.

![SEM images of NaAlg/PVP, NCM-5, NCM-10, and NCM-15 membranes](image)

*Fig. VI.2. SEM images of NaAlg/PVP, NCM-5, NCM-10, and NCM-15 membrane surfaces.*
VI.2.3. DSC analysis

In the filled polymers, the inclusion of inorganic nanoparticles leads to a change in glass transition temperature \( T_g \) because of the favorable interactions between the nanoparticle surface and the polymer, thus restricting the chain mobility. The \( T_g \) can be used as an indicator of the overall segmental mobility, the extent of nanoparticle–polymer surface area created in nanocomposite membranes, both of which will exert substantial effect on the segmental mobility of polymer chains because of the nanoparticle-polymer interactions in addition to physical confinement effects. These perturbations to the bulk of the polymer chain dynamics are often manifested by the changes in \( T_g \) [29, 30].

From the DSC curves of the NaAlg/PVP and NCM-5, NCM-10 and NCM-15 membranes shown in Fig. VI.2, we observe that NaAlg/PVP has a \( T_g \) of 99.4°C, which is shifted to lower temperatures of 94.5°, 89° and 87.9°C for NCM-5, NCM-10 and NCM-15, respectively after the addition of PWA nanoparticle (see Fig. VI.3); this is attributed to the favorable intermolecular interactions between the blend polymer and the surface of PWA nanoparticles. The PWA nanoparticles would perturb the surrounding polymer matrix, thus decreasing its molecular chain mobility at increased PWA loading. This change in polymer chain mobility will also affect the size discrimination and the corresponding penetrant diffusivity characteristics of the membrane matrix.

VI.2.4. DMTA

Dynamic mechanical thermal analysis (DMTA) was carried out on NCMs to obtain information on their microstructures. Also it allows the evaluation of thermal and viscoelastic properties of the material over the large temperature interval [31]. The storage modulus \( (E') \) and tan \( \delta \) curves as a function of temperature were measured for NCMs. The \( T_g \) is defined as the peak of tan \( \delta \) curves whose values are given in Table VI.1. From the DMTA curves, we observe that by increasing the amount of PWA nanoparticles, a shift toward lower \( T_g \) of
\(\tan \delta\) peak was observed with a higher storage modulus in the rubbery region (see Fig. VI.4). This behavior can be attributed to the impediment of the segmental motion of the polymeric chains induced by the presence of PWA nanoparticles in the host polymer matrix. The increase of constraints in segmental motions is mainly due to uniform distribution of PWA nanoparticles, which was also evidenced by SEM micrographs.

![DSC thermograms](image)

**Fig. VI.3.** DSC thermograms of NaAlg/PVP, NCM-5, NCM-10 and NCM-15 membranes.

**VI.2.5. Degree of swelling**

The % degree of swelling calculated from sorption experiments at 27°C for the unfilled blend and PWA-filled NCMs measured as a function of wt. % of water of the feed mixture are displayed in Fig. VI.5. Degree of swelling of NaAlg/PVP membrane increased from 26 to 76 % with increase of feed water
content from 4 to 40 wt. %. The lower swelling values observed for NCM-15 ranging from 17 to 46 % in the same feed composition range of 4-40 wt. % water; compared to NaAlg/PVP blend, suggest the tight matrix composition due to the presence of PWA nanoparticles.

Pure solvent uptake data were used to calculate volume-fraction ($\phi_i$) as:

$$\phi_i = \left( \frac{W_i / \rho_i}{W_i / \rho_i + 1 / \rho_m} \right)$$

(VI.1)

where $W_i$ is solvent uptake in terms of g/g of the dry membrane of component $i$ at equilibrium; $\rho_i$ and $\rho_m$ are the densities of solvent and membrane, respectively.

The membrane density ($\rho_m$) was calculated using:

$$\rho_m = \left( \frac{M_a}{M_a - M_i} \right) \times \rho_o$$

(VI.2)

where $M_a$ is weight of dry membrane in air, $M_i$ is weight of dry membrane in auxiliary liquid, and $\rho_o$ is density of the auxiliary liquid.

According to Flory-Huggins theory [23,24], the dependence of solvent volume fraction on interaction parameter ($\chi_{ip}$) at a given solvent activity ($\alpha_i$) is given as:

$$\ln \alpha_i = \ln \phi_i + (1 - \phi_i) + \chi_{ip} (1 - \phi_i)^2$$

(VI.3)

When the membrane is immersed in pure solvent, the solvent activity will attain unity, such that eq. (4) can be rewritten in terms of $\chi_{ip}$ to give:

$$\chi_{ip} = -\frac{\ln \phi_i + (1 - \phi_i)}{(1 - \phi_i)^2}$$

(VI.4)

The parameter, $\chi_{ip}$, depicts the chemical compatibility between solvent, $i$ and the membrane; it is related to chemical compatibility between solvent and membrane. Since the chemical compatibility is expressed in terms of the difference in solubility parameter ($\delta$) between the components, the relationship between $\chi_{ip}$ and $\delta$ is given as [25]:

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\[ \chi_{ip} = 0.35 + \frac{V_i}{RT} \left( \delta_i - \delta_p \right)^2 \]  
\quad \text{(VI.5)}

where \( V_i \) is molar volume of the solvent, \( R \) is gas constant (8.314 JK\(^{-1}\) mol\(^{-1}\)), \( T \) is in absolute scale, \( \delta_i \) and \( \delta_p \) are solubility parameters of solvent and membrane polymer, respectively. The \( \delta \) of water is 47.8 J\(^{1/2}\).cm\(^{-3/2}\) and that of ethanol is 26.5 J\(^{1/2}\).cm\(^{-3/2}\) [26]. However, \( \delta_p \) of polymer can be calculated using eq. (6) to give:

\[ \delta_p = \delta_i \pm \left[ \frac{\chi_{ip} - 0.35RT}{V_i} \right]^{1/2} \]  
\quad \text{(VI.6)}

Since, eq. (7) has two roots, so \( \delta_p \) would theoretically assume either of the two values when solvent solubility is determined in a membrane. When sorption of membranes is measured in two different solvents, we can select the one that will better match among both the determinations. Extending these relations further, one can also compute the molar mass between crosslinks, \( \overline{M}_w \) (g/mol) and crosslink density, \( \nu_c \) (mol/cm\(^3\)) from the Flory-Rehner theory [27] to give:

\[ \frac{1}{\overline{M}_c} = \frac{1}{\rho_p V_i} \left[ \ln(1 - \phi_i) + \phi_i + \chi_{ip} \phi_i^2 \right] \frac{\phi_i^{1/3} - \frac{1}{2} \phi_i^2}{\phi_i^{1/3}} \]  
\quad \text{(VI.7)}

Here, the effective number of chains in the networks per unit volume or the effective number of network junctions per unit volume, \( \nu_c \) (mol/cm\(^3\)) is given as:

\[ \nu_c = \frac{\rho_m}{\overline{M}_c} \]  
\quad \text{(VI.8)}
Fig. VI.4. DMTA curves for $E'$, $E''$ and tan $\delta$ of NaAlg/PVP, NCM-5, NCM-10 and NCM-15 membranes.

Further observation suggests that swelling results are in good agreement with the observed $T_g$ values, i.e., $DS$ decrease by a decrease in the same $T_g$ of the membranes, which is dependent on the amount of PWA added to the NaAlg/PVP blend matrix. Membrane swelling also influenced the flux as well as separation factor data. The fluxes of NCMs are comparatively lower than those observed for NaAlg/PVP at all compositions of water in the feed. However, flux decreased with increasing concentration of PWA in NaAlg/PVP matrix. On the other hand,
separation factor of NCMs is higher than NaAlg/PVP, suggesting that the nascent NaAlg/PVP blend attains higher rigidity after incorporation of PWA, giving a decreased swelling; this in turn, will decrease the diffusive pathways of water molecules through the membrane by restricting the transport of ethanol.

![Graph](image)

Fig. VI.5. Variation of $DS (%)$ with (a) wt. % water in feed (b) Wt. % PWA .

VI.2.6. Flory-Huggin interaction parameter, solubility parameter and cross linking density of membranes.

The affinity between polymer and solvent was evaluated in terms of the interaction parameter, $\chi_{ip}$. The values of $\chi_{ip}$ show a decrease, suggesting increased affinity between polymer and penetrant molecules. In other words, as the affinity or interaction between the polymer and the penetrant increases, the amount of liquid inside the polymer also increases, while that of $\chi_{ip}$ decreases. Flory-Huggin interaction parameters, $\chi_{p1}$ and $\chi_{p2}$ calculated from eq. (VI.5) and given in Table VI.1, suggest that NCMs interact preferentially more with water than with ethanol, whereas the nascent blend has higher interactions for both water and ethanol molecules.
The solubility parameter difference ($\Delta \delta$) between the polymer and the liquid molecule may be interpreted as a measurement of the affinity between them. For small $\Delta \delta$ values, the affinity between polymer and liquid is high. From Table VI.1, the calculated solubility parameter ($\delta$) values are 55.12 J$^{1/2}$/cm$^{3/2}$ for NaAlg/PVP, whereas for NCM-5, NCM-10 and NCM-15 these values are 55.64, 55.65 and 55.69 J$^{1/2}$/cm$^{3/2}$ respectively. For instance, the $\Delta \delta$ value of NaAlg/PVP and ethanol (26.5 J$^{1/2}$/cm$^{3/2}$) is the least compared to NCMs, confirming that ethanol would dissolve more easily in NaAlg/PVP than in NCMs at increasing loading of PWA in the host polymer; thus, solubility of ethanol in the membrane has decreased.

The $M_c$ and $\nu_c$ data calculated from the Flory-Rehner equation (eq.VI.7) show an influence on the nature of the blend matrix. For instance, $M_c$ value for NaAlg/PVP is high (724g/mol), whereas for NCM-15, it is the least (107g/mol), whereas $\nu_c$ is highest for NCM-15 (8.20mol/cm$^3$) and smallest for NaAlg/PVP (1.22mol/cm$^3$). These trends reveal that increased amount of PWA particles in the host matrix would cause rigidity to the polymer (see data in Table VI.1).

**V.2.7. Contact angle analysis and surface properties**

When a liquid is in contact with a solid, it will exhibit a contact angle ($\theta$), which depends upon the surface tensions of the liquid and the solid as well as the interfacial tension between them. A smooth surface with a lower surface energy has a higher contact angle and lower hydrophilicity. The contact angle measured between water drop and the membrane surface showed an increasing trend with increasing filler loading. For instance, the sequence NaAlg/PVP ($\theta = 46^0$) < NCM-5 ($\theta = 52^0$) < NCM-10 ($\theta = 60^0$) < NCM-15 ($\theta = 89^0$), indicating decreasing trend in hydrophilicity (see Fig. VI.5). The possible reason for such a decrease in hydrophilicity is due to the presence of hydrophilic groups such as -OH and COO$^-$. Na$^+$ present in NaAlg will possibly interact with carbonyl groups of PVP as well as...
PWA nanoparticles, resulting in increase of crosslink density of the matrix; hence, hydrophilicity of the membrane decrease with increasing amount of PWA nanoparticles in the polymer matrix.

In PV separation, feed liquid comes in contact with the membrane surface first, and then the upstream sorption of the mixture occurs onto the surface, which induces the initial partitioning of the feed that is mainly dependent on the surface properties of the polymer. Therefore, surface free energy and wettability of the membranes exert significant influence on the membrane performance. However, the surface free energy per unit area of the membrane is a fundamental property, which determines the surface and interfacial behavior during wetting and adhesion.

Surface energy of NaAlg/PVP and all the NCMs are presented in Table VI.1. The surface free energy ($\gamma_s$) of the membrane in equilibrium with the saturated vapor of water show a decrease from 55.3 to 27.7 mJ/m$^2$ from NaAlg/PVP to NCM-15, whereas the interfacial tension ($\gamma_{ls}$) between membrane and water show an increase from 5.3 to 26.5 mJ/m$^2$ from NaAlg/PVP membrane to NCM-15, clearly indicating the effect of addition of PWA nanoparticles, due to which the membrane surface has been modified and hence, the bulk properties. Decreasing trends of surface free energies and increasing interfacial tensions due to increasing loading of PWA filler nanoparticles show a decrease in wettability of the membranes from NaAlg/PVP to NCM-15. This is further supported by the calculation of work of adhesion, $W_a$. i.e., the strength of adhesion to a solid membrane surface was estimated from the thermodynamic work of adhesion and the results of $W_a$, also compiled in Table 1, show a decrease from 117.1 mJ/m$^2$ for NaAlg/PVP to 74.1 mJ/m$^2$ for NCM-15.
VI.2.8. Membrane performance

Membrane performances of the pristine blend and the nanocomposites containing different amounts of PWA nanoparticles were assessed in terms of flux and separation factor.

VI.2.8.1. Effect of filler

Figure VI.6 displays typically the plots of flux and separation factor of all the membranes for 4 wt. % water-containing feed mixture vs the amount of PWA (wt. %) in NaAlg/PVP blend matrix. It is evident that with increasing amount of PWA in NaAlg/PVP blend host matrix, the membrane permselectivity to water increased remarkably due to increased hydrophilic–hydrophilic interactions between NCMs and water. From the results given in Table VI.1, notice that a separation factor of 386 observed for nascent blend membrane increased remarkably to a highest value of 3766 even at 5 wt. % of PWA in the NaAlg/PVP blend matrix. The NaAlg/PVP, being a polyhydroxy mixed blend polymer, would absorb a large quantity of water, but since the PWA nanoparticles would fill-up the free volume spaces of the NaAlg/PVP blend matrix, a further increase in membrane affinity to water molecules is likely compared to ethanol, thus resulting in an unusual increase of separation factor by sacrificing the flux. At higher loading of PWA, the NCMs will be more rigid, causing a reduction in free volume, thereby, exhibiting lower flux. In the case of NCMs containing lower loadings of PWA (i.e., 5 and 10 wt. %), the membrane selectivity is comparably lower. Thus, in case of NCM-5 and NCM-10, separation factor values increased 3766 and 4685, respectively giving
Table VI.1. Some relevant data on membrane performance and their PV performances in 4 wt. % feed water mixture at 30°C.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>DS (%)</th>
<th>F-H interaction parameters</th>
<th>δ_p (J^{1/2}cm^{-3/2})</th>
<th>(δ_p-δ_i)</th>
<th>M_c (g/mol)</th>
<th>n_e x 10^3 (mol/cm^3)</th>
<th>θ (mJ/m^2)</th>
<th>γ_sv (mJ/m^2)</th>
<th>Wa (mJ/m^2)</th>
<th>J (kg/m^2*h)</th>
<th>β_ij</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaAlg/PVP</td>
<td>114.7</td>
<td>9.54</td>
<td>0.737 1.78</td>
<td>55.12</td>
<td>7.32</td>
<td>724</td>
<td>1.22</td>
<td>46</td>
<td>55.3</td>
<td>5.3</td>
<td>386</td>
</tr>
<tr>
<td>NCM-5</td>
<td>101.6</td>
<td>7.69</td>
<td>0.793 1.89</td>
<td>55.64</td>
<td>7.84</td>
<td>492</td>
<td>1.79</td>
<td>52</td>
<td>51.8</td>
<td>7.5</td>
<td>3766</td>
</tr>
<tr>
<td>NCM -10</td>
<td>88.97</td>
<td>5.78</td>
<td>0.795 2.10</td>
<td>55.65</td>
<td>7.85</td>
<td>216</td>
<td>4.07</td>
<td>60</td>
<td>46.5</td>
<td>10.5</td>
<td>4685</td>
</tr>
<tr>
<td>NCM -15</td>
<td>81.06</td>
<td>5.42</td>
<td>0.798 2.15</td>
<td>55.69</td>
<td>7.89</td>
<td>107</td>
<td>8.20</td>
<td>89</td>
<td>27.7</td>
<td>26.5</td>
<td>7128</td>
</tr>
</tbody>
</table>

DS: degree of swelling; F-H: Flory-Huggin; δ_p: solubility parameter of polymer; δ_i: 47.8 J^{1/2}cm^{-3/2} solubility parameter of water; M_c: number average molecular weight between cross-links (g/mol); n_e: cross-linking density (mol/cm^3); θ: contact angle in deg; γ_sv: surface energy of membrane in equilibrium with saturated vapor; γ_sl: interfacial tension between membrane and water; Wa: work of adhesion; J: flux; β_ij: separation factor.
the fluxes of 0.738 and 0.706 kg/m²h for 4 wt. % water-containing feed mixture. However, in the case of NCM-15, the separation factor is still higher i.e., 7128 and the flux is somewhat lower i.e., 0.544 kg/m²h. This clearly demonstrates the effect of addition of PWA nanoparticles in NaAlg/PVP blend matrix to enhance membrane selectivity to water, but with a lower flux.

**Fig. VI.6.** Separation factor and flux as a function of filler loading at 30°C for 4 wt. % water-containing feed mixture.

**VI.2.8.2. Effect of feed water composition**

In this investigation, we find that crosslink density increases by varying the amount of PWA in the NaAlg/PVP blend, because the PWA nanoparticles will act as the reinforcing bridge between the polymer chain segments of NaAlg and PVP, while the PWA will help to establish this bridge through the electrostatic interactions. Hence, all the NCMs of this study will exhibit higher separation
factors than NaAlg/PVP blend alone. However, the fluxes of all the NCMs are lower even compared to NaAlg/PVP membrane at all the compositions of water in the feed mixture (see Fig. VI.7). By an incremental increase of loading of PWA nanoparticles in NaAlg/PVP blend matrix, flux decrease, but separation factor increase considerably over and above that of the pristine NaAlg/PVP base membrane.

The amount of water in the feed mixture also exerts a significant influence on flux and separation factor. For instance, as the amount of water in the feed increased from 4 to 40 wt. %, the flux for NaAlg/PVP increased from 0.072 to a maximum of 1.044 kg/m²h, while for NCM-15, the separation factor is highest, i.e., 7148 for 4 wt.% water-containing feed, which decreased drastically to 182 at 40 wt.% of water in the feed. Thus, the present NCMs are able to dehydrate ethanol effectively even at lower concentration of water. Since water–ethanol form an azeotrope at 4 wt. % of water and hence, the present membranes can be used in separating azeotropic mixtures.

**Fig. VI.7.** Separation factor and flux as a function of feed water composition at 30°C.
VI.2.8.3. Diffusion coefficient

Transport of binary liquid mixtures through NCMs can be conventionally explained by the sorption-diffusion mechanism [32], which takes place in three steps: sorption, diffusion, and permeation evaporation. Permeation and selectivity are rather governed by solubility and diffusivity of the feed components. In order to understand the process of permeation, we need to calculate the concentration-independent diffusion coefficient, $D_i$ of the permeating molecules using the Fick’s diffusion equation [14]:

$$J_i = -D_i \left( \frac{dC_i}{dx} \right)$$  \hspace{1cm} (VI.9)

where $J_i$ is permeation flux/unit area (kg/m².s), $D_i$ is diffusion coefficient (m²/s), $C_i$ is concentration of permeate (kg/m³); subscript $i$ stands for water or ethanol and $x$ is diffusion path length. For simplicity, we assume that the concentration profile along the diffusion pathway is linear and hence, concentration-independent, $D_i$ can be calculated using [11]:

$$D_i = \frac{J_i \cdot h}{C_i}$$  \hspace{1cm} (VI.10)

where $h$ is membrane thickness (50 µm in the present study).

Calculated values of diffusion coefficient of water and ethanol between 40° and 70°C shown in Fig. VI.8 show that with increasing temperature from 40° to 70°C, flux increased, but separation factor ($\beta_{ij}$) decreased. The $D$ values of water are higher than those of ethanol by two orders of magnitude, further signifying the water-selective nature of the membranes. It is observed that diffusion coefficients of water as well as ethanol increased systematically with increasing temperature, a trend that is consistent with the conventional Arrhenius principles [14].
Fig. VI.8. Diffusion coefficients vs. temperature.

Fig. VI.9. Separation factor and flux as a function of temperature.
VI.2.8.4. Effect of temperature on pervaporation

Temperature affects the PV performance. As can be seen in Fig. VI.9, the flux increases with increasing temperature, but the overall temperature effect on flux or diffusivity can be described through Arrhenius-type relationship, from which activation parameters can be computed. The effect of temperature on PV performance was studied for all the membranes at fixed feed water composition of 4 wt. % under 5 mbar pressure. The temperature dependencies of permeation and diffusion have been calculated using the Arrhenius-type relationship [30-32]:

\[ X = X_o \exp\left(\frac{-E_a}{RT}\right) \]  

(VI.11)

where \( X \) represents the diffusion coefficient (\( D \)) or permeation flux (\( J_p \)), \( X_o \) is a constant representing the pre-exponential factors, \( D_o \) or \( J_o \) and \( E_a \) represents the activation energy for permeation or diffusion and \( RT \) is the conventional energy term. As the feed temperature increases, vapor pressure in the feed side compartment also increases, but vapor pressure on permeate side is not affected, resulting in an increased driving force.

Since the Arrhenius plots are linear (not shown) and positive values of activation energies suggest an increase of permeation flux as well as diffusion coefficient with increasing temperature. As per the free volume theory, an increase in temperature will increase the thermal mobility of polymer chains by generating extra void spaces due to increased sorption and diffusion. However, the driving force for permeation is the concentration gradient that results from a difference in partial vapor pressure of the permeant molecules between feed and permeate mixtures. As the feed temperature increases, vapor pressure in the feed compartment also increases, but vapor pressure on the permeate side will not be affected, resulting in an increased driving force; the latter is closely related to phase transition in PV process, but is dependent on temperature. Activation energies of permeation and diffusion are higher for NCMs than NaAlg/PVP (see Table VI.2). Apparent activation energies for water \( E_{p, w} \), are 21.7, 22.8, 24.9 and
28.1kJ/mol for NaAlg/PVP, NCM-5, NCM-10 and NCM-15 while activation energy for ethanol $E_{pe}$ are 56.2, 62.8, 65.3 and 69.3kJ/mol for NaAlg/PVP, NCM-5, NCM-10 and NCM-15 respectively; lower activation energies for water than ethanol suggest water selective nature of NCMs compared to NaAlg/PVP.

Table VI.2. Arrhenius parameters of membranes.

<table>
<thead>
<tr>
<th>Arrhenius parameters in Kj/mol</th>
<th>NaAlg/PVP</th>
<th>NCM-5</th>
<th>NCM-10</th>
<th>NCM-15</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_p$</td>
<td>25.3</td>
<td>23.3</td>
<td>25.1</td>
<td>28.4</td>
</tr>
<tr>
<td>$E_{pw}$</td>
<td>21.7</td>
<td>22.8</td>
<td>24.9</td>
<td>28.1</td>
</tr>
<tr>
<td>$E_{pe}$</td>
<td>56.2</td>
<td>62.8</td>
<td>65.3</td>
<td>69.3</td>
</tr>
<tr>
<td>$E_d$</td>
<td>22.0</td>
<td>22.8</td>
<td>24.7</td>
<td>28.2</td>
</tr>
</tbody>
</table>

**VI.4. CONCLUSIONS**

This investigation clearly demonstrates the effect that by incorporating PWA nanoparticles into NaAlg/PVP blend host matrix, it is possible to enhance remarkably the PV performance of the filled blend matrix membranes over that of unfilled NaAlg/PVP blend membrane for ethanol dehydration. However, higher loadings of PWA nanoparticles rendered the NaAlg/PVP matrix more rigid with a loss of flux, but giving increased separation factor to water. Membrane characterization by XRD, SEM, DSC, DMTA and contact angle measurement revealed an adequate thermal and mechanical stability as well as surface free energy of the membranes, which are essential for PV dehydration above the ambient temperature. Flory-Huggins equation enabled accurate predictions of the interaction parameters and solubility parameters of the membranes and these are useful in satisfactorily explaining the thermodynamics of dissolution and permeation processes. Modified Flory-Rehner equation was used to calculate
crosslink density of the matrix in effectively predicting the rigidity of NCMs. Feed water composition has played a significant role in water permeation flux, but has only a slight influence on ethanol permeability. The membranes exhibited significantly lower Arrhenius activation energies for water than ethanol, suggesting higher separation ability and water-selective nature of the membranes.

VI.5. REFERENCES


