Using a solution technique, polyelectrolyte complex (PEC) membranes were prepared by the complexation of sodium alginate (SA) with gelatin (Ge). The physico-chemical properties of these PEC membranes were studied by FTIR, WAXD, DSC, TGA and SEM. The pervaporation characteristics of membranes were investigated with water-isopropanol mixtures. The effects of Ge content and feed compositions on the pervaporation performance of the membranes were analyzed. The data thus obtained were employed to explain permeation behavior of water and isopropanol through PEC membranes. The experimental results showed that the membrane containing 10 mass% of Ge exhibits the highest separation selectivity of 4,277 with a flux of $8.47 \times 10^{-2}$ kg/m$^2$h at 30 °C for 10 mass% of water in the feed. The total flux and flux of water are found to be overlapping each other particularly for PEC membranes, manifesting that the developed membranes could be used effectively to break the azeotropic point of water-isopropanol mixtures. From the temperature dependent diffusion and permeation values, the Arrhenius activation parameters were estimated. The activation energy values obtained for water permeation ($E_{pw}$) are significantly lower than those of isopropanol permeation ($E_{pIPA}$), suggesting that the Ge
incorporated membranes have higher separation ability for water-isopropanol system. The negative heat of sorption ($\Delta H_s$) values was obtained for all the membranes, suggesting that Langmuir’s mode of sorption is predominant.

Work of this Chapter has been communicated to *Journal of Membrane and Separation Technology*.

**VI.1. INTRODUCTION**

As the modern industry keeps growing, energy saving becomes a worldwide concern and membrane technology gains more and more importance due to its energy saving character [1]. Pervaporation (PV) is one of the representative membrane-based techniques for separation of azeotropes [2], close-boiling liquids [3] and aqueous organic mixtures [4]. The past decade had witnessed substantial progress and exciting breakthroughs in both the fundamental and application aspects of PV [5-7]. Among the applications of PV, dehydration of organics is probably the best known and well-developed.

Commonly used membrane materials for PV dehydration include naturally occurring polymers [8,9], synthetic hydrophilic polymers [10,11] and inorganic polymers [12,13]. Recently, organic-inorganic hybrids [14-16] and layer-by-layer assembled multilayer [17-20] also attracted great interest. From all these, it was found that an important issue for dehydration is to control the swelling degree of membranes in aqueous feed [1]. Therefore, membrane should be hydrophilic to ensure large flux and at the same time it should not be excessive swelling to ensure good selectivity. It is well known that relaxation is an intrinsic characteristic of common polymeric materials and may result in the falling of its PV performance [21] and therefore, enhancing the durability of a common polymeric membrane in
PV is questionable. To resolve this seemingly paradox, a new strategy of preparation of polyelectrolyte complexes (PECs) with ionic crosslinking is proven [22].

Therefore, recently polyelectrolyte complexes have attracted special interest as membrane materials that can facilitate the PV separation with high flux and selectivity. Generally, PECs or polyanion complexes form when macromolecules of an opposite charge are allowed to interact. The interaction constitutes the main attractive force but hydrogen bondings, ion-dipole forces and hydrophobic interactions frequently play significant roles in determining the structures [23] and hence, PECs are ideal materials for PV dehydration [24].

In search of new environment friendly polymeric materials to develop a new type of novel polyelectrolyte membranes for the dehydration of isopropanol, we thought of combining the properties of sodium alginate (SA) and gelatin (Ge). Sodium alginate has received a great deal of attention due to its considerable applications either pure or composite with other materials. It is a natural hydrophilic and an anion electrolytic polysaccharide, extracted from seaweeds having major industrial importance [25,26]. Sodium alginate possesses not only strong hydrophilicity due to large number of hydroxyl and carboxyl groups, but also has large free-volume between the chains because of the loose structure [26,27]. On the other hand, Ge is a natural protein, obtained from partially hydrolyzed collagen and is regarded as an attractive green polymer as well as a polyampholyte [28]. Gelatin contains free carboxyl and amino groups on its backbone, and carries positive charges in aqueous solution. It has shown a
superior permselectivity towards water in vapor permeation [29]. Furthermore, the flexible backbone of Ge is favorable for the compact and ordered chain packing, which ensures high permselectivity. The complementary properties such as hydrophilic groups, charges and chain stiffness between these two hydrophilic materials may render the promising performance of SA-Ge PEC membranes for dehydration processes. Further, by systematic variation of Ge into SA matrix is expected to be a useful method to improve the mechanical properties of SA as well as to tackle the isopropanol (IPA) separation. However, despite many investigations on their performance in medicine, pharmacy and agriculture applications [30], rare reports have concerned about SA-Ge as a separation membrane.

Therefore, in the present investigation we have made an attempt to develop PV membranes by incorporating Ge into SA matrix. While keeping the amount of SA constant, we have varied the amount of Ge so as to improve the membranes performance. The resulting membranes demonstrated excellent mechanical properties and homogeneity. Incorporation of Ge introduces \(-\text{NH}_3^+\) and \(-\text{COOH}\) groups in SA matrix, and thereby increases the ionic interaction and hydrogen bonding between SA and Ge through PEC formation. The physico-chemical changes in the resulting membranes were investigated using different techniques. The membranes were successfully employed for PV separation of water-IPA mixtures at different feed compositions. The values of permeation flux and separation selectivity were determined. The diffusion coefficient and Arrhenius
activation parameters were also estimated. The results were discussed in terms of PV separation efficiency of the membranes.

VI.2. EXPERIMENTAL

VI.2.1. Materials

Sodium alginate (SA) (medium viscosity grade), isopropanol (IPA) and hydrochloric acid (HCl) were purchased from s. d. fine Chemicals Ltd., Mumbai, India. Gelatin (Ge) was procured from E. Merk Ltd., Mumbai, India. All the chemicals were of reagent grade and used without further purification. Double distilled water was used throughout the investigation.

VI.2.2. Membrane Preparation

Sodium alginate (3 g) was dissolved in 100 ml of deareated distilled water with a constant stirring for about 24 h at room temperature. It was then filtered and the resulting homogeneous solution was spread onto a clean glass plate with the aid of a casting knife in a dust-free atmosphere. It was allowed to dry at ambient temperature for about 2-3 days. The completely dried membrane was subsequently peeled-off and was designated as M.

To prepare PEC membrane, a known amount of Ge and a few drops of concentrated HCl were consecutively added into a homogeneous SA solution. The solution was stirred initially for 24 h at room temperature and then for about 1 h at 70 °C so as to improve the dispersion and formation of polyelectrolyte complex between Ge and SA matrix. The resulting complex solution was poured onto a glass plate and the rest of the procedure was followed as similar to membrane M. The amount of Ge with respect to SA was varied as 5, 10 and 15 mass%, and the
membranes thus obtained were designated as M-1, M-2 and M-3, respectively. The chemical structure and reaction route of the PEC membrane is illustrated in Fig. VI.1.

Fig. VI.1. Scheme for the preparation and structural representation of SA-Ge PEC membrane.
The thickness of the membranes was measured at different points using a Peacock dial thickness gauge (Model G, Ozaki MFG Co. Ltd., Japan) with an accuracy of ± 2 μm. The thickness of the membranes was found to be 45 ± 2 μm.

**VI.2.3. Fourier Transform Infrared Spectroscopy**

The interaction and hydrogen bonding between SA and Ge were confirmed by FTIR Spectrometer (Nicolet, Impact-410, USA). The rest of the procedure was followed as discussed in Chapter III (Section III.2.3).

**VI.2.4. Wide-Angle X-ray Diffraction**

The crystallinity of plane SA and its Ge incorporated PEC membranes were studied at room temperature using a Philips Analytical X-ray Diffractometer. The X-ray source was nickel-filtered Cu-Kα radiation (40 kV, 30 mA). The rest of the procedure was followed as discussed in Chapter III (Section III.2.4).

**VI.2.5. Differential Scanning Calorimetry**

The glass transition temperature ($T_g$) of pure SA and its Ge incorporated PEC membranes was measured using a Differential Scanning Calorimeter (DSC Q 20, TA Instruments, Waters LLC, New Castle, Delawave, USA). The rest of the procedure was followed as discussed in Chapter III (Section III.2.5).

**VI.2.6. Thermogravimetric Analysis**

Thermal properties of pure SA and its Ge incorporated PEC membranes were measured using Perkin-Elmer Diamond Thermogravimetric Analyzer (TGA). The rest of the procedure was followed as discussed in Chapter III (Section III.2.6).
VI.2.7. Scanning Electron Microscopy

The surface and cross-section views of pure SA and its Ge incorporated PEC membranes were examined using a Scanning Electron Microscope (JEOL, JSM-400 Å, Tokyo, Japan). The rest of the procedure was followed as discussed in Chapter III (Section III.2.7).

VI.2.8. Swelling Measurement

The equilibrium sorption experiments were performed in different compositions of water-IPA mixtures using an electronically controlled oven (WTB Binder, Jena, Germany). The masses of the dry membranes were first determined and then the same samples were equilibrated by soaking in different compositions of water-IPA mixtures in sealed vessels at 30 °C for 24 h. The procedure including the calculation of degree of swelling was followed as discussed in Chapter III (Section III.2.8).

VI.2.9. Pervaporation Experiment

PV experiments were performed using the in-house designed set-up as shown in Chapter III [Fig. III.2 (A and B)]. The experiments were carried out at 30, 40 and 50 °C. The water composition in the feed was varied from 5 to 25 mass%.

The rest of the procedure was followed as described in Section III.2.9 of Chapter III. Membrane performance was studied by calculating the total flux \((J)\), separation factor \((\alpha)\) and pervaporation separation index \((PSI)\). These were calculated, respectively, using the Eqs. III.2-III.4 given in Chapter III.
VI.3. RESULTS AND DISCUSSION

VI.3.1. Membrane Characterization

VI.3.1.1. FTIR studies

FTIR spectra of pure SA membrane and its Ge incorporated PEC membranes are presented in Fig. VI.2.

![FTIR spectra of SA and Ge incorporated PEC membranes](image)

**Fig. VI.2.** FTIR spectra of SA and its Ge incorporated PEC membranes: pure Ge; (M) 0 mass%; (M-1) 5 mass%; (M-2) 10 mass%; (M-3) 15 mass% of Ge.
A characteristic strong and broad band appeared at around 3440 cm\(^{-1}\) in membrane M corresponds to O-H stretching vibrations of the hydroxyl groups. The strong bands appeared at around 1610 and 1420 cm\(^{-1}\) were respectively attributed to antisymmetric and symmetric stretching vibrations of the carboxyl groups of SA [32]. Ge has the following characteristic absorption bands: 3400 cm\(^{-1}\) (NH stretching), 1656 cm\(^{-1}\) (amide I, CO, and CN stretching), 1544 cm\(^{-1}\), 1238 cm\(^{-1}\) (amide II and III, respectively, mainly NH bending and CN stretching) [33]. Upon incorporating the Ge into SA matrix, the band assigned to OH stretching was broadened and shifted to a lower frequency, suggesting that H groups were involved in the formation of intermolecular hydrogen bonding with the OH groups of Ge. Further, it is clearly observed that the intensity of strong absorption bands appeared at 1610 and 1420 cm\(^{-1}\) of pure SA membrane (M) was decreased gradually with increasing the content of Ge, indicating that there is an electrostatic attraction between COO\(^-\) groups of SA and NH\(_3^+\) groups of Ge. All these evidences explicitly support the establishment of good interaction between SA and Ge.

**VI.3.1.2. WAXD studies**

Figure VI.3 illustrates the WAXD patterns of pure SA and Ge incorporated PEC membranes along with the pattern of Ge. Membrane (M) shows a broad peak at around \(2\theta = 13.7^\circ\), indicating that SA exists in the form of amorphous nature [34]. The diffractogram of Ge membrane shows clearly two diffraction peaks at around 8 and 18\(^\circ\). According to Bigi et al. [35], the peak appeared at around 8\(^\circ\) is related to diameter of the triple helix, whereas its intensity is associated with the triple-
helix content of the Ge membrane. However, the peak at 18° is attributed to semicrystalline nature. After incorporating the Ge into a SA matrix, the peak of SA (13.7°) was shifted to higher degree.

Fig. VI.3. Wide-angle X-ray diffraction patterns of SA and its Ge incorporated PEC membranes: pure Ge; (M) 0 mass%; (M-1) 5 mass%; (M-2) 10 mass%; (M-3) 15 mass% of Ge.

Further, its intensity was gradually enhanced as the content of Ge was increased. This indicates that the diffraction peaks of Ge become flat in the PEC membranes, suggesting that the presence of SA decreases the triple-helix content
of Ge. This is because of the formation of strong intermolecular interaction due to hydrogen bonding and electrostatic attraction between SA and Ge.

VI.3.1.3. DSC study

The thermal properties of the membranes can be judged by its solid state properties such as glass transition temperature. The DSC curves of pure SA and Ge incorporated PEC membranes were recorded and thermograms thus obtained are presented in Fig. VI.4.

![DSC thermograms of SA and its Ge incorporated PEC membranes](image)

**Fig. VI.4.** DSC thermograms of SA and its Ge incorporated PEC membranes: (M) 0 mass%; (M-1) 5 mass%; (M-2) 10 mass%; (M-3) 15 mass% of Ge.

A special care was taken during DSC measurements since membranes are prone to adsorb moisture, which strongly affects on $T_g$. To eliminate this effect, two cycles of heating and cooling runs were adopted, ensuring that the temperature
range employed in the study would not cause thermal degradation in the first heating run [36].

From the thermogram, it is noticed that pure SA membrane exhibits its $T_g$ at 94 °C. However, when we incorporated Ge from 5 to 10 mass%, the $T_g$ of the membranes was increased from 97 to 108 °C. This is due to an establishment of electrostatic force of attraction and hydrogen bonding between Ge and SA matrix. However, membrane containing 15 mass% of Ge (M-3), exhibited lower $T_g$ than that of membrane M-2. The decline of $T_g$ is unexpected, but it can be due to non-availability of sites in SA matrix for the establishment of electrostatic attraction and hydrogen bonding with the further added Ge. The further added Ge could not form ionic bond with SA and moved freely than those ionically fixed ones. Therefore, the resulting polymer network becomes relaxed and disordered the arrangements in the membrane matrix.

VI.3.1.4. TGA studies

The thermal stability and degradation behaviour of Ge incorporated PEC membranes were investigated by TGA under nitrogen flow. The resulting thermograms are shown in Fig. VI.5. From the thermograms, it is clear that under nitrogen flow non-oxidative degradation occurred in two stages for all membranes. The first weight loss occurred between ambient temperature and 200 °C corresponds to the physically absorbed water molecules. Most of these absorbed water molecules exist in a bound state rather than in a free molecular state [37] and seem to be bound directly to the polymer chain through hydrogen bonds. Such weight loss is about 24% for SA membrane, whereas its Ge incorporated PEC
membranes exhibited slightly lower loss ranging from 16 to 22%. This indicates that the PEC membranes have low water retention capacity. Further, this was decreased correspondingly with increasing the mass% of Ge from 5 to 10%. However, the loss was increased for membrane containing 15% of Ge. This is because of increased hydrophilic nature of membrane, owing to non-availability of sites in SA matrix for electrostatic attraction as well as hydrogen bonding.

Fig. VI.5. Thermogravimetric analysis of SA and its Ge incorporated PEC membranes: (M) 0 mass%; (M-1) 5 mass%; (M-2) 10 mass%; (M-3) 15 mass% of Ge.
The second stage of decomposition temperature of all the Ge incorporated membranes was slightly increased with increasing the mass% of Ge content. Especially, the highest thermal stability was observed for membrane M-2 compared to other membranes, suggesting that the thermal stability of the Ge incorporated membrane was increased. The second stage of decomposition was started from 205 to 500 °C, which is attributed to major weight loss due to decomposition of polymeric network. If we consider the temperature at 50% weight loss as a measuring point, the Ge incorporated PEC membranes exhibit around 10 to 230 °C higher thermal stability than that of pure SA membrane. This clearly indicates that Ge incorporated PEC membranes demonstrated higher thermal decomposition temperature compared to SA membrane.

**VI.3.1.5. SEM study**

The surface and cross-sectional views of pure SA and Ge incorporated PEC membranes were studied using scanning electron microscope and the resulting photographs are shown in Fig. VI.6. When we observe the both surface and cross sectional views of the photographs carefully, it is observed that the membranes are smooth and homogeneous with no porosity upto 10 mass% of Ge. However, when the content of Ge was increased to 15 mass%, the membrane surface becomes rough with foliaceous. This clearly suggests that upto 10 mass% of Ge, there is a good compatibility between Ge and SA. This is very well supported by the WAXD, DSC and TGA data. This compatibility no longer remains when Ge content was reached to 15 mass%.
**Fig. VI.6.** SEM micrographs of SA and its Ge incorporated PEC membranes: (A) surface view and (B) cross-sectional view.
VI.3.2. Swelling Study

VI.3.2.1. Effects of feed composition and Ge content on membrane swelling

To study the effects of feed composition and Ge content on membrane swelling, the percent degree of swelling of all the membranes was plotted as a function of mass% of water in the feed at 30 °C as shown in Fig. VI.7.

![Graph showing variation of degree of swelling with different mass% of water in the feed for SA and its Ge incorporated PEC membranes.]

Fig. VI.7. Variation of degree of swelling with different mass% of water in the feed for SA and its Ge incorporated PEC membranes.

It is observed that the degree of swelling was increased almost linearly for all the membranes with increasing mass% of water in the feed. This is because of strong interaction occurring between water molecules and the membrane, since water causes a greater degree of swelling than that of isopropanol. This is quite obvious as membranes contain interactive groups such as \(-\text{OH}, \ -\text{NH}_3^+\) and -
COOH. On the other hand, the degree of swelling was decreased from membrane M to M-2 throughout the investigated feed compositions. This is because, the added Ge contains \(-\text{NH}_3^+\) and OH, which establish the ionic crosslinks and hydrogen bonding respectively with –COO\(^-\) and H of SA matrix, leading to more compact structure and making the free carboxyl groups of SA unavailable for solvent interaction. However, when content of Ge was increased to 15 mass%, the degree of swelling was increased. This is because of non-availability of sites in SA matrix for the establishment of electrostatic attraction and hydrogen bonding with Ge. Therefore, the Ge polymer becomes relaxed and thereby \(-\text{NH}_3^+\) and OH groups are freely available for solvent interaction, resulting to greater swelling throughout the water composition. This is very well supported by the DSC, TGA and SEM photograph of the membranes.

**VI.3.3. Pervaporation Study**

**VI.3.3.1. Effects of feed composition and Ge content on pervaporation**

Figure VI.8 shows the total pervaporation flux as a function of water composition in the feed for pure SA and Ge incorporated PEC membranes. It is observed that the permeation flux was increased linearly for all membranes upon increasing the water composition in the feed. This is expected owing to selective interaction between water molecules and the membrane. On the other hand, the permeation flux was decreased for the membrane M to M-2. This is because of a significant reduction of free-volume owing to chain stiffness caused by electrostatic attraction and hydrogen bonding.
Fig. VI.8. Variation of total pervaporation flux with different mass% of water in the feed for SA and its Ge incorporated PEC membranes.

On the contrary, the observed permeation flux of membrane M-3 was more than that of M-2 throughout the range of feed composition. This is because, when excess Ge was added, the interactable groups of Ge could not able to form ionic and hydrogen bonding with SA. As a result, the network of Ge was relaxed in the SA matrix and thereby the free hydrophilic groups were increased in the membrane matrix, leading to enhanced permeation flux which is more than that of M-1 membrane. To assess the extent of permeation of individual components, we
plotted the total flux and fluxes of water and IPA as a function of Ge content in the membranes for 10 mass% of water in the feed as shown in Fig. VI.9.

![Plot of flux and fluxes (Fig. VI.9)](image)

**Fig. VI.9.** Variation of total flux, and fluxes of water and isopropanol with different mass% of Ge at 10 mass% of water in the feed.

From the plot, it is observed that the total flux and flux of water are overlapping each other, particularly for Ge incorporated membranes, suggesting that the membrane developed in the present study by the incorporation of Ge demonstrated an excellent permselectivity towards water. The overall selectivity of a membrane in PV process, generally explained on the basis of interaction between membrane and the permeating molecules and the molecular size of the permeating species. Figure VI.10 displays the effects of feed composition and Ge content on the selectivity of all the membranes.
Chapter VI

Fig. VI.10. Variation of separation selectivity with different mass% of water in the feed for SA and its Ge incorporated PEC membranes.

It is observed that the selectivity of water was decreased almost exponentially for all the membranes with increasing mass% of water in the feed. At higher concentration of water in the feed, the membrane swells greatly because of establishing strong interaction between membrane and the water molecules. Therefore, a decrease of selectivity is apparent at higher concentration of water irrespective of the content of Ge in the membrane matrix. On the contrary, the selectivity was increased significantly from membrane M to M-2 at all feed compositions. This is attributed to increased selective interaction between membrane and the water molecules, owing to an establishment of ionic crosslinks and hydrogen bonding. On the other hand, the selectivity was decreased for M-3
membrane. This is because, the interactable groups of Ge could not able to form ionic and hydrogen bonds with SA. The added Ge simply relaxed in the SA matrix and thereby disordered the arrangements which would cause for the declined selectivity. This is expected due to an establishment of Ge phase in the membrane matrix as evidenced by the SEM photograph (M-3). This was further demonstrated from Fig. VI.11, in which the flux and selectivity were plotted as a function of Ge content at 10 mass% of water in the feed. The permeation flux was decreased with increasing Ge content in SA and reached minimum when Ge content was 10 mass%, and it was then increased.

![Graph](image)

**Fig. VI.11.** Variation of total flux and selectivity with different mass% of Ge at 10 mass% of water in the feed.
On the contrary, the selectivity increased steeply up to 10 mass% of Ge and then decreased for 15 mass% Ge. Here, Ge was acted as ionic crosslinking agent to interlock the SA main chains. The higher is the Ge content, the more will be the packing in SA matrix, thus lowering the available free-volume of the membrane, resulting to decreased flux. Since, the characteristic size of IPA molecule is much larger than that of water, IPA molecules were moved through the polymer matrix with more difficulty when the free-volume was reduced, and separation selectivity was accordingly enhanced. On the other hand, when excess quantity of Ge was added, the Ge could not form ionic and hydrogen bonds with SA, and moved more freely than those ionically fixed ones. The resulting polymer network attains relaxed and disordered state and thereby the free-volume of the membrane was increased. As a result, permeation flux was increased while declining the selectivity.

**VI.3.3.2. Effect of Ge on pervaporation separation index**

The PSI is the product of total permeation flux and separation factor, which characterizes the membrane separation ability. This index can be used as a relative guideline for the design of new membranes for pervaporation separation process and also to select a membrane with an optimal combination of flux and selectivity.

Figure VI. 12 illustrates the variation of PSI as a function of mass% of Ge at 30 °C for 10 mass% of water in the feed. When we look at the PSI plot, it is observed that all the Ge incorporated membranes have shown higher PSI values than that of plane SA membrane (M). This is because of high selectivity exhibited by the Ge incorporated membranes. If we look at only Ge incorporated membranes, the PSI
values were increased with increasing the Ge content from 0 to 10 mass%. As discussed in both swelling and flux data, this was attributed to the formation of ionic crosslinking and hydrogen bonding between SA and Ge. A further increase of Ge beyond 10 mass%, significantly enhanced the hydrophilic character, which decreases the selectivity. As a result, PSI value of membrane M-3 almost remained same as of M-2.

![Fig. VI.12. Variation of pervaporation separation index with different mass% of Ge at 10 mass% of water in the feed.](image)

**VI.3.4. Diffusion Coefficients**

Mass transport of binary liquid mixtures through a non-porous polymer membrane is generally described by the solution-diffusion mechanism, which occurs in three steps: sorption, diffusion and evaporation [38]. Thus, permeation rate and selectivity are governed by the solubility and diffusivity of each component of the
feed mixture to be separated. In PV process, because of the establishment of fast equilibrium distribution between bulk feed and the upstream surface of a membrane, the diffusion step controls the transport of permeants [39,40]. It is, therefore, important to estimate the diffusion coefficient \( (D_i) \) of penetrating molecules to understand the mechanism of transport. The diffusion coefficients have been calculated at 30 °C using the Eqs. III.5 and III.6 given in Chapter III [41,42]. The calculated values of \( D_i \) at 30 °C are presented in Table VI.1.

**Table VI.1.** Diffusion coefficients of water and isopropanol for all the membranes at different mass% of water in the feed

<table>
<thead>
<tr>
<th>Mass% of water</th>
<th>( D_w \times 10^7 ) (m²/s)</th>
<th>( D_{IPA} \times 10^9 ) (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M</td>
<td>M-1</td>
</tr>
<tr>
<td>5</td>
<td>2.81</td>
<td>2.57</td>
</tr>
<tr>
<td>10</td>
<td>2.71</td>
<td>2.50</td>
</tr>
<tr>
<td>15</td>
<td>2.60</td>
<td>2.48</td>
</tr>
<tr>
<td>20</td>
<td>2.54</td>
<td>2.35</td>
</tr>
<tr>
<td>25</td>
<td>2.30</td>
<td>2.02</td>
</tr>
</tbody>
</table>

Similar to PV study, the diffusion coefficients of water were decreased significantly from membrane M to M-2 and then increased for membrane M-3, while the diffusion coefficient of IPA were suppressed. This further confirms that the membranes developed in the present study have remarkable separation ability for the separation of water-IPA mixtures. As discussed above, this was attributed
to increased electrostatic attraction and hydrogen bonding in the membrane matrix due to the incorporation of Ge. However, it is found that there was a considerable decrease in diffusion coefficient for all the membranes when the amount of water was increased in the feed. This is expected, because of the observed deterioration of membranes’ selectivity as discussed in PV study. In spite of this, the magnitude of the diffusion coefficients of water is quite high in comparison with that of IPA, suggesting that even at higher concentration of water in the feed, the membranes developed in present study still have remarkable separation selectivity towards water.

VI.3.5. Effect of Temperature on Membrane Performance

Effect of operating temperature on PV performance for water-IPA mixtures was studied for all the membranes at 10 mass% of water in the feed, and the resulting values are presented in Table VI.2.

Table VI.2. Pervaporation flux and separation selectivity of all the membranes for different temperature at 10 mass% of water in the feed

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>$J \times 10^2$ (kg/m²h)</th>
<th>$\alpha_{sep.}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M</td>
<td>M-1</td>
</tr>
<tr>
<td>30</td>
<td>12.15</td>
<td>10.73</td>
</tr>
<tr>
<td>40</td>
<td>15.05</td>
<td>11.96</td>
</tr>
<tr>
<td>50</td>
<td>16.16</td>
<td>15.92</td>
</tr>
</tbody>
</table>

It is observed that the permeation rate was found to increase from 30 to 50 °C for all the membranes, while suppressing the separation factor. This is because,
higher temperature not only decreases the intermolecular interaction between permeants, but also decreases the intramolecular interaction within the membrane material, which predominate the plasticizing effect on the membrane due to greater swelling. Consequently, permeation of diffusing molecules and the associated molecules through the membrane becomes easier, leading to an increase of total permeation flux, while suppressing the selectivity. This effect prompted us to estimate the activation energies for permeation and diffusion by the extensively used Arrhenius type equation Eq. given in III.7 of Chapter III [43].

The resulting Arrhenius plots of log $J$ and log $D$ versus temperature are shown in Figs. VI.13 and VI.14 for the temperature dependence of permeation flux and diffusion, respectively.

Fig. VI.13. Variation of log $J$ with temperature for SA and its Ge incorporated PEC membranes at 10 mass% of water in the feed.
Fig. VI.14. Variation of log $D$ with temperature for SA and its Ge incorporated PEC membranes at 10 mass% of water in the feed.

From the least-squares fits of these linear plots, the activation energies for total permeation ($E_p$) and diffusion ($E_D$) were calculated. In similar way, activation energies for permeation of water ($E_{pw}$) and IPA ($E_{pIPA}$), and diffusion of water ($E_{Dw}$) were calculated, but the plots are not given to avoid the crowdness. The values thus obtained are presented in Table VI.3. From the Table VI.3, it is observed that pure SA membrane (M) exhibits lower $E_p$ and $E_D$ values compared to those of Ge incorporated PEC membranes. This suggests that both permeation and diffusion processes require less energy for transport of molecules through the pure SA membrane. Obviously, Ge incorporated membranes consumed more energy because of its ionic crosslinking and hydrogen bonding. This has resulted noticeably from membrane M to M-2 with increasing the amount of Ge. Although, $E_p$ values are slightly lower than those of $E_D$ values in all the
membranes, the difference is insignificant, suggesting that both sorption and diffusion contribute equally to the PV process. The same trend is also observed for $E_{pw}$ and $E_{Dw}$ values.

Table VI.3. Arrhenius activation parameters for permeation and diffusion, and heat of sorption

<table>
<thead>
<tr>
<th>Parameters (kJ/mol)</th>
<th>M</th>
<th>M-1</th>
<th>M-2</th>
<th>M-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_p$</td>
<td>11.67</td>
<td>15.97</td>
<td>23.10</td>
<td>13.53</td>
</tr>
<tr>
<td>$E_D$</td>
<td>12.16</td>
<td>16.57</td>
<td>23.91</td>
<td>14.05</td>
</tr>
<tr>
<td>$E_{pw}$</td>
<td>11.43</td>
<td>15.88</td>
<td>23.01</td>
<td>13.45</td>
</tr>
<tr>
<td>$E_{pIPA}$</td>
<td>16.33</td>
<td>33.11</td>
<td>51.28</td>
<td>37.28</td>
</tr>
<tr>
<td>$E_{Dw}$</td>
<td>11.98</td>
<td>16.63</td>
<td>23.95</td>
<td>14.10</td>
</tr>
<tr>
<td>$\Delta H_s$</td>
<td>-0.49</td>
<td>-0.60</td>
<td>-0.81</td>
<td>-0.52</td>
</tr>
</tbody>
</table>

However, a significant difference was noticed between the apparent activation energy values for water ($E_{pw}$) and IPA ($E_{pIPA}$), and the difference was increased correspondingly with increasing the Ge. This further suggests that membranes incorporated with higher amount of Ge demonstrated greater separation efficiency toward water. The $E_p$ and $E_D$ values ranged between 11.67 and 23.10, and 12.16 and 23.91 kJ/mol, respectively. Using these values, we have further calculated the heat of sorption using the Eq. given in Section III.8 of Chapter III. The resulting $\Delta H_s$ values are included in Table VI.3. The $\Delta H_s$ values give the additional information about the transport of molecules through the polymer matrix. It is a composite parameter involving the contributions of both...
Henry’s and Langmuir’s types of sorption [44]. The Henry’s law states that the heat of sorption will be positive for liquid transport, leading to the dissolution of chemical species into that site within the membrane, giving an endothermic contribution to the sorption process. However, the Langmuir’s sorption requires the pre-existence of a site in which sorption occurs only by a hole filling mechanism, giving an exothermic contribution. The $\Delta H_s$ values obtained in the present study are negative for all the membranes, suggesting that Langmuir’s sorption is predominant, giving an exothermic contribution.

**VI.4. CONCLUSIONS**

Novel polyelectrolyte complex (PEC) membranes were prepared by varying the amount of Ge in SA matrix. Thermogravimetric study reveals that PEC membranes exhibited better thermal stability compared to pure SA membrane (M). The performance of membranes was systematically evaluated for the separation of water-IPA mixtures. An increase of Ge content in the membrane matrix results to increase overall performance of the membrane. This was explained on the basis of ionic crosslinking, hydrogen bonding, chain stiffness and significant enhancement of hydrophilicity. Among the PECs membranes, the membrane containing 10 mass% of Ge exhibited the highest separation selectivity of 4,277 with a flux of $8.47 \times 10^{-2}$ kg/m$^2$h at 30 °C for 10 mass% of water in the feed.

Experimental data also reveal that the total flux and flux of water are overlapping each other particularly for Ge incorporated membranes, suggesting that the developed membranes ensure high selectivity towards water. This is in
accordance with the diffusion data. The temperature effect study indicated that the membranes show significant lower activation energy values for water permeation ($E_{pw}$) than that of isopropanol permeation ($E_{pIPA}$), suggesting that membranes developed in the present study have higher separation ability towards water. The estimated $E_p$ and $E_D$ values were ranged between 11.67 and 23.10, and 12.16 and 23.91 kJ/mol, respectively. All the membranes exhibited negative $\Delta H_s$ values, indicating that sorption is mainly dominated by the Langmuir’s mode of sorption, giving an exothermic contribution.

VI.5. REFERENCES


*Chapter-VI*


