Sodium Montmorillonite Clay Loaded Novel Mixed Matrix Membranes of Poly(Vinyl Alcohol) for Pervaporation Dehydration of Aqueous Mixtures of Isopropanol and 1,4-Dioxane

ABSTRACT

In this chapter, we will discuss poly(vinyl alcohol)-based mixed matrix membranes loaded with 5 and 10 wt % of sodium montmorillonite (Na⁺MMT) clay particles i.e., (PVA/Na⁺MMT-5 and PVA/Na⁺MMT-10) fabricated by solvent casting method. The uncrosslinked membranes were used in pervaporation (PV) dehydration of aqueous solutions of isopropanol and 1,4-dioxane at 30°C. Membrane morphology was characterized by scanning electron microscopy. Differential scanning calorimetry, thermogravimetric analysis, and dynamic mechanical thermal analysis were used to understand thermal properties. Universal testing machine was used to study mechanical strength properties. PV results are discussed in terms of water flux, separation factor, permeation separation index, enrichment factor, and activation energy of permeation. Sorption and PV experiments were carried out for the thermally crosslinked and glutaraldehyde crosslinked PVA/Na⁺MMT mixed matrix membranes for 10 wt % water-containing feed mixtures at 30°C. A small increase in separation factor with a slight sacrifice in flux was observed without showing any great difference as compared to uncrosslinked mixed matrix membranes. The hydrophilic nature of Na⁺MMT clay and the formation of PVA/Na⁺MMT mixed matrix membranes are responsible to offer such increased separation to water over the organic components of the feed mixtures.

VI.1. INTRODUCTION

Recently, mesoporous/microporous molecular sieves/clay particles are continued to be interesting filler materials into polymers in developing cost-effective high performance membranes in pervaporation (PV) separation and purification technologies. Particularly, extensive research has been devoted to develop polymer-layered nanocomposites, wherein filler inorganic particles in a polymer matrix could exhibit improved physical and mechanical properties of the virgin polymers. The easily tailored pore size and compositional variability available with montmorillonite clay particles when embedded into polymer network will provide the versatile range of applications that span from material development to membrane separations in addition to drug delivery devices [1,2]. One of the most widely used fillers in such applications is montmorillonite (MMT), a common clay mineral from the smectite family. Its rich intercalation chemistry allows it to be chemically modified and to become compatible with various polymers. Since the use of sodium montmorillonite (Na⁺MMT) clay, which belongs to the class of smectite clay i.e., the family of 2:1 phyllosilicates, many efforts have been made to use them as fillers to develop novel composite materials [3,4]. Na⁺MMT is composed of the units made up of two silica tetrahedral sheets centered with alumina octahedral sheet. Smectite clays have the properties of cation exchange and intercalation of molecules, which will tend to swell in solvents to a certain extent [5]. However, when these particles are intercalated into polymeric matrices, they are known to increase the overall mechanical strength and barrier properties of the mixed matrix membrane.

Of late, membrane technology is considered to be one of the most effective and energy saving methods to separate the desired component from the mixed media. Ultrafiltration, reverse osmosis, pervaporation (PV) and gas separation [6] have all been well recognized as successful membrane-based techniques in commercial applications because of their ease of operation and eco-friendly nature. Among these techniques, PV is particularly popular in recent years due to the availability of a variety of novel mesoporous/microporous filler particles, which when incorporated are responsible to create free channels for an easy transport of water molecules from
the aqueous-organic feed mixtures. PV membranes incorporated with such mesoporous/microporous particles could offer applications in separating aqueous-organic mixtures or azeotropes that are otherwise difficult to separate by the conventional distillation process [7]. In PV, the feed mixture permeates across the barrier membrane, while permeate is collected on the downstream side as a vapor under high vacuum (low pressure) [8]. Liquid is collected after condensation under liquid nitrogen atmosphere. Thermodynamic driving force for liquid transport across the filled dense membrane is the difference in chemical potential of the individual permeating components between feed and permeate sides [9]. Thus, PV allows for selective separation of a component from the aqueous-organic mixtures. An additional advantage is that PV can be performed under ambient conditions, but distillation/extraction requires higher temperatures and therefore, energy inputs are more. In this respect, PV has an advantage in separating azeotropic and/or closely boiling liquid mixtures, isomers as well as recovery or removal of small quantities of impurities from aqueous streams that are organically contaminated [10-15].

Because of the excellent film-forming properties, good chemical resistance and hydrophilic nature, poly(vinyl alcohol), (PVA) has been the most widely chosen polymer as a membrane in PV separation studies [16]. However, its major drawback when used alone is its weak mechanical strength due to its extensive swelling in the presence of hydrophilic liquids; this is the major cause of concern in the usage of PVA membranes. In order to overcome these problems, crosslinking, blending or grafting of PVA have been attempted [17-19]. Other efforts include the development of composite membranes of PVA with polyacrylonitrile support, commercialized under the trade name GFT membranes, mainly developed in Germany. However, research efforts have been actively pursued to develop the laboratory level PV test protocols that will utilize the filled matrix PVA membranes. In this direction, several zeolite or clay particles as fillers have been incorporated into PVA matrix to boost its performance in terms of flux and separation factor [20-22]. Particularly, in case of Na’MMT, two types of structures are possible when these are incorporated into PVA matrix; the first one is the intercalated structure, wherein one or two extended polymer chains are inserted into interlayer spaces of the layered clay, and the second
one is the exfoliated structure in which clay layers are dispersed into PVA matrix. In either case, clay fillers give a stable layer to the PVA base polymer [23].

As a part of our continuing effort [24,25], in the present investigation, mixed matrix membranes were developed by incorporating Na⁺MMT clay particles into PVA to test their ability and stability in PV experiments as compared to pristine PVA membrane for the selective separation of water from isopropanol and 1,4-dioxane feed mixtures at 30°C. Two mixed matrix membranes were fabricated by adding 5 and 10 wt. % Na⁺MMT clay particles into PVA to improve their performances over the pristine PVA membrane. It may be noted that PV has been the widely studied technique in separating aqueous-organic mixtures [26-28] as well as organic-organic mixtures [27-29]. However, PV membranes of this study have exhibited high separation factors and/or permeability to water from the chosen feed mixtures in addition to having sufficient mechanical strength properties [30]. Particularly, while dehydrating organic components, membrane should be hydrophilic and is expected that after the addition of hydrophilic Na⁺MMT particles, one can increase the water selective nature of the mixed matrix membranes. Improved performances of such membranes can be assessed for different compositions of feed mixtures containing water + isopropanol and water + 1,4-dioxane. The flux, \( J \), separation factor (selectivity), \( \alpha \), permeation separation index, \( PSI \) and enrichment factor, \( \beta \), were computed to judge the quality of the membranes developed in dehydrating isopropanol and 1,4-dioxane. It is also demonstrated that by incorporating the mesoporous clay particles, one can not only increase the mechanical strength properties of the membranes, but also increase the membrane barrier performance.

For a clear understanding of the performance of the uncrosslinked membranes, sorption and PV experiments were carried out with the crosslinked mixed matrix membranes. The values obtained were nearly in agreement with the uncrosslinked mixed matrix membranes. Therefore, a detailed study was undertaken only for the uncrosslinked mixed matrix membranes, which was rather the main objective of this work.
VI.2. RESULTS AND DISCUSSION

VI.2.1. Particle Size Measurement of Sodium Montmorillonite

Zeta average diameter of Na⁺MMT particles dispersed in water was 0.8 µm size as shown in Fig. VI.1.

Fig. VI.1. Particle size distribution histogram of Na⁺MMT clay particles

VI.2.2. Membrane Characterization

VI.2.2.1. Membrane Morphology

Figure VI.2 shows the surface SEM micrograph of PVA/Na⁺MMT-10 filled membrane in which Na⁺MMT particles are distributed homogeneously throughout the PVA matrix. This uniform distribution of Na⁺MMT particles when present in PVA matrix facilitates an easy separation of water.
VI.2.2.2. Differential Scanning Calorimetry (DSC)

DSC curves of pristine PVA and PVA/Na⁺MMT membranes are shown in Fig.VI.3. The DSC curve for pristine PVA membrane shows an endotherm at 190.5°C [31], which corresponds to its melting point. The melting endotherm has shifted to higher temperatures viz., 191.5°C and 194°C, respectively for 5 and 10 wt. % Na⁺MMT-loaded PVA membranes. However, increase in $T_m$ of PVA is due to increasing amount of Na⁺MMT filler particles that are inorganic in nature. Notice that as the clay particles have higher melting temperature, $T_m$ of PVA matrix also increases.
VI.2.2.3. Thermogravimetric Analysis (TGA)

TGA/DTA thermograms of pristine PVA, PVA/Na⁺MMT-5 and PVA/Na⁺MMT-10 membranes are shown in Fig.VI.4. Major weight losses are observed between 250° and 500°C. However, a single stage degradation was observed for pristine PVA with an onset of degradation at 276°C with a major weight loss occurring between 276°C and 383°C. Thermal decomposition curves for PVA/Na⁺MMT-5 and PVA/Na⁺MMT-10 mixed matrix membranes have shifted to higher temperatures due to the presence of Na⁺MMT clay particles. A two-step decomposition was observed for PVA/Na⁺MMT-5 mixed matrix membrane; the first step was between 279°C and 386°C, while the second step was between 411°C and 478°C. The onset decomposition temperature increased further for the PVA/Na⁺MMT-10 mixed matrix membrane with the first step observed between 297°C and 378°C, while the second step between 402°C and 482°C; this confirms the increase
in thermal stability of the mixed matrix membranes due to the intercalation of PVA segments into the clay layers of Na⁺MMT.

**Fig.VI.4.** TGA/DTA curves of (a) pristine PVA, (b) PVA/Na⁺MMT-5 and (c) PVA/Na⁺MMT-10 mixed matrix membranes

**VI.2.2.4. Dynamic Mechanical Thermal Analysis (DMTA)**

Tanδ curves of pristine PVA, PVA/Na⁺MMT-5 and PVA/Na⁺MMT-10 membranes are shown in Fig.VI.5. Pristine PVA has a \( T_g \) of 61°C [32], which was shifted to 66°C and 71°C after incorporation of Na⁺MMT particles into PVA, suggesting a restricted segmental motion of PVA chains due to intercalation. This will inhibit an excessive sorption of PVA in the presence of hydrophilic solvents, thereby facilitating water selectivity of the membrane.
VI.2.2.5. Universal Testing Machine (UTM)

The elongation at break of the pristine PVA was 269% with a maximum tensile strength of 30 N/mm², whereas for PVA/Na⁺MMT-5 membrane, it was 170%; for PVA/Na⁺MMT-10 membrane, it was 140%, with the tensile strength values of 5 N/mm² and 14 N/mm², respectively. Thus, mechanical strength properties of the filled matrix membranes are better than those of the pristine PVA membrane.

VI.2.3. Sorption

Figure VI.6 displays the results of % sorption of pristine PVA and PVA/Na⁺MMT filled matrix membranes at 30°C for 10, 20, 30 and 40 wt. % water-containing feed mixtures. The efficiency of a membrane lies in its selective nature
towards the preferred liquid component of the feed mixture, which depends upon the extent of sorption of the membrane. Notice that PVA membrane sorbs to a larger extent in water + 1,4-dioxane feed mixture than water + isopropanol feed mixture, due to higher-level interactions of 1,4-dioxane than isopropanol with the PVA membrane. Sorption of PVA/Na⁺MMT filled matrix membranes in both the feed mixtures is smaller than observed for pristine PVA membrane. When 10 wt. % of Na⁺MMT particles are added to PVA to obtain the filled matrix membrane, an increase in membrane sorption is observed due to the presence of excess of hydrophilic Na⁺MMT particles as compared to 5 wt. % Na⁺MMT loaded PVA; however, sorption is smaller than observed for pristine PVA membrane, since Na⁺MMT is less hydrophilic than the pristine PVA (see Fig. VI.6). Such a decrease in membrane sorption is attributed to the insertion of PVA chain segments into layered structure of Na⁺MMT galleries, thus causing an intercalation between PVA and Na⁺MMT particles [23]; this will further decrease solvent uptake capacity of the membrane from the feed mixture. Therefore, an increase in separation factor of the filled matrix membranes to water compared to pristine PVA membrane is related to the decrease in solvent uptake capacity of the mixed matrix membranes.
VI.2.4. Membrane Performance

The PV performance of the uncrosslinked PVA/Na⁺MMT membranes has been tested and results are compared with the crosslinked pristine PVA membrane, since the uncrosslinked pristine PVA membrane did not withstand the PV conditions for feed mixtures of this study even under the residual vacuum. However, the present uncrosslinked mixed matrix membranes are better suited than the crosslinked pristine PVA membrane. The uncrosslinked mixed matrix membranes showed nearly 10-20 times higher separation factors for water + isopropanol feed mixture and about 4-8 times higher for water + 1,4-dioxane feed mixture, than the crosslinked PVA membrane. PV results exhibited a dependence on the amount of clay added to PVA
matrix as filler particles in addition to feed water composition. Hence, PV results of this study have been analyzed in terms of filler concentration and feed water compositions.

**VI.2.4.1. Effect of Clay Content on Pervaporation Results**

MMT is a clay mineral containing stacked silicate sheets measuring ~ 10 Å in thickness and ~ 2200 Å in length. Therefore, it has a high aspect ratio and platelet morphology. The chemical structure of MMT contains two fused silica tetrahedral sheets, sandwiching an edge-shared octahedral sheet of either magnesium or aluminum hydroxide. Hence, MMT has a sorption capacity, which is significant for an efficient intercalation of hydrophilic PVA. Its stacked silicate sheets will provide improved thermal stability, mechanical strength and barrier properties.

Results of the effect of clay content on flux and separation factor of the membranes are given in Fig.VI.7. Pristine PVA membrane exhibited a flux of 0.095 kg/m².h with a $\alpha$ value of 77 for 10 wt. % water in the feed mixture of isopropanol. As seen from Fig.VI.7, the $\alpha$ of PVA membrane was increased after adding Na⁺MMT clay particles into PVA matrix. Thus, for PVA/Na⁺MMT-5 membrane, an increase in $\alpha$ of 1,116 was shown for 10 wt. % water-containing isopropanol feed mixture. This $\alpha$ value was further increased at higher loadings of clay filler particles i.e., in case of PVA/Na⁺MMT-10 membrane, which showed the separation factor of 2,241 for 10 wt. % water-containing isopropanol feed. However, flux data for PVA/Na⁺MMT-5 and PVA/Na⁺MMT-10 membranes are 0.051 kg/m².h and 0.075 kg/m².h, respectively; these values are comparatively lower than those observed for pristine PVA membrane. A similar trend was observed for water + 1,4-dioxane feeds, but with lower $\alpha$ values of 216 and 369 coupled with higher flux values of 0.076 kg/m².h and 0.093 kg/m².h, respectively. Comparatively, pristine PVA membrane has a much smaller $\alpha$ of 52 with a higher flux of 0.124 kg/m².h.
As seen in Figs. VI.8 and VI.9, the $\alpha$ of PVA/Na⁺MMT-5 membrane increased significantly due to adsorption of water molecules onto the clay layers of the filled PVA matrix membranes as compared to the pristine PVA membrane. Thus, a large number of organic molecules are retained on the feed side of the membrane due to electrostatic interactions between water molecules and the positively charged sodium ion sites of Na⁺MMT particles that are incorporated in the membrane matrix; this makes the membrane more selective to water than organic components of the feed mixtures. Na⁺MMT clay particles have the intercalation layers, which tend to accommodate more of PVA chains in their galleries, thereby increasing the adsorption of a large number of water molecules at higher loading (i.e., at 10 wt. % of Na⁺MMT) of clay particles. However, due to increased hydrophilic nature of the membrane as a result of addition of 10 wt. % of Na⁺MMT clay particles, membrane sorption capacity has increased, but the overall sorption is smaller than that observed.
for the pristine PVA membrane due to lesser hydrophilicity of the clay particles. Flux of the membranes has reached almost close to the value found for pristine PVA membrane. Membranes prepared by adding more than 10 wt. % of Na\textsuperscript{+}MMT particles were found to be more brittle than those containing lower amount of Na\textsuperscript{+}MMT i.e., <10 wt % and hence, these were not useful in the present PV study. Therefore, we restricted the PV experiments with membranes having loadings of only 5 and 10 wt. % of Na\textsuperscript{+}MMT particles into PVA matrix. Montmorillonite is known to compose of units made up of two silica tetrahedral sheets centered with the alumina octahedral sheet. Its layers are stacked by weak dipolar or van der Waals forces, leading to intercalation of water or polar organic molecules, thereby causing the crystal lattice to expand in the $c$ direction [13,14]. Therefore, not only adsorption on the external surface, but also absorption (intercalation) in the galleries can occur.

Since both PVA polymer and Na\textsuperscript{+}MMT particles are hydrophilic in nature and therefore, membrane performance can be explained on the basis of solution-diffusion theory [33,34] in addition to adsorption-diffusion-desorption concepts [35]. In pristine PVA membrane, the permeating water molecules first get absorbed into the microvoids and then diffuse out on the permeate side due to the existence of concentration gradient. In case of filled matrix membranes, the overall separation can be explained by the hydrophilic interactions between clay layers and the PVA matrix. The clay layers may be distributed throughout the PVA matrix, thus forming a strong intercalation. However, majority of water molecules are adsorbed in the hydrophilic clay region, which in turn will get absorbed by the hydrophilic regions of the PVA matrix for an easy diffusion through the barrier membrane. Notice that flux of the clay-filled PVA membrane is slightly lower than the pristine PVA membrane (see Figs. VI.8 and VI.9). Therefore, separation takes place due to the selective adsorption of water molecules onto the hydrophilic sites of the clay particles, which will then diffuse through the hydrophilic PVA membrane, by inhibiting the transport of organic components (isopropanol or 1,4-dioxane) from the feed mixtures. This further promotes for an increased flux due to increase in driving force. It may be noted that molecular transport occurs due to the faster desorption rate of water molecules on the permeate side. This effect is more beneficial for water transport, since water
molecules will occupy most of the channels in the hydrophilic regions of the mixed
matrix membranes. This also justifies a marked increase in water separation factor
with a recovery of higher amount of water on the permeate side by sacrificing the
flux. In any case, the complimentary effects of Na⁺MMT on water transport will help
to improve the membrane performance, thereby offering a high separation factor to
water.
Fig. VI.8. Water flux and separation factor vs wt. % of water for (a) pristine PVA, (b) PVA/Na\(^+\)MMT-5 and (c) PVA/Na\(^+\)MMT-10 mixed matrix membranes for water + isopropanol feed mixtures at 30°C. Symbols: (Δ) separation factor and (○) flux.
Fig. VI. 9. Water flux and separation factor vs wt. % of water for (a) pristine PVA, (b) PVA/Na⁺MMT-5 and (c) PVA/Na⁺MMT-10 mixed matrix membranes for water + 1,4-dioxane feed mixtures at 30°C. Symbols: (Δ) separation factor and (○) flux.
VI.2.4.2. Permeation Separation Index and Enrichment Factor

The PV results have been discussed in terms of permeation separation index (PSI) and enrichment factor ($\beta$) at 30\(^\circ\)C as shown in Figs. VI.10 and VI.11 and at 40\(^\circ\)C to 60\(^\circ\)C as given in Table VI.1. Both PSI and $\beta$ values decrease systematically with increasing water concentrations of the feed mixtures. The values of PSI and $\beta$ are higher for the PVA/Na\(^+\)MMT-10 mixed matrix membrane when compared to PVA/Na\(^+\)MMT-5 and pristine PVA membranes; the pristine PVA membrane exhibited the lowest PSI and $\beta$ values. These trends for all the membranes are in line with the $\alpha$ values discussed before. The $\beta$ values of PVA/Na\(^+\)MMT-5 and PVA/Na\(^+\)MMT-10 membranes are somewhat identical because the differences in wt. % of water in the permeate for both the membranes are quite smaller.
Fig.VI.10. PSI vs wt. % of water in feed mixture of (a) isopropanol and (b) 1,4-dioxane for pristine PVA (○), PVA/Na⁺MMT-5 (□), PVA/Na⁺MMT-10 (x) mixed matrix membranes at 30°C
Fig. VI.11. $\beta$ vs wt. % of water in feed mixture of (a) isopropanol and (b) 1,4-dioxane for pristine PVA (*), PVA/Na\(^+\)MMT-5 (+), PVA/Na\(^+\)MMT-10 (−) mixed matrix membranes at 30\(^\circ\)C
Table VI.1. Pervaporation Data for 10 wt. % Water Containing Feed Mixtures of Water + Isopropanol and Water + 1,4-Dioxane Feeds at 40°, 50° and 60°C

<table>
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<tr>
<th>Temperature (°C)</th>
<th>Wt. % of water in permeate</th>
<th>Water flux (J) (kg/m².h)</th>
<th>Separation factor (\alpha)</th>
<th>PSI</th>
<th>(\beta)</th>
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VI.2.4.3. Effect of Feed Composition on Pervaporation Results

Pristine PVA membrane has a large number of hydroxyl groups and hence, it sorbs to a greater extent upon contact with hydrophilic water, thus rendering the PVA membrane mechanically weak for performing the PV experiments. Therefore, it is necessary to prepare PVA membranes that can be used in PV dehydration studies of water-organic feed mixture by blending, grafting, etc., [17,36,37]. In the present investigation, it is demonstrated that by incorporating Na⁺MMT clay particles, one can improve the solvent stability of PVA membrane, thus facilitating the membrane performance. As presented in Figs.VI.8 and VI.9, flux values of PVA/Na⁺MMT mixed matrix membranes are slightly lower than those of the pristine PVA. For PVA/Na⁺MMT mixed matrix membranes, flux values increased with increasing feed water composition from 10 to 40 wt. %. However, even at a lower amount of water i.e., 10 wt. % of the feed mixture, there is a strong tendency of water molecules to get adsorbed onto Na⁺MMT clay layers. Therefore, any increase in water composition of the feed mixture will decrease the separation factor to water quite considerably by increasing the flux value. As can be seen in Fig.VI.6, at higher water concentration of the feed mixture, PVA membrane swells to a large extent due to large number of hydroxyl groups, thereby reducing the effect of clay particles in the PVA matrix. Generally, PVA membranes crosslinked with glutaraldehyde (GA) or urea formaldehyde (UF) are used in PV studies to reduce the excessive swelling, but crosslinked membranes have shown increased water selectivity at the expense of flux. The PVA/Na⁺MMT filled uncrosslinked membranes are able to withstand the cyclic PV conditions even at higher concentrations of water in the feed. This is due to the intercalation of PVA segments into the clay structured layers, leading to the formation of a filled matrix structure. At higher concentration of water in the feed mixture, water will exert the induced plasticization effect to PVA.

Notice that for 40 wt. % of water containing water + isopropanol feed mixture, the α values are 53 and 71, but the flux values are enhanced from 0.150 kg/m².h to 0.160 kg/m².h, respectively for PVA/Na⁺MMT-5 and PVA/Na⁺MMT-10 membranes. For the pristine PVA membrane, a lower α of 11, with a higher flux of
0.181 kg/m².h is observed. At the same concentration of water in the feed mixture of water + 1,4-dioxane, separation factors are 11 and 13, with the corresponding flux values of 0.182 kg/m².h and 0.193 kg/m².h, respectively for PVA/Na⁺MMT-5 and PVA/Na⁺MMT-10 membranes. In case of pristine PVA membrane, separation factor and flux values are 4 and 0.265 kg/m².h, respectively. PVA chain segments have followed the non-ordered trends, which might have blocked the sites provided by Na⁺MMT particles, thereby creating the loose leaks for the organic components (isopropanol or 1,4-dioxane) to be retained back on the feed side. Differences observed in flux and separation factors for water + isopropanol and water + 1,4-dioxane feed mixtures are attributed to the differences in thermodynamic interactions of isopropanol and 1,4-dioxane with PVA/Na⁺MMT filled matrix membranes as well as between liquid components of the mixed feed media. However, the extent of interaction of liquids with the membrane polymers depends upon the nature of organic components. Due to higher polar nature of isopropanol (dielectric constant of 19.92) than 1,4-dioxane, (dielectric constant of 2.21), the observed flux is lower for isopropanol than for 1,4-dioxane. This is consistent with the sorption data of the membranes discussed before.

**VI.2.5. Effect of Temperature on Membrane Performance**

In this research, the membrane performance was studied at higher temperatures viz., 40°, 50° and 60°C for 10 wt. % water-containing feed solutions of isopropanol as well as 1,4-dioxane. The present membranes were quite stable at higher temperatures under the PV conditions. Results of flux and separation factors for 10 wt. % of water in the feed solutions of isopropanol or 1,4-dioxane at 40°, 50° and 60°C are presented in Table VI.1. As expected, flux has increased with increasing temperature, but separation factor decreased. The temperature dependency of flux was analyzed by Arrhenius equation of the type:

\[
J_p = J_{po} \exp \left(-\frac{E_p}{RT}\right)
\]  

(VI.1)
where $J_p$ is permeation flux of water, $J_{p0}$ is permeation rate constant, $E_p$ is activation energy for permeation, $R$ is molar gas constant and $T$ is temperature in Kelvin. If activation energy is positive, permeation flux increases with increasing temperature, which is indeed observed in most PV separation experiments [33,38]. The driving force represents the concentration gradient, resulting from a difference in partial vapor pressure of the permeants between feed and permeate mixtures. As the feed temperature increases, vapor pressure in the feed compartment also increases, but vapor pressure at the permeate side is not affected. This results in an increase of driving force with increasing temperature of the PV experiment.

Arrhenius plots of $\ln J_p$ vs. $1/T$ are displayed in Figs. VI.12 and VI.13 for pristine PVA, PVA/Na$^+$MMT-5 and PVA/Na$^+$MMT-10 membranes, respectively for water + isopropanol and water + 1,4-dioxane feed mixtures. The $E_p$ values for water + isopropanol feed mixture with pristine PVA, PVA/Na$^+$MMT-5 and PVA/Na$^+$MMT-10 filled matrix membranes are, respectively 28 kJ/mol, 34 kJ/mol and 35.6 kJ/mol, indicating a gradual increase with increasing Na$^+$MMT loadings, due to the difficulty involved in liquid transport to crossover the Eyring’s energy barrier. For water + 1,4-dioxane feed mixture, a similar trend was observed i.e., $E_p$ values are, respectively 25.66 kJ/mol, 33.03 kJ/mol and 35.08 kJ/mol for the three membranes. The increase in $E_p$ values are more considerable for water + 1,4-dioxane than for water + isopropanol feeds, further suggesting a greater difficulty to crossover Eyring’s energy barrier in case of the former mixture. This suggests that membranes with lesser separation factor to water will have lower $E_p$; this is indeed observed in the present systems. Activation energies obtained from the flux data have revealed that in the presence of clay particles, a lesser energy is required for the penetrant molecules to penetrate through the barrier membrane.
Fig. VI.12. Arrhenius plots of $\ln J_p$ vs $1/T$ for (a) pristine PVA, (b) PVA/Na$^+$MMT-5 and (c) PVA/Na$^+$MMT-10 mixed matrix membranes for 10 wt. % water in feed mixture of water + isopropanol
Fig. VI.13. Arrhenius plots of $\ln J_p$ vs $1/T$ for (a) pristine PVA, (b) PVA/Na$^+$MMT-5 and (c) PVA/Na$^+$MMT-10 mixed matrix membranes for 10 wt. % water in feed mixture of water + 1,4-dioxane.
VI.2.6. Comparison of PV Results with Vapor Liquid Equilibrium (VLE) Data

PV has gained increasing attention in many chemical and process engineering applications as an effective and energy-saving membrane-based technique to separate azeotropic mixtures. PV performance is mainly regulated by the physico-chemical structure of the membrane rather than the VLE of the system of interest. This is demonstrated by comparing the PV results with VLE curves for both the feed mixtures in Fig.VI.14. Water + isopropanol forms an azeotrope at 12.5 wt. % of water, while water + 1,4-dioxane has an azeotropic composition at 18.1 wt. % of water. Separation of these azeotropes by distillation is possible only by adding a third component (as an entrainer) such as benzene or toluene, which are hazardous liquids. Instead, in PV separation, the membrane acts as a third phase to break the azeotrope, thereby saving the energy. This effect can be seen in Fig.VI.14. (a) and (b), respectively for water + isopropanol and water + 1,4-dioxane mixtures. Notice that in both the cases, PV curves are well above the literature reported VLE curves throughout the feed mixture composition, suggesting that PV is more effective in separating azeotropes as compared to distillation. Moreover, in PV, one need not use benzene or toluene, which makes the PV process environmentally more benign than distillation.
VI. 2.7. PV Results of Crosslinked Membranes

To test the reliability of the present PVA/Na\textsuperscript{+}MMT uncrosslinked mixed matrix membranes, which were successfully adopted for several cycles of PV experiments, sorption and PV experiments were also carried out for thermally crosslinked and glutaraldehyde crosslinked pristine PVA and PVA/Na\textsuperscript{+}MMT mixed matrix membranes at 30\textdegree{}C for 10 wt. % of water-containing feed mixtures of water + isopropanol and water + 1,4-dioxane. Crosslinked mixed matrix membranes could withstand the same number of cycles of PV operation as uncrosslinked mixed matrix membranes. Pristine PVA and mixed matrix membranes were thermally crosslinked at 110\textdegree{}C for 3 h. As seen in Fig. VI.15, there is not much difference in the sorption

Fig. VI.14. Comparison of vapor liquid equilibrium curve (●) with PV data (▲) at 30\textdegree{}C for (a) water + isopropanol and (b) water + 1,4-dioxane feed mixtures.
capacities of uncrosslinked, thermally crosslinked and glutaraldehyde crosslinked PVA/Na⁺MMT mixed matrix membranes. Since the Na⁺MMT particles have high melting points, thermal crosslinking did not exert much effect on PVA sorption.

When the mixed matrix membranes were crosslinked with glutaraldehyde, there was not much crosslinking possible, since most of the -OH groups of PVA were held firmly in between the layers of Na⁺MMT due to the intercalation phenomenon. This indicates that there is no direct reaction between -CHO groups of glutaraldehyde and -OH groups of PVA, unlike in pristine PVA membrane, to form the crosslinked ether linkage. But, glutaraldehyde crosslinking is slightly more as compared to thermal crosslinking, which reduced the sorption accordingly. The variation in flux and separation factor are presented in Figs. VI.16 and VI.17, respectively for thermally crosslinked and glutaraldehyde crosslinked pristine PVA and PVA/Na⁺MMT mixed matrix membranes, where no drastic enhancements in separation factors of mixed matrix membranes are observed. Thermally crosslinked PVA/Na⁺MMT-5 and PVA/Na⁺MMT-10 membranes showed the separation factors of 1130 and 2269 with the flux values of 0.049 kg/m².h and 0.073 kg/m².h for 10 wt. % of water-containing feed mixture of water + isopropanol. However, for the similar crosslinking, the pristine PVA membrane showed a separation factor of 65 with flux a value 0.108 kg/m².h. For water + 1,4-dioxane feed mixture, separation factors were found to be 221 and 377, whereas the flux values were 0.065 kg/m².h and 0.088 kg/m².h, respectively. On the other hand, for pristine PVA membrane, these values were found to be 40 and 0.137 kg/m².h, respectively. Glutaraldehyde crosslinked PVA/Na⁺MMT-5 and PVA/Na⁺MMT-10 membranes showed the separation factors of 1145 and 2299 with the flux values of 0.048 kg/m².h and 0.072 kg/m².h, respectively for 10 wt. % of water-containing feed mixture of water + isopropanol. The separation factors of 228 and 381 with the flux values of 0.063 kg/m².h and 0.086 kg/m².h, respectively were observed for water + 1,4-dioxane feed mixture.
Fig. VI.15. % Sorption of 10 wt. % of water in water + isopropanol (white box) and water + 1,4-dioxane (black box) feed mixtures vs pristine PVA (M1), PVA/Na⁺MMT-5 (M2) and PVA/Na⁺MMT-10 (M3) mixed matrix membranes at 30°C for (a) thermally crosslinked membranes and (b) glutaraldehyde crosslinked membranes.
Fig. VI.16. Water flux of 10 wt. % of water in water + isopropanol (white box) and water + 1,4-dioxane (black box) feed mixtures vs pristine PVA (M1), PVA/Na’MMT-5 (M2) and PVA/Na’MMT-10 (M3) mixed matrix membranes at 30°C for (a) thermally crosslinked membranes and (b) glutaraldehyde crosslinked membranes.
Fig. VI.17. Separation factor of 10 wt. % of water in water + isopropanol (white box) and water + 1,4-dioxane (black box) feed mixtures vs pristine PVA (M1), PVA/Na⁺MMT-5 (M2) and PVA/Na⁺MMT-10 (M3) mixed matrix membranes at 30°C for (a) thermally crosslinked membranes and (b) glutaraldehyde crosslinked membranes.
VI.2.8. Comparison of the Present Uncrosslinked Membrane Performance with Literature Data

After incorporating Na\textsuperscript{+}MMT particles into PVA matrix, the membrane properties of PVA have greatly improved. As highlighted in Table VI.2, the PV performances of the present membranes are dependent upon the operating conditions, which make a meaningful comparison of the data almost impossible, since these will obscure the effect of driving force in PV. Therefore, we have evaluated the PV performance in terms of flux and separation factor to understand the effects of incorporated clay particles. Table VI.2 compares our data with those of the published reports on flux and separation factors for various types of other PVA-based membranes reported in the earlier literature. The present $\alpha$ values are quite higher than those of the previously published reports. However, flux values of the present membranes are somewhat lower than those of the published reports. An effort to improve flux is necessary and this will be undertaken in future.
Table VI.2. Comparison of PV Performance of The Present Membranes with Literature Data at 30°C.

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>Water in feed (Wt. %)</th>
<th>Water flux ( (J) ) (kg/m²·h)</th>
<th>Separation factor ( (\alpha) )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Water + Isopropanol</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVA/Na⁺MMT-5</td>
<td>10</td>
<td>0.051</td>
<td>1116</td>
<td></td>
</tr>
<tr>
<td>PVA/Na⁺MMT-10</td>
<td>10</td>
<td>0.085</td>
<td>2241</td>
<td>Present work</td>
</tr>
<tr>
<td>NaAlg / PVA (75:25, wt./wt.)</td>
<td>10</td>
<td>0.125</td>
<td>195</td>
<td>37</td>
</tr>
<tr>
<td>NaAlg / PVA (50:50, wt./wt.)</td>
<td>10</td>
<td>0.170</td>
<td>119</td>
<td></td>
</tr>
<tr>
<td>NaAlg / PVA (25:75, wt./wt.)</td>
<td>10</td>
<td>0.195</td>
<td>91</td>
<td></td>
</tr>
<tr>
<td>PVA / KA</td>
<td>10</td>
<td>0.179</td>
<td>410</td>
<td>21</td>
</tr>
<tr>
<td>PVA / NaA</td>
<td>10</td>
<td>0.183</td>
<td>328</td>
<td></td>
</tr>
<tr>
<td>PVA / CaA</td>
<td>10</td>
<td>0.193</td>
<td>233</td>
<td></td>
</tr>
<tr>
<td>PVA / NaX</td>
<td>10</td>
<td>0.216</td>
<td>233</td>
<td></td>
</tr>
<tr>
<td><strong>Water + 1,4-Dioxane</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVA/Na⁺MMT-5</td>
<td>10</td>
<td>0.068</td>
<td>216</td>
<td>Present work</td>
</tr>
<tr>
<td>PVA/Na⁺MMT-10</td>
<td>10</td>
<td>0.091</td>
<td>369</td>
<td></td>
</tr>
<tr>
<td>NaAlg + 10 wt. % PEG + 5 wt. % PVA</td>
<td>10</td>
<td>0.285</td>
<td>351</td>
<td>36</td>
</tr>
<tr>
<td>PVA/NaAlg (5:95, wt./wt.)</td>
<td>10</td>
<td>0.200</td>
<td>60</td>
<td>18</td>
</tr>
<tr>
<td>PVA/NaAlg (10:90, wt./wt.)</td>
<td>10</td>
<td>0.250</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>PVA/NaAlg (20:80, wt./wt.)</td>
<td>10</td>
<td>0.270</td>
<td>48</td>
<td></td>
</tr>
</tbody>
</table>

PVA-Poly(vinyl alcohol); Na⁺MMT-Sodium montmorillonite; NaAlg-Sodium alginate; KA, NaA, CaA, NaX-Zeolites; PEG-Poly(ethylene glycol).
VI.3. CONCLUSIONS

In the published literature, many efforts have been made to develop various types of membranes (asymmetric, composite, mixed matrix, etc.) for PV applications. In all these studies, polymeric membranes have been generally used, because they are inexpensive and can be economically processable at lower operating costs. Realizing the importance of mixed matrix membranes, we thought of preparing such membranes by incorporating 5 and 10 wt. % of Na⁺MMT clay particles into PVA matrix. By doing so, it is demonstrated that it is possible to enhance water separation factor over that of pristine PVA membrane quite considerably by obtaining a reasonable flux. For the type of mixed matrix membranes developed here, Na⁺MMT particles did not readily form the continuous phase, but isolated clay particles are surrounded by PVA chains in the matrix. Expectedly, clay particles, through the molecular sieving effect, selective sorption as well as selective diffusion could increase the mobility of preferentially permeating species (water in this case) in the mixed matrix of PVA membranes. At the same time, it decreases the mobility of component that is less permeable (isopropanol or 1,4-dioxane).

Our present experimental data indicated that due to the strong intercalated structure of PVA formed with Na⁺MMT galleries as a result of incorporation of Na⁺MMT clay particles into PVA, it is possible to obtain the layered crystalline structures in the PVA matrix derived. It was observed that the crystalline and hydrophilic nature of Na⁺MMT particles could hinder the transport of organic components of the mixed aqueous media to offer an easy passage to water molecules through the membranes. An increase in flux and separation factor of the PVA/Na⁺MMT-10 membrane can be attributed to the increased membrane swelling as a result of more number of water selective sites available for such hydrophilic-hydrophilic interaction. As the water content of the feed mixture is increased, flux also increased due to hydrophilic-hydrophilic interactions, but separation factor has decreased due to a decrease in crystallinity in addition to increased plasticization effect of the PVA membrane in the presence of a large amount of water during PV extraction process. In the present research, PV performances of the mixed matrix
membranes were evaluated and found to be superior over that of the pristine PVA (unfilled) membrane in terms of flux and separation factors. Thus, the presently developed mixed matrix membranes are useful, at least in the laboratory level set up as envisaged in the present study or even on a pilot scale, in dehydrating isopropanol or 1,4-dioxane from their aqueous mixtures. Activation parameters of the permeation process for mixed matrix membranes revealed the requirement of a lesser activation barrier energy values for the penetrant molecules to pass through these membranes.
VI.4. REFERENCES


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