

Composite Chitosan Membranes for the Separation of Methanol/methyl *tert*-butyl Ether Mixtures

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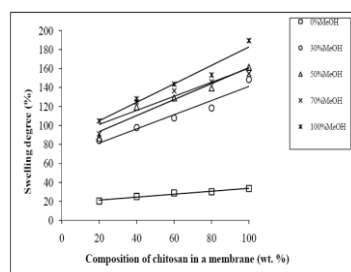
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Graphical abstract



Abstract

Composite membranes from chitosan blended with different ratios of chitosan were developed for the pervaporation of methanol/methyl *tert*-butyl ether mixtures. The composite membranes were characterized for surface morphology and sorption. Surface morphology showed chitosan and PVA were homogenously blend for all chitosan composition. Swelling characteristics of composites membrane were affected by methanol concentration as well as chitosan composition in the blend. Increasing feed temperatures and methanol concentration in the feed in pervaporation increased the flux and decreased the separation factor. The composite membranes containing 20 to 40 wt% chitosan was chosen as the preferred membrane formulation to yield fluxes ranging from 50 to 70 g/m²hr with separation factors ranging from 55 to 80 at optimum operating conditions of 30 wt% methanol in the feed and feed temperature of 50 °C.

Keywords: Chitosan; poly(vinyl alcohol); composite membrane; pervaporation; methanol; methyl *tert*-butyl ether

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1.0 INTRODUCTION

Chitosan is the second most abundant biopolymer in nature [1]. Its chemical structure contains both reactive amino and hydroxyl groups that readily react with chemicals. These hydrophilic groups are considered to play an important role in preferential water sorption and diffusion through the chitosan as membrane. Chitosan based membranes have been known to exhibit good filming properties [2], chemically resistant and high permselectivity towards water [3].

Nawawi and Huang [4] however concluded that chitosan has a reasonably poor stability in water and in aqueous mixtures due to the amino group in its structure. Various modification techniques have been applied namely crosslinking [5, 6], blending [7] and incorporation of zeolite [8, 9] in order to improve overall properties of chitosan as well as its separation performance. Blending is the most common modification method applied as it provides a convenient way of developing materials with novel or selectively enhanced properties which are possibly superior to those of the components, besides offering the possibility in tailoring end-products' properties [2, 5, 6, 7, 8].

PVA is an attractive polymer that has high anti-fouling potential, thermally and chemically resistant and accompanied by high water permeability [10]. Incorporation of PVA in membrane will greatly improve mechanical strength and hydrophilicity [11]. Blended chitosan/PVA membranes in this research will be

developed in the form of composite to achieve high membrane productivity at the same time retain the necessary mechanical strength. Composite chitosan membrane has been reported to exhibit better pervaporation separation index (PSI) for pervaporation of isopropanol compared to dense chitosan membrane [4].

Pervaporation is a process for the separation of mixtures of liquids by partial vaporization through a non-porous or porous membrane. It is a versatile process in which a feed liquid mixture is brought into contact with a membrane which allows the removal of one or more components into vapour stream on the other side of the membrane. Pervaporation is commonly applied for dehydration of organic solvents (water removal from organics), removal of organic compounds from aqueous solution (organic removal from water) and the separation of organic mixtures. The process has been proven to be highly efficient and economical particularly for the separation of azeotrope-forming aqueous-organic mixtures [12, 13, 14, 15].

Methyl *tert*-butyl ether (MTBE) is mainly used as an additive in gasoline, besides being used as chemical platform for production of high purity isobutylene and as reaction solvent in pharmaceuticals industry [13]. The use of MTBE in gasoline can impose adverse environmental effects when the spill contaminates surface and groundwater. In MTBE synthesis, the product contains residual methanol which will subsequently distilled off and recovered. Separation of MTBE/methanol mixtures is very difficult

process since methanol forms minimum-boiling azeotropes with MTBE at composition of 14.3 wt% methanol at 760 mmHg [14]. The separation of methanol/MTBE mixtures via pervaporation process was the focus of this research. The pervaporative separation at different feed concentration of methanol and feed temperature was performed using chitosan/PVA composite membrane and its performance was evaluated in terms of permeation flux and separation factor. The composite membranes were characterized and their productivity was compared with pristine chitosan composite membrane.

2.0 EXPERIMENTAL

2.1 Materials

Chitosan polymer (MW:50,000-100,000) and acetic acid was supplied by Mallinckridt Baker. Polyvinyl alcohol (approx. MW: 8600) was from ACROS Organics, New Jersey. Polysulfone was supplied by Amoco Polymers Inc.. Ethylene glycol (MW: 6,000-7,000) was purchased from Fisher Scientific, Hong Kong, and N,N-dimethylacetamide (DMAc) was purchased from Fluka Chemical & AG, Switzerland. Methyl tert-butyl ether (MTBE) and methanol were purchased from Fisher Scientific, U.K., and Merck, Germany, respectively.

2.2 Preparation of Chitosan Based Composite Membrane

The porous polysulfone substrate was prepared through phase inversion process from a casting solution consisting 12 wt% polysulfone, 11 wt% polyethylene glycol and 77 wt% N,N-dimethylacetamide which was casted onto polyester non-woven fabric held on a glass plate with the aid of Gardner knife. The cast film was immediately immersed into a gel bath consisting of 50 wt% DMAc in deionized water at room temperature for 10 min. The resulting porous membrane was washed with deionized water for 24 hours and dried in air at room temperature.

The composite membranes were prepared by coating 0.5 wt% of chitosan solution to produce pristine chitosan composite membrane. 1 wt% chitosan and 5 wt% PVA was blended at 20, 40, 60, 80, and 100 wt% of chitosan to produce chitosan/PVA composite membrane. Respective coating solution was poured onto the porous polysulfone membrane with the aid of dropper and glass rod adjusted to the appropriate thickness.

2.3 Scanning Electron Microscopy (SEM)

The morphological structures of chitosan based composite membranes were analyzed using SEM. The membranes were sputter-coated with gold prior to macroscopic observation. The surface and cross-sectional views obtained from SEM were evidence of the structural composition of the developed chitosan based composite membranes.

2.4 Swelling Studies

Swelling studies were conducted using chitosan/PVA composite membrane at various concentrations of methanol/MTBE solutions (0–100 wt% methanol in MTBE) for 24 hours to reach equilibrium at room temperature. The dry composite membrane was weighed beforehand. After 24 hours, the membranes were carefully blotted off the liquid at surface with tissue paper as quickly as possible to remove the excess liquid and wet membranes were weighed. The liquid absorbed in the membranes was collected and analyzed for the composition by refractometer. The amount of liquid adsorbed

in the membrane is expressed as the degree of swelling (DS %), which can be calculated using Eq. 1,

$$DS\% = \frac{(W_s - W_d)}{W_d} \times 100\% \quad (1)$$

where W_s is the weight of wet membrane at equilibrium of sorption and W_d is the weight of dry membrane.

2.5 Pervaporation Experiments

Pervaporation separation experiments were performed in an apparatus set up as described by Tan *et al.*, [16]. Separation performance of the chitosan/PVA composite membrane was compared to the pristine chitosan composite membrane. Methanol feed concentration of 30, 50 and 70 wt% at constant temperature of 30 °C was used to study the effect of feed concentration on pervaporation process. On the other hand, methanol concentration was fixed at 30 wt% to study the effect of feed temperature from 25 – 50 °C on the process. Throughout the process, permeate pressure was maintained at about 3–5 mmHg.

Membrane performance in pervaporation was studied by calculating the total permeation flux (J) and separation factor (α), presented in Eq. 2 and Eq. 3, respectively,

$$\text{Flux, } J = Q/At \quad (2)$$

where Q is the weight (g) of the permeate, t is the permeation time (h), and A is the membrane area (m²).

$$\text{Separation factor, } \alpha = \frac{(Y_{MeOH}/Y_{MTBE})}{(X_{MeOH}/X_{MTBE})} \quad (3)$$

where Y is the permeate composition and X is the feed composition.

Since solubility and diffusivity of the feed mixture component in polymeric membranes are generally dependent on the operating temperature, pervaporation characteristic in the terms of flux is also dependent on the temperature. When the temperature of the feed is increased, the permeation rate generally follows an Arrhenius type law as calculated in Eq. 4,

$$J = A_p \exp(E_p/RT) \quad (4)$$

where J is the total permeation flux (kg/m².hr); A_p , the pre-exponential factor (kg/m².hr); E_p , the activation energy of permeation (kJ/mol); R , the gas constant (kJ/mol.K); and T the operation temperature (K).

The value of the apparent activation energy of permeation varies in the range 17 – 63 kJ/mol. The apparent activation energy indicates the amount of energy required to facilitate diffusion of the permeating components through the membrane. Thus, the activation energy for diffusion of methanol should be lower than that for MTBE if the membrane is relatively more selective to methanol.

3.0 RESULTS AND DISCUSSION

3.1 Surface Morphology

Figure 1 and 2 showed the surface area and cross-sectional area of SEM micrographs for pristine chitosan composite membrane and chitosan/PVA composite membrane at 40 and 80 wt% chitosan blends, respectively. Surface area of pristine chitosan composite membrane in Figure 1a showed uninformed overall surface with visible pores. Whilst, Figure 1b showed the composite structure of the membrane having a top dense layer consists of a solid homogeneous chitosan film and sponge-like porous polysulfone

substrate. This is as the result of very high precipitation rates (short gelation time) during immersion in gel bath which lead to asymmetric membrane with a sponge-like structure [17].

Figure 2a and 2b showed the surface area of chitosan/PVA composite membranes at different compositions of polymer mixtures. The micrograph images of the blended chitosan and PVA membrane revealed the absence of pores on the surface area and the increasing surface smoothness as the percentage of chitosan in the respective membranes decreased.

3.2 Degree of Swelling

In Figure 3, methanol concentrations significantly affect the degree of swelling of the composite membranes, in which degree of swelling increased with increasing methanol concentration and composition of chitosan in the membrane. Composite membranes swelled from 80% to ~160% in 30% of methanol in MTBE with the addition of 20% to 40% chitosan in the blend. From the figure, composite membranes prepared swelled considerably in solution containing higher concentration of methanol for all chitosan compositions. For example, composite membranes swelled from 90% to 120% in 30% and 70% of methanol in MTBE, respectively, for composite containing 40 wt% of chitosan in the composition. The tendency of the composite membranes to swell in solution with more methanols was expected since membranes prepared were structurally consisted of similar functional groups with methanol, causing membrane to absorb methanol compared to MTBE and hence causing better sorption of methanol through composite membrane

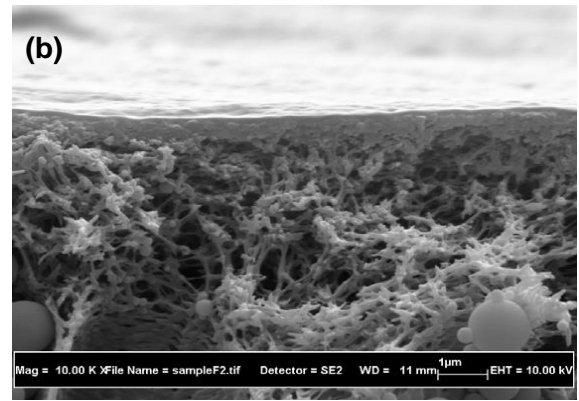
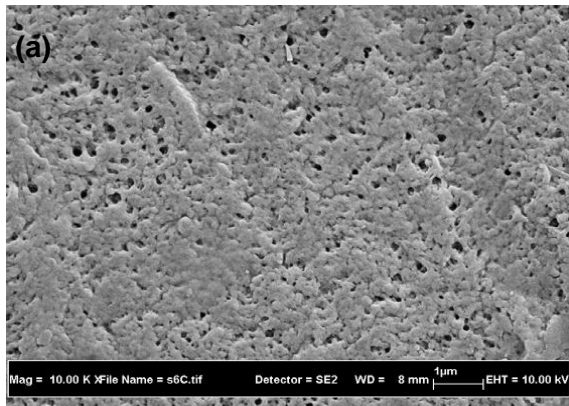


Figure 1 SEM for composite membrane; (a) surface area, (b) cross-sectional area

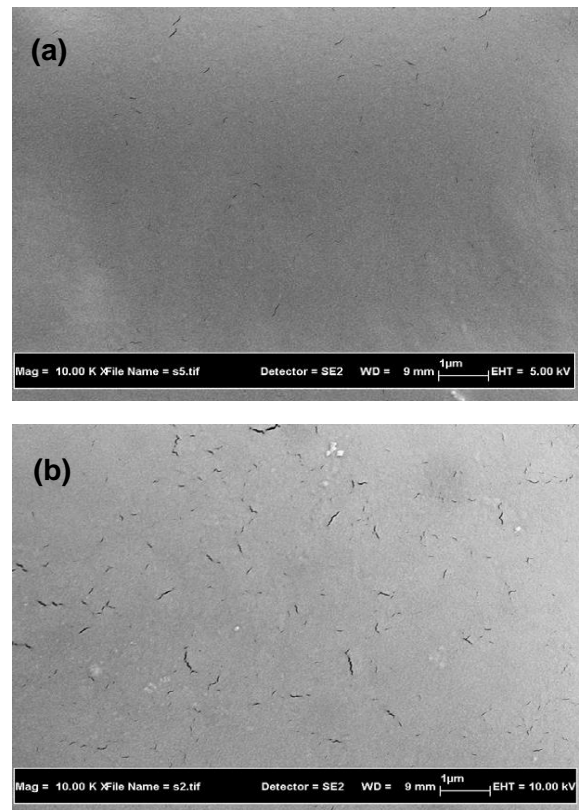


Figure 2 SEM of surface area for blended chitosan and PVA composite membrane at different compositions of polymer mixture; (a) 40 wt% chitosan, (b) 80 wt% chitosan

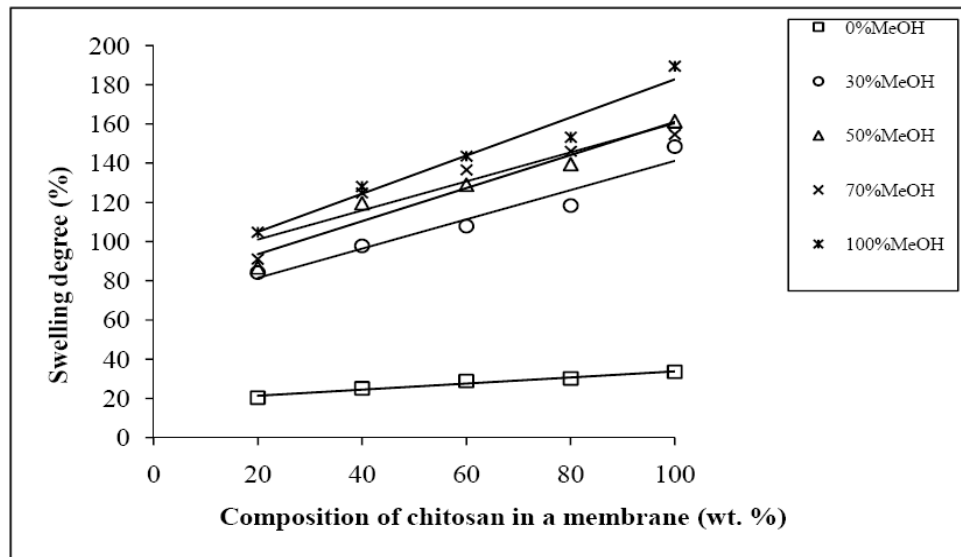


Figure 3 Effects of chitosan composition in membranes on the degree of swelling

3.3 Pervaporation Results

3.3.1 Effect of Methanol Concentration in the Feed

Figure 4 plotted the comparison of fluxes between different blending ratios of chitosan/PVA composite membranes and pristine chitosan composite membrane at room temperature versus methanol concentration in the feed. The pristine chitosan composite membrane exhibited the highest permeation flux at 259 g/m².h in 70 wt% feed concentration. Overall, increasing

the methanol feed concentration resulted in the increased of permeation flux. This can be attributed to several reasons, i.e., (1) methanol is more polar compared to MTBE in the solution mixtures. Since both chitosan and PVA are hydrophilic, the membrane readily swelled in solution mixtures with high methanol concentration due to the interaction between polymers and permeant [13]. Swelling caused polymer chains become more flexible, increases the space available for diffusion and hence, transport of permeating species become easier, (2) molecular size of methanol is smaller than MTBE.

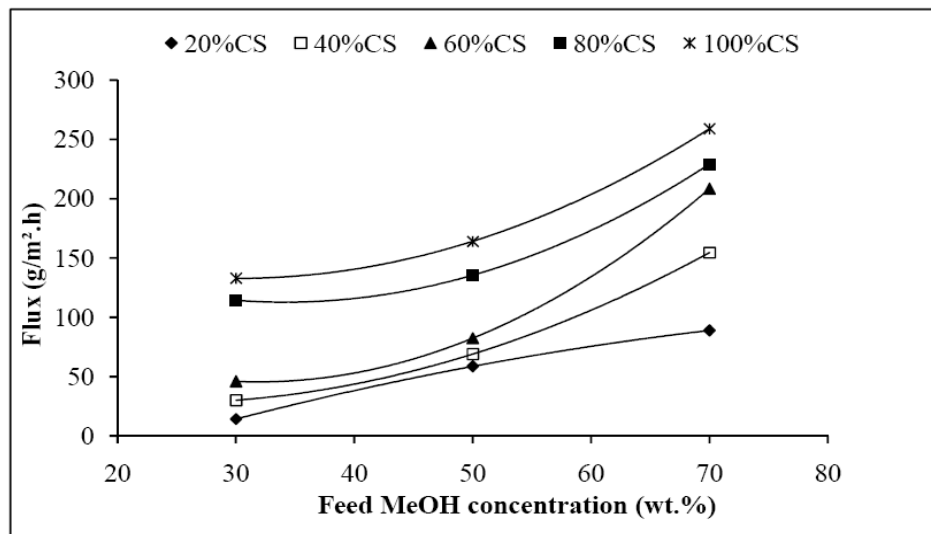


Figure 4 The permeation flux of different membranes in the different feed concentrations

3.3.2 Effect of Chitosan Composition in Composite Membrane

Figure 5 shows the total and individual component (methanol and MTBE) permeation flux at 30 wt% methanol concentration for different composition of chitosan (wt%) in composite membranes. The permeation fluxes of the permeating components increase with the increase in the composition of

chitosan in the membrane. As shown, the permeation flux of methanol is higher than that of MTBE for the whole range of the composition of chitosan in the membrane. It should be noted that for the whole range of composition of chitosan in the membrane the methanol flux is almost identical to the total flux which indicates that the membrane is more selective to methanol as compared to MTBE.

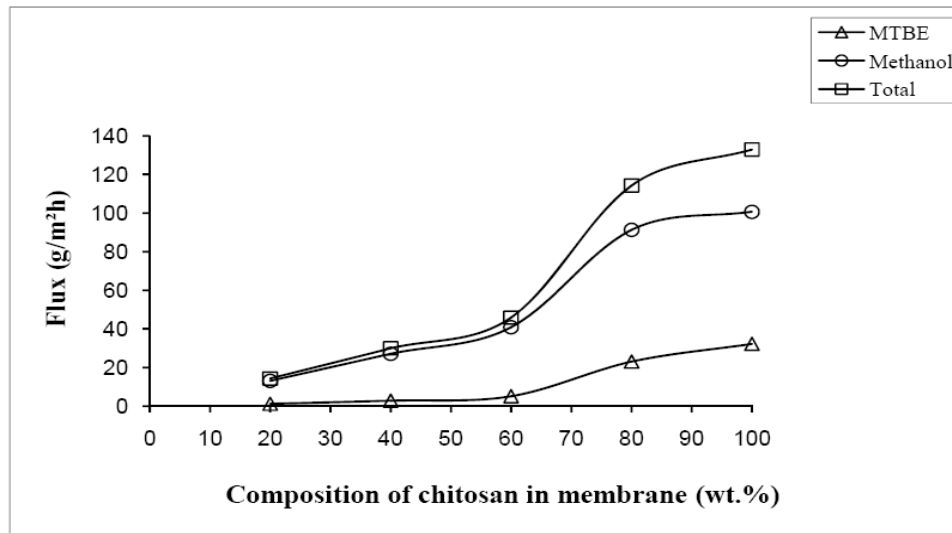


Figure 5 The permeation flux versus the concentration of chitosan for each component at 30 wt% methanol concentration

The membrane containing 20 wt% chitosan has the lowest total permeation flux. This is due to the high composition of more condensed polymer network of PVA. The insertion of small amount of chitosan could have made certain parts of PVA compact network distorted and lead to higher free volume in the network. Therefore, further increase of chitosan in the membrane will allow higher permeation rate [19].

The separation factor of methanol and MTBE is shown in Figure 6. The separation factor decreased as both the chitosan

composition in the membrane and methanol feed concentration increased. The highest separation factor achieved was between 20-40 wt% chitosan compositions in the membrane at 30 wt% methanol concentration. As shown by the figure, at 20 wt% of chitosan in the membrane, the highest separation factor ($\alpha \sim 24$) was achieved using 30 wt% of methanol as the liquid feed. The separation factor reduced to about 23 when the chitosan composition in the membrane increased to 40 wt% using the same liquid feed.

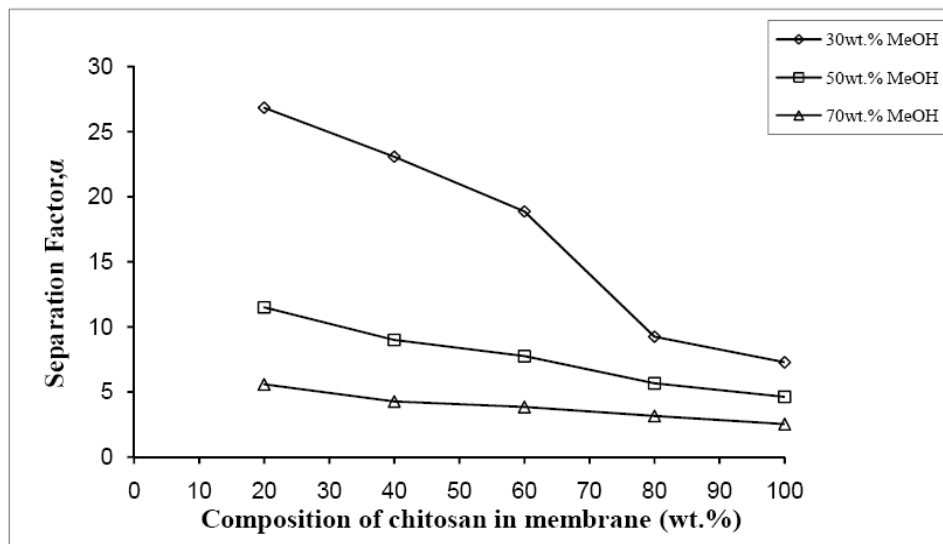


Figure 6 Separation factor versus composition of chitosan in the membrane

Similar trends can be observed for the whole range of composition of chitosan in the membrane; the separation factor decreases with the chitosan content in the membrane. This may be attributed to a decrease in density of the membrane as higher dosage of chitosan added to the membrane. As the membrane become relatively less dense and the polymer network loosen, the membrane becomes less selective.

Since both chitosan and PVA can preferentially interact with methanol, they have the polarity factor. As the chitosan content

in membrane increases, the selective diffusivity decreases because of the loosening of the polymer network. When the content of chitosan is high, the selectivity is low [13].

3.3.3 Effect of Feed Temperature

In the attempt to investigate the effect of temperature, the pervaporation separation was conducted at feed concentration of 30 wt% methanol. The variables are the composition of chitosan

in the membrane and the feed temperature. Figure 7 shows the effect of feed temperature on the total permeation flux at different chitosan composition in the membrane at feed concentration of 30 wt% methanol. The total flux increased significantly with increasing feed temperatures with composite containing 80 wt% of chitosan in the blend gave out the highest permeation 160 g/m²hr at 50 °C. Increasing of flux could be due to the fact that the increase of feed temperature elevates the polymer thermal mobility and consequently leads to the rise of mass transport across the membrane. This is an agreement with physical reasoning that a larger driving force for flux leads to a higher flux [2].

Increasing temperature also brings about higher molecular diffusivity [4]. Higher diffusivity allows molecules to penetrate through membrane faster and results in an increase of total flux. In addition, the increased of feed temperature could result in earlier phase transition of liquid inside the membrane because the required enthalpy for the transition is achieved faster when there is more heat supplied. The diffusivity of vapour is higher than liquid; therefore, the mass transport is faster and the total flux increases [5].

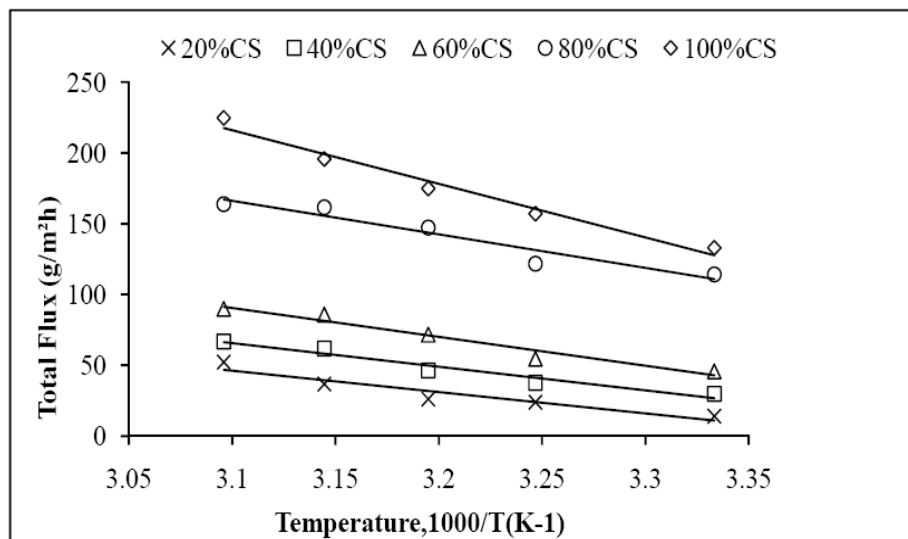


Figure 7 Effects of feed temperature on total permeation flux

Figures 8 and 9 illustrate the effects of temperature on the individual flux of methanol and MTBE, respectively, and separation factor of the composite membranes. Figures 8a and 8b show the Arrhenius relationships between methanol and MTBE with the feed temperature respectively. Overall, both of the individual flux increased with increasing feed temperatures. By comparing Figures 8a and 8b, it could be concluded that for all the temperature range, the methanol flux is higher than that of MTBE; methanol flux for composite membrane with 80 wt% chitosan at 50 °C was ~150 g/m²hr while MTBE flux was only ~30 g/m²hr for the same membrane blend and temperature.

Increasing feed temperature also increased the separation factor as shown in Figure 9. Thermal motion of polymer chain intensified at higher temperature creating more free volume in the polymer matrix. In other word, polymers possess larger free volumes at high temperature enhancing diffusivity of permeating species. Similar observation was reported by Nam and Lee [15]

in their research where they concluded that increasing the pervaporation temperature affects the permeation flux ethylene glycol-water mixtures. In general, as the temperature increased, the thermal motion of polymer chain is intensified creating more free volume in the polymer matrix, i.e., polymers possess larger free volumes at higher temperature. However, pristine chitosan composite membrane and composite membrane with 80 wt% chitosan in the blend gave the lowest separation factor despite of having highest permeation flux previously when compared to other chitosan/PVA composite membranes. This is the normal trade off between the permeation flux and separation factor where high permeation flux gives low separation factor and vice versa.

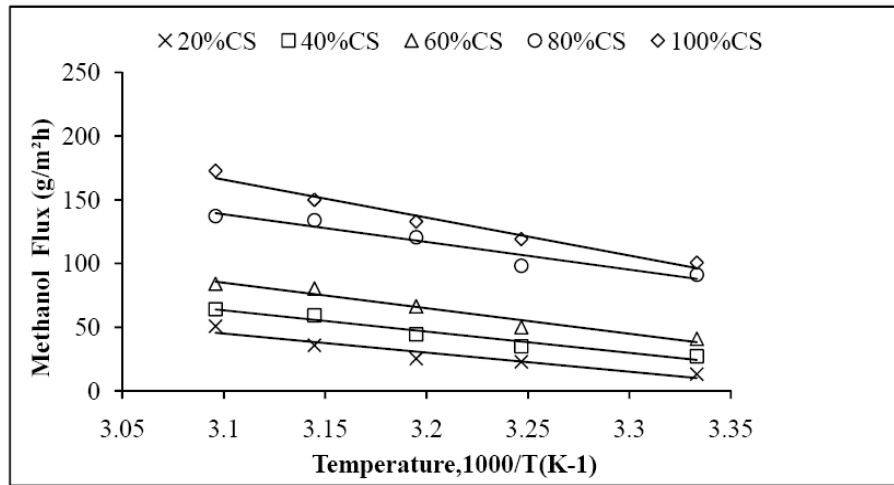


Figure 8(a) Effects of feed temperature on methanol flux

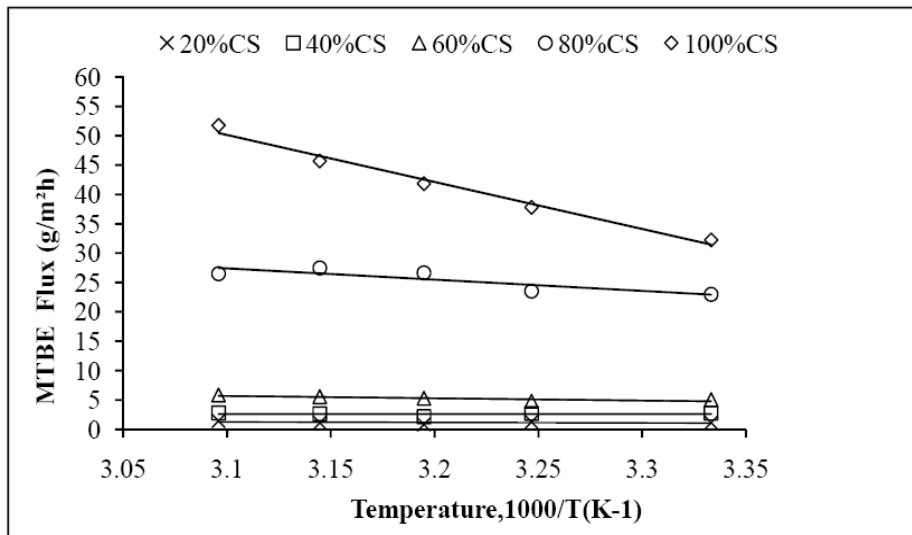


Figure 8(b) Effects of feed temperature on MTBE flux

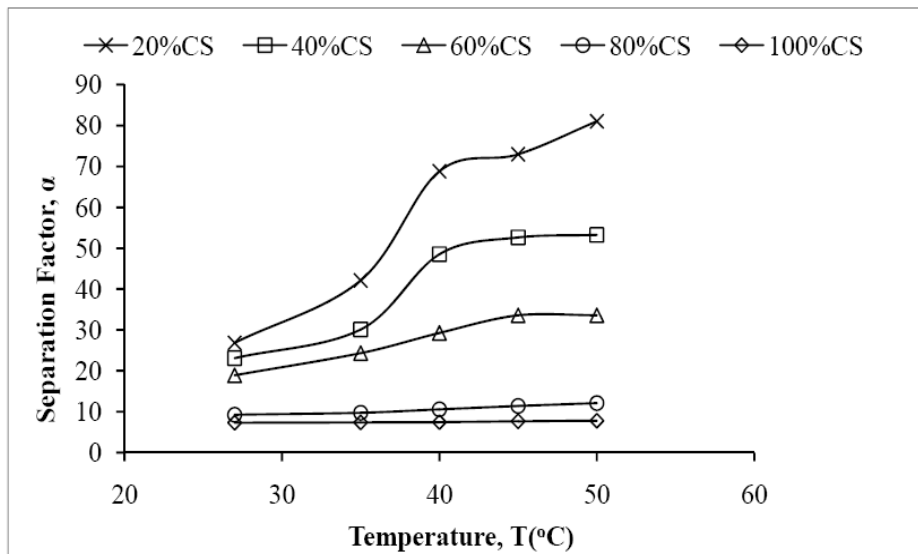


Figure 9 Separation factor at different feed temperature

4.0 CONCLUSION

Composite membranes of chitosan/PVA have shown the absence of pores on the surface area while pristine composite chitosan membrane showed visible pores even at low level of magnification. Swelling characteristics of the composite membranes showed an increased with respect to chitosan composition in the blend and concentration of methanol. Composite membrane with 20 wt% chitosan in the blend gave the lowest swelling degree in all methanol concentration. Composite membranes containing lower composition of chitosan in the blend has better permeation flux and separation factor for solution mixtures containing low methanol concentration in the feed. Feed temperature improved the total flux by two-fold to 60 g/m²hr for composite membrane with 40 wt% chitosan operated at 50 °C in 30 wt% methanol in the feed. Therefore, the composite membranes containing 20 to 40 wt% chitosan was chosen as the preferred membrane formulation to yield fluxes ranging from 50 to 70 g/m²hr with separation factors ranging from 55 to 80 at optimum operating conditions of 30 wt% methanol in the feed and feed temperature of 50 °C.

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