

Polyion Complex Chitosan Membrane Consisting of Sodium Alginate/Chitosan for the Pervaporation Separation of Methanol/Methyl *tert*-butyl Ether Mixtures

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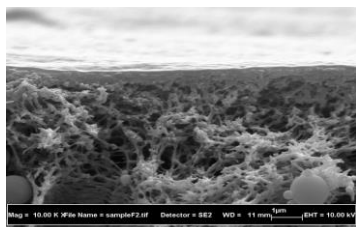
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Graphical abstract



Abstract

The polyion complex (PIC) composite membranes consisting of chitosan (CS) and sodium alginate (SA) were prepared for the separation of methanol/methyl *tert*-butyl ether (MTBE) mixtures via pervaporation process. Membrane morphologies showed that CS and SA were homogenously intermixed for all blended ratio tested. Swelling characteristics observed all membranes were readily swelled in the solution mixtures containing more methanols. Separation performance of the membranes via pervaporation was performed on the effect of SA composition in the membrane blend, effect of MTBE concentration in the feed and effect of feed temperature. Overall separation performances showed that the membranes were highly permselective towards methanol due to the affinity and polarity for all the studied parameters.

Keywords: Chitosan; sodium alginate; membrane, pervaporation

Abstrak

Membran komposit berbilang ion rumit yang mengandungi kitosan (CS) dan sodium alginat (SA) telah disediakan bagi pemisahan campuran metanol/ metil *tert*-butil eter melalui proses pervaporasi. Morfologi membran menunjukkan bahawa CS da SA bercampur secara homogen bagi semua nisbah campuran yang diuji. Sifat-sifat pembengkakan memperlihatkan bahawa membran mudah membengkak dalam larutan campuran yang mengandungi lebih metanol. Prestasi pemisahan membran-membran melalui pervaporasi telah dilakukan ke atas kesan komposisi SA dalam adukan membran, kesan kepekatan MTBE dalam suapan dan kesan suhu suapan. Prestasi keseluruhan pemisahan menunjukkan bahawa membran-membran adalah lebih kememilisherapan kepada metanol disebabkan afiniti dan kepolaran bagi semua pemboleh ubah-pemboleh ubah yang dikaji.

Kata kunci: Kitosan; natrium alginat; membran; pervaporasi

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1.0 INTRODUCTION

Chitosan (CS) is a partially deacetylated polymer of chitin, composed of an amino and hydroxyl group that can be readily reacted to form salt or complex ion [1]. It is widely used in membrane applications because of its high hydrophilicity, good film-forming character, functional groups that can easily modified, good mechanical and excellent chemical-resistant properties [2]. These hydrophilic groups play an important role in preferential water sorption and diffusion through chitosan membrane. Sodium alginate (SA) is a polyelectrolyte with negative charges on its backbone. Once dissolved in water, the polymer will form a homogenous film-forming solution, which later produces a coherent film with wide range of applications in food and non-food industries [3]. Blending of these two ionic

polymers will result in a spontaneous formation of polyion complex (PIC) membranes which occurs via ionic interaction between counter ion groups [4]. The PIC membranes made from anionic and cationic have been reported to have an excellent selectivity and permeability with good stability for the separation of alcohol and water [5].

In the petrochemical industries, methyl *tert*-butyl (MTBE) is produced from the reaction of isobutene in excess methanol. The residual methanol is subsequently distilled off and recovered. It is very difficult to separate, because methanol forms minimum-boiling azeotropes with MTBE product at a composition of 14.3 wt. % methanol at 760 mmHg. Moreover, it is reported that the conventional separation process used to separate the mixtures involved high capital and energy extensive. Therefore for this work, pervaporation is recognized as an alternative separation

technique to replace the conventional separation. Pervaporation is especially effective to separate azeotropic mixtures, close-boiling point mixtures, isomers and mixtures consisting of heat-sensitive compounds [6].

Similar work also has been reported by Kim *et al.*, [4] using PIC composite membrane at different CS content in the blend to study the effect of feed concentration and feed temperature on pervaporation performances on the separation of methanol/MTBE mixtures. They found that PIC composite membranes prepared have high permselectivity and permeability

due to the excellent polarity and relatively high free volume of the membrane network.

In this work, different approach to the method was applied by manipulating the blending ratio of SA in the membrane. The prepared PIC composite membranes were first characterized for their morphologies and swelling characteristics in the solution mixtures. Separation performances for the separation of methanol/MTBE mixtures were evaluated on the effect of SA composition in the membrane blend, effect of MTBE concentration in the feed and effect of feed temperature.

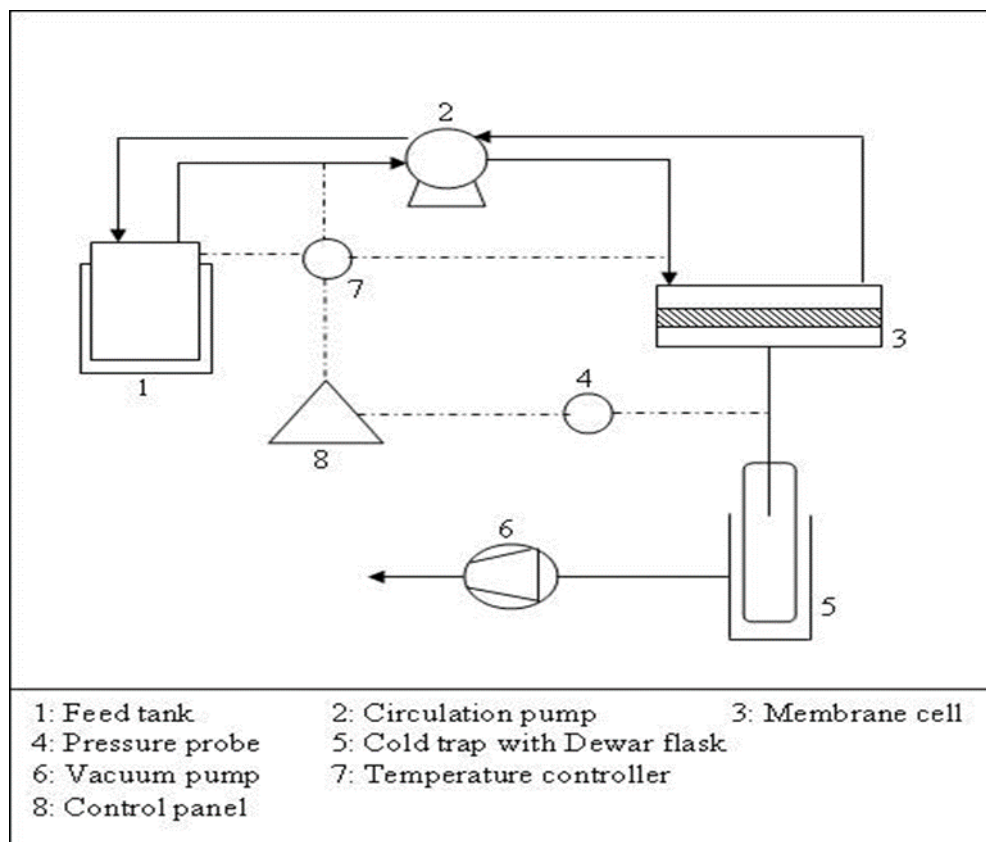


Figure 1 Schematic diagram of the pervaporation system

2.0 EXPERIMENTAL

2.1 Materials

CS powder (MW 50000-100000) and acetic acid from Mallinckrodt Baker. Polysulfone of Amoco Polymers Inc., ethylene glycol (MW 6000-7000) of Fisher Scientific, Hong Kong, and N,N-dimethylacetamide of Fluka Chemical & AG, Switzerland. SA powder was from Sigma. MTBE and methanol were purchased from Fisher Scientific, U.K., and Merck, Germany, respectively. Water was deionized before use.

2.2 Membrane Preparation

Porous support for composite membranes was prepared from polysulfone. Porous support solution containing polysulfone, dimethylformamide and ethylene glycol was casted on backing material. The casted porous membranes were immediately immersed in aqueous dimethylformamide, rinsed thoroughly with distilled water and left to dry. Blends of CS and SA were prepared with composition ranging from 0 to 2 wt% of SA; CS

amount was fixed at 2 wt% in all blend solutions. Membrane solutions were casted onto the porous support as coating layer to form composite membranes and air dried before further analysis.

2.3 Scanning Electron Microscopy (SEM) Analysis

SEM analysis of the composite membranes was performed by JEOL 5400 with 1000X magnification operating at 7 kV. The membranes were sputter-coated with gold before analysis.

2.4 Swelling Experiment

The dried samples of composite membranes were weighed beforehand. Samples were immersed in solution with methanol/MTBE mixtures from 30 to 100 wt% MTBE for 24 hours at room temperature. The swollen samples were weighed after excess liquid was removed with filter paper. The degree of swelling (DS%) was calculated according to Eq. 1,

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

Where W_s and W_d are the weight of swollen and dried samples, respectively.

2.5 Pervaporation Experiment

Separation of methanol/MTBE mixtures was performed by pervaporation process at predetermined operating conditions to evaluate the effect of SA content in membrane blend, effect of operating parameters of the developed PIC composite membranes on feed concentration and feed temperature. Schematic representation of pervaporation process is shown in Figure 1, which operated in batch mode. The effective area for membrane permeation is 56.75 cm². Pervaporation was run for 1 hour; permeate sample was collected in the flask attached to cold trap and its composition was sent for analysis using refractometer. The separation performance of the developed composite membranes was evaluated in terms of permeation flux (J) and separation factor (α) calculated from Eq. 2, and Eq. 3, respectively,

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

Where Q is the weight of collected permeate (g), A is the membrane effective area (m²), and t is pervaporation time (h).

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

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, permeation flux is also dependent on temperature. When the feed temperature increased, the permeation flux generally follows an Arrhenius type law as in Eq. 4,

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

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

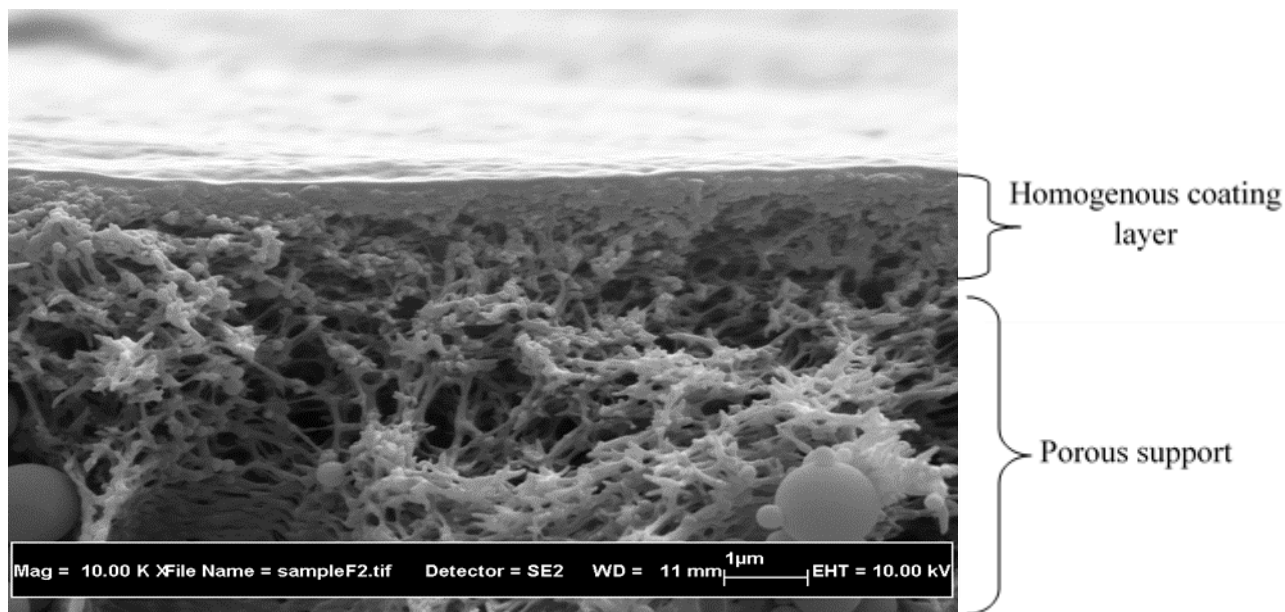
3.0 RESULTS AND DISCUSSION

3.1 SEM Analysis

Figure 2a to 2e shows the cross sectional area of PIC composite membranes at different SA content in the blend. The thickness of coating layer increased with increasing SA content in the blend as can be seen in Figure 2b to 2e. The coating layer of CS/SA of PIC composite membrane is not phase separated with increasing SA content which indicates that the two polymers are homogeneously intermixed and in the state of polyion complex.

3.2 Swelling Characteristics

Figure 3 shows swelling degree decreased with increasing MTBE concentration in the feed. At low MTBE concentration, swelling degree for all PIC composite membranes showed the highest indicating membranes interact exclusively with methanol than MTBE. At higher concentration of methanol in the feed, the membranes swelled greatly due to the formation of a strong interaction between the membrane and methanol molecules while suppressing the interactions within the membranes material. Increasing SA content in the blend also decreases the swelling degree because membrane has compact network structure, making it less permeable for component to pass through the membrane.



(a)

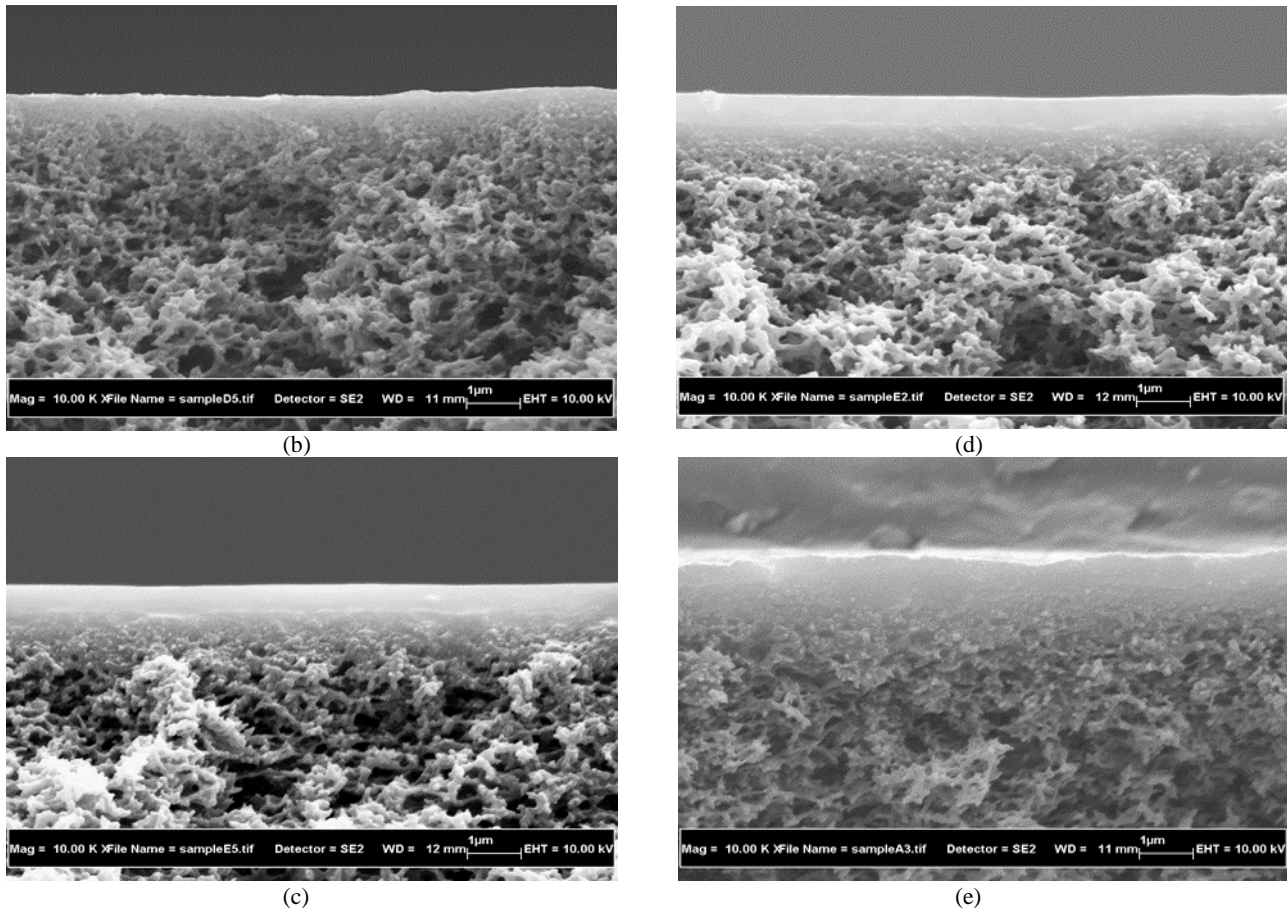


Figure 2 The cross-sectional morphologies of PIC composite membranes for (a) 0 wt% SA, (b) 0.5 wt% SA, (c) 1.0 wt% SA, (d) 1.5 wt% SA, and (e) 2.0 wt%

3.3 Pervaporation Experiment

3.3.1 Effect of SA Composition in the Blend

Figure 4 showed the permeation flux and separation factor of PIC composite membranes at different SA content in the blend. Feed composition was fixed at 70/30 wt% of MTBE/methanol mixtures and operated at feed temperature of 30°C. Selectivity is

high at higher SA content due to the increasing affinity of PIC composite membranes towards polar compound, which is methanol. However, higher SA content decreases the permeation flux due to the formation of more ionic complex, causing rigidity and compactness in membrane network. Transportation of larger MTBE molecules was hampered due to this hence reducing the permeation flux.

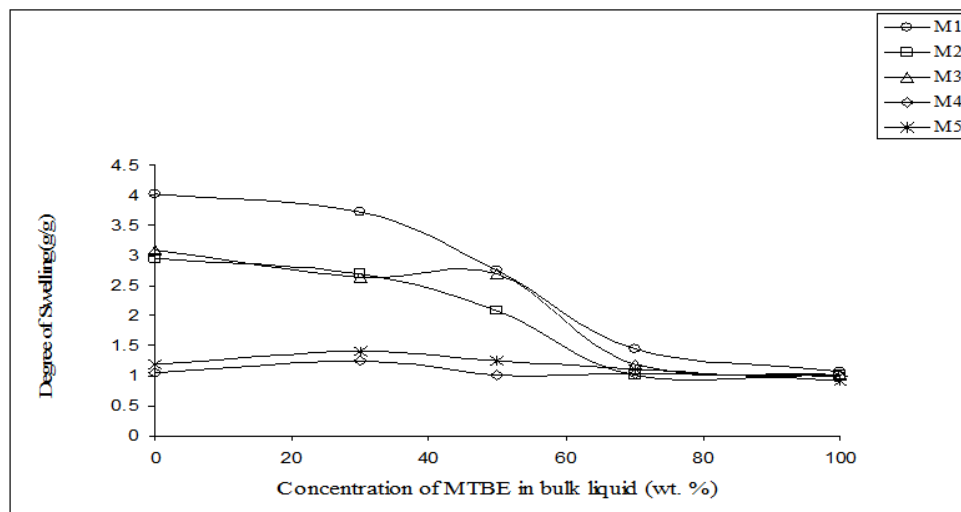


Figure 3 Swelling degree of PIC membranes at different SA content (wt%)*. *M1: 0 wt%, M2: 0.5 wt%, M3: 1.0 wt%, M4: 1.5 wt%, and M5: 2.0 wt%

3.3.2 Effect of Feed Concentration

Figure 5 illustrated the PSI on the effect of MTBE concentration on the feed. PSI increased with the increasing MTBE concentration. PSI also improved with the increasing SA content in the blend. Comparing to M1, the PSI for all PIC composite

membranes improved greatly up to three folds. M4 (1.5/2.0 wt% SA/chitosan) was found to give the highest PSI of 3211 with 96% methanol in the permeate. M5 has higher swelling degree than M4 because insertion of SA enhance swelling due to improve hydrophilicity and affinity towards polar compound.

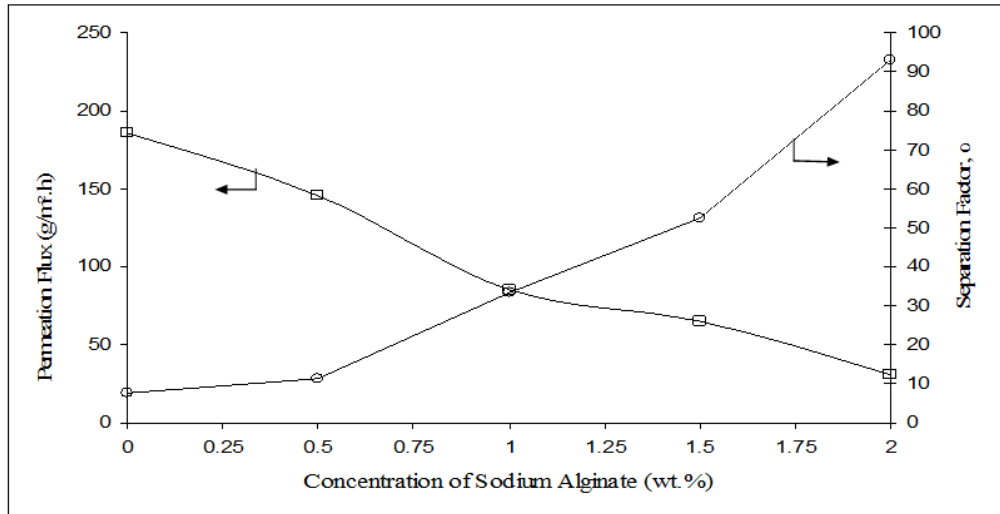


Figure 4 Permeation flux and separation factor of PIC membranes at different SA content (wt%) in the blend

3.3.3 Effect of Feed Temperature

Figure 6 and 7 show effect of temperature on permeation flux and separation factor, respectively, for different SA content in PIC composite membranes. Increase in temperature increases the permeation flux. The supplied heat leads to increasing in mobility of polymer chains in membrane, amplifying the frequency of chain jumping which resulted in higher free volumes. This will facilitate the mass transport of component through the membrane thus increasing the permeation flux. Elevated temperatures also increase the separation factor. Increasing the temperature causes the mobility of polymer chains to increase but the frozen free

volume formed during preparation step decreases due to relatively very rigid and bulky structural properties of PIC membrane [4]. Increase in mobility of polymer chains obstructs the diffusion of MTBE molecules, which has larger molecular size than methanol, which eventually increased the separation factor.

It is very interesting to note that the membrane containing 2.0wt % sodium alginate showed a very low permeation flux while having a very high separation factor. This phenomenon is due to the relaxation of polymeric chains during the pervaporation which affects the membrane mobility [7].

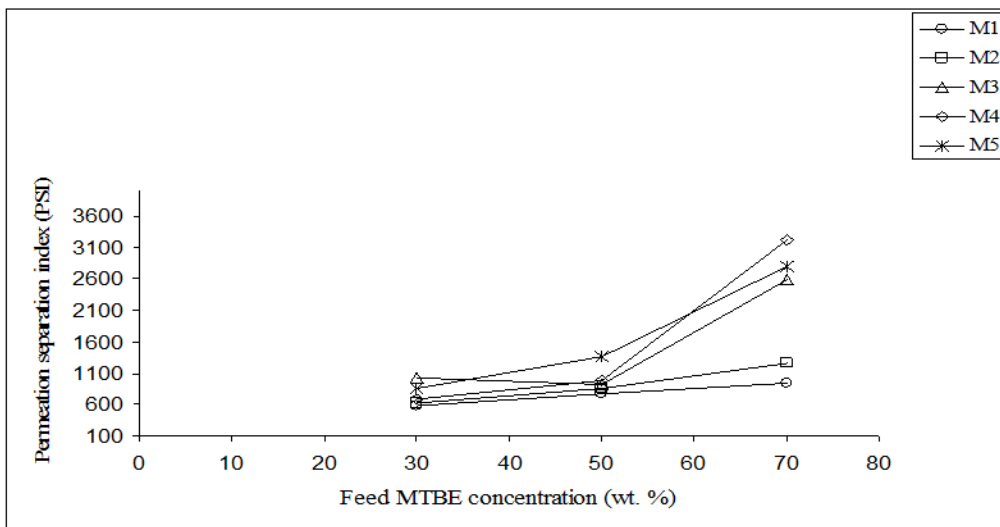


Figure 5 Effect of MTBE concentration on PSI of PIC membranes at different SA content (wt%)*. *M1: 0 wt%, M2: 0.5 wt%, M3: 1.0 wt%, M4: 1.5 wt%, and M5: 2.0 wt%

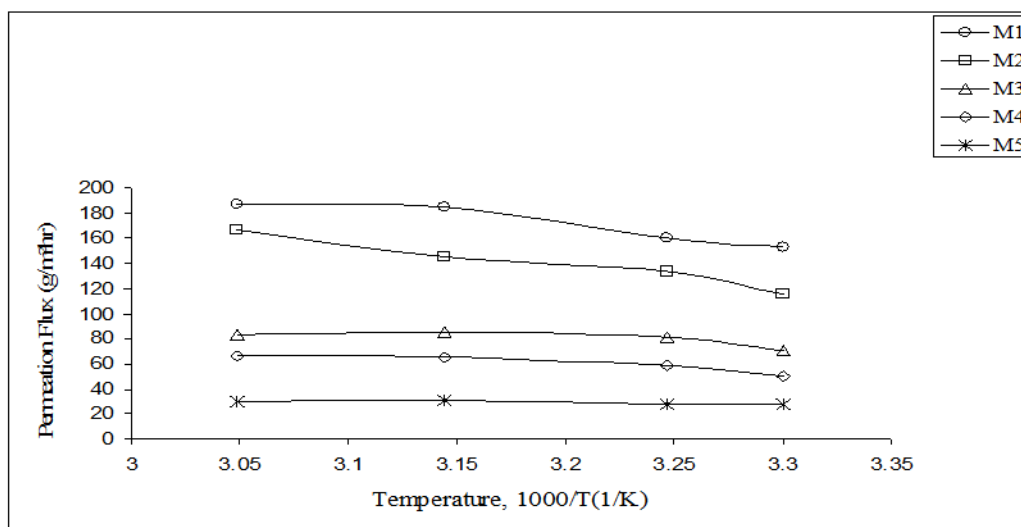


Figure 6 Permeation flux of PIC membranes for various feed temperatures at different SA content (wt%)*. Feed concentration: 70 wt% MTBE in the mixtures, permeate pressure: 0.07 bar. *M1: 0 wt%, M2: 0.5 wt%, M3: 1.0 wt%, M4: 1.5 wt%, and M5: 2.0 wt%

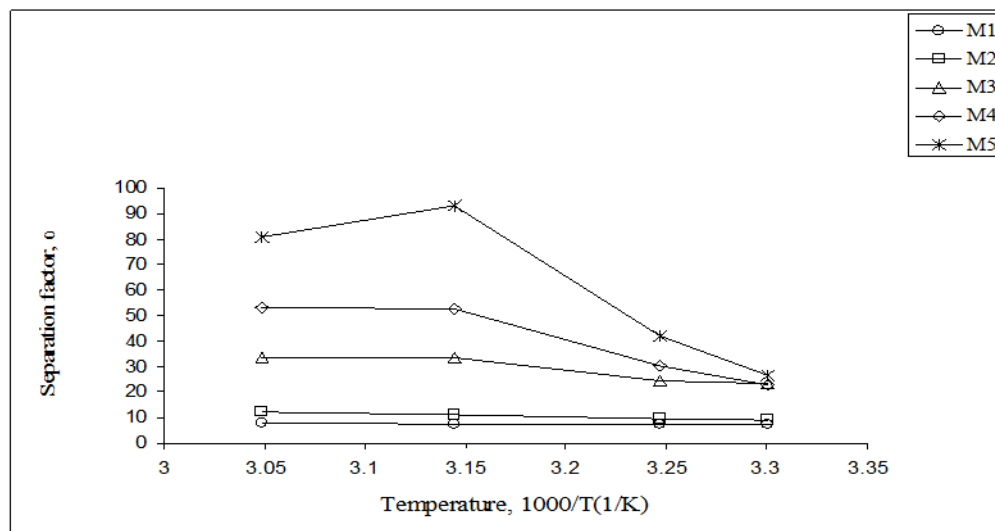


Figure 7 Separation factor of PIC membranes for various feed temperatures at different SA content (wt%)*. Feed concentration: 70 wt% MTBE in the mixtures, permeate pressure: 0.07 bar. *M1: 0 wt%, M2: 0.5 wt%, M3: 1.0 wt%, M4: 1.5 wt%, and M5: 2.0 wt%

4.0 CONCLUSIONS

Modification via polyion complex sodium alginate/chitosan blend membranes improved the overall performance of this type of composite membranes in pervaporation separation of methanol/methyl tert-butyl ether (MTBE); the membranes were preferentially permeable to methanol in the entire feed composition and were affected by the sodium alginate content. Higher methanol concentrations leading to a greater extent of membrane swelling. Selectivity of the membranes improved with more sodium alginate in the membrane blend. This is because polyion complexation increased at higher sodium alginate composition making membrane more attracted towards polar compound. Pervaporation separation index increased with increasing sodium alginate composition and MTBE concentration mainly due to the polarity effect of the membrane structure which sorbed methanol preferentially. Permeation flux

and separation factor increased significantly at high temperature due to the free volume in the membrane.

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