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Synthetic PDMS composite membranes for pervaporation dehydration of ethanol

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ABSTRACT

Cross-linked polydimethylsiloxane (PDMS) membranes supported on cellulose acetate (CA) and polyamide (PA) microfiltration membranes were prepared by pre-wetting technique for pervaporation (PV) dehydration of ethanol. Laboratory CA supports were initially prepared and characterized and compared with commercial PA supports. The experiments were carried out to investigate the effects of support layer and permselective thickness on the separation performance of membranes at different operating conditions particularly initial ethanol concentrations (0.3–3.0 wt.%) and temperatures (30–50˚C). The results revealed that increasing feed concentration and temperature increases total permeation flux. PDMS/PA membrane showed better overall performance than PDMS/CA membrane.

Keywords: Membranes; Mass transfer; Solubility; Permeation; Diffusion

1. Introduction

Alcohol obtained from fermentation, as a renewable resource, among alternative fuels, may become one of the most important fuels. The advantage of combined pervaporation (PV) and fermentation in membrane bioreactors offers the continuous processing [1].

In the past two decades, membrane has established itself as one of the most promising technologies in the molecular-level liquid/liquid separation and continuously receives global attention and efforts in biorefinery, petrochemical, pharmaceutical industries, etc. [2–8]. It has especially received many attentions in connection with the dehydration of ethanol from biomass fermentation. Since production of ethanol from biomass using conventional technologies (e.g. distillation, adsorption, etc.), is so energy-intensive, PV is being investigated to provide an economical alternative for such especial separation processes [9–11]. This position has motivated a substantial attitude to explore diverse membranes and their efficiency in current fields.

So far many researches have been carried out regarding PV [12–16]. PV is one of the membrane technologies that utilize a non-porous membrane for separation of liquid mixtures. PV using dense membranes has emerged as a promising new method for water removal from aqueous solutions. Polydimethylsiloxane (PDMS) membrane is a well-known hydrophobic membrane [17–21] for removing organics from aqueous mixtures.

Many researchers have focused on membrane materials selection, modification, and development of

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permselective layers. Recently, importance of the support layer on PV performance has been noticed; since it can modify permeation properties of membranes, in addition to providing mechanical stability. In Table 1, selected PV literature data for several systems are summarized for the separation of ethanol/water mixtures using different PDMS supported and unsupported membranes. Support layers with nanopores can dominate the overall mass transfer resistance and affect the membrane performance.

Due to the various attractive properties of composite membranes as compared with other membranes, this research is especially contributed to provide a comprehensive investigation regarding the current state-of-art technologies for preparation methodology of support layer and the pros and cons of various operational conditions in PV processes. This work presents in details and systematically the performance of different PDMS composite membranes in PV separation of ethanol/water mixtures. As an indispensible orientation for development of PV, firstly cellulose acetate (CA) supports were initially prepared by means of the phase-inversion method and compared with commercial polyamide (PA) supports. Thereafter, PDMS/CA and PDMS/PA composite membranes were prepared by the conventional pre-wetting technique. Effects of the support layer, permselective thickness, and different operating conditions, such as feed concentration and temperature were investigated in detail. Finally, the superiority of composite membranes over other membranes in the separation performance was highlighted. The outcome of this experimental study can be useful to evaluate technical feasibility of support layer in dehydration of water using composite membranes.

2. Experimental

2.1. Materials

Dehesive 944 silicone as a solvent-based addition cross-linkable silicone was purchased from Wacker Silicones Corporation, Adrian; MI. The proprietary cross-linker (V24/Catalyst OL system) was provided by Wacker; containing SiH groups in polymer chain together with platinum, acting as a catalyst in the hydrosilylation reaction. 1-Methyl-2-pyrrolidone (NMP), n-hexane and toluene were also purchased from Merck and used as received. Commercial PA porous membrane was supplied from Sartorius AG. CA with an average molecular weight of 52,000 g/mol (Fluka) was used as a polymeric material to form microporous support.

2.2. CA support preparation

Initially, CA powder (15.5 wt.%) was added to NMP. The prepared solution was stirred and degassed in an ultrasonic bath for about 2 h to remove any air bubbles. Then, the solution was cast on a glass plate using a casting knife. Subsequently, the cast film was immersed in a distilled water bath to complete the phase separation, where exchange between the solvent (NMP) and the non-solvent (water) was induced.

Table 1
PV performance of different PDMS composite membranes

Membrane	Membrane thickness (μm)	Feed ethanol concentration (wt.%)	Temperature (℃)	J (kg/m^2 h)	α	Ref.
PDMS	40	11.9	25	0.014	7.1	[11]
PDMS-PS graft copolymer supported on a PES	20	10	60	0.130	6.2	[29]
PDMS-PS block copolymer	39	10	25	0.027	6.2	[30]
PDMS-PPP graft copolymer	30	7	30	0.019	40.0	[31]
PDMS-PI graft copolymer	20	6.6	48	0.032	6.6	[32]
PDMS-PS IPN supported membrane	15	10.0	60	0.160	5.5	[33]
PDMS/silicate	30	5.0	30	0.110	37	[34]
PDMS/PEI/PPP	40	5.0	40	0.270	3.7	[35]
PDMS/CA	8	5.0	40	1.300	8.5	[36]
Silicalite-1 filled PDMS/PEI	20	5.1	22	0.150	34	[37]
Silicalite-1 filled PDMS/PEI	12	6.5	22	0.150	16	[37]
Silicalite-1 filled PDMS/PEI	4	7.0	22	0.560	14	[37]
ZSM-5 filled PDMS/PVDF	10	5.0	50	0.821	13.7	[38]
ZSM-5 filled PDMS/PVDF	10	5.0	60	1.290	13.4	[38]
ZSM-5 filled PDMS/PVDF	10	5.0	70	2.011	12.6	[38]

Finally, the polymer film was heat-treated in a distilled water bath at 50˚C for 10 min to remove the excess NMP. The prepared microporous support was kept in a container of distilled water to be ready for characterization as well as preparation of the composite membrane. Detailed description of the support formation mechanism was presented in our previous studies.

2.3. Porosity measurement

As mentioned, porosity of the composite membranes plays an important role in describing support layer on PV performance [22]. In order to evaluate porosity of the support, the samples were initially impregnated with distilled water then weighed after wiping superficial water with filter papers. After that the wet samples were placed in an air-circulating oven at 80˚C for 24 h to be completely dried and finally, the dry samples were weighed. The porosity of samples was calculated using the following equation [22]:

$$P(\%) = \frac{Q_0 - Q_1}{Ah} \times 1000 \tag{1}$$

where P is the microporous membrane support porosity; Q_0 and Q_1 are the weights of wet and dry samples (g), respectively; A is the sample surface area (cm^2) and h is the sample thickness (mm).

2.4. PDMS/CA composite membrane preparation

The thin film PDMS/CA composite membranes were made via the following procedure: A mixture of 20 wt.% PDMS in toluene was prepared. The solution was then stirred for 1 h to ensure that the silicone oil was completely dissolved. Before casting, the proprietary cross-linker and catalyst were added to the polymer solution. Finally, it was degassed in an ultrasonic bath for about 1 h to remove any air bubbles. The prepared CA supports were impregnated with distilled water and fixed on a glass plate. The water was used to fill the pores to prevent intrusion of the polymer solution into the support layer. The excess water was wiped off with a wet tissue. Casting was performed over the less porous side of the support. Before casting the solution over the support, the glass plate was inclined (30˚C) to allow flowing of the polymer solution down over the support. After 5 min, the glass plate was turned upside down and the coating procedure was repeated. Casting was repeated five times. Afterwards, the membranes were put into an oven at 80˚C for 2 h to remove the residual solvent and to fully cross-link the polymer. Finally, the cross-linked composite membranes were cooled to room temperature.

2.5. PDMS/PA composite membrane preparation

The preparation procedure of PDMS/PA membranes is similar to that of PDMS/CA membranes with a series of minor differences. However, the thin film composite PDMS/PA membranes were made as follows: Casting solutions were initially prepared from n-hexane solution containing 20 wt.% silicone with proper ratios of cross-linker and catalyst. Simultaneously, a PA porous membrane was put on water surface in a basin to act as the support. Then the casting solution was cast on the PA membrane impregnated with distilled water and the solvent was evaporated at ambient temperature for 48 h.

The thickness of permselective layer was determined with a digital micrometer (MitutoyoModelMDC-25SB) readable to ±1 μm by subtracting the thickness of composite membrane from that of support. Each composite membrane was synthesized with two different skin layers (5 and 8 μm). Thicknesses of the synthesized CA and the commercial PA supports are in the range of 145.8 ± 1.2 and 120 μm, respectively.

3. PV experiment

Effects of support layer, permselective thickness, and different operating conditions including feed composition and temperature were studied. PV experiments were carried out using a lab scale setup as shown in Fig. 1. The membrane was placed in a plate and frame module with an effective area of 16.6 cm^2. Rubber O-rings were used to provide a pressure-tight seal between the membrane and the cell. In all tests, permeate pressure was maintained at a low level (2 mbar) by a vacuum pump (MOTO GEN 80-4B with R.P.M. 1380, Iran). Permeate samples were condensed and collected in a glass condenser kept inside a liquid nitrogen vessel. Permeates were condensed and collected in a Pyrex glass condenser kept inside a cryogenic trap at −35˚C. An accurate refractometer (DR-A1) was employed to analyze alcohol concentration in permeate samples.

4. Results and discussion

4.1. Effect of support layer on PV performance

There are several reports that present the support layer effect on separation performance of PV process

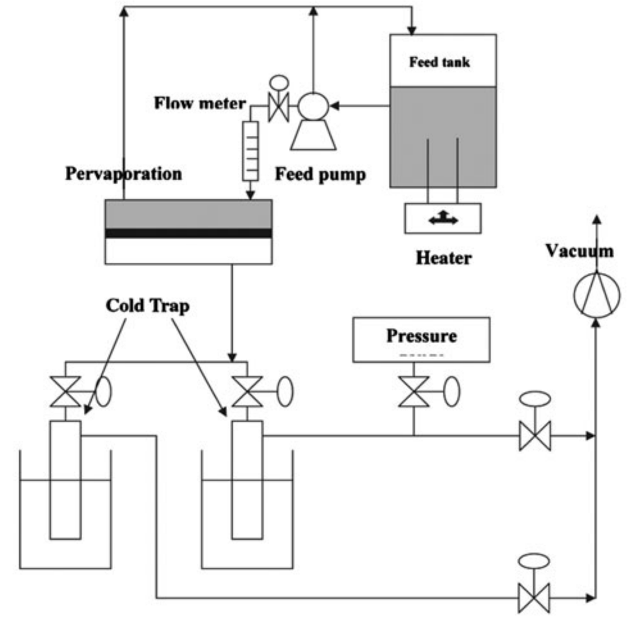

Fig. 1. Schematic diagram of the lab scale setup.

and many researchers have investigated the recovery of ethanol from its aqueous solution [23–25].

It should be pointed out that the permeation properties of the composite membranes are not only affected by their active layer thicknesses, but also by their physical structure of support layers. Therefore, it was tried to provide a comprehensive investigation regarding the effects of microporous support layers on the PV performance. The results revealed that the prepared PDMS composite membranes are reasonably and acceptably selective for ethanol. The presence of microfiltration support layers enhances the PV performance of the membranes in terms of permeation flux and separation factor. For instance, in the case of ethanol recovery with 0.3 wt.% ethanol concentration at 30˚C, the composite PDMS/CA and PDMS/PA membranes with permselective layer thickness of 5 μm exhibit ethanol permeation fluxes of 0.0047 and 0.0237 kg/m^2 h and ethanol selectivities of 3.01 and 11.87, respectively.

Characteristics of different synthesized composite membranes depend on both support layer and preparation method. PA and CA supports are two types of highly hydrophilic materials. In the pre-wetting method, prior to casting, the pores of the PA and CA supports are filled with solvent (water). This mitigates mass-transfer resistance caused by intrusion of the PDMS solution into the porous support layers during preparation of the composite membranes. As a result, thin and defect free dense PDMS permselective layers are formed on PA and CA support layers confidently. Therefore, support layer and PDMS permselective layer can be completely matched. Consequently, high total permeation flux and acceptable selectivity for the PDMS composite membranes are achieved.

Additionally, utilization of the more hydrophilic PA support provides both higher ethanol and water fluxes as compared with the less hydrophilic CA support and shows lower selectivity than PDMS/PA.

The enhancement in total flux may also be due to the larger porosity of the microporous PA support layer compared with the CA support, as demonstrated in Fig. 2. The porosity values of the PA and CA supports are 71 and 63%, respectively.

There is a pressure drop when permeating molecules penetrate through the microporous support layer depending on its microporous structure. The permeation can be described by convective flow. Hence, a pressure gradient between the interface layer and the permeate channel applies a driving force on the permeating molecules. However, the effect of pressure drop on mass transfer is determined by total permeation flux, pore diameter, and sensitivity of the permeating molecules towards pressure changes [26]. Hence, the existence of very small pores and pressure-sensitive molecules with low vapor pressures, can affect the mass transport significantly.

Condensation of permeating molecules in the pores is another important parameter which affects the performance of composite membranes. Pore condensation depends only on structure of the support and not on its chemical nature. This effect becomes significantly important for membranes with small pore diameters and pressure-sensitive molecules with low-equilibrium vapor pressures [26]. In order to prevent permeate condensation and permeate pressure drop, pore diameters have to be optimized.

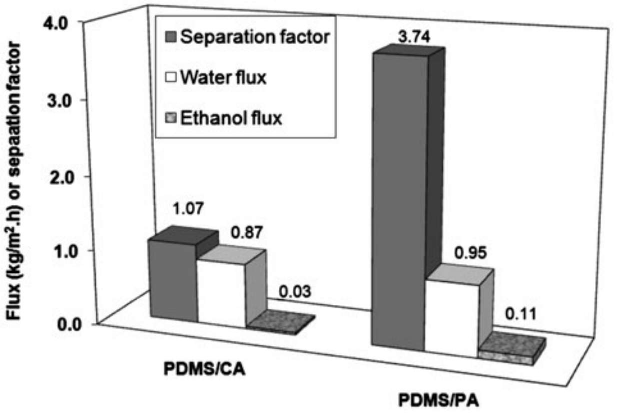

Fig. 2. Effect of microporous support layer on the performance of PDMS composite membrane for ethanol/water mixture at 3.0 wt.% of ethanol.

4.2. Effect of feed concentration

Effect of ethanol concentration in the feed on PV performance of the composite membranes is presented in Fig. 3(a–c). As observed, increasing ethanol concentration increases ethanol permeation flux significantly. It is due to the fact that increasing ethanol concentration increases ethanol sorption. It also enhances the membrane swelling because of the ethanol plasticizing effect and promotes free rotation of the polymer segments about the main chain resulting in lower activation energy for diffusion. Diffusion compared with sorption seems more significantly effective on ethanol permeation flux. When ethanol is highly sorbed into the composite membranes, the major part of the membranes contains the permeating liquid and diffusion of the incoming permeants through this part of the membranes is faster than that through the rest of the polymer matrices [23,25].

Although ethanol concentration increases ethanol permeation flux, water permeation flux increases more significantly than ethanol permeation flux, resulting in the membrane selectivity reduction. This phenomenon can be attributed to more free volume and simultaneously more side chains mobility at the higher ethanol concentration. Consequently, water molecules can permeate more easily through the free volume due to their smaller size. Meanwhile, diffusion of water molecules through the membranes increases leading to the membrane selectivity reduction [23–25]. At ethanol concentration range of 0.3–3.0 wt.%, all the membranes exhibit an ethanol selective behavior, it means ethanol concentration in the permeate side is more than that in the feed side (Fig. 4). At ethanol concentration below 1.0 wt.%, the membrane selectivity reduction is more significant than that at higher ethanol concentration. With a closer look, for the case of PDMS/CA membrane, it can be seen that by increasing the concentration from 0.3 to 1.0 wt.%, selectivity diminishes up to 55%, while the membrane selectivity reduction is about 45% when ethanol concentration increases from 1.0 to 3.0 wt.%, whereas, for the PDMS/PA membrane, these values are 34 and 53%, respectively. It can be concluded that at concentrations more than 1.0 wt.%, the ethanol permeation flux increases and this enhancement is more significant for the PDMS/PA membrane.

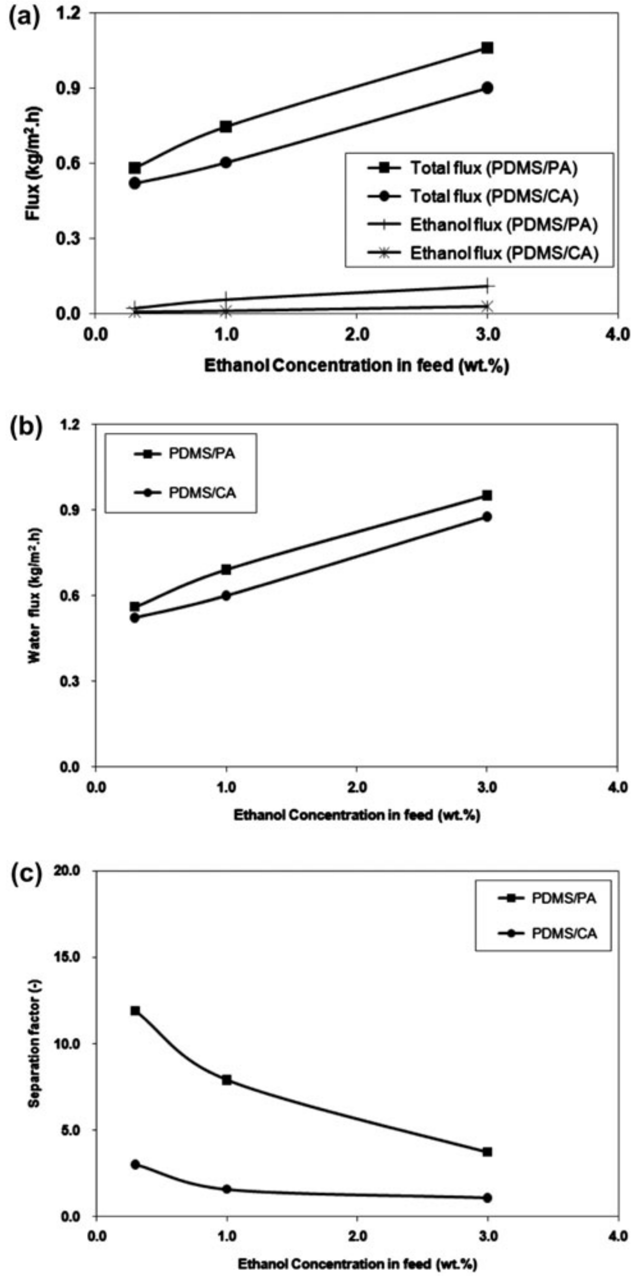

Fig. 3. Effect of ethanol concentration in feed on permeation fluxes and selectivity of ethanol/water mixtures; permselective thickness was 5 μm.

4.3. Effect of feed temperature

Effect of feed temperature of the composite membranes on PV performance was investigated. As observed in Fig. 5(a–c), increasing the feed temperature at different feed compositions, increases permeation fluxes of both ethanol and water in all the experiments, while decreases the membranes selectivities. Increasing rate of water permeation flux is greater than that of ethanol permeation flux and this reduces the membrane selectivity significantly. At higher feed temperatures, swelling degree of the membrane matrix increases more significantly and these result in the more polymer segmental motions. Moreover,

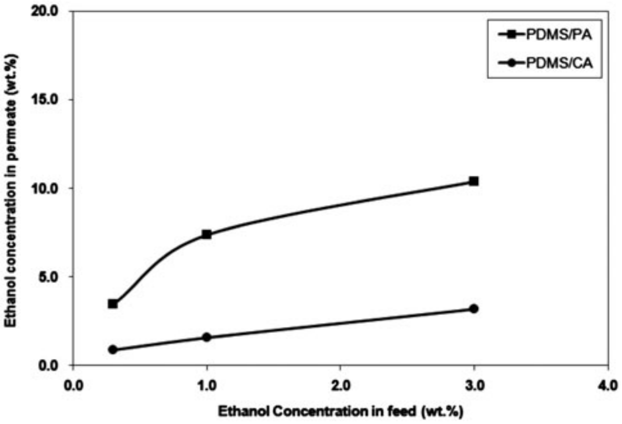

Fig. 4. Variation of ethanol concentration in permeates with ethanol concentration in feed; permselective thickness was 5 μm.

according to the free volume theory, free volume is strongly related to random thermal movement [25,27]. As temperature increases, the frequency and amplitude of the chain jump increase accordingly and this results in the larger free volume, along with the more activity of permeating molecules. This facilitates transport of water and ethanol molecules; which increases the total permeation flux and consequently reduces the membranes selectivity.

The results revealed that, increasing feed temperature from 30 to 50˚C, at different feed compositions (0.3–3.0 wt.%), increases the total permeation fluxes of PDMS/CA and PDMS/PA membranes up to 200 and 240%, respectively. At higher temperature (above 40˚C), the effect of feed temperature on total permeation flux is more significant. Increasing total permeation flux with temperature is likely due to the higher diffusion rate of the feed molecules.

The temperature dependency of permeation flux can be computed using the Arrhenius type equation as follows [27,28]:

$$J_p = J_{p0} \exp\left(\frac{-E_p}{RT}\right) \tag{2}$$

where J_p is the permeation rate of permeating molecules through the membrane, J_{p0} is the pre-exponential constant, R is the universal gas constant, T is temperature, and E_p is the activation energy of permeation. Arrhenius plots of ln J_p vs. $1000/T$ are depicted in Fig. 6. As observed, with a reasonable accuracy ($R^2>$ 92), Arrhenius plots are linear in the temperature range studied, confirming that the temperature dependency of permeation flux follows the Arrhenius equation (Fig. 6). E_p values for the PDMS/CA and PDMS/PA composite membranes calculated from the slopes of the straight lines of the Arrhenius plots are 43.35 and 39.03, respectively. In all the experiments, E_p values are positive confirming that permeation flux increases with increasing temperature. Since increasing temperature enhances permeation flux, it can be deduced that the sorption process is not significant compared with the diffusion process [23]. Since sorption is less significant and the support layer has little

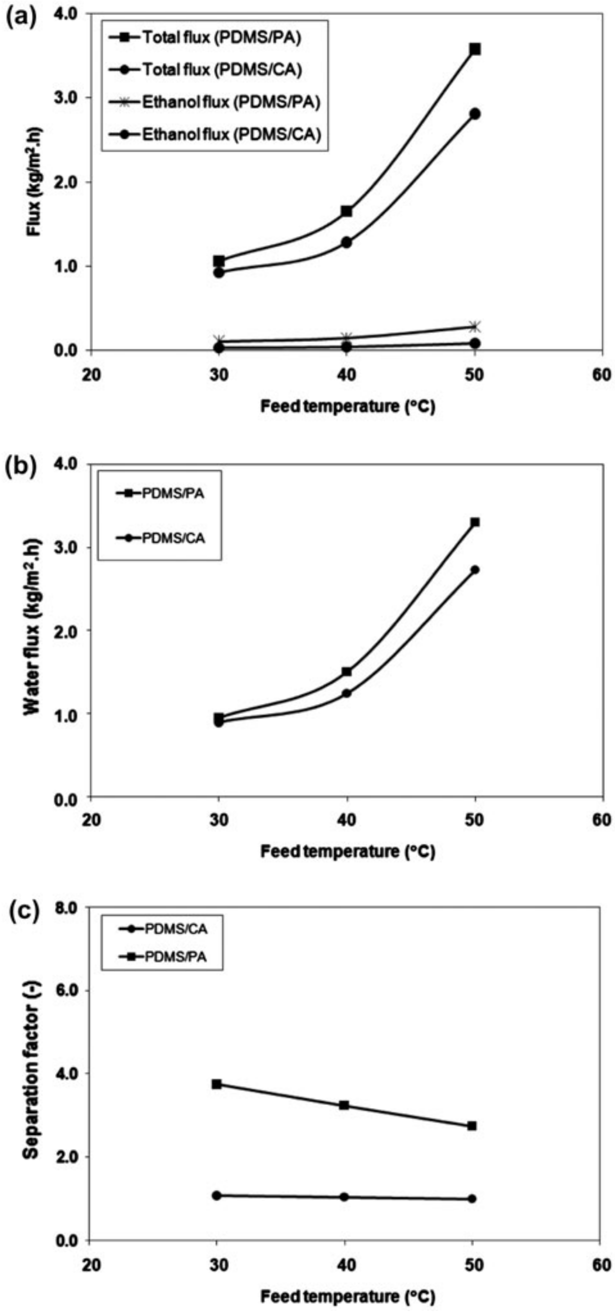

Fig. 5. Effect of feed temperature on permeation fluxes and selectivity of ethanol/water mixtures; permselective thickness was 5 μm.

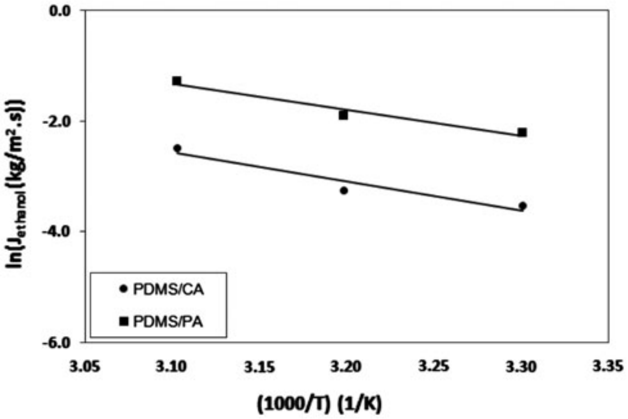

Fig. 6. Arrhenius plot of ln J_p vs. $1000/T$ for the PDMS composite membranes at 3.0 wt.% of ethanol; permselective thickness was 5 μm.

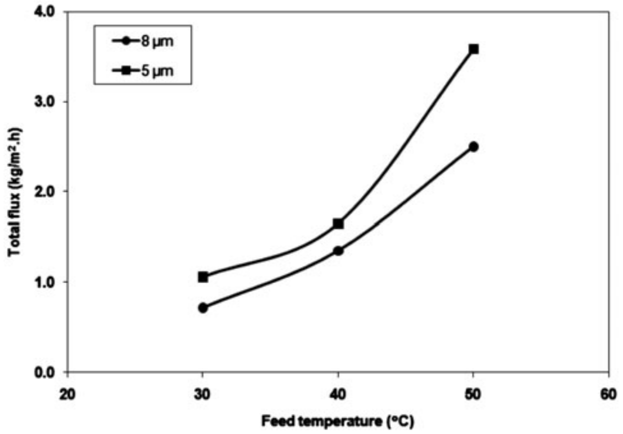

Fig. 7. Effect of permselective thickness on PV performance of PDMS/PA composite membrane at 3.0 wt.% of ethanol.

impact on activation energy, the activation energy of PDMS/PA membrane (39.03 kJ/mol) is approximately in the same order as that of PDMS/CA membrane (43.35 kJ/mol).

4.4. Effect of permselective layer thickness

In Fig. 7, the effect of PDMS permselective layer thickness on PV performance is presented. As the permselective thickness increases from 5 to 8 μm, total fluxes of both PDMS/PA and PDMS/CA membranes decrease. For both the membranes, ethanol selectivity increases. It can be said that the PV performance of composite membranes can be controlled by adjusting their permselective layer thicknesses.

5. Conclusion

PV performance of ethanol/water mixtures using the synthesized PDMS/CA and PDMS/PA composite membranes were investigated at different feed concentrations and feed temperatures. Total permeation flux of ethanol/water mixtures through the PDMS/CA and PDMS/PA composite membranes were found to vary from 0.52 to 0.90 and 0.58 to 1.06 $kg/m^2 h$ over a concentration range of 0.3–3.0 wt.% at 30°C. The results revealed that, increasing feed temperature from 30 to 50°C, increases total permeation fluxes of PDMS/CA and PDMS/PA membranes up to 200 and 240%, respectively. At higher temperature (above 40°C), effect of feed temperature on total permeation flux is more significant. The results clearly revealed that the permselective layer thickness and the support layer morphology have significant effects on the PV performance. Since both permeation flux and selectivity are influenced by the support layer, the selection of appropriate supports seems to be very important in the preparation of composite membranes for PV applications. The results indicated that porosity of the support layers should be as high as possible, to diminish the diffusion paths through the membranes.

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