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Short communication

Preparation of cellulose acetate membrane filled with metal oxide particles for the pervaporation separation of methanol/methyl *tert*-butyl ether mixtures

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ABSTRACT

In this work, a new pervaporation cellulose acetate (CA) membrane filled with metal oxide particles was prepared to intensify the separation of methyl *tert*-butyl ether (MTBE)/methanol mixtures. The SEM and Raman spectrometry revealed that the particles of metal oxide were evenly dispersed in the membrane matrix and made a denser membrane. When the content of Al_2O_3 and ZnO was 1.98 wt% and 4 wt%, respectively, both the permeation flux and separation factor of blended CA membrane were higher than those of pure CA membrane. In comparison with the pure CA membrane, the maximum flux of blended membrane filled with Al_2O_3 and ZnO improved 96.5% and 111.1%, respectively; the maximum separation factor improved 48.0% and 37.8%, respectively. In addition to the substantially improved permeation flux and selectivity, the CA membrane filled with metal oxide was found easy to prepare and with low cost.

1. Introduction

MTBE as an additive in gasoline is produced by reacting methanol with isobutylene from a mixed-C_4 stream in the liquid phase over an acidic ion-exchange resin catalyst. In order to utilize isobutylene to the greatest extent, excessive methanol is often used. Therefore, a mixture of MTBE and methanol will form at the end of the reaction. However, methanol forms azeotropic mixtures with both MTBE and butanes at 760 mmHg, which presents a challenge to the conventional distillation technology [1]. As an alternative, pervaporation (PV) is an attractive technique due to its simplicity and potential for energy savings, especially for mixtures with high volatility and mixtures with thermal or chemical sensitivity [2–4].

Cellulose acetate is an easily available source of membrane material for pervaporation, preferably for permeation of hydrophilic compounds [5]. Cao et al. [6] have studied the influence of the acetylation degree of cellulose acetate on pervaporation for a methanol/MTBE system. Zhang et al. [7] investigated the pervaporation of methanol/MTBE/C_5 ternary mixtures through a CA membrane. Their research work showed that CA could be used to separate the mixture of methanol/MTBE, but the flux of methanol was low. A modified technology is to make the CA membrane more hydrophilic to improve the performance flux and separation factor. Niang et al. [1] prepared a pervaporation CA membrane blended with cellulose acetate hydrogen phthalate to separate the mixture of MTBE and methanol. This membrane demonstrated good separation performance, however, cellulose acetate hydrogen phthalate was not easy to obtain. Thereafter, Dubey et al. [8] used a novel chitosan-impregnated bacterial cellulose membrane to separate ethanol/water azeotrope by pervaporation and found an improved flux of ethanol; Cai et al. [9] found that the composite membranes with polyvinylalcohol (PVA) as separating layer material and CA as supporting layer had good pervaporation performance for the MTBE/MeOH system.

In addition to the organic membrane, the inorganic zeolite membrane can separate MTBE/methanol by pervaporation. Kita et al. [10] reported that the separation factor of zeolite membrane reached 5000 for MTBE/methanol, which is higher than that of organic membrane. However, the cost of zeolite membrane is much higher than that of organic membrane and it is not easy to fabricate.

Recently, blending the organic membrane with inorganic compounds was also reported to be able to improve the pervaporation performance of membranes. Kittur et al. [11] prepared ZSM-5 zeolite-incorporated polydimethylsiloxane (PDMS) membranes to separate an isopropyl alcohol/water mixture. They found that both the permeation flux and selectivity increased simultaneously with increasing zeolite content in the membrane matrix. In additional, Lu et al. [12] prepared the PVDF ultrafiltration membrane containing the nanosized Al_2O_3 particles, and Al_2O_3 was claimed to have made the PVDF more hydrophilic, the contact angle changed from 83.64° of pure PVDF to 57.42° of composite membrane containing 2% Al_2O_3 particles, the water flux was improved from 100 L/m^2 h for pure PVDF membrane to 200 L/m^2 h for the composite membrane at the pressure of 0.4 MPa.

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In methanol manufacture process, Al_2O_3 and ZnO are often selected as the catalyst for methanol synthesis, which indicated that the methanol molecules has interaction with Al_2O_3 and ZnO molecules [13,14]. Inspired by this fact, Al_2O_3 and ZnO were selected as additives to the base CA membrane and used for separation of MTBE/methanol mixture in this study. It was also to explore the possibility of improving the separation performance by utilizing organic membrane filled with metal oxide particles.

2. Experimental

2.1. Materials

Cellulose acetate (CA: 39.6% acetyl content, average M_w = 50,000) was obtained from Wuxi Chemical Plant. ZnO, Al_2O_3, *N*,*N*-dimethylformamide (DMF) and methanol were purchased from Beijing Chemical Factory and MTBE was obtained from Weisi Chemical Company. Methanol, MTBE and DMF of analytical grade were directly used without any purification.

2.2. Membrane preparation

Pervaporation membrane was prepared by the phase-inversion method [15,16]. 8 g of CA was dissolved in 72 g of DMF in a flask. Then the flask was placed in a shaker with a 75 °C water bath for 12 h. A known amount of metal oxide particles was added into the solution and dispersed by ultrasound for 5 h, then the mixture was placed on a table for 5 h, allowing the mini bubbles to ascend and separate from the blend. About 10 g of blend was cast on a glass plate and spread with a rod to form a flat membrane. The membrane was stored at 20 °C for 24 h to allow the solvent to evaporate from the membrane. Finally, the membrane was removed from the glass plate. The resulting membrane was completely transparent and dense, with a thickness of about 25 μm. The membrane morphology was observed by a Scanning Electron Microscopy instrument (SEM, LEO1530), and the Raman spectroscopy of metal oxide in blend membrane was detected (RS, Renishaw, RM2000). The weight content of metal oxide in blend membrane was measured by a Thermal Gravimetric Analyzer (TGA, TA 2050).

2.3. Pervaporation experiment

Fig. 1 shows the experimental setup used for the pervaporation measurements. The membrane module is an annular chamber made of stainless steel, in which a membrane supported by a porous sintered stainless steel in the permeate side was mounted. The effective area of the membrane was 2.83×10^{-3} m^2. 2.5 L of a mixture of MTBE and methanol (31%, w/w) were placed into the tank and kept at a certain temperature with an electric heater. The feed liquid was pumped through the feed compartment of the membrane cell, where it came into direct contact with top layer of membrane surface. After then, it was circulated back to the tank, and methanol and MTBE permeated through the membrane under the force of vacuum. Vacuum on the permeate side was kept below 500 Pa and was monitored with a digital vacuometer. The permeate methanol and MTBE vapor was condensed into liquid at the membrane downstream side in a cold tube, which was cooled by liquid nitrogen. Before starting the vacuum pump, the feed liquid was circulated for 15 min to make the feed liquid fully contact and impregnate with the membrane. To minimize the effect of unsteady operation, one experiment point was last for 5 h. The permeate mixture was weighed by a balance and its composition was determined by a HP6890 gas chromatograph equipped with a thermal conductivity detector. Unless otherwise stated, the feed temperature was 40 °C. In one experiment point, about 3 g of mixture permeated through the membrane, the total weigh of feed liquid is about 2 kg, so within the 20 experimental points, the composition of feed liquid could be assumed constant. Each experiment point replicated for three times.

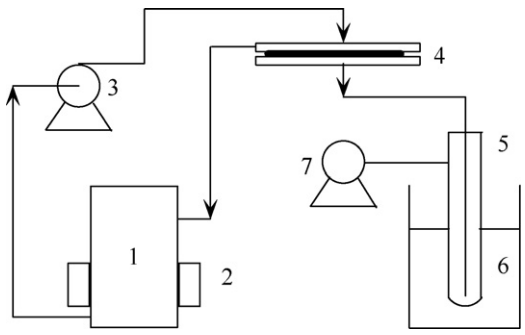

Fig. 1. Schematic diagram of experimental setup—1: feed tank; 2: electric heater; 3: pump; 4: membrane contactor; 5: cold trap; 6: liquid nitrogen tank; 7: vacuum pump.

The separation performance of pervaporation can be expressed by two factors: the flux J and separation factor α which are defined as follows:

$$J = \frac{m\delta}{St} \quad (1)$$

where the permeation time t is equal to 2.5 h in this work; the effective membrane surface area S is equal to 28.3 cm^2; m is the mass weight of the permeate mixture; and δ is the membrane thickness, which is equal to 25 μm that is determined by the SEM photos.

$$\alpha = \frac{y_1/x_1}{y_2/x_2} \quad (2)$$

where y_1 and y_2 are the methanol concentrations in the permeate mixture and feed, respectively; x_1 and x_2 are the MTBE concentration in the permeate mixture and feed.

3. Results and discussion

3.1. Membrane morphology

The morphologies of pure CA and CA filled with ZnO and Al_2O_3 are shown in Fig. 2(a) indicates the smooth surface of pure CA membrane, and Fig. 2(b) shows that the top and bottom of the pure CA membrane were dense layers, but there were some hollow spongy holes inside the membrane. Unlike the pure CA membrane, there were many protrusions on the surface of the blended CA membrane, which consisted of particles of metal oxide or their aggregates (Fig. 2(c) and (e)). The diameters of Al_2O_3 and ZnO aggregates were about 100 μm and 10 μm on the membrane surface, respectively. Furthermore, the metal oxide led to a denser membrane, evidenced by no spongy holes in the cross-section (Fig. 2(d) and (f)). The addition of metal oxide particles into the polymer solution resulted in a larger viscosity than of the pure polymer. The viscosity of blend would increase with the increase of mass content of metal oxide, which reduced the vaporation rate of DMF accordingly and a dense membrane was formed.

3.2. Raman spectra

The spectrum of ZnO, Al_2O_3 and blended membrane are shown in Fig. 3. The absorbance peaks at 416.94 cm^{-1} and 437.44 cm^{-1}

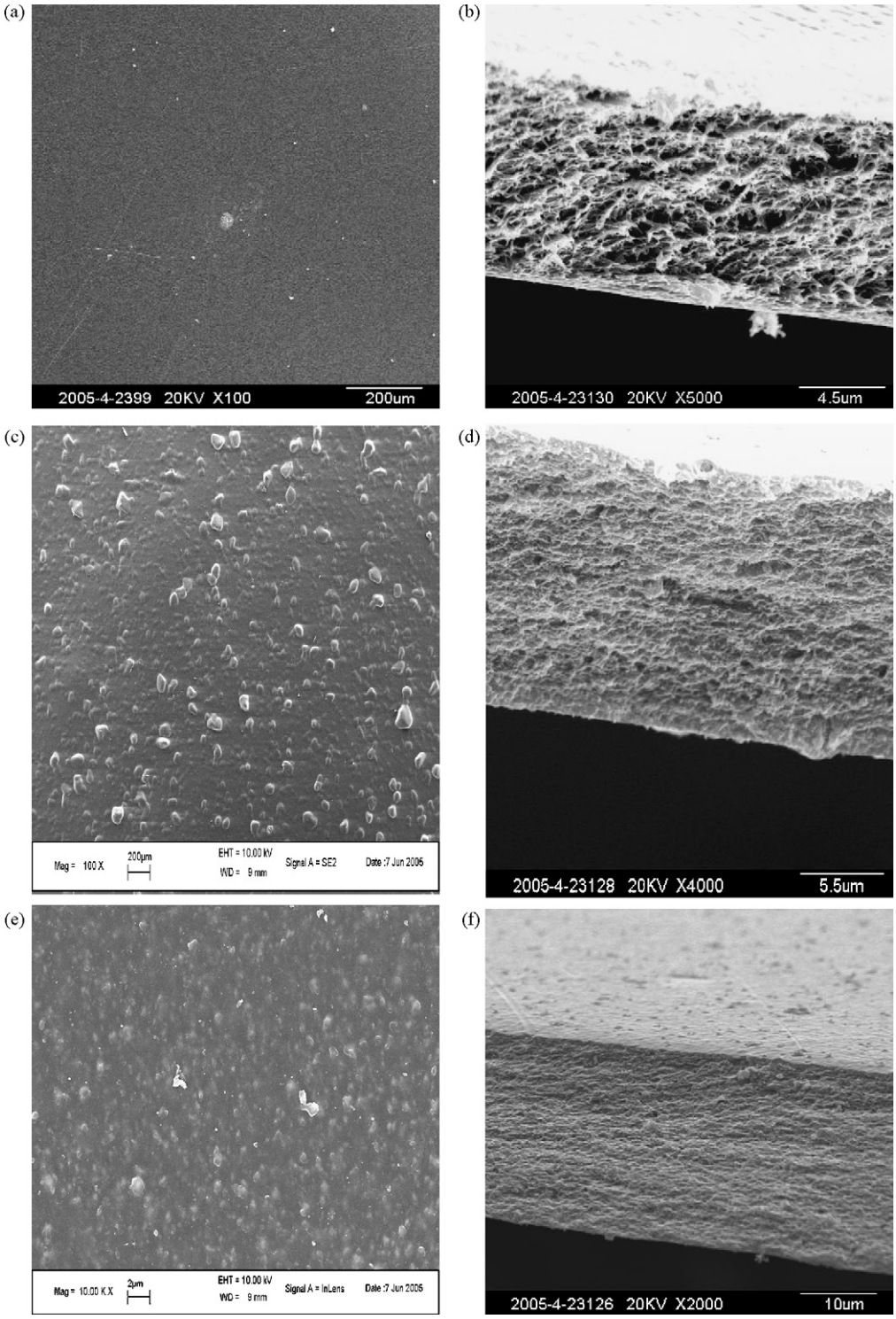

Fig. 2. Morphology of pure CA membrane and blended membrane: (a) surface of pure CA membrane; (b) cross-section of pure CA membrane; (c) surface of CA membrane filled with Al_2O_3; (d) cross-section of membrane filled with Al_2O_3; (e) surface of CA membrane filled with ZnO; (f) cross-section of membrane filled with ZnO.

are attributed to the Al–O band of Al_2O_3 and the Zn–O band of ZnO, respectively. The absorbance peaks at 656 cm^{-1} and 910 cm^{-1} correspond to the circle of CA molecules.

3.3. TGA curves of CA membrane filled with metal oxide particles

The TGA curves of blended membrane filled with Al_2O_3 metal oxide particles with 7.21 wt% are shown in Fig. 4 When the temperature was lower than 300 °C, the mass fraction decreased slowly. When the temperature was within 300–400 °C, the mass fraction of the membrane decreased rapidly, which indicated that the CA had decomposed into CO_2 and H_2O; when the temperature was higher than 550 °C, the mass remained constant, which showed that the residue was metal oxide. According to the mass of the residue, the mass fraction of metal oxide in the blended membrane can be obtained.

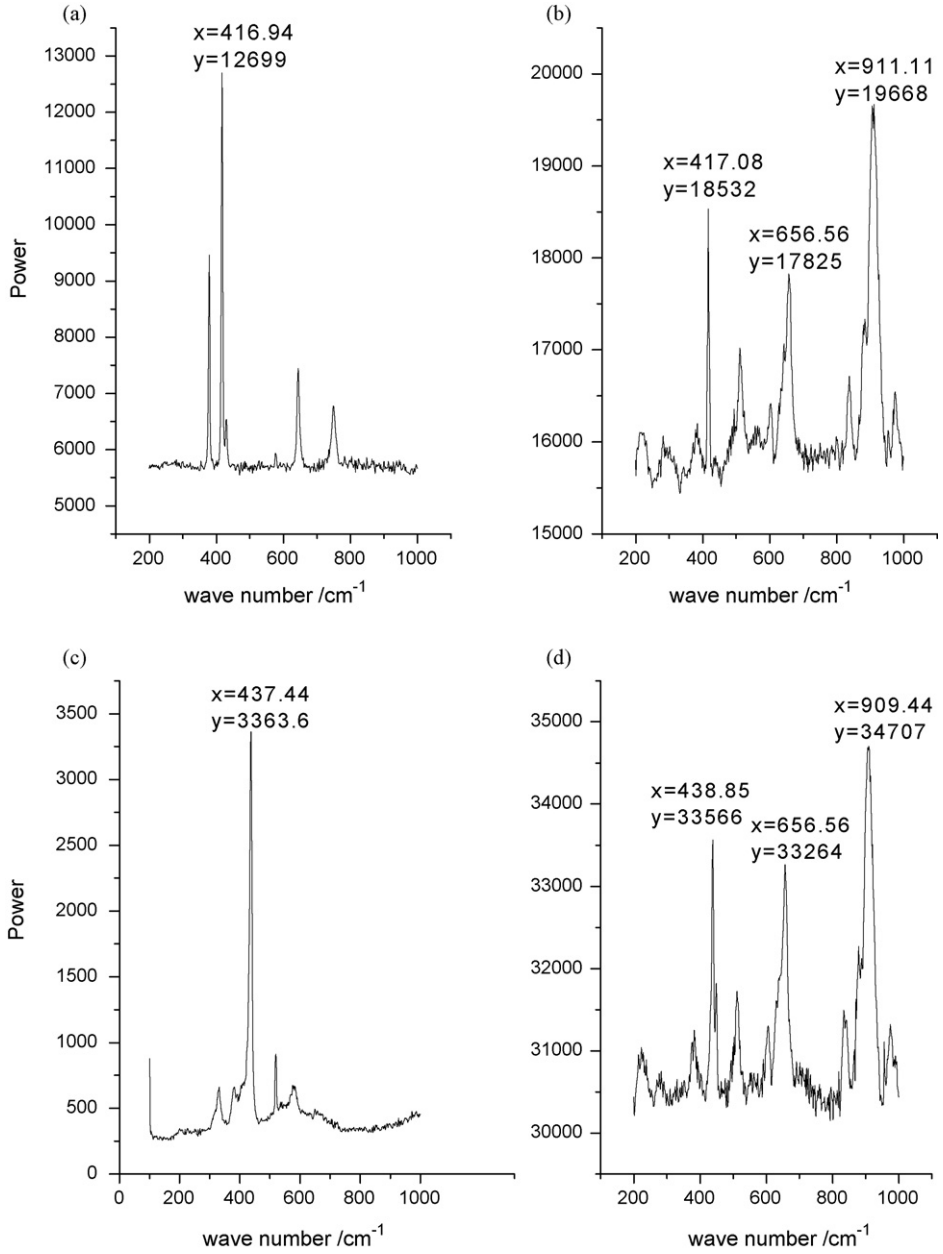

Fig. 3. Raman spectra of metal oxide and blended CA membrane: (a) standard spectrum of Al_2O_3 crystals; (b) spectrum of CA membrane filled with Al_2O_3 particles; (c) standard spectrum of ZnO crystals; (d) spectrum of CA membrane filled with ZnO particles.

3.4. Effect of mass fraction of Al_2O_3 on separation performance

The separation factors and flux of CA membrane filled with different mass fractions of Al_2O_3 are shown in Fig. 5 When the mass fraction of Al_2O_3 was 1.98%, the separation factors were 859.3, which was larger than the separation factor of pure CA membrane, 560.4. When the mass fraction of Al_2O_3 was 3.21%, the flux reached a maximum; when the mass fraction of Al_2O_3 was 1.98%, the flux was 2.50 kg/m^2 h, which was nearly twice that of pure CA, 1.27 kg/m^2 h. The adding of metal oxide particles made the membrane dense, which slowed down the diffusion of methanol and MTBE. However, the methanol molecules has interaction with the Lewis acid site on the surface of Al_2O_3 particles [17], as a result, the solubility of methanol in the CA membrane filled with metal oxide become larger than that in pure CA membrane. The product flux is determined by solubility and diffusion rate, in this study a greater increase of solubility and a relatively lower decrease of diffusion rate were believed to obtain with the increase of metal oxide in the membrane. When the metal oxide content was too high, there were some faults in the structure of the blended membrane, which decreased the separation efficiency.

In the figure, the error of experimental point was calculated by the data obtained through duplicating three times corresponding to one experimental condition. It was found that the real flux value was within 5% of the error of the average value of three groups of data.

3.5. Effect of mass fraction ZnO on separation performance

The flux of CA membrane filled with different mass fractions of ZnO is shown in Fig. 6. For the membrane filled ZnO, the solubility of methanol increased due to the strong interaction between

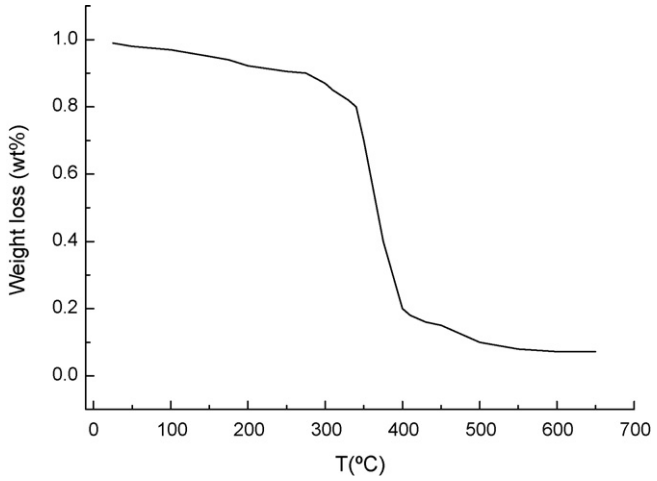

Fig. 4. TGA curves of CA membrane filled with Al_2O_3 metal oxide particles with weight 7.21%.

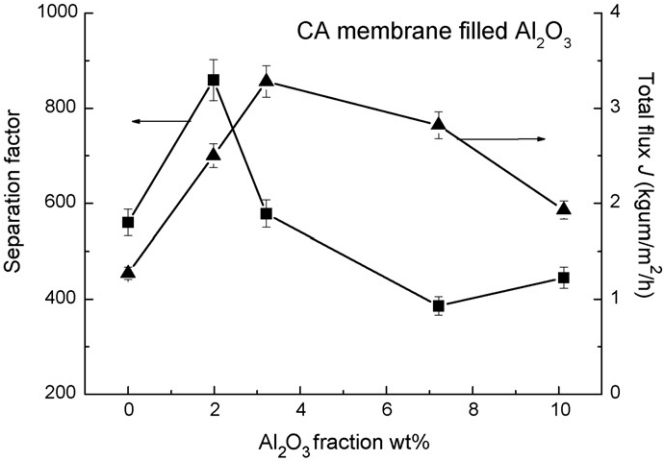

Fig. 5. Effect of Al_2O_3 weight fraction on separation performance.

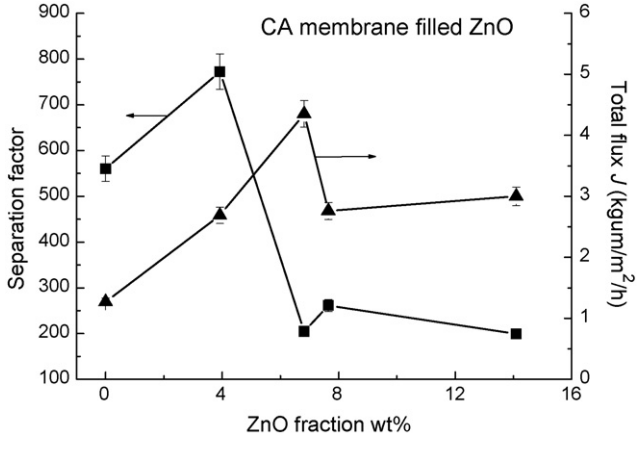

Fig. 6. Effect of ZnO weight fraction on separation performance.

methanol and the hydroxyl group on the surface of ZnO [18]. When the mass fraction of ZnO was 6.82%, the flux reached a maximum, which was nearly three and a half times that of pure CA. When the mass fraction of ZnO was 4.01%, the flux was twice that of pure CA. Thus, when the mass fractions of ZnO were 4.01%, both the separation factor and flux could be improved.

4. Conclusion

The addition of Al_2O_3 and ZnO particles into CA membrane at 1.98% and 4.01% (w/w), respectively improved both the permeation flux and separation factor of methanol/MTBE system. Comparing with pure CA membrane, the maximum flux of blended membrane filled with Al_2O_3 and ZnO improved 96.5% and 111.1%, respectively; the maximum separation factor of blended membrane filled with Al_2O_3 and ZnO improved 48.0% and 37.8%, respectively. Compared with previous work, the CA membrane filled with metal oxide is found to be inexpensive and easy to prepare.

Acknowledgements

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