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Pervaporation dehydration of ethanol by hyaluronic acid/sodium alginate two-active-layer composite membranes

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ABSTRACT

The composite membranes with two-active-layer (a capping layer and an inner layer) were prepared by sequential spin-coatings of hyaluronic acid (HA) and sodium alginate (NaAlg) on the polyacrylonitrile (PAN) support layer. The SEM showed a mutilayer structure and a distinct interface between the HA layer and the NaAlg layer. The coating sequence of two-active-layer had an obvious influence on the pervaporation dehydration performance of membranes. When the operation temperature was 80 °C and water concentration in feed was 10 wt.%, the permeate fluxes of HA/Alg/PAN membrane and Alg/HA/PAN membrane were similar, whereas the separation factor were 1130 and 527, respectively. It was found that the capping layer with higher hydrophilicity and water retention capacity, and the inner layer with higher permselectivity could increase the separation performance of the composite membranes. Meanwhile, effects of operation temperature and water concentration in feed on pervaporation performance as well as membrane properties were studied.

1. Introduction

Pervaporation, as a promising membrane-based separation technology for the dehydration of solvents, has undergone a rapid development in recent years. Solution–diffusion mechanism is proposed and widely accepted (Binning, Lee, Jennings, & Martin, 1961; Lonsdale, 1982) to elucidate the mass transfer of pervaporation process: selective sorption of feed species on the membrane surface, selective diffusion through the membrane and desorption into a vapor phase on the permeate side. Among these three steps, selective sorption and diffusion in membranes are often the rate-governing steps. At present, the composite membrane, which comprises a separation layer (active layer) and a support layer is the most commonly used configuration. Ideally, the separation layer of membranes should possess the surface with high sorption capacity and selectivity, and the bulk with low diffusion resistance and high diffusion selectivity. Materials for the separation layer of the one-active-layer pervaporation membranes have to bear these properties all-in-one, which limits the selection scope of materials. It is well known that the composite membranes assign the separation performance and the mechanical strength demands into the separation layer and the support layer individually. The performance can be highly improved by choosing the appropriate materials for the separation layer and the support layer. It is thus envisaged that if the similar strategy is adopted, the separation layer is further divided into the capping layer and the inner layer (two-active-layer) to intensify the adsorption and diffusion individually, as shown in Fig. 1, the selection scope of the materials for separation layer may be dramatically expanded and the separation performance may be improved in a much broader range, since the surface and bulk properties could be varied by the rational tuning of the capping layer and the inner layer.

Rational screening of hydrophilic materials for capping layer and inner layer is of great importance for the separation performance of two-active-layer membranes. Till now, several kinds of polymer-based materials have been employed in the dehydration process of ethanol–water aqueous solution by pervaporation. Young Moon, Pal and Huang (1999) prepared two-ply membranes by successive castings of NaAlg and CS solutions for the pervaporation dehydration of 95 wt.% ethanol–water mixture. When CS was selected as capping layer facing to the feed solution, the separation factors was 147, while that of the membranes with NaAlg facing to the feed solution was 1062. These results suggested that coating sequence had an obvious effect on membrane separation performance. In our previous study (Ding, Zhang, Jiang, Li, Ma, & Zhao, 2012), composite membranes with two-active-layer, HA and CS, were constructed

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Nomenclature

A	effective membrane area (m^2)
C_i	concentration of component i in the membrane (g/m^3)
J	permeation flux (g/m^2 h)
l	thickness of the active layer (m)
m_d	weight of the dry membrane (g)
m_s	weight of the swollen membrane (g)
P	permeability
Pi/l	permeance
p_{il}	partial pressure of component i in the permeate side
p_{i0}^{sat}	saturated vapor pressure of pure component i
Q	total mass of the permeate solution in time t (g)
t	time (h)
W_f, E_f	weight fractions of water and ethanol in the feed solution
W_p, E_p	weight fractions of water and ethanol in the permeate solution
W_M	weight fractions of water and ethanol in the membrane
x_{i0}^L	mole fraction of component i in the feed solution

Greek letters

α	selectivity
α_s	sorption selectivity
α_D	diffusion selectivity
β	separation factor
γ_{i0}^L	activity coefficient of component i in the feed solution

through alternative self-assembly and spin-coating. It was found that the separation factor of the HA/CS/PAN membrane (704) with CS as inner layer was remarkably higher than that of CS/HA/PAN membrane (104) with HA as inner layer. A probable explanation was HA layer had higher water sorption selectivity and CS layer had higher diffusion selectivity. In the above studies, the capping layer and the inner layer are fabricated from cationic polyelectrolyte and anionic polyelectrolyte, individually. Herein, we want to explore the separation performance of the two-active-layer membranes where the capping layer and the inner layer are both fabricated from anionic polyelectrolytes.

As one common hydrophilic carbohydrate polymer, sodium alginate (NaAlg), which is extracted from marine brown algae, has exhibited excellent performance as a pervaporation membrane material (Bhat & Aminabhavi, 2006, 2007; Kalyani, Smitha, Sridhar, & Krishnaiah, 2006; Kanti, Srigowri, Madhuri, Smitha, & Sridhar, 2004; Kumar Naidu, Sairam, Raju, & Aminabhavi, 2005; Kurkuri, Kumbar, & Aminabhavi, 2002; Kurkuri, Toti, & Aminabhavi, 2002; Magalad, Supale, Maradur, Gokavi, & Aminabhavi, 2010; Uragami & Saito, 1989). The carboxylic and hydroxyl groups play a crucial role in preferential water sorption and diffusion through the membranes (Yeom & Lee, 1998). Since alginate has the excellent permselectivity toward water, it may be the suitable material to offer higher separation performance (Huang, Pal, & Moon, 1999; Shi, Wang, Chen, Golemme, Zhang, & Drioli, 1998). As another common hydrophilic carbohydrate polymer, hyaluronic acid (HA) (Kim, Yoon, Lee, Kim, & Kim, 2004; Ma, Zhang, Jiang, Nie, & Liu, 2010; Tomihata & Ikada, 1997) has demonstrated high water sorption selectivity in ethanol aqueous solution and high water retention capacity (500 mL/g) due to a large number of hydroxyl groups and carboxyl groups. Therefore, HA may have potential to intensify the sorption/dissolution of water.

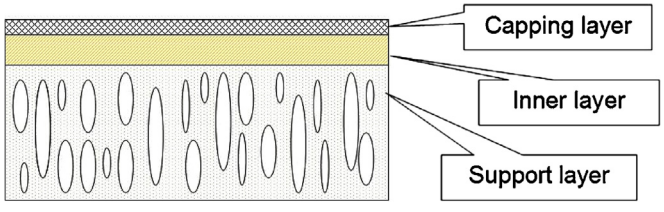

Fig. 1. Schematic structure of the two-active-layer composite membrane.

In this study, two-active-layer composite membranes were fabricated by sequential spin-coatings of HA and NaAlg on the PAN support layer. Effect of coating sequences and operation conditions on structure and performance variation of the two-active-layer membranes for dehydration of 90 wt.% ethanol–water mixture were explored.

2. Experiments

2.1. Materials

The flat-sheet ultrafiltration membrane, which had a molecular weight cut-off of 100,000 and was made up of PAN porous layer and polyethylene terephthalate nonwoven fabric substrate, was obtained from Shanghai MegaVision Membrane Engineering & Technology Co. Ltd. (Shanghai, China). NaAlg (viscosity of 1 wt.% aqueous solution at 20 °C: 0.02 Pa s) was purchased by Tianjin Guangfu Ltd. (Tianjin, China). HA (MW 1,200,000 Da, sodium salt) was obtained by Qufu Haixin Industrial Co. Ltd. (Qufu, China). Glutaraldehyde (GA; 25 wt.%), hydrochloric acid (HCl), calcium chloride and absolute ethanol were purchased from Tianjin Kewei Ltd. (Tianjin, China). Deionized water was used in all experiments.

2.2. Membrane preparation

The flat-sheet PAN membrane was immersed into deionized water for 2 days to remove glycerol on the membrane surface, and air-dried at room temperature. The NaAlg solution was prepared by dissolving NaAlg into deionized water with stirring for 2 h, and then kept aside for 1 h to remove the bubble in the solution. HA solution was prepared by dissolving hyaluronic acid into deionized water with stirring for 2 h, and then added GA solution to initiate cross-linking and adjusted pH to about 4.5 with 0.01 M HCl. After half an hour, stirring was stopped and the sample was kept aside for degassing

Membranes were prepared by two-step spin-coating. NaAlg solution was firstly coated on PAN support layer by spin-coater and dried at room temperature. Then the NaAlg membrane was cross-linked by immersing into the $CaCl_2$ aqueous solution for 10 min and then rinsed with deionized water and air-dried. After that, the second coating was carried on. HA solution was spin-coated on the membrane surface and air-dried. The resultant membrane was denoted as HA/Alg(X)/PAN, where X (unit: mol/L) meant Ca^{2+} concentrations of solutions that were used to cross-link NaAlg membrane. Similarly, the Alg(X)/HA/PAN membrane was prepared by sequential spin-coatings of first hyaluronic acid and then sodium alginate.

2.3. Characterization

FT-IR spectra for each layer of the composite membrane were acquired by using a Nicolet-560 Fourier transform infrared spectrometer with scan range of 4000–600 cm^{-1}.The static water contact angles of the membrane surfaces were measured by contact angle goniometer (JC2000C, Powereach Co., Shanghai, China) for the investigation of the hydrophilic/hydrophobic property. The contact angle of each membrane sample was measured ten times

at different locations. The cross-section morphology of membranes was observed by a Nanosem 430 field emission scanning electron microscope (FESEM). Samples were freeze-fractured in liquid nitrogen and then were sputtered with gold prior to scanning.

2.4. Swelling and sorption measurement

The swelling degree of homogenous HA and NaAlg membranes was measured by immersing membranes into deionized water and 90 wt.% ethanol–water mixture for 24 h. Then the membranes were carefully wiped off the surface liquid with tissue paper. The mass swelling degree(MSD) was calculated as follows:

$$MSD = \frac{Ms - Md}{Md} \times 100\% \quad (1)$$

where, M_s and M_d are the mass of the swollen and dry membranes. The adsorbed liquid in membranes was desorbed by an apparatus with a vacuum pump and condensed in a liquid nitrogen trap, which was analyzed by gas chromatography. All the experiments were repeated three times.

Sorption selectivity (α_s) was calculated by Eq. (2):

$$\alpha_s = \frac{W_M/E_M}{E_f/E_f} \quad (2)$$

where W_M and E_M are the weight fractions of water and ethanol in the membrane, respectively; W_f and E_f are the weight fractions of water and ethanol in the feed solution, respectively.

According to solution–diffusion theory, diffusion selectivity (α_D) was calculated by Eq. (3):

$$\alpha_D = \frac{\alpha}{\alpha_s} \quad (3)$$

where α is the separation factor of single-active-layer HA/PAN or CS/PAN membranes.

2.5. Pervaporation experiment

Pervaporation experiments were carried out for dehydration of ethanol–water mixtures. The pervaporation apparatus were described in our previous study (Peng, Lu, Hu, Wu, & Jiang, 2005). The effective surface area was 25.6 cm^2. The concentrations of the feed solution and the permeate were measured by gas chromatography (USA Agilent 4890). The permeate flux (J) and the separation factor (β) was calculated as follows:

$$J = \frac{Q}{At} \quad (4)$$

$$\beta = \frac{W_p/E_p}{W_f/E_f} \quad (5)$$

where Q is the mass of the permeate collected in time t, and A is the effective membrane area. W_p and E_p are the weight fractions of water and ethanol in the permeate solution, respectively; W_f and E_f are the weight fractions of water and ethanol in the feed solution, respectively.

Generally, permeate flux and separation factor are affected strongly by operation conditions (such as temperature and water concentration in the feed), which change vapor pressure difference between two sides of membrane (driving force), as well as membrane intrinsic properties. In order to investigate the intrinsic properties of membranes with variation of feed concentration and temperature, effect of the driving force should be removed. Baker, Wijmans, and Huang (2010) presented a method in term of permeability (P_i), permeance (P_i/l) and selectivity (α), which normalized the driving force. They were used to evaluate variations of membrane properties with operation conditions.

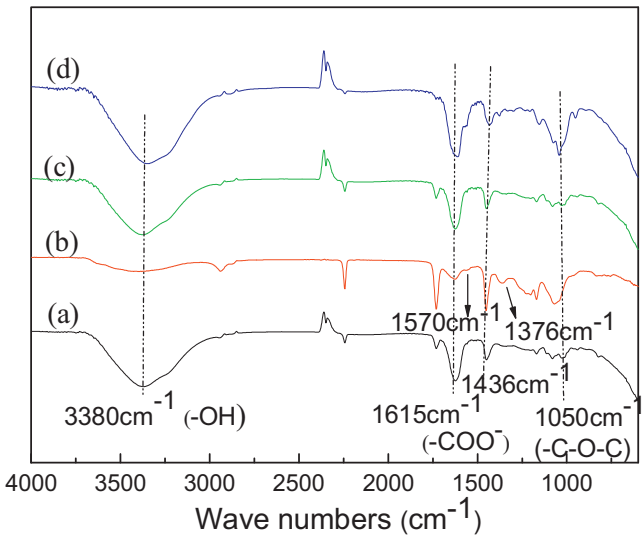

Fig. 2. FTIR spectra of (a) Alg(0.5)/PAN; (b) HA/PAN; (c) Alg(0.5)/HA/PAN; and (d) HA/Alg(0.5)/PAN membranes

The component flux can be written as:

$$J_i = \frac{P_i}{l}(\gamma_{i0}^L x_{i0}^L p_{i0}^{sat} - p_{il}) \quad (6)$$

where for component i, J_i is the partial permeate flux, P_i is the permeability, l is the thickness of the active layer in the composite membranes, γ_{i0}^L is the activity coefficient in the feed solution, x_{i0}^L is the mole fraction in the feed solution, p_{i0}^{sat} is the saturated vapor pressure of pure component i, p_{il} is the partial pressure in the permeate vapor. It is implicit in Eq. (6) that the concentration polarization effect is negligible. Therefore the permeance (P_i/l) was calculated as follows:

$$\frac{P_i}{l} = \frac{J_i}{(\gamma_{i0}^L x_{i0}^L p_{i0}^{sat} - p_{il})} \quad (7)$$

Since the vacuum pump is used in the permeate side and the vapor pressure is approximately vacuum, p_{il} can be considered as zero. The activity coefficient and the pure component vapor pressure can be calculated by computer simulation programs (ChemCad, HYSYS, ProSim or Aspen Plus).

The selectivity (α) is defined as the ratio of the permeability or the permeance of two components:

$$\alpha_{ij} = \frac{P_i}{P_j} = \frac{P_i/l}{P_j/l} \quad (8)$$

3. Results and discussion

3.1. Membrane characterization

3.1.1. FT-IR

Fig. 2 shows FT-IR spectra of Alg(0.5)/PAN, HA/PAN, Alg(0.5)/HA/PAN and HA/Alg(0.5)/PAN membranes, respectively. The spectra of Alg(0.5)/PAN, HA/PAN, Alg(0.5)/HA/PAN and HA/Alg(0.5)/PAN membranes showed the same peak at 3380 cm^{-1} which was ascribed to –OH, 1050 cm^{-1} which was ascribed to C–O–C (Ma et al., 2010), 1615 cm^{-1} and 1436 cm^{-1} which were ascribed to asymmetric COO^- stretching vibration and symmetric COO^- stretching vibration (Papageorgiou, Kouvelos, Favvas, Sapalidis, Romanos, & Katsaros, 2010). In addition, the bending vibration of the N–H (1570 cm^{-1}) and $-CH_3$ (1376 cm^{-1}) were presented in the spectra of HA/PAN and HA/Alg(0.5)/PAN, respectively. It implied that HA was successfully deposited on

Table 1
Water contact angles of Alg(*X*)/HA/PAN, Alg(*X*)/PAN, HA/Alg(*X*)/PAN and HA/PAN membranes.

Membrane	Contact angle (°)	Membrane	Contact angle (°)
Alg(0)/HA/PAN	52 ± 3	Alg(0)/PAN	51 ± 3
Alg(0.02)/HA/PAN	34 ± 2	Alg(0.02)/PAN	33 ± 2
Alg(0.1)/HA/PAN	24 ± 1	Alg(0.1)/PAN	25 ± 2
Alg(0.5)/HA/PAN	23 ± 1	Alg(0.5)/PAN	23 ± 1
HA/Alg(0)/PAN	37 ± 2	HA/PAN	36 ± 2
HA/Alg(0.02)/PAN	34 ± 2	–	–
HA/Alg(0.1)/PAN	33 ± 2	–	–
HA/Alg(0.5)/PAN	33 ± 2	–	–

Table 2a
The swelling behavior of HA and NaAlg homogenous membranes in 90 wt.% ethanol–water mixture and water.

	Degree of swelling	
	90 wt.% ethanol–water	Water
HA	0.06	41
NaAlg	0.03	0.64

HA/PAN and HA/Alg(0.5)/PAN. Meanwhile, the absorption peak of Alg(0.5)/HA/PAN was similar to that of Alg(0.5)/PAN which was also indicated that NaAlg was successfully deposited on Alg(0.5)/HA/PAN and Alg(0.5)/PAN.

3.1.2. SEM

Fig. 3 shows SEM cross-section images of Alg(0.5)/PAN, HA/PAN, Alg(0.5)/HA/PAN and HA/Alg(0.5)/PAN membranes, respectively. It was indicated that the active layer with a thickness about 500 nm was uniformly and tightly deposited on the porous PAN support layer. The cross-section of Alg(0.5)/HA/PAN and HA/Alg(0.5)/PAN membranes in Fig. 3(c and d) clearly shows the two-active-layer structure and a distinct interface between those two layers. The thickness of capping layers of HA/Alg/PAN and Alg/HA/PAN membranes was about 150 nm, while the thickness of inner layers was about 400 nm.

3.1.3. Water contact angle

Table 1 shows water contact angles of Alg(*X*)/HA/PAN, Alg(*X*)/PAN, HA/Alg(*X*)/PAN and HA/PAN membranes. It was observed that with the increase of Ca^{2+} concentrations (*X*) in the aqueous solutions that used to crosslink NaAlg layer, the contact angle of Alg(*X*)/HA/PAN and Alg(*X*)/PAN membranes became smaller, indicating that hydrophilicity was enhanced by Ca^{2+} crosslinking. When *X* value was the same, contact angles of Alg(*X*)/HA/PAN and Alg(*X*)/PAN membranes were similar, which indicated that alginic acid layer was completely deposited. Similarly, contact angles of HA/Alg(*X*)/PAN and HA/PAN membranes proved that HA was also completely deposited on membranes.

3.2. Pervaporation studies

3.2.1. Swelling, sorption and diffusion characteristics

The equilibrium sorption percentage of crosslinked HA and NaAlg homogenous membranes, which were cross-linked by glutaraldehyde and 0.5 M Ca^{2+} respectively, were investigated and results are shown in Table 2a. Both HA and Alg membranes suffered much less swelling in 10 wt.% water–ethanol mixture than in water, which meant that the membranes were stable for pervaporation under low water concentration. Although Ca^{2+} cross-linked Alg layer showed higher hydrophilicity, HA swelled more evidently than Alg in both water and the feed solution. The swelling degree of polymer in various solvents was determined not only by the polymer–solvent affinity but also its spatial structure.

Table 2b
The sorption and diffusion behavior of HA and NaAlg homogenous membranes in 10 wt.% water–ethanol mixture.

	C_i (10^{-2} g/g)		α_s	D_i (10^{-12} m^2/s)		α_D
	Water	Ethanol		Water	Ethanol	
HA	5.41	0.59	83	1.75	1.12	1.6
NaAlg	1.42	1.58	8.1	3.73	0.05	91.1

The three dimensional cross-linking of alginate acid chains by Ca^{2+} can effectively suppress the swelling. The extended chains of HA with lower crosslinking degree in the solvent lead to a looser network, which can be accessed by more solvent molecules.

Sorption selectivity indicated the affinity of the membrane toward the components to be separated. The sorption amount of water and ethanol and the sorption selectivity of HA and NaAlg in the feed (10 wt.% water–ethanol mixture) are also shown in Table 2b. A big difference in the sorption amount with respect to water and ethanol can be observed which indicated that both the HA and NaAlg had high affinity toward water. And the HA ($\alpha_s = 83$) exhibited much higher sorption selectivity than that of NaAlg ($\alpha_s = 8.1$).

To discriminate the effects of solubility and diffusivity on permeability, diffusion selectivity was calculated by Eq. (3). The flux and separation factor of Alg/PAN one-active-layer composite membranes were 925 g/m^2 h and 738, while those of HA/PAN membranes were 1705 g/m^2 h and 130. It showed that diffusion selectivity of Alg (α_D = 91.1) was higher than that of HA (α_D = 1.6). It can be explained by concentration-averaged diffusion coefficients ($\overline{D_i}$) of water and ethanol in HA and NaAlg layer in the active layer of HA/PAN and Alg(0.5)/PAN composite membrane. According to the Fick's law, when the concentration profile is assumed linear along the diffusion length in the active layer for simplicity,

$$\overline{D_i} = \frac{J_i l}{C_i} \tag{9}$$

the concentration-averaged diffusion coefficients $\overline{D_i}$ can be calculated by Eq. (9). Diffusion coefficient of water molecules were higher both in HA and NaAlg, while diffusion coefficients of ethanol molecules in crosslinked alginate were smaller than that in HA. One reason was that the water molecules (dynamic diameter, 0.26 nm) were smaller than ethanol molecules (dynamic diameter, 0.52 nm). Furthermore, large free volume voids of HA in the feed, indicated by the swelling degree, promoted the diffusion coefficient of ethanol. But the voids was too large to identify water and molecules, thus, the diffusion coefficient of ethanol in HA was much higher than that in alginate. In a word, HA exhibited much higher water sorption selectivity than that of NaAlg, whereas NaAlg exhibited higher water diffusion selectivity than that of HA.

3.2.2. Effect of the cross-linking of alginate layer on the separation performance

Ca^{2+} cross-linking was a common method to improve alginate membrane performance. Fig. 4 shows the effect of Ca^{2+} concentration on pervaporation performance of Alg(*X*)/PAN, Alg(*X*)/Alg(*X*)/PAN, Alg(*X*)/HA/PAN and HA/Alg(*X*)/PAN membranes for dehydration of 90 wt.% ethanol–water mixture at 80 °C. The permeate flux of those four membranes displayed the similar trend with the increase of Ca^{2+} concentration. Membranes made of alginate which was not cross-linked by Ca^{2+} exhibited lower flux and separation factor, compared with cross-linked membranes. With the increase of Ca^{2+} concentration, both of the hydrophilicity and the crosslinking degree were increased, which improved the permselectivity of the membranes. Thus separation factors of these membranes were all increased.

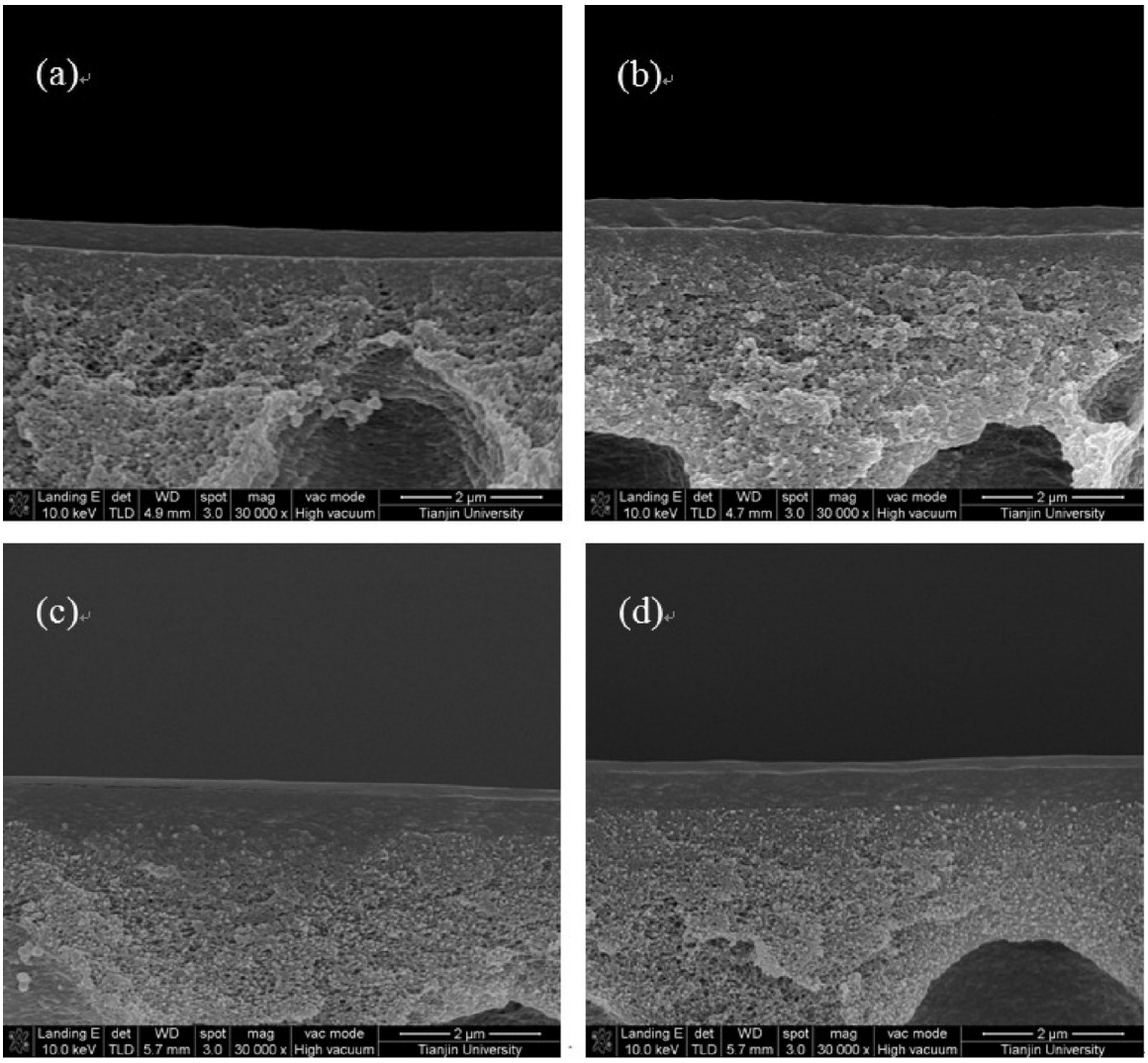

Fig. 3. SEM images of cross-section: (a) Alg(0.5)/PAN; (b) HA/PAN; (c) Alg(0.5)/HA/PAN; and (d) HA/Alg(0.5)/PAN. Scale: 2 μm.

3.2.3. Effect of coating sequences on the separation performance

Separation performance of various composite membranes is shown in Fig. 4. Comparison between the separation performance of HA/Alg/PAN and Alg/Alg/PAN membranes showed that HA/Alg/PAN possessed a higher separation factor, while their fluxes were similar. It showed that HA with high water sorption selectivity and water retention capacity was more suitable as the capping layer than alginate. When it was used as capping layer, more water was adsorbed by HA layer, which increased the driving force of water diffusion through the membranes. It can be

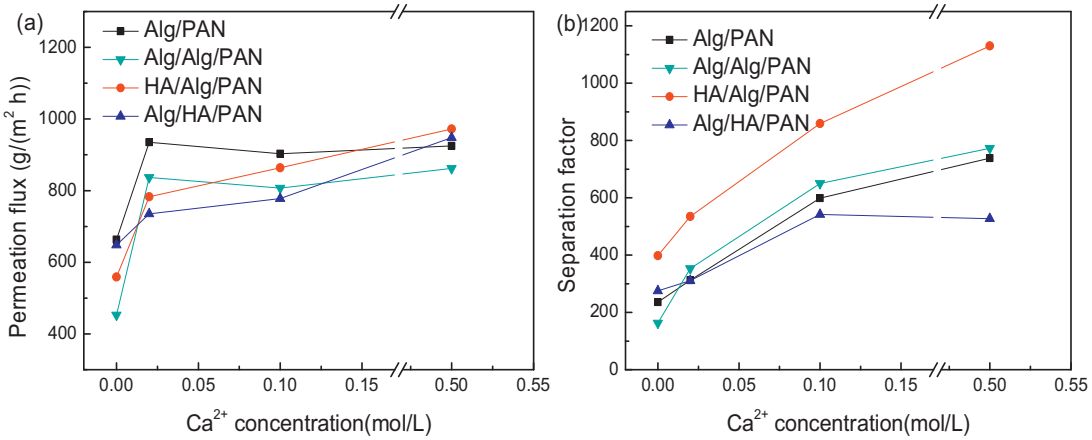

Fig. 4. Effect of Ca^{2+} concentration on pervaporation performance of membranes, Alg/PAN, Alg/Alg/PAN, Alg/HA/PAN and HA/Alg/PAN, for dehydration of 90 wt.% ethanol–water mixture at 80 °C.

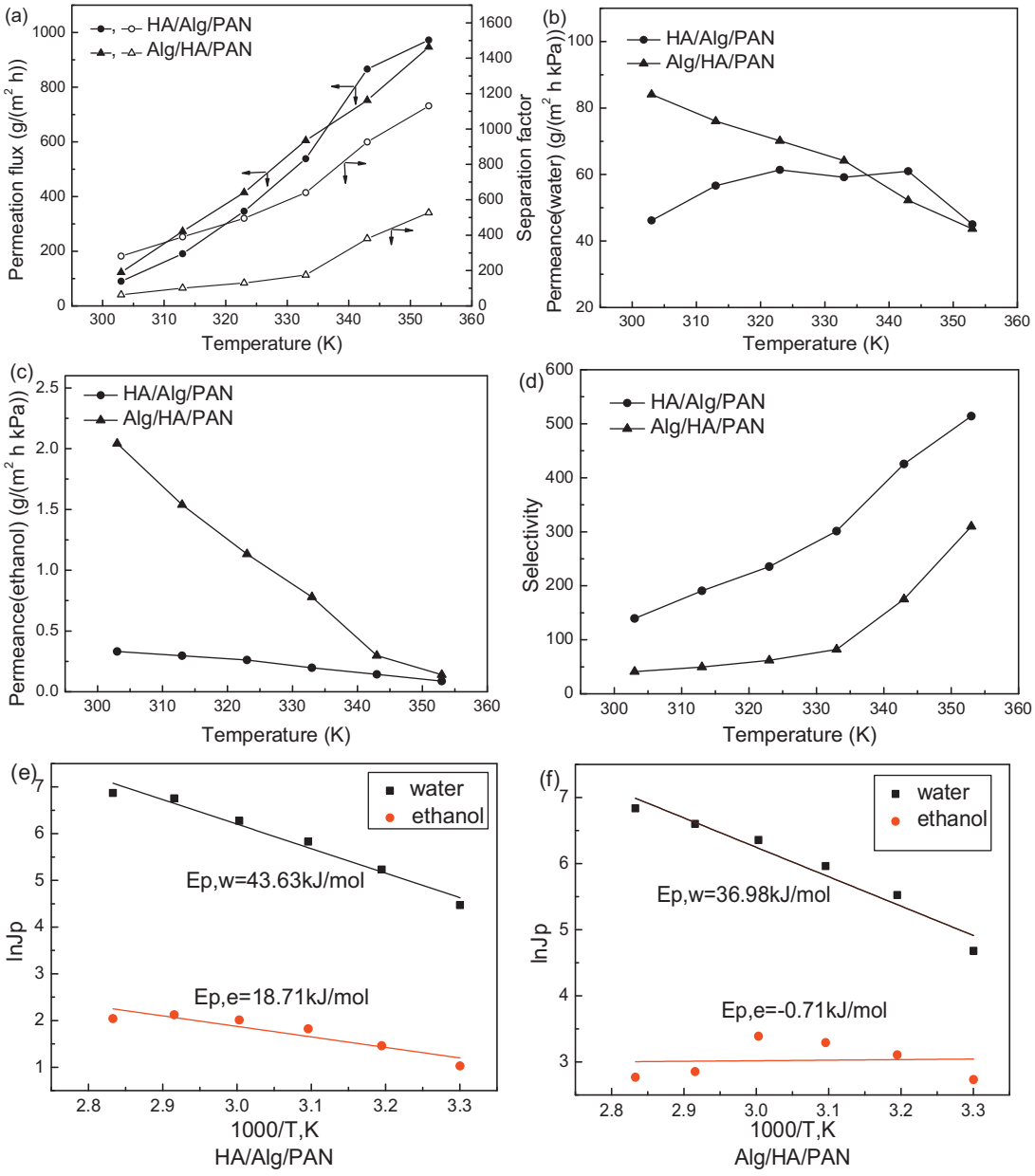

Fig. 5. Effect of operation temperature on pervaporation performance of HA/Alg/PAN and Alg/HA/PAN membranes for dehydration of 90 wt.% ethanol–water mixture. (a) Effect of operation temperature on permeation flux and separation factor of HA/Alg/PAN and Alg/HA/PAN membranes. (b) Effect of operation temperature on water permeance of HA/Alg/PAN and Alg/HA/PAN membranes. (c) Effect of operation temperature on ethanol permeance of HA/Alg/PAN and Alg/HA/PAN membranes. (d) Effect of operation temperature on selectivity of HA/Alg/PAN and Alg/HA/PAN membranes. (e) Arrhenius plots of permeation flux for separation of ethanol–water mixture by the HA/Alg/PAN membrane. (f) Arrhenius plots of permeation flux for separation of ethanol–water mixture by the Alg/HA/PAN membrane.

concluded that materials as capping layer should possess higher hydrophilicity and larger sorption capacity to intensify solution process.

Comparison between the separation performance of Alg/HA/PAN and Alg/Alg/PAN membranes showed that Alg/Alg/PAN after crosslinked possessed a higher separation factor, while their fluxes were similar. It showed that alginate was more suitable as the inner layer than HA. Crosslinked alginate had higher diffusion selectivity than that of HA. When it was used as inner layer, the membranes possessed high separation factor, which proved that materials as inner layer should possess higher diffusion selectivity and small swelling degree.

Separation performance of HA/Alg/PAN and Alg/HA/PAN two-active-layer composite membranes was studied to verify the validity of the selection rules. It was found that the separation factor of HA/Alg/PAN was higher remarkably than that of Alg/HA/PAN membranes. HA/Alg(0.5)/PAN membrane possessed a separation factor of 1130 and Alg(0.5)/HA/PAN membrane possessed a separation factor of 527, while their permeate fluxes were 972 g/m^2 h and 948 g/m^2 h respectively. This further proved that capping layer with higher hydrophilicity and water capacity, and inner layer with higher permselectivity could increase the separation performance of the composite membranes. Meantime, compared with our previous study, HA/Alg(0.5)/PAN membrane with Alg as the inner layer have higher separation factor(1130) than that of HA/CS/PAN(704) which further verified that Alg have higher diffusion selectivity than that of CS.

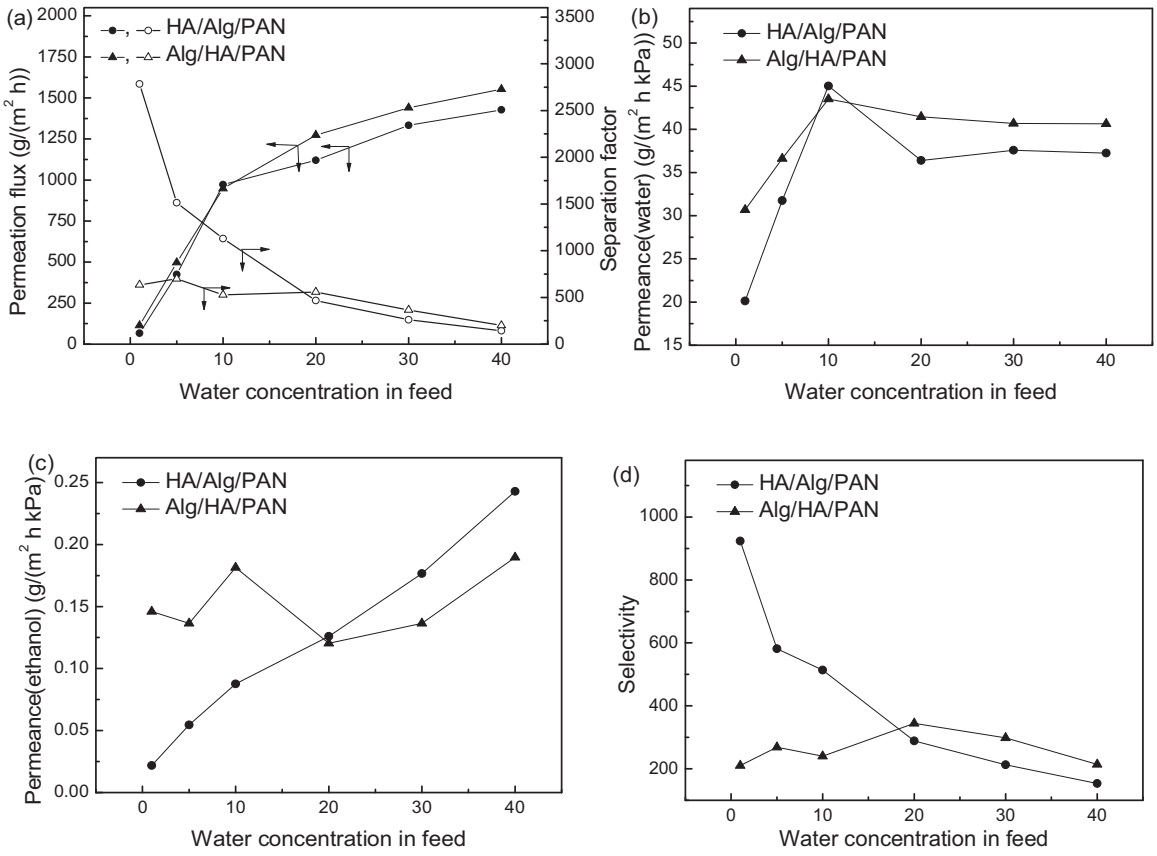

Fig. 6. Effect of water concentration in feed on pervaporation performance of HA/Alg/PAN and Alg/HA/PAN membranes for dehydration of ethanol–water mixtures containing 1 wt.%, 5 wt.%, 10 wt.%, 20 wt.%, 30 wt.% and 40 wt.% water at 80 °C. (a) Effect of water concentration on permeation flux and separation factor of HA/Alg/PAN and Alg/HA/PAN membranes. (b) Effect of water concentration on water permeance of HA/Alg/PAN and Alg/HA/PAN membranes. (c) Effect of water concentration on ethanol permeance of HA/Alg/PAN and Alg/HA/PAN membranes. (d) Effect of water concentration on selectivity of HA/Alg/PAN and Alg/HA/PAN membranes.

3.2.4. *Effect of operation temperature on the separation performance*

Operation conditions had a remarkable influence on flux and separation factor, and its variation not only changed the driving force of species permeating through membranes, but also the intrinsic properties of membranes. Fig. 5 shows effect of operation temperature on pervaporation performance of HA/Alg(0.5)/PAN and Alg(0.5)/HA/PAN membranes for dehydration of 90 wt.% ethanol–water mixture. With increasing temperature, both flux and separation factor of two membranes went up markedly (as shown in Fig. 5 (a)). However, the separation factor of HA/Alg/PAN was higher than that of Alg/HA/PAN at all the temperature point, while fluxes of these two membranes were similar.

The flux was mainly affected by ethanol and water vapor pressure (driving force) and membrane properties. With the increase of temperature, ethanol and water vapor pressure increased and the permeating driving force was enhanced, which was favorable to increase of flux. In order to study the effect of temperature on membrane intrinsic properties, driving force normalized permeance and selectivity are presented in Fig. 5(b–d). It could be found that water and ethanol permeances of Alg/HA/PAN membrane varied in a wider range than those of HA/Alg/PAN, indicating that properties of Alg/HA/PAN membranes were more temperature-depended. The dependence of permeation flux on temperature could be expressed by Arrhenius equation (Eq. (10)) and the apparent activation energy could be obtained by Eq. (10).

$$J_p = A_p \exp\left(-\frac{E_p}{RT}\right) \quad (10)$$

where A_p, J_p, E_p, R and T are the pre-exponential factor, permeation flux, apparent activation energy, gas content and feed temperature, respectively.

The Arrhenius plots of $\ln J_p$ versus $1000/T$ for water and ethanol are shown in Fig. 5(e and f). A linear relationship was observed, indicating the permeability followed the Arrhenius law. With the temperature ranging from 303 to 353 K, the apparent activation energy for water in HA/Alg(0.5)/PAN membrane and Alg/HA/PAN membrane were 43.63 kJ/mol and 36.98 kJ/mol, respectively. Simultaneously, the apparent activation energy for ethanol in HA/Alg(0.5)/PAN membrane and Alg/HA/PAN membrane were 18.71 kJ/mol and −0.71 kJ/mol, respectively. It could be found that the apparent activation energy for water and ethanol in HA/Alg(0.5)/PAN membrane were larger than that in Alg/HA/PAN membrane. Therefore, with the increase of temperature, the increasing rate of water flux and ethanol flux in HA/Alg(0.5)/PAN membrane were greater than that in Alg/HA/PAN membrane. So the data of selectivity showed that the HA/Alg/PAN membrane was more advantageous than that of Alg/HA/PAN membrane for dehydration of 90 wt.% ethanol–water mixture.

3.2.5. *Effect of water concentration in feed on the separation performance*

Fig. 6 shows effect of water concentration in feed on pervaporation performance of HA/Alg(0.5)/PAN and Alg(0.5)/HA/PAN membranes for dehydration of ethanol–water mixtures containing 1 wt.%, 5 wt.%, 10 wt.%, 20 wt.%, 30 wt.% and 40 wt.% water at 80 °C. With increasing water concentration in feed, fluxes of both membranes increased and separation factors decreased, which resulted

from enhanced swelling with increasing water concentration. Driving force normalized permeance and selectivity are presented in Fig. 6(b–d). It was shown that permeances of water and ethanol increased remarkably, suggesting that membrane became more relaxed with the increase of water concentration and was favorable to feed species through membrane.

When water concentration was below 20 wt.%, water selectivity of HA/Alg/PAN was higher than that of Alg/HA/PAN; When water concentration was equal to or above 20 wt.%, reverse. It was probably because the swelling of HA capping layer increased with the increase of water concentration, resulting in the decrease of selectivity. So HA/Alg/PAN membranes were advantageous for dehydration of ethanol–water solution with low water concentration, while Alg/HA/PAN membranes were advantageous for high water concentration, because of better anti-swelling property of Ca^{2+} cross-linked NaAlg layers.

4. Conclusion

The two-active-layer composite membranes, which comprise the capping layer and the inner layer, were prepared by sequential coating of HA and NaAlg on the PAN support layer and utilized for pervaporation dehydration of ethanol–water mixtures. It was shown that membranes with different coating sequences had an obvious difference in the dehydration performance. Under the operation condition of 80 °C and 10 wt.% water concentration in feed, HA/Alg/PAN membrane possessed a separation factor of 1130 and Alg/HA/PAN membrane possessed a separation factor of 527, while the permeate fluxes of both membranes were similar. It suggested that materials with higher hydrophilicity and larger sorption capacity could be selected for constructing the capping layer to intensify solution process, while materials with less diffusion resistance and high diffusion selectivity could be used for constructing the inner layer to enhance the diffusion process.

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