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The Study on Pervaporation Behaviors of Dilute Organic Solution Through PDMS/PTFE Composite Membrane

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Abstract As an energy-efficient alternative to distillation, pervaporation has been widely combined with fermentation to remove organic compounds from their dilute solutions in a fermentation broth. In this work, the organic permselective composite membrane is prepared by coating polydimethylsiloxane (PDMS) cross-linked with n-heptane on the substrate of polytetrafluoroethylene(PTFE) membrane. The separation behavior is studied in different dilute organic solutions, which include acetone dilute solution, butanone dilute solution, cyclohexanone dilute solution, ethanol dilute solution, isopropanol dilute solution, n-butyl alcohol dilute solution, acetic acid dilute solution, and ethyl acetate dilute solution. Most of these solutions are main reaction products or by-products from fermentation process. The effects of solubility of organics in the membrane, molecular weight, and polarity of the organics on the pervaporation performance are investigated. The effects of operating temperature and organic concentration in the feed solutions on the performance of composite membrane are studied as well. The experimental results show that molecular volume has less influence than solubility and molecular polarity for these organic solvent. The selectivity of PDMS membrane to ethyl acetate is relative high due to good solubility and diffusion of ethyl acetate molecules in polymer.

Keywords Pervaporation · Dilute organic solution · Molecular volume · Molecular polarity · Solubility

Introduction

In last decades, pervaporation (PV) has been established as a promising membrane technology that is potentially useful in such applications as the dehydration of organic compounds, the removal/recovery of organic compounds from aqueous solutions and the separation of close-boiling organic mixtures (e. g., structural isomers) and azeotropic mixtures [1]. With the

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development of pervaporation technology, the combination of PV and other unit operation has attracted more and more attention. Among these combinations, PV-distillation and PV-reaction hybrid processes are already applied in industrial practices [2]. PV applications in bio-process are also reported [3], such as PV-fermentation, which utilize PV to remove main fermentation reaction products or by-products. Cho and Hwang [4] studied the integration of continuous fermentation and membrane separation, increased ethanol productivity by 10–20%. O' brien and Craig [5] coupled a continuous yeast fermentation system with a PV membrane system to recover an ethanol enriched stream from the fermentation broth continuously, in which the PV module is consistently producing an ethanol enriched (~20–30%) permeate while maintaining the ethanol content in the fermentor at a level of 4–6%. Since PV technology is widely used to separate the organics from fermentation broth, where the organic contents in the feed is generally low, it is important to study the pervaporation behaviors of dilute organic solution through membrane.

Most of PV membranes are composite ones, which consist of a selective dense top layer and a porous support layer. Usually the dense layer plays a dominant role in realizing selective separation of organics, and these organics-permselective ones are mainly polymeric membranes. One of the commonly used polymeric materials for organic separation is polydimethylsiloxane (PDMS), also known as silicone rubber, which has an alternating –O–Si–O– unit structure and has very good stability in operation [6, 7]. This membrane has very good processing properties and is suitable for manufacturing ultrathin composite membranes. The selectivity of PDMS for organics is higher than that for water. Even in cases where PDMS exhibits moderate selectivity, this material can still meet the requirements of most applications [8–10].

The support layer of composite membrane mainly serves to increase the mechanical strength of the membrane. Polytetrafluoroethylene (PTFE) is attractive in membrane applications due to its superior chemical resistance, good thermal stability, and high mechanical strength. Because of its poor surface hydrophilicity and adhesive compatibility to other polymer, a PTFE membrane with micrometer pores is an excellent hydrophobic support for the removal of organics from aqueous solution.

The mass transport in PV is usually described by three steps: selective sorption of components into the membrane, molecular diffusion of the components through the membrane, and evaporation of the components at the membrane surface on the permeate side [11]. Among them, the solubility and diffusivity of the components in the membrane play an essential role in component transport [12]. Thus, PV separation is usually governed by the chemical nature of the macromolecules that comprise the membrane, the physical structure of the membrane, the physicochemical properties of the mixtures to be separated, and the permeant–permeant and permeant–membrane interactions [13]. Although many studies focus on the PV membrane and its effect on the PV performance, there are only a few research on the interaction between PV membrane and different kind of organic solvents, which is necessary for modeling PV process. In this paper, the pervaporation experiments of eight different organic/water mixtures have been carried out to study the dissolution and diffusion of small molecules in dense polymer membranes during the PV process.

Experimental

Material

α, ω-Dihydroxypolydimethylsiloxane with average molecular weight within the range of 30,000–60,000 was purchased from Beijing Second Chemical Plant, China. Tetraethylorthosilicate (TEOS), dibutyltin dilaurate, *n*-heptane, acetone, butanone, cyclohexanone, alcohol, isopropanol, n-butyl alcohol, acetic acid, and ethyl acetate were obtained as analytical reagents from Tianjin Fuchen Chemical Reagent Company, China. Polytetrafluoroethylene (PTFE) membranes, with an average pore size of 2 μm and a thickness of 15 μm, were provided by Shanghai Linfulong Film Technology CO., LTD.

Membrane Preparation [14]

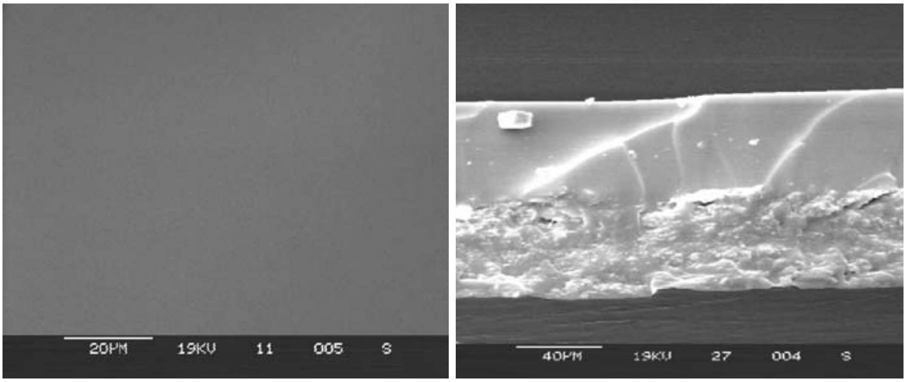
PDMS, crosslinking agent TEOS, and catalyst dibutyltin dilaurate were mixed according to a 100/10/2 weight ratio in n-heptane. Prior to coating, the PTFE membrane was laid and spread out on the surface of plexiglass plate, then the PDMS solution was poured over its surface quickly. The composite membrane system was kept under ambient temperature for 48 h to complete the cross-linking reaction.

Since the PTFE membrane was very thin, PDMS solution intruded into the membrane pores completely and was integrated with the PTFE membrane. Thickness of the composite membrane prepared for this work was approximately 50 μm. Figure 1 is SEM photographs of PDMS/PTFE composite membrane. In Fig. 1, the upper part is the PDMS dense layer, the lower part is PTFE support layer. It can be seen that the close bonding layer was formed between this two parts.

Pervaporation Set-Up and Procedure

The apparatus used for pervaporation is illustrated in Fig. 2. Feed tank and membrane cell were maintained at constant temperature by water jacket and circulating water bath. To keep feed concentration and temperature uniform, a magnetic stirrer was used. The pressure at the downstream side was kept at approximately 15 mmHg. The effective membrane area was 19.62 cm^2.

As Hasanoglu [15] and Kalyani [16] referred to related definition in the article about pervaporation, the selectivity (α) is calculated from the equation below, where Y_O and Y_W



(a) surface (b) cross-section

Fig. 1 SEM photographs of PDMS/PTFE composite membrane

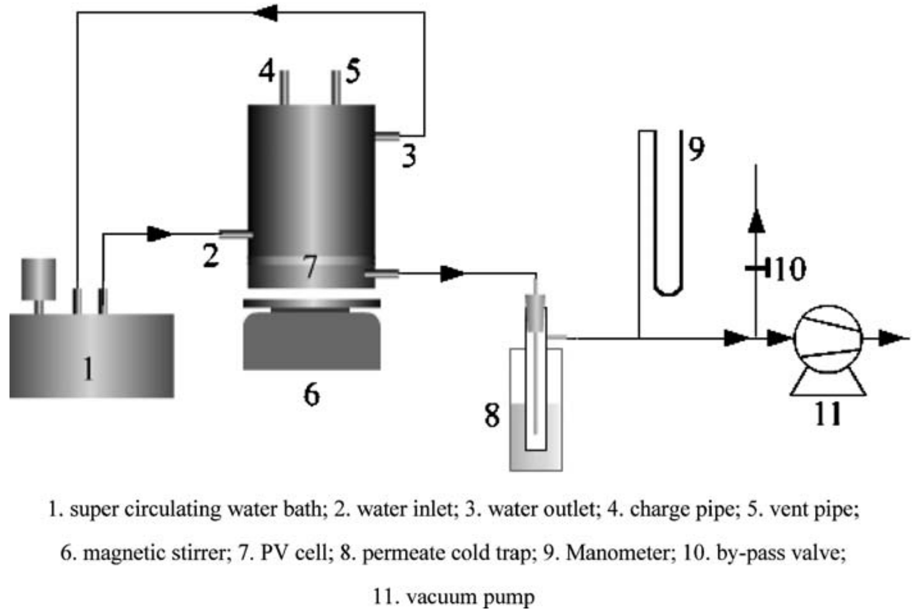


Fig. 2 The schematic diagram of pervaporation experiment

are the weight percentages of organic and water in the permeate, X_{O} and X_{W} are the weight percentages of organic and water in the feed, respectively:

$$\alpha = \frac{Y_{\mathrm{O}}/Y_{\mathrm{W}}}{X_{\mathrm{O}}/X_{\mathrm{W}}} \tag{1}$$

The flux was defined as:

$$J = \frac{W}{A \times t} \tag{2}$$

where J is the total flux (g·m^{-2} h^{-1}); W, mass of permeate (g); A, effective mass transfer area of membrane (m^2); and t, time elapsed (h).

The determined permeate fluxes are normalized to thickness of 1 μm to eliminate the effect of thickness. According to the following relation [17]:

$$J_{\mathrm{N}} = J \times \theta \tag{3}$$

where J_{N} and θ denote the normalized flux (Kg·μm·m^{-2} h^{-1}) and the membrane thickness (μm), respectively.

Permeate compositions were determined by using abbé refractometer [18].

Table 1 lists selected physicochemical properties of water and the organic components investigated, where acetone, butanone, and cyclohexanone have the same organic functional group, –*CH* = C [19]. While n-butyl alcohol, butanone, and ethyl acetate have the same carbon atomicity and different functional group.

Table 1 Physicochemical data for components.

Component	Molar volume (cm^3/mol)	Solubility parameter, $\delta[(J/cm^3)^{0.5}]$
Water	18.02	47.4
Acetone	73.53	20.4
Butanone	89.53	19.0
Cyclohexanone	103.64	20.2
Alcohol	58.37	27.0
Isopropanol	77.92	23.6
n-butyl alcohol	91.26	23.8
Acetic acid	57.24	25.8
Ethyl acetate	97.87	19.0

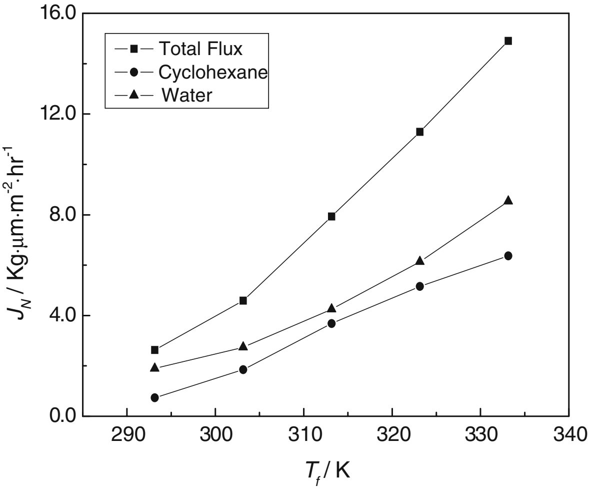
Results and Discussion

Pervaporation Separation of Ketone/Water Mixtures

The experimental results in Figs. 3 and 4 depict the effect of feed temperature on PV performances at 0.99 wt.% of cyclohexanone in the feed. From these figures, it is clearly noticed that the total flux, cyclohexanone flux, and water flux increase monotonically with feed temperature increasing. From Fig. 4, it is observed that the selectivity of cyclohexanone to water increases with increasing temperature in the range of 296–313 K, but decreases with the further increase in feed temperature. The results are evidently different from those reported in many literatures where selectivity decreases with feed temperature increasing [20].

PV performance is affected by many factors, such as the interaction between membrane and permeate molecules, molecular size of permeate components, the swelling degree of membrane, etc. The effect of feed temperature on the pervaporation performance of

Fig. 3 Variation of permeates flux with feed temperature at 0.99 wt.% of cyclohexanone in the feed



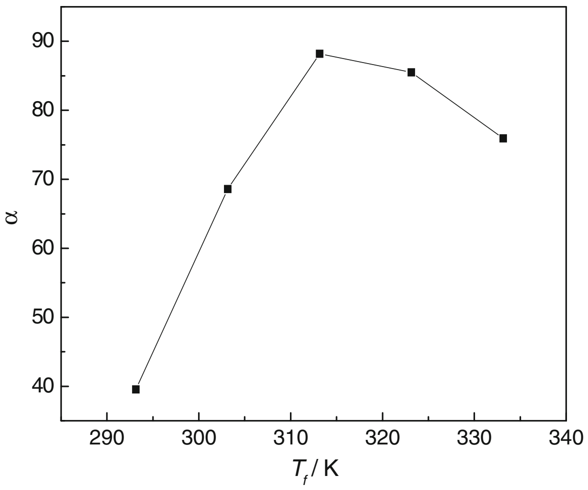


Fig. 4 Variation of selectivity with feed temperature at 0.99 wt.% of cyclohexanone in the feed

composite membrane is mainly shown in three aspects: the solubility of components in the membrane, the activity of polymer chain, and the free volume of polymer chain. With increasing operating temperature, the free volume of PDMS molecules and the diffusion of permeating molecules increase due to thermal expansion of polymer chains [9].

It can be explained based on the fact that during PV process, permeating molecules diffuse through free volumes of the membrane. Thermal motions of polymer chains in amorphous regions randomly produce free volumes. As feed temperature increases, frequency and amplitude of polymer jumping chains increases, which leads to more free volume of the membrane. Meanwhile, the mobility of permeating molecules is enhanced. As a result, when feed temperature goes up, diffusion rate of individual permeating molecule ascends, which results in high permeation fluxes.

This phenomenon showed in Figs. 3 and 4 indicates that the effect of feed temperature on the solubility of components is more significant than the other factors in the range of 296–313 K. Preferential adsorbability and solubility of cyclohexanone in the PDMS membrane is significant with increasing of feed temperature in the range of 296–313 K. Thus, the cyclohexanone flux increases significantly and the selectivity also increases during the initial temperature increasing period. Cyclohexanone molecular size is about sixfold of water molecules (the molar volumes of cyclohexane and water are 103.64 cm^3/mol and 18.02 cm^3/mol, respectively, Table 1), more water molecules are able to permeate through the interstitial space between polymer chains than cyclohexanone molecules when the temperature is further increased. As a result, the increasing feed temperature tends to magnify the diffusivity difference between water and ethanol molecules and hence reduces the selectivity.

Figures 5 and 6 show the effect of feed concentration on PV performance at 303 K feed temperature. It is observed that both the total flux and cyclohexanone flux increase linearly with increasing feed concentration, but the water flux almost remains the same. The driving force of mass transfer and the swelling degree of the membrane could be enhanced owing to the increase in feed concentration. As the flux is very small in the process of pervaporation, the effect of concentration polarization can be neglected. Consequently, the permeate flux takes on an increasing trend, but the water flux is almost unchanged because of the hydrophobicity of the membrane.

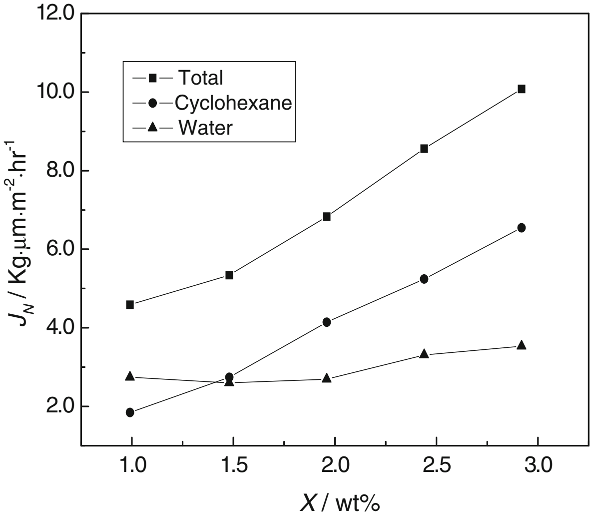


Fig. 5 Variation of permeates flux with feed concentration at 303 K of feed temperature

Figure 6 indicates that the selectivity of cyclohexanone to water increases when feed concentration increases from 0.99 wt.% to 2.5 wt.%. However, with the further increasing of feed concentration, the increase in feed concentration can result in higher swelling degree of the membrane which further increases the free volume of the membrane. This change is more favorable to the permeation of water than that of cyclohexanone.

Pervaporation Separation of Alcohol/Water Mixtures

The PV experiments of ethanol/water, iso-propanol/water, and n-butyl alcohol mixtures at different temperatures were carried out to investigate the temperature dependence of

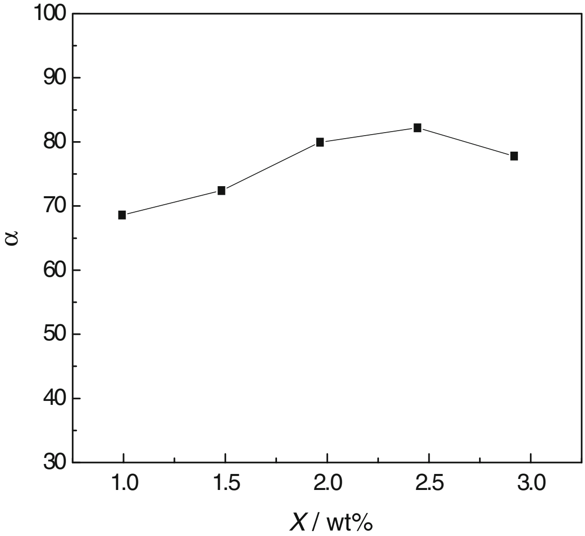
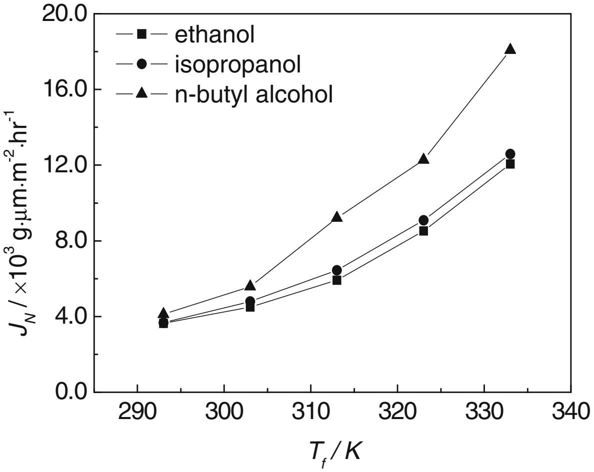


Fig. 6 Variation of selectivity with feed concentration at 303 K of feed temperature

Fig. 7 Variation of permeates flux with feed temperature at 0.99 wt.% of alcohol in the feed



pervaporation performances, and the results are shown in Figs. 7 and 8. It can be seen that the total flux of three kinds of alcohol/water mixtures increase monotonically with feed temperature increasing and it is also observed from Fig. 9 that the temperature dependence of the flux is consistent with Arrhenius equation, for both alcohol/water and cyclohexane/water. The effects of temperature on the selectivity of the PDMS/PTFE membrane to ethanol, iso-propanol, and n-butyl alcohol are different from each other. With the increase of feed temperature, the selectivity of the PDMS/PTFE membrane to iso-propanol and n-butyl alcohol first increases and then decreases, while the selectivity of the PDMS/PTFE membrane to ethanol decreases in the range of 290–330 K.

Figure 10 shows the effect of feed concentration on PV performance at 303 K feed temperature. It can be seen that, with the increase of ethanol content in the feed, the selectivity of the PDMS/PTFE membrane to ethanol first increases and then decreases, while the total flux of ethanol/water mixtures increases.

Fig. 8 Variation of selectivity with feed temperature at 0.99 wt.% of alcohol in the feed

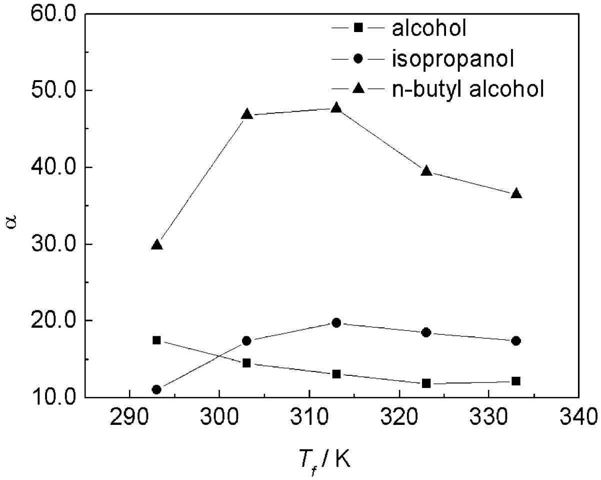
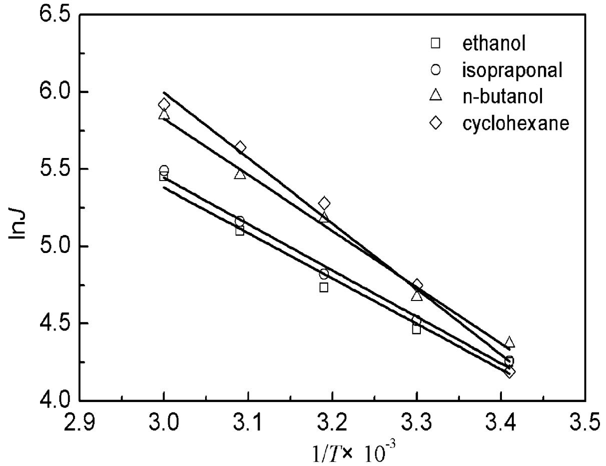


Fig. 9 Variation of PV performance with feed temperature at 0.99 wt.% of alcohol in the feed



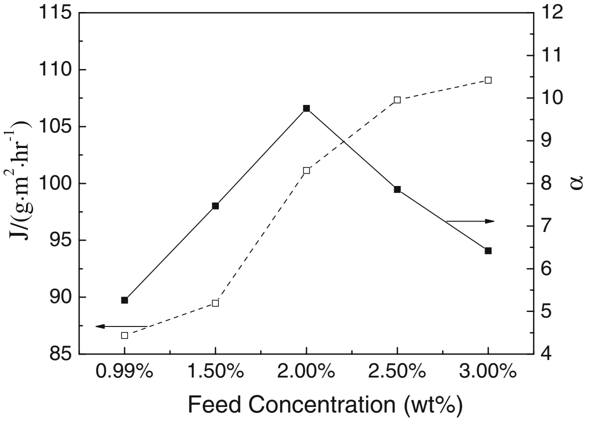
During the PV process, the increase of ethanol concentration cause more ethanol dissolved into the membrane, which makes the selectivity of the PDMS/PTFE membrane to ethanol increase with the ethanol concentration in the range of 0.99% to 2.00%. Well, with the further increase of feed concentrations, it will result in the polymer swelling, which increases the free volume of the membrane, thus more H_2O molecules are dissolved into the membrane material because of its small molar volume and the selectivity decrease.

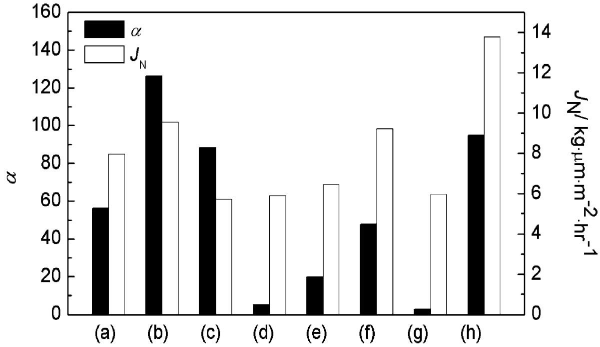
Comparison of Pervaporation Behaviors of Different Organic–Water Mixtures

Figure 11 shows the total fluxes of the different dilute organic aqueous solutions and selectivity of acetone, butanone, cyclohexanone, alcohol, isopropanol, n-butyl alcohol, acetic acid, and ethyl acetate to water, the organic concentration is 0.99 wt.% in the aqueous solution, at operating temperature of 313 K.

As seen in the Fig. 11, the total flux and selectivity of dilute butanone aqueous solution are higher than that of the acetone and cyclohexanone.

Fig. 10 Variation of PV performance with ethanol concentration at 303 K of feed





(a) acetone, (b) butanone, (c) cyclohexanone, (d) alcohol, (e) isopropanol, (f) n-butyl alcohol, (g) acetic acid, (h) ethyl acetate

Fig. 11 Pervaporation separation of different organic solvent/water mixtures through PDMS/PTFE membrane at T=303 K, C=0.99%

The PV behavior is related to the molar volume of organics and its solubility parameter, which affect the diffusion and solubilization of organic components in the membrane, respectively. Comparison of molar volume and solubility parameter between acetone, butanone, and cyclohexane is shown in Table 1. It is observed that the PDMS/PTFE membrane does not show higher pervaporation performance to smaller organics during PV process. The result in Fig. 11 can be explained that the solubility parameter of PDMS is closer to butanone than acetone and cyclohexanone as shown in Table 1(δ_{PDMS}=14.9–15.5(J/cm^3)$^{0.5}$) [21]. Thus, PDMS is more selective to butanone than to other components. The solubility parameter is a measure of the affinity between polymer and permeate. As the affinity between permeate and polymer increases, the absorbed liquid inside the polymer increases, and consequently the permeate flux increases.

It is also noticed that the total flux of ethanol/water, isopraponal/water, and n-butanol/water mixtures and selectivity of ethanol, isopraponal, and n-butanol both increase, respectively. Table 1 shows that molar volume of these three organics increases in turn and solubility parameter of them are similar. Therefore, molar volume and solubility parameter are not the main factors to influence pervaporation of these three alcohol/water mixtures.

Based on the solution–diffusion mechanism, the components are dissolved in the polymer, reach the equilibrium, and diffuse to downstream side of the membrane. There is no significant difference among the solution of ethanol, isopropanol and n-butanol in polymer. Thus, the different permselectivity of PDMS membrane for three alcohols may be caused by the different diffusivity in polymer. In addition, the molecular polarities decrease with the order of ethanol>isopraponal>n-butanol, and the interaction between alcohol molecules and polymer chain decreases, respectively. Therefore, n-butanol molecules are more likely to diffuse in polymer compared with the other alcohol molecules.

Although the carbon number is the same for ethanol and acetic acid, and their solubility in water are similar, the PV performance of acetic acid through the membrane is lower than that of ethanol. Except for the higher polarity of acetic acid, the hydrogen bond association among acetic acid molecules may inhibit the diffusion of acetic acid in polymer.

For the pervaporation separation of acetic ether/water mixtures, the membrane has high selectivity to acetic ether because the solubility parameter of PDMS is close to it. And compared with the other organic/water mixtures, its low molecular polarity will enhance the diffusion in PDMS. Therefore, the PV performance of PDMS membrane to acetic ether/water mixtures is better.

Conclusion

In this study, the effects of feed temperature and concentration on PV performance of PDMS/PTFE membrane are investigated. With feed temperature increasing, the total flux increases monotonically, but the selectivity only increases in the feed temperature range of 296–313 K, and then begins to decrease with the further increase in temperature. With feed concentration increasing, the total flux increases, but the selectivity decreases. Pervaporation results show that PDMS membrane is much more selective to butanone than to acetone and cyclohexanone. This may be attributed by the fact that the solubility parameter of PDMS is closer to butanone than to acetone and cyclohexanone. It can be concluded the solubilization of ketone in the membrane plays a critical role during the PV process. And for the three kind of alcohol/water mixtures, J_N(ethanol/water)<J_N(isopraponol/water)<J_N(n-butanol/water), and the selectivity of n-butanol is higher than ethanol, isopraponal, and n-butanol. The main reason is n-butanol molecules are more likely to diffuse in polymer compared with the other alcohol molecules. The solubility and diffusion coefficient of acetic ether in polymer are comparatively good, and there is a comparatively good PV performance for it.

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