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Comparison between the pervaporation and vapor permeation performances of polycarbonate membranes

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Abstract

The pervaporation and vapor permeation performance of symmetrical and asymmetrical polycarbonate membranes, prepared via a dry-phase inversion and wet-phase inversion methods, respectively, were studied by measuring the permeation rate and separation factor. It was found that the polymer concentration effect on the pervaporation performance for the symmetrical polycarbonate membrane was lower than that for the asymmetrical polycarbonate membrane. Compared with pervaporation, vapor permeation has a significantly increased separation factor with a decreased permeation rate for the symmetrical polycarbonate membrane. Water molecules preferentially dissolve into the symmetrical polycarbonate membrane and diffuse easily through the membrane.

Keywords: Pervaporation; Vapor permeation; Symmetric; Asymmetric; Polycarbonate

1. Introduction

Since the pervaporation technique is considered as an energy saving process, it has gained greater interest in the separation of azeotropic mixtures, close boiling point mixtures or isomers, and for the removal or recovery of trace substances. In recent years, pervaporation has established itself as one of the most promising membrane technologies for the treatment and recycling of volatile organic compounds and pollution prevention [1,2]. In the membrane research field, many efforts have been made to prepare pervaporation membranes with good performance and good stability. Many researchers focused their attention on improving the membrane separation performance, including: membrane formation process, ^{60}Co γ-ray irradiation or plasma grafting, polymer blending, chemical grafting, and preparing new polymers [3–10]. Furthermore, it has been reported that the addition of salt in membranes can enhance the permeation rate of pervaporation [11–13]. It has also been observed that adding a small amount of salt in the feed can elevate the membrane selectivity of membranes drastically [14]. However, the key to successful pervaporation lies in the membrane performance. The permselectivity and permeation rates are two important characteristics that determine membrane performance. Polycarbonate membranes possessing excellent

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mechanical strength have been regarded as promising membrane materials for separation. We have previously reported that transition metal additives in a polycarbonate casting solution are capable of improving the oxygen permeability by dry-phase inversion [15]. In addition, wet-phase inversion is used in preparing asymmetric membrane to improve the gas separation and pervaporation performance. In these reports, the effects of membrane formation processes, types of additive such as: transition metal or nonsolvent in the casting solution, have been carefully investigated [16,17]. However, because organic feed mixtures directly contact the polymer membranes in the pervaporation process, the feed mixtures through the swelling or shrinking effects often influence the physical and chemical properties of the membranes. Vapor permeation, a membrane separation technique developed by Uragami et al. and Okamoto et al. [18,19], was proposed to improve the disadvantages of pervaporation. In this vapor permeation technique, the feed solution is first vaporized and then permeated through the membrane. Thus, polymer membrane swelling or shrinking due to the feed solution can be prevented. In this paper, water pervaporation and vapor permeation separation from aqueous alcohol mixtures was performed using polycarbonate membranes. The feed composition, degree of swelling, and alcohol molecular size effects on the pervaporation and vapor permeation performances were investigated.

2. Experimental

2.1. Materials

Polycarbonate (Upervaporation separation indexlon S-2000) (M_w = 28,000) was purchased from Mitsubishi gas Chemical Co. Dichloromethane, methanol, ethanol *n*-propanol, and *t*-butanol were supplied by Merck Co. The above mentioned chemicals are all of reagent grade.

2.2. Membrane preparation

The asymmetric PC membranes were prepared from the formation system of PC/CH_2Cl_2/CH_3OH (polymer/solvent/coagulation medium) with 2 ml C_2H_5OH as the additive in the casting solution. Casting the solution onto a glass plate to a predetermined thickness using a Gardner Knife formed the membranes. The glass plate was immersed in the coagulation medium. Then the membrane was peeled off and dried in vacuum for 24 h. The average membrane thickness was about 50 μm. In addition, the symmetric PC membranes were prepared from the casting solution of polycarbonate in dichloromethane. Casting the solution onto a glass plate to a predetermined thickness using a Gardner Knife at room temperature formed the membranes. The membrane was dried at room temperature for 30 min. The membrane was then peeled off and put in vacuum for 24 h before sorption and pervaporation measurement. According to the SEM analysis, the prepared membranes are dense symmetric membranes with a thickness ranging from 25 to 30 μm.

2.3. Sorption measurement

The membranes were immersed in alcohol–water mixtures for 24 h at 25 °C. They were subsequently blotted between tissue paper to remove excess solvent and placed in the left tube of a twin tube set-up. The system was evacuated while the left tube was heated with hot water and the right tube was cooled in liquid nitrogen. GC determined the composition of the condensed liquid in the right tube.

2.4. Pervaporation and vapor permeation measurement

A traditional pervaporation and vapor permeation process [20] was used. In pervaporation, the feed solution is in direct contact with the membrane. The effective area was 10.2 cm^2. The permeation rate was determined by measuring the weights of permeate. The compositions of the feed solution and the permeate were measured by gas chromatography (G.C. China Chromatography 8700 T). Using the same apparatus as pervaporation carried out the experiment of vapor permeation, except that the feed solution is not in contact with the membrane. The feed solution was vaporized first and then permeated through the membrane. The separation factor

$$\alpha_{A/B} = (Y_A/Y_B)/(X_A/X_B)$$

where X_A, X_B and Y_A, Y_B are the weight fractions of A and B in the feed and the permeate (A being the more permeative species), respectively. In vapor permeation, X_A and X_B are the weight fractions of water and alcohol vapors in the feed, and Y_A and Y_B are the weight fractions of the water and alcohol in the permeates.

2.5. Contact angle measurements

The contact angle of water was measured with a face contact angle meter CA-D type (Kyowa Interface Science Co. Ltd.) at 25 °C and 60% relative humidity.

2.6. Degree of swelling

The degree of swelling of the membrane was defined by the following equation:

$$\text{Degree of swelling} = (W_w - W_d)/W_d \times 100\%$$

where W_d and W_w denote the weight of dry and swollen membranes, respectively.

3. Results and discussion

3.1. Membrane formation process effect on the pervaporation and vapor permeation performance

The membrane formation process effect on the pervaporation and vapor permeation performance through various prepared polycarbonate membrane compositions are shown in Fig. 1. The data shows that the separation performance of the symmetrical PC membranes prepared via a dry-phase inversion for pervaporation and vapor permeation were not affected by polymer concentrations in the 6–12 wt% range. However, the permeation rates of the asymmetrical PC membranes prepared via a wet-phase inversion decreased rapidly from 632 to 109 g/m^2 h for 8 wt% and 12 wt% polymer concentrations, respectively. These phenomena might be because a dense homogeneous membrane was obtained using the dry-phase inversion method, resulting in high pervaporation and vapor permeation stability when the symmetrical PC membranes were used to separate the aqueous ethanol solution. The asymmetrical PC membrane was obtained via a wet-phase inversion method. The pervaporation performance was affected by the polymer concentration, resulting from the top layer thickness increasing with increasing polymer concentration. The asymmetrical PC membrane structures were studied with a Hitachi S-570 scanning electron microscope (SEM). The SEM photographs are shown in Fig. 2. Fig. 2 shows that the thickness of the top membrane layer increases with increasing polymer concentration. This observation agrees with the result shown in Fig. 1. To further compare the stability between the symmetrical and asymmetrical PC membranes, the membrane durability was tested using a 90 wt% ethanol solution at 25 °C for two months. Defects were present in the top layer of the asymmetrical PC membranes (Fig. 3(D) and (F)). However, this was not found in the symmetrical PC membranes (Fig. 3(B)). Thus, the high stability symmetrical PC membranes will be discussed further in the following sections.

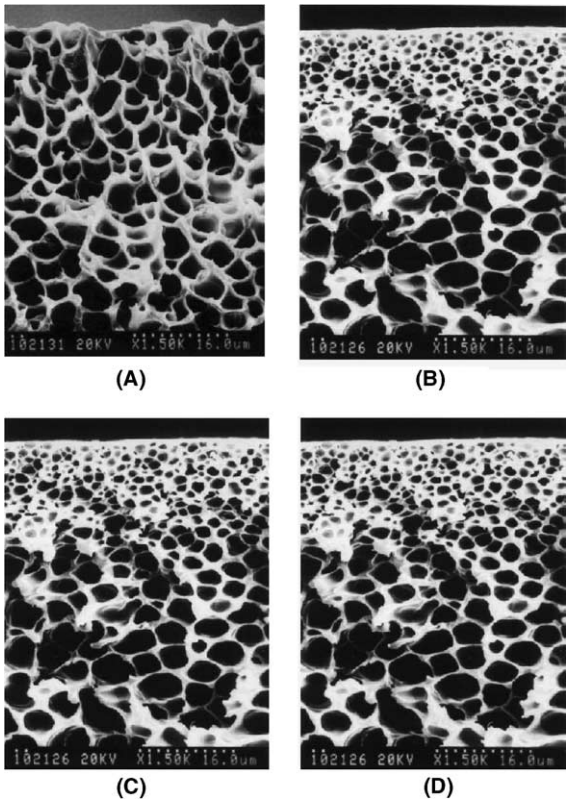

Fig. 2. The SEM photographs of the asymmetrical PC membranes. (A) 8 wt%, (B) 9 wt%, (C) 10 wt%, (D) 12 wt%.

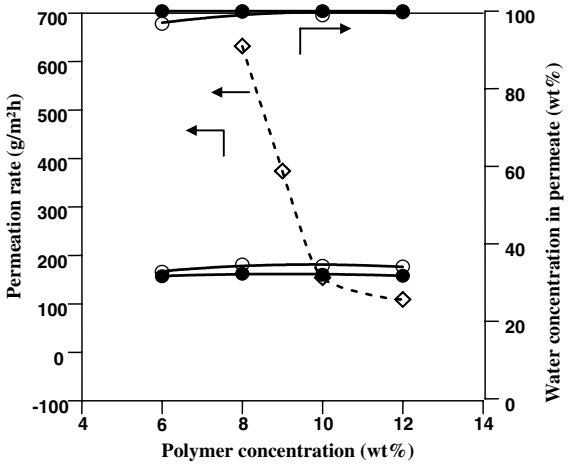

Fig. 1. Effect of polymer concentration on the pervaporation and vapor permeation performance. (○) symmetrical PC membrane for pervaporation, (●) symmetrical PC membrane for vapor permeation, (□) asymmetrical PC membrane for pervaporation.

3.2. Feed composition effect on the pervaporation and vapor permeation performances

The feed composition effects on the pervaporation and vapor permeation performance for the symmetrical polycarbonate membranes are shown in Fig. 4. As the ethanol feed concentration increases, the permeation rate decreases accordingly for the symmetrical PC membranes. These results might be due to the plasticizing effect of ethanol. Generally, hydrophobic membranes have stronger interactions with alcohol than with water. Hence, the degree of swelling in the symmetrical PC membranes increased with increasing ethanol concentration, as shown in Fig. 5. In addition, the difference in the solubility parameters between the polymer membrane

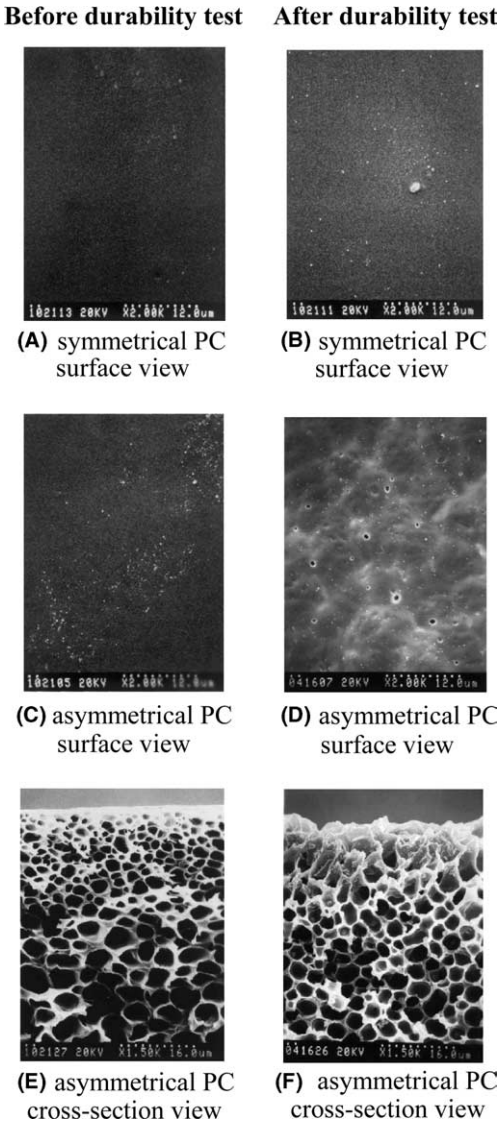

Fig. 3. Membrane durability test for 90 wt% ethanol solution at 25 °C for two months. (A) Symmetrical PC membrane, before durability test; (B) symmetrical PC membrane, after durability test; (C) asymmetrical PC membrane, before durability test; (D) asymmetrical PC membrane, after durability test; (E) asymmetrical PC membrane, before durability test; (F) asymmetrical PC membrane, after durability test.

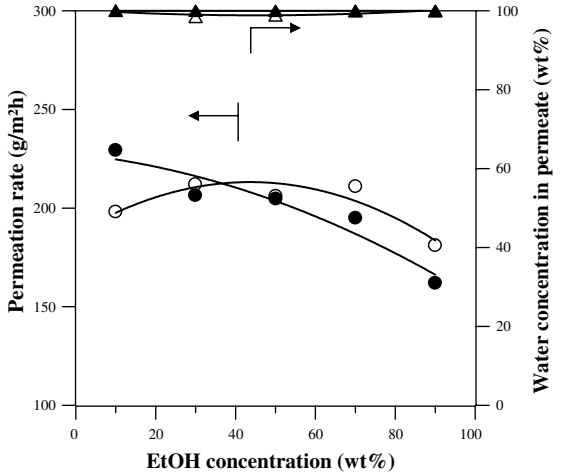

Fig. 4. Effect of feed composition on the pervaporation and vapor permeation performances of the symmetrical PC membrane. (○, □) pervaporation, (●, ▲) vapor permeation. Polymer concentration: 10 wt% PC/CH_2Cl_2.

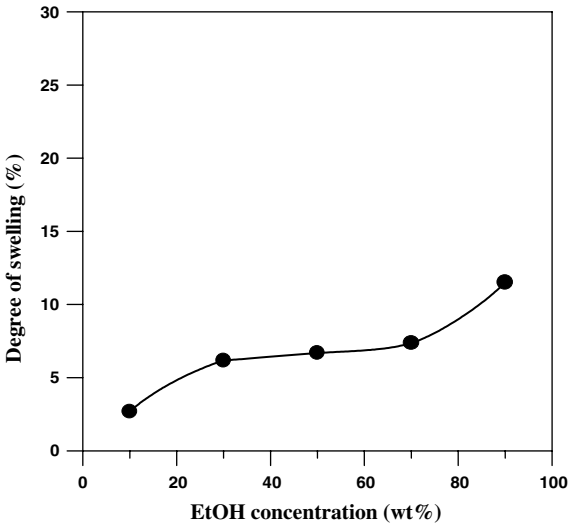

Fig. 5. Effect of feed composition on the degree of swelling of the symmetrical PC membrane. Polymer concentration: 10 wt% PC/CH_2Cl_2.

and ethanol $\Delta\delta_{PC\text{-}EtOH} = 4.8(cal/cm^3)^{1/2}$ was lower than that between the polymer and water $\Delta\delta_{PC\text{-}H2O} = 13.7(cal/cm^3)^{1/2}$. These results support the data shown in Fig. 5. The higher the ethanol concentration in the feed solution results the higher the degree of membrane swelling. However, compared with the swelling degree results, an opposite trend was obtained for the permeation rate. This result shows that the diffusivity of water is higher than that for ethanol. Thus, lower water content in the higher ethanol feed concentration results in a decreasing permeation rate. In addition, the vapor permeation experiment was carried out using the same apparatus used for the pervaporation experiment, except that the feed solution was not in contact with the membrane. The feed solution was vaporized first and then permeated through the membrane. Fig. 4 shows that the vapor permeation rate was higher than that for the pervaporation with the aqueous ethanol feed concentration up to 30 wt%. Beyond this concentration, an

opposite trend was obtained. These phenomena might be because at vapor–liquid equilibrium, the ethanol concentration in the vapor phase is much higher than that in the liquid phase at lower ethanol feed concentrations (10–30 wt%). Thus, the swelling effect plays an important role in the vapor permeation separation process. However, the ethanol clustering effect results in a lower vapor permeation rate than that for the pervaporation method at higher ethanol feed concentrations (>30 wt%).

3.3. Ethanol sorption of symmetric PC membranes

In order to investigate the solubility and diffusivity effects on membrane permselectivity, sorption experiments for the polycarbonate membranes were performed. The feed composition effects on the ethanol concentration in the permeate in the symmetrical PC membrane are shown in Fig. 6. The permeate and sorption composition curves lie under the diagonal line, indicating that the water molecules were selectively dissolved into the membrane and diffused through the membrane. The ethanol concentration in the membrane was higher than that in the permeate for ethanol feed concentrations in the 10–90 wt% range. These results can be explained by the very strong affinity between the ethanol molecules and the symmetrical PC membrane and the large ethanol molar volume. Conversely, once the water molecules are incorporated into the symmetrical PC membrane, they are easily diffused through the membrane because the interaction between the water molecules and the membrane is very weak. The smaller water molecular size contributes to this process. Consequently, the water molecules are permeated through the hydrophobic symmetrical PC membrane. Sorption experiments were performed to determine the solution separation factor, $\alpha_{solution}$, for the symmetrical PC membranes. The pervaporation permeability coefficient represents the product of the solution coefficient and the diffusion coefficient. Thus, the pervaporation separation factor, $\alpha_{pervaporation}$, is also expressed as the product of the solution, $\alpha_{solution}$, and that for diffusion, $\alpha_{diffusion}$, as follows:

$$\alpha_{pervaporation} = \alpha_{solution} \times \alpha_{diffusion}$$

The solution separation factor and diffusion separation factor results are shown in Table 1. The table shows that the solution separation factor increases with increasing feed ethanol concentration. These phenomena might be because of the high affinity between the ethanol molecules and the symmetrical PC membrane results in a more swollen membrane. Hence, the water molecules can easily dissolve into membrane, resulting in increased solution separation factor. Compared with the solution separation factor, a higher diffusion separation factor was obtained. In general, the diffusion separation factor is strongly related to the membrane structure. A denser symmetrical membrane structure results in a higher diffusion separation factor. Therefore, the pervaporation behavior is caused by both the diffusion separation and the solution separation factors. However, the former has a greater contribution.

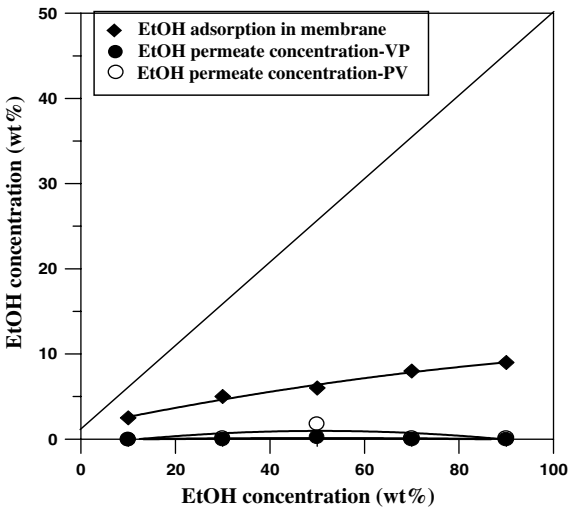

Fig. 6. Effect of the feed composition on the ethanol concentration in the permeate and in the symmetrical PC membrane. (□) absorbed, (●) permeated; vapor permeation (○) permeated; pervaporation. Polymer concentration: 10 wt% PC/CH_2Cl_2.

3.4. Symmetrical PC membrane pervaporation and vapor permeation properties with different aqueous alcohol mixtures

Table 2 shows the pervaporation and vapor permeation performance for a 90 wt% aqueous alcohol solution through symmetrical PC membranes. The figure

Table 1
Effect of feed ethanol concentration on the separation factor of pervaporation, solution, and diffusion for the symmetrical PC membrane[a]

Feed ethanol concentration (wt%)	$\alpha_{pervaporation}$	$\alpha_{solution}$	$\alpha_{diffusion}$
10	6.2	1.3	4.9
30	27	3.3	8.2
50	83	5.9	14.1
70	2150	9.3	232.1
90	9008	38.1	236.5

[a] Polymer concentration: 10 wt% PC/CH_2Cl_2; feed solution temperature: 25 °C.

Table 2
Effect of feed alcohol mixtures on the pervaporation and vapor permeation performance through the symmetrical PC membranes[a]

Aqueous alcohol mixture (90 wt%)	Molar volume (ml/mol)	Pervaporation		Vapor permeation	
		Permeation rate (g/m^2h)	Water concentration in permeate (wt%)	Permeation rate (g/m^2h)	Water concentration in permeate (wt%)
Ethanol	58.6	175	99.9	160	99.9
n-Propanol	75.1	205	99.8	190	–[b]
t-Butanol	91.9	210	99.8	195	–[b]

[a] Polymer concentration: 10 wt% PC/CH_2Cl_2.
[b] Water in permeate 100 wt%; alcohol cannot be measured by GC.

shows that an increase in the number of carbon atoms in the alcohol results in an increase in the water concentration in the permeate. According to the solution–diffusion mechanism [21], the size of the permeating species and the affinity between the permeating species and the membrane are important in both the solution and diffusion processes. A higher water concentration in the permeate for the longer chain alcohol is explained by the molar volume. The molar volumes of ethanol, *n*-propanol, and *t*-butanol are 58.6, 75.1, and 91.9 (ml/mol), respectively. The above data explains why the water concentration in the permeate increases with increasing numbers of carbon atoms in the alcohol. Table also shows that the permeation rate increases when the carbon atom number in the alcohol increases. These phenomena might be due to the interaction between the alcohol and the symmetrical PC membrane. Table 3 shows the difference in the solubility parameters between the polymer and alcohol following the order: ethanol > *n*-propanol > *t*-butanol. The solubility of pure alcohol in a symmetrical PC membrane increases with increasing carbon atom number. That is, the larger alcohol molecule has a higher affinity for the symmetrical PC membrane than a smaller molecule. Therefore, *t*-butanol produces greater swelling than ethanol. These results correspond well with the permeation rate of the symmetrical PC membrane, as indicated in Table 2.

Table 3
Solubility of water and alcohols in the symmetrical PC membrane and the difference between the solubility parameter (δ) of membrane and alcohol[a]

Permeating molecule	δ $(cal/cm^3)^{1/2}$	$\delta_{PC} - \delta_{alcohol}$	Solubility (g/100 g)
Water	23.4	13.7	2
Ethanol	12.7	3.0	15
n-Propanol	11.9	2.2	18
t-Butanol	10.6	0.9	20

[a] Polymer concentration: 10 wt% PC/CH_2Cl_2; feed solution temperature: 25°C.

4. Conclusions

The polymer concentration effect on the pervaporation performance of a symmetrical polycarbonate membrane is lower than that of an asymmetrical polycarbonate membrane. The durability of the symmetrical membrane is greater than that of the asymmetrical membrane. Compared with pervaporation, vapor permeation effectively increases the permselectivity of water. The swelling effect plays an important role in the vapor permeation separation process at lower ethanol feed concentrations (10–30 wt%). The ethanol clustering effect results in a lower vapor permeation rate than that for pervaporation at a higher ethanol feed concentration (>30 wt%).

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