Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Lee, Kueir-Rarn , Liu, Ming-June and Lai, Juin-Yih(1994) 'Pervaporation Separation of Aqueous Alcohol Solution through Asymmetric Polycarbonate Membrane', Separation Science and Technology, 29: 1, 119 — 134
To link to this Article: DOI: 10.1080/01496399408002472
URL: http://dx.doi.org/10.1080/01496399408002472

SEPARATION SCIENCE AND TECHNOLOGY, 29(1), pp. 119–134, 1994

Pervaporation Separation of Aqueous Alcohol Solution through Asymmetric Polycarbonate Membrane

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ABSTRACT

In the present work the separation of aqueous alcohol mixtures through wet-phase inversion prepared polycarbonate membranes was studied by using the pervaporation process. The formation of asymmetric pervaporation membranes was discussed in terms of the presence of a nonsolvent in the casting solution, the polycarbonate concentration, and the kinds of coagulation media. The effects of feed composition, swelling degree, and the size of the alcohols on the pervaporation performances were investigated. The rate of liquid–liquid demixing increases with a decreasing number of carbon atoms of the alcohol coagulation medium. The permeation rate of the pervaporation process for the nonsolvent-added membrane was much higher than that of the membrane without nonsolvent additive. In binary alcohol mixtures, the permselectivities of small-sized alcohols through the asymmetric membrane are decided by two factors: preferential solubility of larger-sized alcohol and predominant diffusivity of small-sized alcohol.

Key Words. Pervaporation; Wet-phase inversion; Additive; Liquid–liquid demixing; Polycarbonate

INTRODUCTION

Pervaporation is a membrane separation process involving liquid–gas systems which has several interesting potential applications such as the separation of azeotropic and isomeric mixtures, the removal of water from organic liquids, and the removal of organic contaminants from wastewater

(1–5). The separation of alcohol/water mixtures by a pervaporation technique using a dense homogeneous polymer membrane has recently been given much attention. The research emphasis has been on the development of new polymer membranes which have high separation factors, acceptable permeation rates, and good stability in the various mixtures to be separated. Several methods of membrane preparation may be used for this purpose; grafting a selective species onto an inert film, blending and crosslinking (7–9), copolymerization (10, 11), and surface modification (12). Polycarbonate membranes possessing excellent 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 (13). In addition, wet-phase inversion is used in preparing asymmetric membrane to improve gas separation performance. Compared with dry-phase inversion, wet-phase inversion effectively improves the gas separation properties of polycarbonate membranes (14).

This paper discusses the preparation of asymmetric membranes from various polymer concentrations, kinds of coagulation media, and the presence of a nonsolvent in a casting solution. The effects of feed composition, degree of swelling, and the size of the alcohols on the pervaporation performances of asymmetric polycarbonate membranes were studied.

EXPERIMENTAL

Material

Polycarbonate (Uplion S-2000) was supplied by Mitsubishi Gas Chemical Co. Dichloromethane and *N,N'*-dimethylforamide (DMF), supplied by Merck Co., were employed as casting solvents. Methanol, ethanol, propanol, butanol, and all the above chemicals were of reagent grade.

Membrane Preparation

The polycarbonate (PC) membrane was prepared from a casting solution of polycarbonate in dichloromethane (CH_2Cl_2). The asymmetric membranes were prepared from solutions of varying compositions of PC/CH_2Cl_2 with added nonsolvents. The membrane was formed by casting the solution onto a glass plate to a predetermined thickness by using a Gardner knife. The glass plate was immersed in various coagulation media for 5 minutes. Then the membrane was peeled off and dried in vacuum for 24 hours. The average membrane thickness was about 50 μm.

SEM

The structures of the prepared membranes were examined by a Hitachi Medel S570 scanning electron microscope (SEM). The samples were coated with gold to about 150 Å.

Degree of Swelling

The degree of swelling of the membrane was defined by

$$\text{Degree of swelling} = \frac{\text{weight of swollen membrane}}{\text{weight of dry membrane}} \times 100\%$$

where the weight of dry membrane and the weight of swollen membrane denote the weight of dry and solvent-swollen membranes, respectively.

Apparatus and Measurements

Traditional pervaporation and sorption processes were used (15). The effective membrane area was 10.2 cm^2. Most of the experiments were conducted at 25°C. In pervaporation, the permeation rate was determined by measuring the weight of the permeate. The composition of the feed solutions, permeates, and solutions adsorbed in the membrane were measured by gas chromatography (G.C. China Chromatography 8700T). The separation factor, $\alpha_{water/alcohol}$, was calculated from

$$\alpha_{water/alcohol} = (Y_{water}/Y_{alcohol})/(X_{water}/X_{alcohol})$$

For pervaporation, Y_{water}, $Y_{alcohol}$ and X_{water}, $X_{alcohol}$ are the weight fractions of water and alcohol in the permeate and feed, respectively. For sorption, Y_{water} and $Y_{alcohol}$ are the weight fractions of water and alcohol in the membrane, respectively.

RESULTS AND DISCUSSION

Effect of Coagulation Medium on the Membrane Formation and the Pervaporation Performance

The pervaporation performances of 90 wt% aqueous ethanol solution through various coagulation medium-prepared PC membranes are listed in Table 1. The data shows that the larger-sized alcohol was used as the coagulation medium, resulting in a higher separation factor and a lower permeation rate. These phenomena might be due to the fact that the binodal curve was located far from the solvent–polymer axis, resulting in slow liquid–liquid demixing when the larger-sized alcohol was used as the coagulation medium (16, 17). Thus, the lower ratio of coagulation medium

TABLE 1
Effect of Coagulation Media on the Pervaporation Performances for Asymmetric PC Membrane[a]

Coagulation media	H_2O content in permeate (wt%)	Separation factor	Permeation rate ($g/m^2 \cdot h$)
Methanol	98.5	591	374
Ethanol	99.0	891	228
n-Propanol	99.8	5285	125

[a] Coagulation medium: CH_3OH, C_2H_5OH, *n*-C_3H_7OH. Additive nonsolvent: 2 mL C_2H_5OH in casting solution. Operation temperature: 25°C. Feed composition: 90 wt% aqueous ethanol solution.

inflow to solvent outflow creates a membrane with a more compact top layer (17), resulting in an increase of the separation factor. The binodal curves for the system of PC/CH_2Cl_2/coagulation medium (methanol, ethanol, *n*-propanol, *n*-butanol) were determined as described previously (14). A similar trend was obtained by Mulder et al. (17).

Effect of Composition of Coagulation Bath on Pervaporation Performance

The addition of solvent to the coagulation bath is a parameter which strongly influences the type of membrane structure formed. Figure 1

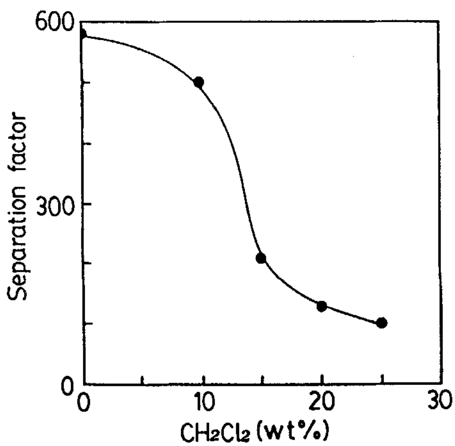

FIG. 1 Effect of composition of coagulation bath on pervaporation performances. PC/CH_2Cl_2/CH_3OH with 2 mL C_2H_5OH additive in casting solution.

shows the effect of CH_2Cl_2 concentration of the coagulation bath on the separation factors for pervaporation of 90 wt% aqueous ethanol solution through an asymmetric $PC/CH_2Cl_2/CH_3OH$ (polymer/solvent/coagulation medium) membrane with 2 mL C_2H_5OH as the additive in the casting solution. The separation factor decreases with increasing CH_2Cl_2 concentration of the coagulation bath. These phenomena might be due to the fact that increasing CH_2Cl_2 content in the coagulation bath leads to a decrease in the polymer concentration in the film at the interface. Another remarkable effect, i.e., delayed demixing, tends to produce nonporous membranes with thick and dense top layers which appear at the same time (16). The effect of the former on the pervaporation performance is higher than that of the latter. The membrane structure was verified by scanning electron microscopy (SEM), as shown in Fig. 2(A)–(D). The pore size and porosity increase with increasing CH_2Cl_2 content in the coagulation bath. This observation agrees with the result shown in Fig. 1.

Effect of Polymer Concentration on Pervaporation Performance

The effect of polycarbonate concentration (8–12 wt%) on pervaporation performances for the system $PC/CH_2Cl_2/CH_3OH$ with 2 mL ethanol additive in the casting solution is shown in Table 2. Table 2 shows that the separation factor increases and the permeation rate decreases with an increase of the polycarbonate concentration of the casting solution from 8 to 12 wt%. These results might be due to the fact that an increase in the initial polymer concentration in the casting solution leads to a much higher polymer concentration at the surface. Thus, the rate of liquid–liquid demixing decreases, resulting in an increase in the top layer thickness of

TABLE 2
Pervaporation Results of Asymmetric Polycarbonate Membranes from the System Polycarbonate/CH_2Cl_2/CH_3OH[a]

Polymer concentration (wt%)	Separation factor	Permeation rate ($g/m^2 \cdot h$)
8	291	632
9	591	374
10	1090	154
12	3903	109

[a] Coagulation medium: CH_3OH. Additive nonsolvent: 2 mL C_2H_5OH in casting solution. Feed composition: 50 wt% aqueous ethanol solution. Operation temperature: 25°C.

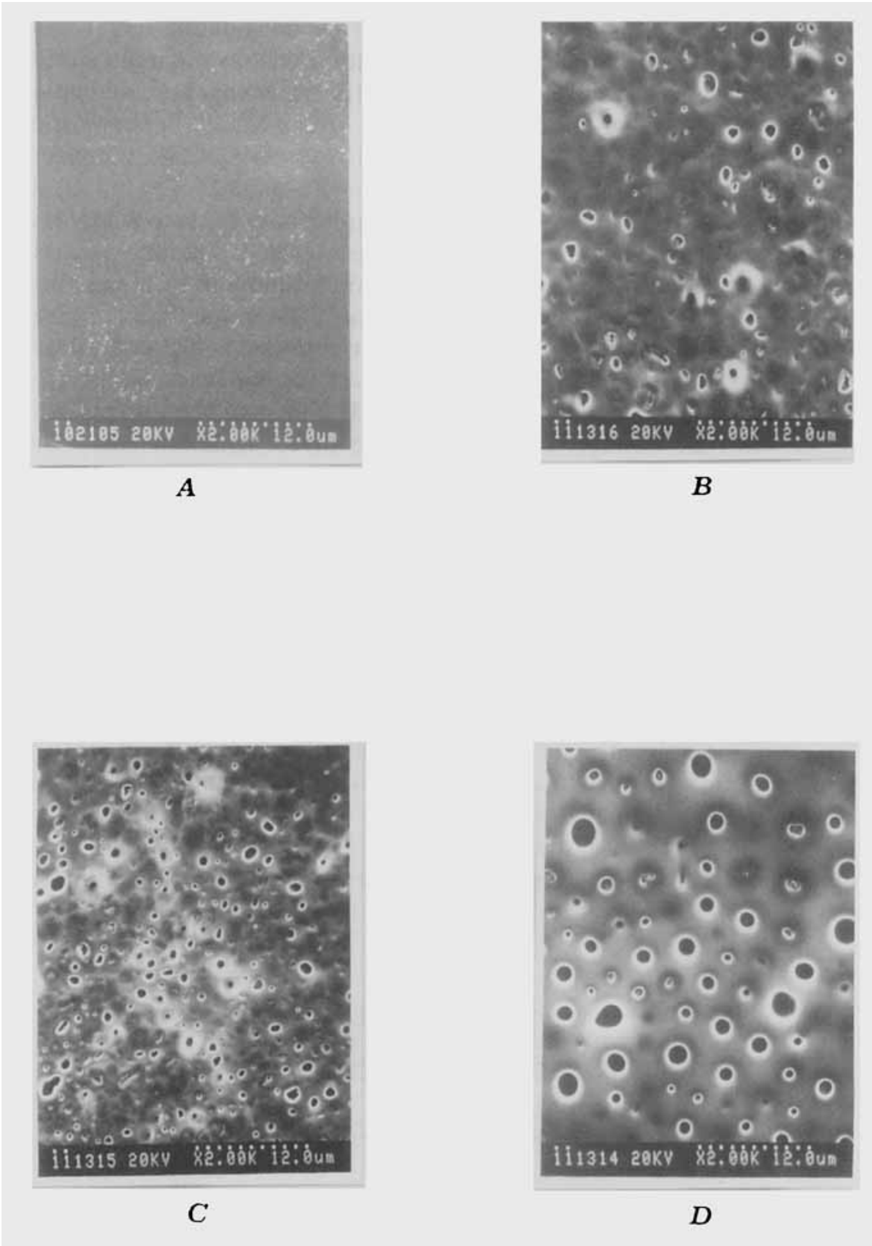

FIG. 2 SEM surface views of asymmetric polycarbonate membrane. CH_2Cl_2 content in coagulation bath: (A) 0 wt%, (B) 15 wt%, (C) 20 wt%, (D) 25 wt%.

the asymmetric membrane. The decrease of the permeation rate results from the increase of the top layer thickness. This implies that the volume fraction of polymer increases and, consequently, a lower porosity is obtained. While investigating the structures of the asymmetric membranes, cross-section views of the membranes were studied with a Hitachi S-570 scanning electron microscope (SEM). The SEM photographs are shown in Fig. 3. They show that the thickness of the membrane top layer increases with increasing polymer concentration. This clearly supports the hypothesis that two different types of phase separation are responsible for the formation of symmetric membranes: gelation for the formation of the top layer and liquid–liquid phase followed by gelation of the concentrated polymer phase for the formation of the porous sublayer. Similar results were obtained by Mulder et al. (17).

Effect of Feed Composition on Pervaporation Performance

In order to investigate the effects of solubility and diffusivity on membrane permselectivity, sorption experiments for the asymmetric polycarbonate membrane were made. Figure 4 shows the influence of the feed ethanol concentration on the permeation rate, the ethanol concentration in the permeate, and in the membrane for the asymmetric PC membrane. The permeate and sorption composition curves lie under the diagonal line, indicating that the water molecules are selectively dissolved into the membrane and are also predominantly diffused through the membrane. Additionally, the ethanol concentration in the membrane is higher than that in the permeate for ethanol feed concentrations in the range of 10–90 wt%. These results can be explained by the very strong affinity between the ethanol molecules and the PC membrane and also the molecular size of ethanol is rather large. On the other hand, once the water molecules are incorporated into the PC membrane, they can easily diffuse through the PC membrane because the interaction between the water molecule and the PC membrane is very weak and also the molecular size of water is smaller than that of ethanol. Consequently, the water molecules are predominantly permeated through the hydrophobic PC membrane. In addition, the permeation rate decreases with increasing ethanol concentration. Table 3 shows the relationship between the ethanol concentration in the feed solution and the degree of swelling of the PC membrane. The degree of swelling of the PC membrane increases with an increase of ethanol content in the feed. These phenomena might be due to the plasticizing effect of ethanol on the hydrophobic PC membrane. However, compared with the results of the degree of swelling, an opposite trend was obtained for the permeation rate. This result shows that the diffusivity of water is

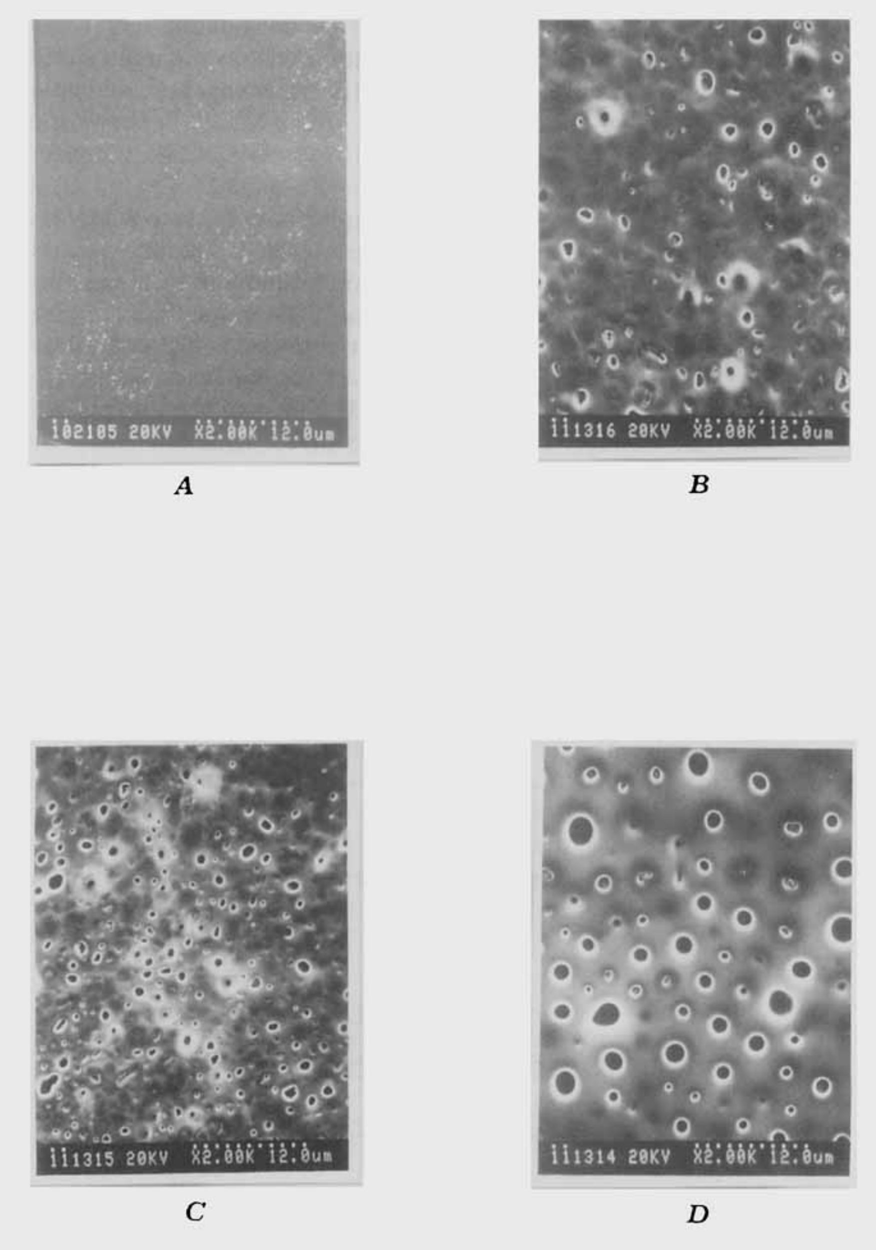

FIG. 3 Cross section of asymmetric membranes from the system PC/CH_2Cl_2/CH_3OH with 2 mL C_2H_5OH additive in casting solution. (A) 8 wt%, (B) 9 wt%, (C) 10 wt%, (D) 12 wt%.

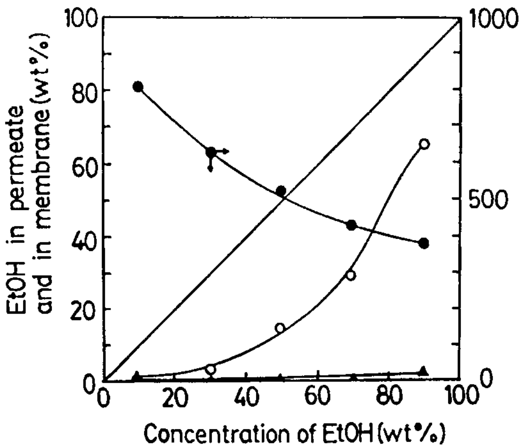

FIG. 4 Effect of feed ethanol concentration on the permeation rate and the composition of the solution adsorbed and permeated through the asymmetric polycarbonate membrane. $PC/CH_2Cl_2/CH_3OH$ with 2 mL C_2H_5OH additive in casting solution. (▲) Permeated, (○) adsorbed, (●) permeation rate.

TABLE 3

Relationship between the Degree of Swelling and Feed Ethanol Concentration for the Asymmetric PC Membrane[a]

Feed ethanol concentration (wt%)	Degree of swelling (g/g)
0	1.04
10	1.19
30	1.25
50	1.39
70	1.50
90	1.57
100	1.59

[a] Coagulation medium: CH_3OH. Additive nonsolvent: 2 mL C_2H_5OH in casting solution.

higher than that of ethanol. Thus, a lower water content of the higher feed ethanol concentration results in a decreasing permeation rate.

Pervaporation Properties of Asymmetric PC Membrane for Different Alcohol–Water Mixtures

According to the solution-diffusion mechanism (9), the size of the permeating species is important in both the solution and diffusion process. The results for pervaporation properties for methanol, ethanol, *n*-propanol, and *t*-butanol mixtures of 90 wt% alcohol in water through an asymmetric PC membrane by pervaporation are shown in Fig. 5. It shows that an increase in the number of carbon atoms in the alcohol results in an increase in the separation factor but also leads to a decrease in the permeation rate. These phenomena can be explained by the molecular size of the feed compound and the affinity between the permeates and the asymmetric PC membrane. The difference of the solubility parameters between the polymer and alcohol, and the degree of swelling of the PC membrane for alcohols, are summarized in Table 4. The separation factor was found to depend on the molecular length of this linear alcohol series. It was also found that the permeation rate increases as the molecular length decreases. The difference of solubility parameter between the polymer and alcohols was in the order of methanol > ethanol > *n*-propanol > *t*-butanol.

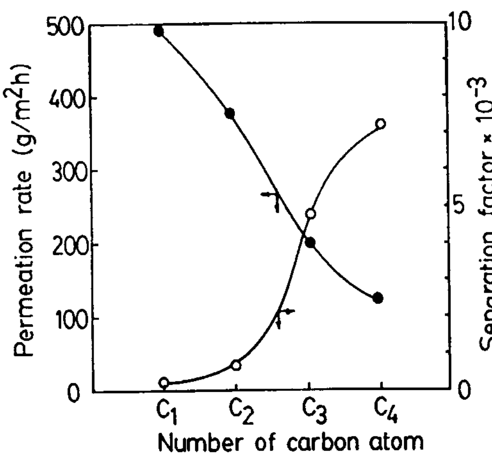

FIG. 5 Effect of molecular size of alcohol on permselectivity of the asymmetric polycarbonate membrane with 90 wt% aqueous alcohol solution. $PC/CH_2Cl_2/C_2H_5OH$ with 2 mL C_2H_5OH additive in casting solution.

TABLE 4
Degree of Swelling of the Asymmetric PC Membrane and the Difference between the Solubility Parameter (δ) of Membrane and Alcohol[a]

Permeating molecule	Degree of swelling	δ $(cal/cm^3)^{1/2}$	$\delta_{PC} - \delta_{alcohol}$
Water	1.04	23.4	13.7
Methanol	1.47	14.5	4.8
Ethanol	1.59	12.7	3.0
n-Propanol	1.62	11.9	2.2
t-Butanol	1.68	10.6	0.9

[a] Coagulation medium: CH_3OH. Additive nonsolvent: 2 mL C_2H_5OH in casting solution. δ_{PC} = 9.7: data taken from J. Brandrup and E. H. Immergut (Eds.), *Polymer Handbook*, Wiley, New York, 1975.

That is, the affinity between membrane and the larger-sized alcohol (*t*-butanol) should become stronger, and the degree of swelling for larger-sized alcohol should become higher than that of small-sized alcohol (methanol). Consequently, this result showed that the solubility of alcohols for the asymmetric PC membrane was higher than that of water, but the diffusivity of water across the membrane was much higher than that of the alcohols. This phenomenon was also observed by Uragami et al. for various hydrophobic membranes (18). The compositions of alcohols incorporated preferentially into the asymmetric PC membrane are shown in Table 5. Table 5 shows that the separation factor of sorption for all binary

TABLE 5
Pervaporation and Sorption Performance of the Asymmetric PC Membrane for Binary Alcohol Mixtures[a]

Binary alcohol mixtures (50/50 wt%)		Separation factor	
a	*b*	Sorption	Pervaporation
Methanol	Ethanol	0.85	20.0
Methanol	*n*-Propanol	0.71	101.0
Ethanol	*n*-Propanol	0.82	2.5

[a] Coagulation medium: CH_3OH. Additive nonsolvent: 2 mL C_2H_5OH in casting solution. Operation temperature: 25°C. Separation factor = $(M_a/M_b)/(F_a/F_b)$, $(P_a/P_b)/(F_a/F_b)$ where *F*, *M*, and *P* are the composition of one component in the feed, membrane, and permeate, respectively.

alcohol mixtures is lower than unity; that is, the higher alcohol was preferential adsorbed into the PC membrane for binary alcohol mixtures. This result agrees with the degree of swelling of the PC membrane for the single component measurement in Table 4. Nevertheless, the separation factor of pervaporation is higher than that of sorption. These trends might be due to the fact that the small-sized alcohol predominantly diffused through the PC membrane. Thus, it may be concluded that both water/alcohol and methanol/other alcohol systems have the same permeation and separation mechanisms.

Effect of Nonsolvent in Casting Solution on Pervaporation Performance

The PC membrane prepared via a wet-phase inversion method has a lower permeation rate of 55 $g/m^2 \cdot h$ and a separation factor of 1421 for 90 wt% ethanol feed concentration. In this work, we attempted to improve the permeation rate for aqueous alcohol solution by pervaporation separation. The effect of nonsolvents in the casting solution on pervaporation performances are listed in Table 6. As the molar volume of nonsolvent additives increases, the resultant asymmetric membranes have an increased free volume and a decreased macromolecular packing density. Therefore, the permeation rate sharply increases and the separation factor decreases. For example, the pervaporation separation index (PSI) for the ethanol-added system (2.2×10^5) was evidently higher than that of the unadditive system (7.8×10^4). Thus, the nonsolvent added to the casting solution by wet-phase inversion could effectively improve pervaporation performance. SEM photographs of nonsolvent additives membrane are

TABLE 6
Effect of Nonsolvent in Casting Solution on the Pervaporation Performances for Asymmetric PC Membrane[a]

Nonsolvent additive	Molar volume (mL/mol)	Separation factor	Permeation rate ($g/m^2 \cdot h$)
—	—	1421	55
Methanol	40.70	891	234
Ethanol	58.68	591	374
n-Propanol	75.14	192	415
n-Butanol	91.96	53	579

[a] Coagulation medium: CH_3OH. Operation temperature: 25°C. Feed composition: 90 wt% aqueous ethanol solution. Additive nonsolvent: 2 mL nonsolvent in casting solution.

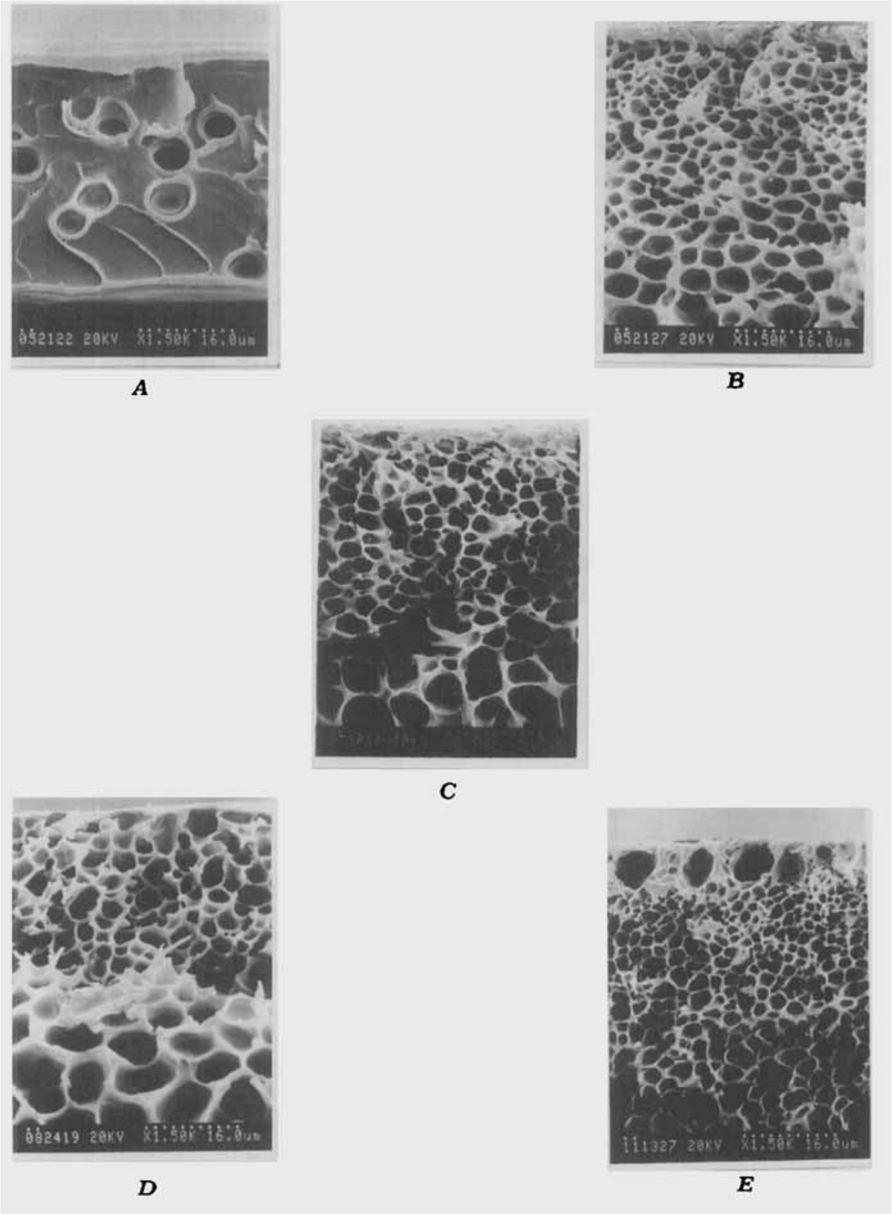

FIG. 6 Cross section of asymmetric membranes from the system $PC/CH_2Cl_2/CH_3OH$ with nonsolvent additive in casting solution. (A) Without additive, (B) methanol, (C) ethanol, (D) *n*-propanol, (E) *n*-butanol.

shown in Fig. 6. The pore size of the membrane sublayer increases and the thickness of the membrane top layer decreases with increasing molar volume of the added alcohols. Note the macrovoid present in the top layer of the *n*-butanol additive system. These results agree well with the data presented in Table 6. Figure 7 shows the effect of nonsolvent (CH_3OH) content in the casting solution on pervaporation performances for 90 wt% aqueous ethanol solution through an asymmetric PC membrane. The separation factor decreases and the permeation rate increases with an increase in the nonsolvent content in the casting solution. The above trend could be explained very well from the ternary phase diagram (14). As a result of the increasing content of nonsolvent in the casting solution, the initial composition profile shifts toward a binodal curve (16–19). These results clearly show that the rate of liquid–liquid demixing increases with increasing nonsolvent content in the casting solution. An asymmetric membrane with a dense top layer and a porous sublayer was obtained by using the wet-phase inversion method. Furthermore, the thickness of the dense top layer decreases with increasing nonsolvent content (14). As a result, the permeation rate increases. The morphology of the above membrane was verified by a study of SEM photographs, as shown in Fig. 8.

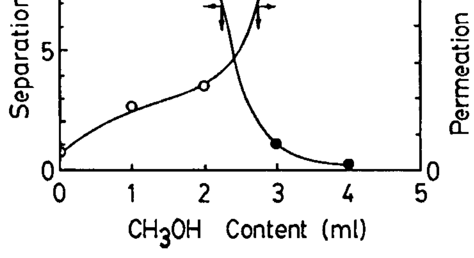

FIG. 7 Effect of methanol content in casting solution on the pervaporation performances for 90 wt% aqueous ethanol solution through the $PC/CH_2Cl_2/CH_3OH$ membrane.

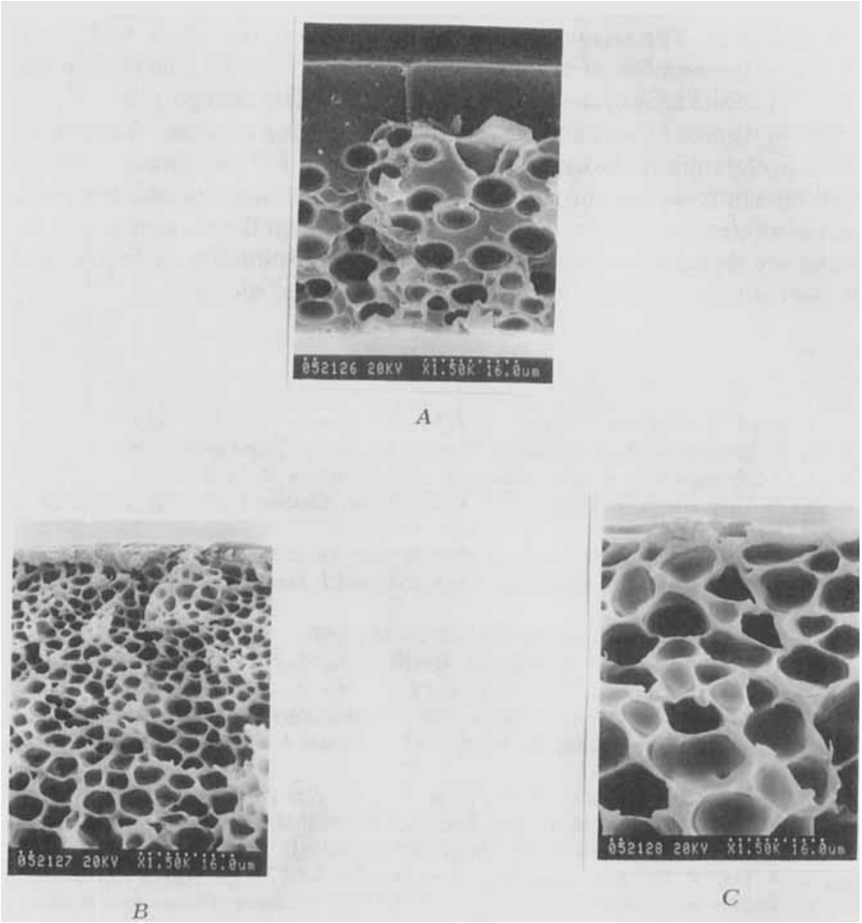

FIG. 8 Cross section of asymmetric membranes from the system $PC/CH_2Cl_2/CH_3OH$ with various nonsolvent contents in casting solution. (A) 1 mL, (B) 2 mL, (C) 3 mL.

CONCLUSION

An asymmetric polycarbonate membrane prepared via the wet-phase inversion method with a nonsolvent added to the casting solution effectively improved the permeation characteristics throughout this study. The key factors affecting membrane morphology include the presence of nonsolvents in the casting solution, kinds of coagulation media, and polymer concentration. The ratio of liquid–liquid demixing decreases with an increase in the number of carbon atoms of alcohol in the coagulation medium. The thickness of the top layer can be varied by changing the polymer concentration or by adding nonsolvent to the casting solution. Water molecules preferentially dissolve in the asymmetric PC membrane and also predominantly diffuse through the membrane. In binary alcohol mixtures, the permselectivities of small-sized alcohol through the asymmetric membrane are decided by two factors: preferential solubility of larger-sized alcohol and predominant diffusivity of small-sized alcohol.

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Received by editor February 11, 1993