Pervaporation of Aqueous Alcohol Solution Through a Polycarbonate/(DMF/Metal Salt) Complex Membrane Prepared via a Wet-Phase Inversion Method

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ABSTRACT: A polycarbonate (PC)/(DMF/metal salt) complex membrane was utilized in the pervaporation of alcohol/water mixtures. The effects of the presence of metal salt in the casting solution, the polycarbonate concentration, and the kinds of coagulation media on the formation of membranes were studied. In addition, the effects of feed composition, size of the alcohol, and the degree of swelling on the pervaporation performances were investigated. Compared with the membrane without additive, the PC/(DMF/metal salt) complex membrane shows an improvement in the pervaporation separation index (PSI). © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1191–1198, 1998

Key words: pervaporation; additive; wet-phase inversion; liquid–liquid demixing; polycarbonate

INTRODUCTION

Pervaporation is an energy-efficient method for separating azeotropic mixtures, compounds with close-boiling point, and heat-sensitive compounds.[1] Therefore, there has been increasing interest in its use. Numerous pervaporation membranes were prepared for the process of dehydration of ethanol–water mixtures.[2–7] The key to successful pervaporation lies in the performance of membranes. Permeation rate and separation factors are two important characteristics determining the performance of membranes. In general, the disadvantage of using dense homogeneous membranes for pervaporation is the low permeation rate. Thus, to improve the permeation rate of the commercial pervaporation membranes are structurally asymmetric, with a dense skin supported by an aporous sublayer. Wet-phase inversion is the most widely used technique for preparing asymmetric membranes. The asymmetric polycarbonate membrane is a potential candidate for the pervaporation separation of aqueous alcohol mixtures because of its good chemical stability and strong mechanical strength. To improve the extremely low permeation rate of PC membranes for the pervaporation separation of alcohol–water mixtures, this study attempts to fabricate asymmetric PC/(DMF/metal salt) complex membranes for pervaporation by a wet-phase inversion process. In this article, the effects of the types of metal salt, the casting polymer concentration, and the concentration of metal salt in DMF on the formation of asymmetric PC complex membranes were studied. In addition, the ef-

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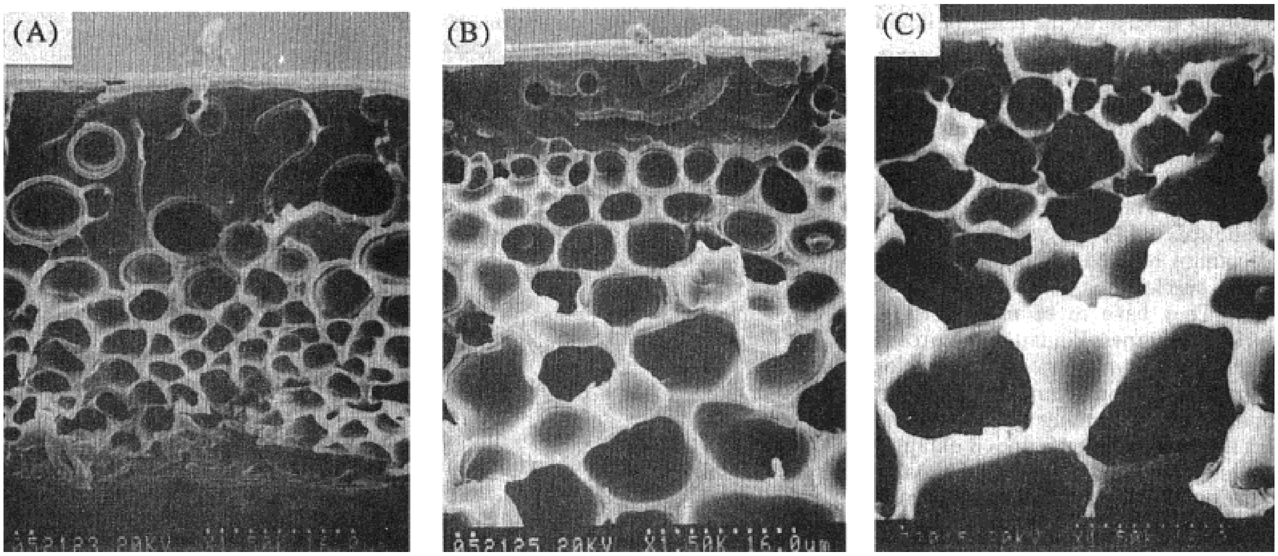

Figure 1 Effect of DMF/CH_2Cl_2 weight ratio in the casting solution on a cross section of the membrane structure. Casting solution: 8 wt % PC in CH_2Cl_2; coagulation medium: CH_3OH. (A) 4 wt %; (B) 8 wt %; (C) 17%.

fect of feed ethanol concentration and degree of swelling on the pervaporation performances were also investigated.

EXPERIMENTAL

Materials

Cobalt(II) chloride, copper(II) chloride, iron(III) chloride, and zinc(II) chloride were used as complex transition metal salts. Polycarbonate (Uplion-2000) was supplied by Mitsubishi Gas Chemical Co. Dichloromethane and *N,N'*-dimethylforamide, supplied by Merck Co., were employed as casting solvents. Methanol, ethanol, *n*-propanol were of reagent grade.

Table I Effect of DMF/CH_2Cl_2 Weight Ratio in the Casting Solution on the Pervaporation Performances

DMF/CH_2Cl_2 Ratio (wt %)	Separation Factor α	Permeation Rate (g m^{-2} h^{-1})	PSI
0	1421	55	78155
4	1277	135	172395
8	491	297	145827
17	36	432	15552

Casting solution: 8 wt % PC in CH_2Cl_2; coagulation medium: CH_3OH; feed ethanol concentration: 90 wt %; feed solution temperature: 25°C; PSI, pervaporation separation index.

Membrane Preparation

The asymmetric membrane were prepared from solution of varying composition of PC/CH_2Cl_2 with metal salt/DMF added. The membrane was

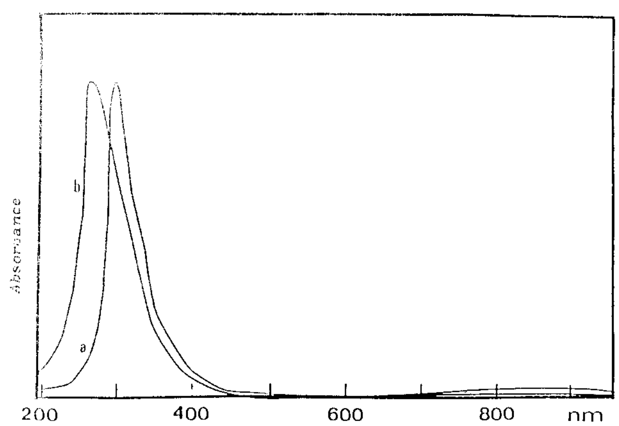

Figure 2 Visible and UV absorption spectra of (A) PC/DMF/$CuCl_2$ solution (B) $CuCl_2$ in CH_2Cl_2/DMF solution.

Table II Effect of S-Value on the Pervaporation Performances

$CuCl_2 \cdot 2H_2O$/DMF Mol Ratio (S)	Separation Factor α	Permeation Rate (g m^{-2} h^{-1})
0.010	1400	125
0.022	1375	210
0.045	1116	305
0.090	891	565

Casting solution: 10 wt % PC in CH_2Cl_2; coagulation medium: CH_3OH.; S-value: the mol ratio of the $CuCl_2 \cdot 2H_2O$/DMF; feed ethanol concentration: 90 wt %; feed solution temperature: 25°C.

formed by casting the solution onto a glass plate to a pervaporation thickness by using a Gardner knife. The glass plate was immersed in the coagulation medium for 5 min. Then, the membrane was peeled off and dried in vacuum for 24 h. The average membrane thickness was about 50 μm.

SEM

The membrane structure were examined by an Hitachi Model S570 scanning electron microscope (SEM). The samples were coated with gold to about 150 Å.

Viscometric Measurement

The viscometric measurements were carried out with an Ubbelohde Viscometer. The PC polymer was dissolved in a dichloromethane casting solvent. The viscosities of the solvent and of the casting solution with different concentrations were measured at 25 ± 0.1°C.

Characterization

FITR spectra were recorded on a Jasco FT/IR-7000 and elemental analysis (EA) carried out using a Perkin–Elmer 240C EA.

Pervaporation

The pervaporation experimentals of the aqueous alcohol solution were performed with a traditional pervaporation processes.[8] The experiments were conducted at 25°C. The analytical measurements for the determination of the water and alcohol concentration in the feed and permeate solutions were carried out by gas chromatography (G.C., China chromatography 8700T). The separation factor, α, was calculated from the following equation:

$$\alpha^{H_2O}_{ethanol} = \frac{Y_{H_2O}/Y_{ethanol}}{X_{H_2O}/X_{ethanol}}$$

where Y_{H_2O}, $Y_{ethanol}$, and X_{H_2O}, $X_{ethanol}$ are the weight fraction of water and alcohol in the perme-

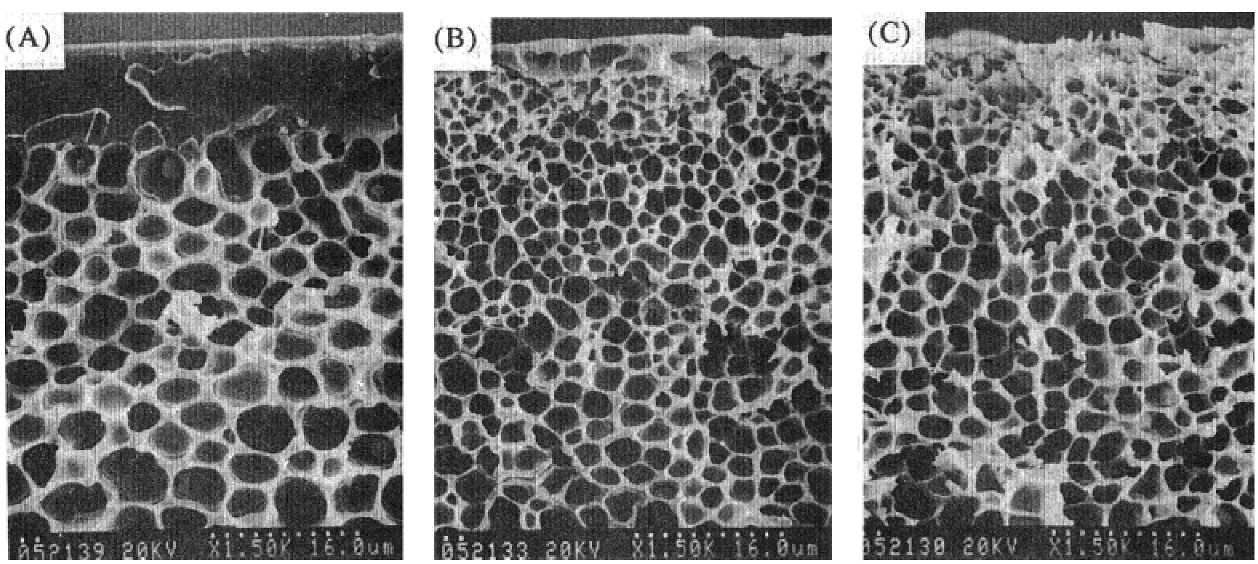

Figure 3 Effect of an S-value on a cross-section of the membrane structure. Casting solution: 10 wt % PC in CH_2Cl_2. (A) S = 0.01; (B) S = 0.045; (C) S = 0.09.

Table III Effect of PC Concentration in the Casting Solution on the Pervaporation Performances and on the FTIR Ratio of (A_{1650}/A_{1598}) and (A_{1775}/A_{1508})

PC Concentration	Relative Absorbance		Separation Factor α	Permeation Rate (g m^{-2} h^{-1})
	(A_{1650}/A_{1508})[a]	(A_{1775}/A_{1508})[b]		
8	0.22	1.31	870	351
10	0.26	1.25	1116	305
12	0.47	1.21	1791	210

$CuCl_2 \cdot 2H_2O$ (0.3 g)/DMF 3 mL additive in the casting solution; coagulation medium: CH_3OH; coagulation time: 5 min; coagulation temperature: 20°C; feed ethanol concentration: 90 wt %.

[a] The relative absorbance of the shift amide carbonyl group to the benzene ring group.

[b] The relative absorbance of the ester group to the benzene ring group.

ate and feed, respectively. The permeation rate was determined by measuring the weight of the permeate.

RESULTS AND DISCUSSION

Effect of the Addition of DMF on the Pervaporation Performances

The effect of the addition of nonvolatile solvent (DMF) in the casting solution on pervaporation performances is listed in Table I. As the ratio of DMF/CH_2Cl_2 (additive/solvent) increases, the pervaporation separation Index (PSI) value reaches a maximum at approximately 4 wt % of the DMF/CH_2Cl_2 ratio. The PSI value of 4 wt % DMF/CH_2Cl_2 is evidently higher than that of the unadditive system. However, the increase in nonsolvent (DMF) concentration of the casting solution enhances the rate of liquid–liquid demixing, resulting in a decrease in the top layer thickness of the asymmetric membrane.[9] Thus, the asymmetric membrane with a lower separation factor were obtained by using a casting solution with a higher DMF/CH_2Cl_2 ratio (17 wt %). The SEM photographs are shown in Figure 1. It shows that the thickness of the membrane top layer decreases with the increase of the DMF/CH_2Cl_2 ratio from 0–17 wt %. This observation agrees with the result shown in Table I.

Effect of Metal Complexes on the Pervaporation Performances

Ultraviolet and FTIR were used to confirm the existence of a metal complex in the membrane. The UV spectra of the $CuCl_2$/DMF solution and the PC/(DMF/$CuCl_2$) casting solution are shown in Figure 2. The spectrum of DMF/$CuCl_2$ system shows a maximum absorption peak at 263 nm. The absorption band at 263 nm shifts to 295 nm in the spectrum of the PC/(DMF/Cu_2Cl_2) casting

Table IV Effect of Metal Salt Additives in the Casting Solution on the Pervaporation Performances of Polycarbonate Membrane

Kinds of Salts	*N* Content (%)	Casting Solution Viscosity (dL/g)	Separation Factor α	Permeation Rate (g m^{-2} h^{-1})
$FeCl_3$	0.79	2.36	2036	111
$ZnCl_2$	0.50	2.34	1491	208
$CuCl_2$	0.49	2.29	1116	305
$CoCl_2$	0.30	1.95	947	454

Casting solution: 10 wt % PC in CH_2Cl_2; casting temperature: 20°C; coagulation temperature: 25°C; coagulation medium: 5 min; feed ethanol concentration: 90 wt %.

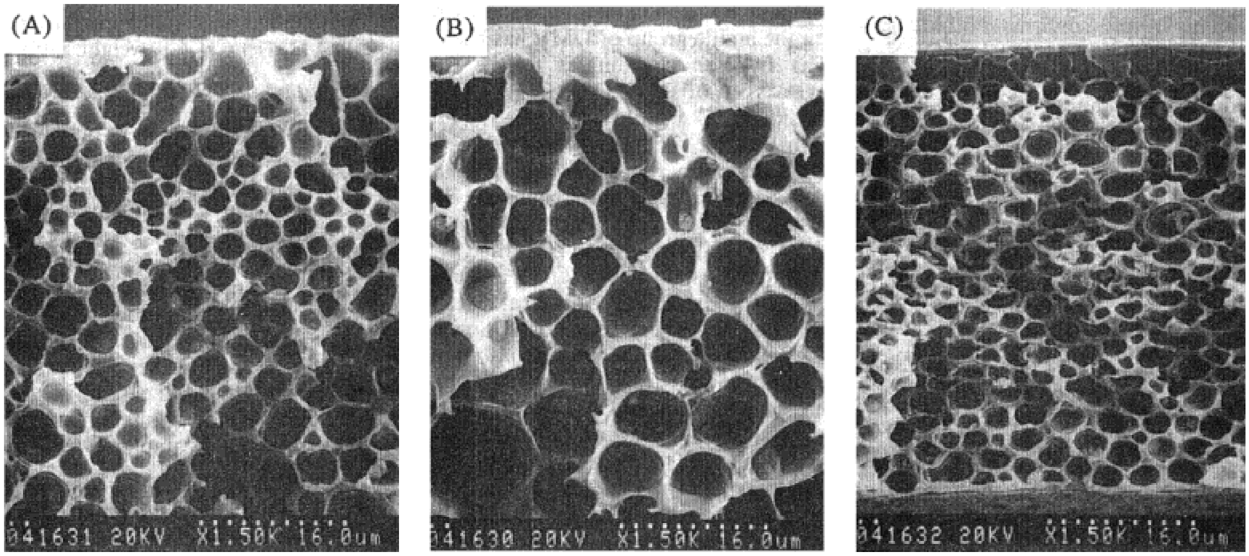

Figure 4 Effect of polymer concentration in the casting solution. The PC/(DMF/$CuCl_2$)/C_2H_5OH system with S = 0.045 additive on a cross section of the membrane structure. (A) 8 wt %; (B) 10 wt %; (C) 12 wt %.

solution. This result suggests that the metal complex forms in the system of PC/(DMF/$CuCl_2$).

Effect of the DMF/$CuCl_2$ Concentration on the Pervaporation Performance

S-value is defined here as the molar ratio of $CuCl_2$ to DMF in the casting solution . The effect of the S-value on the pervaporation performance of the PC/(DMF/$CuCl_2$)/CH_3OH membrane is shown in Table II. Table II shows that the separation factor decreases and the permeation rate increases with an increase of the S-value in the casting solution. From the ternary phase diagram an increase in the concentration of the added metal salt could shift the initial casting composition toward the binodal curve, indicating the casting solution is easier to proceed rapid liquid–liquid demixing.[10] A higher concentration of added metal salt results in a more porous membrane that possesses a higher permeation rate. This deduction was verified by scanning electron microscopy, as shown in Figure 3(A–C). It can be seen from Figure 3 that the thickness of the dense top layer decreases with increasing S-value in the casting solution.

Effect of Polymer Concentration on the Pervaporation Performances

The effect of the PC concentration in the casting solution on the pervaporation performance of the PC/(DMF/$CuCl_2$)/C_2H_5OH membrane is shown in Table III. It shows that the permeation rate decreases and the separation factor increases with increasing polycarbonate concentration in the casting solution from 8–12 wt %. These results can be reasoned by the fact that an increase in PC concentration results in a decrease in the rate of liquid–liquid demixing and, hence, an increase in the thickness of the top layer. Moreover, increasing the initial polymer concentration in the casting solution leads to higher volume fraction of the polymer, and consequently, a membrane with lower porosity is obtained. The C=O stretching band of the ester group of the PC polymer at 1775 cm^{-1} was found to be independent of the PC concentration. However, the relative absorbance decreases with decreasing PC concentration. In addition, another relative absorbance C=O stretching band also increases. The increase of relative absorbance indicates that the amount of complexs increases, resulting in a lower permeation rate and a higher separation factor. Besides, it can be observed from Figure 4 that the thickness of the top layer increases with increasing polymer concentration. This observation corresponds well with the results shown in Table III.

Effect of Metal Salt Additives in the Casting Solution on the Pervaporation Performances

The effects of four types of mental salt such as: $FeCl_3$, $ZnCl_2$, $CuCl_2$, and $CoCl_2$ on the pervapora-

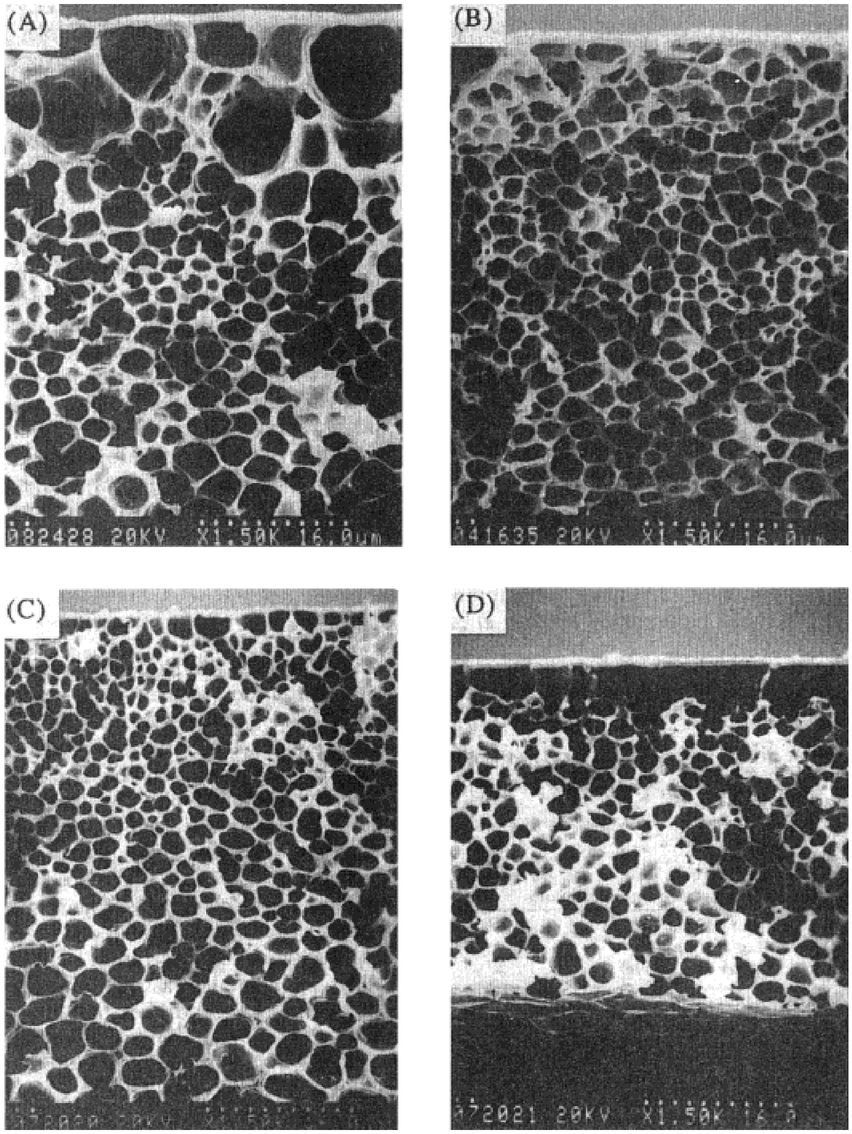

Figure 5 Effect of various metal salt additives on the membrane structure. Casting solution: 10 wt % PC in CH_2Cl_2 and (salt/DMF)/CH_2Cl_2 12.7 wt %. (A) $CoCl_2 \cdot 6H_2O$; (B) $CuCl_2 \cdot 2H_2O$; (C) $ZnCl_2$; (D) $FeCl_3 \cdot 6H_2O$.

tion performances were investigated. The result was shown in Table IV. The membrane with the highest separation factor was obtained by using CH_3OH as the coagulation medium and adding $FeCl_3$/DMF (S = 0.045) in the casting solution. The separation factors of the four membranes follow the order of $FeCl_3 > ZnCl_2 > CuCl_2 > CoCl_2$. It was also observed that the separation factor increases with the increase of the viscosity of the casting solution. In addition, on basis of the EA results, the nitrogen content of the PC/(DMF/metal salt) membrane increases with an increase of the casting solution viscosity. These phenomena might be accounted for the fact that the casting solution viscosity was enhanced by the increasing of the interaction between the PC structure and the metal salt solution, resulting in the intensity of complex formation increases. Thus, the pore size of the membrane reduces and then results in an increase in the separation factor. The SEM photographs of the four membranes prepared by various types of metal salt additives are shown in Figure 5. The thickness of the top layer of the asymmetric membrane increases with the increasing of the viscosity of the casting solution. These observations correspond well with the results described in Table IV.

Effect of the Feed Ethanol Concentration in the Feed on Pervaporation Performance

Table V shows the influence of the feed ethanol concentration in the feed on the pervaporation performance through the asymmetric PC membrane prepared by adding ($CuCl_2$/DMF) metal salt solution (S = 0.045) in the casting solution. The results show that the permeation rate decreases and the separation factor increases with increasing ethanol concentration. The affinity between the permeates and the PC membrane can further illustrate the above phenomenon. The difference of the solubility parameter between the alcohol and the PC membrane ($\delta_{PC} - \delta_{EtOH} = 3.0$ $(cal/cm^3)^{1/2}$) is lower than that of the water and the PC membrane ($\delta_{PC} - \delta_{H_2O} = 13.7$ $(cal/cm^3)^{1/2}$).[11,12] Water molecules can easily diffuse through the PC membrane because the interaction between the water and the PC membrane is very weak and the molar volume of water is small. Thus, a lower water content (higher feed ethanol concentration) results in a decreasing permeation rate. Moreover, the degree of swelling increases as the feed ethanol concentration increases, as shown in Figure 6. This can be explained by the fact that the strong affinity between ethanol and the PC membrane plasticizes the asymmetric membrane. This clearly supports that the deffusivity of water is higher than that of ethanol.

Table V Effect of Ethanol Concentration on the Pervaporation Performances through the Asymmetric Polycarbonate Membrane, PC/(DMF/$CuCl_2$)/CH_3OH System

Feed Ethanol Concentration (wt %)	Separation Factor α	Permeation Rate (g m^{-2} h^{-1})
90	1116	305
70	945	399
50	743	465
30	487	587
10	211	631

Casting solution: 10 wt % PC in CH_2Cl_2; coagulation medium: CH_3OH; feed solution temperature: 25°C; S-value: 0.045.

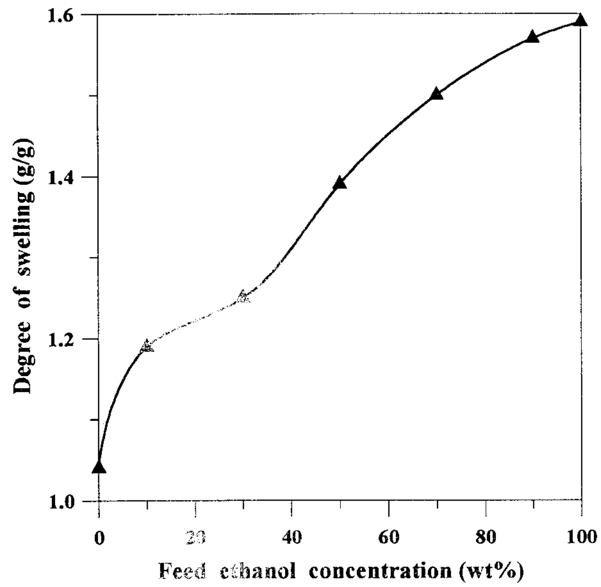

Figure 6 Effect of feed ethanol concentration on the degree of swelling through the PC/($CuCl_2$/DMF)/CH_3OH system membrane with S = 0.045 additive.

CONCLUSION

It has been shown in this work that, depending on the types of metal salt additive and the polycarbonate concentration, a series of polycarbonate complex membranes can be prepared. Thickness of the top layer can be varied by changing the polymer concentration or by adding nonsolvent/metal salt solution in the casting solution. Compared with the membrane without additive, which has a PSI of 7.8×10^4, the PC/(DMF/metal salt) complex membrane shows an improvement in the pervaporation separation index (PSI = 3.4×10^5). Thus, these results suggest that using a metal salt additive to prepare a complex membrane can effectively improve the pervaporation performances of separating aqueous ethanol solution.

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