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

Pervaporation Separation of Water/Ethanol Mixtures through Polycarbonate/Cobalt(III) Acetylacetonate Membranes

Shih-Hsiung Chen; Sing-Peng Chua; Da-Ming Wang; Kueir-Rarn Lee; Juin-Yih Lai

To cite this Article Chen, Shih-Hsiung , Chua, Sing-Peng , Wang, Da-Ming , Lee, Kueir-Rarn and Lai, Juin-Yih(1998) 'Pervaporation Separation of Water/Ethanol Mixtures through Polycarbonate/Cobalt(III) Acetylacetonate Membranes', Separation Science and Technology, 33: 13, 1955 — 1967
To link to this Article: DOI: 10.1080/01496399808545039
URL: http://dx.doi.org/10.1080/01496399808545039

SEPARATION SCIENCE AND TECHNOLOGY, 33(13), pp. 1955–1967, 1998

Pervaporation Separation of Water/Ethanol Mixtures through Polycarbonate/Cobalt(III) Acetylacetonate Membranes

SHIH-HSIUNG CHEN*
DEPARTMENT OF ENVIRONMENTAL ENGINEERING AND HEALTH
CHIA NAN COLLEGE OF PHARMACY AND SCIENCE
TAINAN, TAIWAN 717, REPUBLIC OF CHINA

SING-PENG CHUA and DA-MING WANG
DEPARTMENT OF CHEMICAL ENGINEERING
CHUNG YUAN UNIVERSITY
CHUNG LI, TAIWAN 32023, REPUBLIC OF CHINA

KUEIR-RARN LEE
DEPARTMENT OF CHEMICAL ENGINEERING
NANYA JUNIOR COLLEGE
CHUNG LI, TAIWAN 32034, REPUBLIC OF CHINA

JUIN-YIH LAI
DEPARTMENT OF CHEMICAL ENGINEERING
CHUNG YUAN UNIVERSITY
CHUNG LI, TAIWAN 32023, REPUBLIC OF CHINA

ABSTRACT

In the present work, cobalt(III) acetylacetonate [$Co(acac)_3$] was added to polycarbonate (PC) to improve its performance on pervaporation separation of water/ethanol mixtures. By adding 3 wt% of $Co(acac)_3$, the resulting PC/$Co(acac)_3$ complex membrane possessed a permeation rate similar to a pure polycarbonate membrane, but the separation factor (water/ethanol) was about three times higher. The stability of the complex membrane was tested, and it was found that, after being immersed in an aqueous ethanol solution for 72 hours, the complex membrane was still stable.

* To whom correspondence should be addressed.

In addition, the effects of the added amount of $Co(acac)_3$ and the feed composition on pervaporation performance are presented in this work, and the mechanism of the improvement in pervaporation performance is briefly discussed.

Key Words. PC/cobalt(III) acetylacetonate membrane; Pervaporation separation index value; Solubility ratio; Pervaporation

INTRODUCTION

Pervaporation is an efficient process for the separation of azeotropic mixtures, close-boiling-point mixtures, and structural isomers (1–3). In the present work, preparation of membranes suitable for the pervaporation separation of water–ethanol solutions is discussed. Both ethanol-selective and water-selective membranes can be applied to the pervaporation of water/ethanol solutions (4–6). Although many researchers have focused on synthesizing ethanol-selective membranes (7–9), water-selective membranes are, in fact, more common. It is known that the pervaporation performance of water-selective membranes can be improved by elevating the hydrophilicity of the membranes. For example, it has been reported that γ-ray irradiation, chemical grafting, and plasma deposition (10–12) can increase the hydrophilicity of membranes, and the pervaporation performance can thus be improved. Another efficient method to improve pervaporation performance is to add salt to the casting solution to form polymer/salt complex membranes (13–15), which is the focus of the present work.

It has been reported that the addition of salt in membranes can enhance the pervaporation flux (13–15). It has also been observed that adding a small amount of salt in the feed can elevate the selectivity of membranes drastically (16). However, when polymer/salt complex membranes are used as pervaporation membranes, the stability of the salt content in the membranes has always been a problem because the salt might dissolve in the liquid feed (17). How to retain the stability of the salt in membranes is very important in the application of polymer/salt complex membranes to pervaporation.

In the present work a cobalt salt, cobalt(III) acetylacetonate [$Co(acac)_3$], was added in the polycarbonate (PC) membranes to improve its performance on pervaporation separation of water/ethanol mixtures. It will be shown that this polymer/salt complex membranes possesses good stability and has a separation factor three times higher than that of the pure polycarbonate membranes.

EXPERIMENTAL

Materials

Polycarbonate (Upsilon S-2000) (MW = 28,000) was purchased from Mitsubishi Gas Chemical Company, and dichloromethane and cobalt(III) acetyla-

cetonate [$Co(acac)_3$] were supplied by Merck Company. The above-mentioned chemicals were all of reagent grade.

Membrane Preparation

The PC membranes were prepared from a casting solution of polycarbonate in dichloromethane. The PC/$Co(acac)_3$ membranes were prepared from PC/dichloromethane casting solutions containing various amounts of cobalt(III) acetylacetonate (1–7.5 wt%). The membranes were formed by casting the solution onto a glass plate to a predetermined thickness (350 μm) using a Gardner knife at room temperature. The membranes were dried at room temperature for 30 minutes. The membranes were then peeled off and put in a vacuum for 24 hours before sorption and pervaporation measurements. According to SEM analysis, the prepared membranes are dense and symmetric, with a thickness ranging from 25 to 30 μm. It should be noted that the membrane thickness is independent of the cobalt salt content.

Pervaporation Experiment

A traditional pervaporation setup was used (9). In pervaporation the feed solution is in direct contact with the membrane. The effective membrane area was 10.2 cm^2. The upstream pressure was 1 atm and the downstream was vacuumed to about 3 mmHg (400 Pa). The feed temperature was controlled at 25°C. Before sampling, 90 minutes was allowed to let the system reach the steady state. The permeate collection time was 30 minutes. The permeation rate was determined by measuring the weight of permeate, and the compositions of the feed solution and the permeate were determined by gas chromatography (GC China Chromatography). The separation factor, $\alpha_{A/B}$, is defined as

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

where X_A, X_B and Y_A, Y_B are the weight fractions of A and B in the feed and in the permeate (A represents the more permeative species), respectively.

Contact Angle Measurements

The contact angle of water was measured with a FACE contact angle meter (CA-D type, Kyowa Interface Science Co.). The reported data for each sample were the average of three measurements, and the standard deviation was about 3%.

Sorption Measurements

The membranes was immersed in the ethanol–water mixture for 24 hours at 25°C. They were subsequently blotted between tissue paper to remove

excess solvent and were then placed in the left half of a twin tube setup. Desorption was then performed: the system was evacuated for 30 minutes while the left tube was heated with hot water (90°C), and the right tube was cooled in liquid nitrogen. The composition of the condensed liquid in the right tube was determined by GC. The selectivity of sorption was calculated from

$$\alpha_{sorp} = (Y_w/Y_e)/(X_w/X_e)$$

where X_e, X_w and Y_e, Y_w are the weight fractions of ethanol and water in the feed and in the membranes, respectively.

RESULTS AND DISCUSSION

Stability of the Cobalt Salt

For salt-containing membranes the stability of salt is usually a problem because the salt might dissolve in the liquid feed. Therefore, the stability of cobalt(III) acetylacetonate [$Co(acac)_3$] in the polycarbonate membranes was examined by performing the dissolution test of PC/$Co(acac)_3$ membranes in a aqueous ethanol solution. The membranes were placed in a solution of ethanol and water (90 wt% ethanol) for 72 hours to investigate if the salt, complexed in membranes, would dissolve in the solution. Ultraviolet studies were carried out to examine if cobalt ion existed in the solution. When the solution contained a small amount of cobalt salt (0.05 wt%), a peak was observed in the UV spectrum of the solution, as shown in Fig. 1 (Line a). However, for solutions in which membranes containing various amounts of cobalt salt were immersed for 72 hours, no obvious peaks were found in the UV spectra, as shown in Fig. 1 (Lines b–e). The absence of any absorption peak in the UV spectrum indicates that the cobalt ion is almost undetectable in the dissolution solution. In other words, loss of cobalt salt from the membranes did not occur after 72 hours of immersion of the membranes in the ethanol aqueous solution, indicating the cobalt salt in the polycarbonate membranes is very stable.

Effect of $Co(acac)_3$ Content on the Pervaporation Performance

The effect of the salt content in the membrane on pervaporation performance is reported in Table 1. By comparing the result for the pure PC membrane with that for the PC membrane containing 1 wt% $Co(acac)_3$, it was found that the addition of cobalt salt elevates the separation factor but reduces the permeation flux. Similar phenomena were also observed when the same membranes were applied to gas separation (18), and can be accounted for by

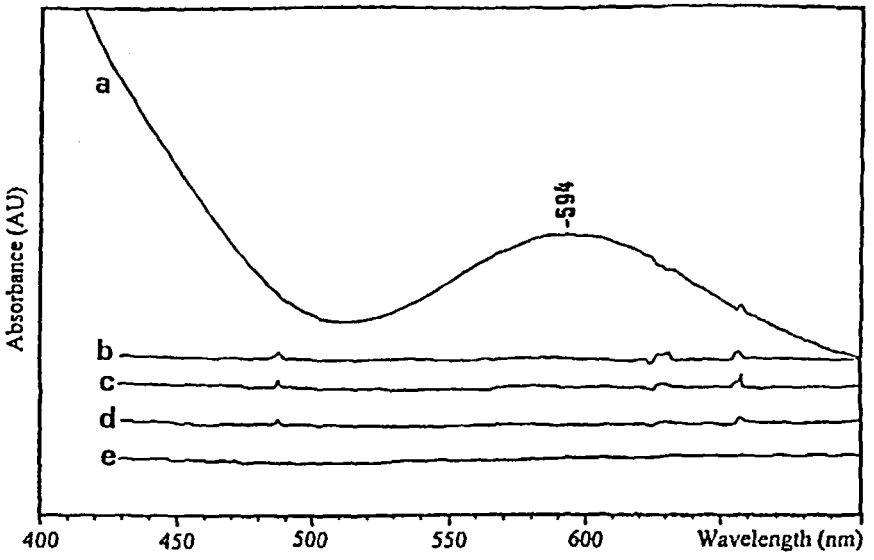

FIG. 1 UV spectra of the dissolution solutions. The dissolution experiments were performed by immersing the PC/$Co(acac)_3$ membranes in an aqueous ethanol solution with 90 wt% ethanol. The amount of $Co(acac)_3$ dissolved in the solution was: (a) 0.05 wt%, (b) 5 wt%, (c) 10 wt%, (d) 15 wt%, and (e) 20 wt%.

TABLE 1
Effect of $Co(acac)_3$ Content in the PC/$Co(acac)_3$ Membrane on the Pervaporation Performance[a]

$Co(acac)_3$ content (wt%)	Permeation flux ($g/m^2 \cdot h$)	Separation factor, α_{per}	PSI[b]
Pure PC	168	110	19,200
1	126	373	46,500
3	162	370	61,200
5	175	233	38,500
7.5	188	175	28,700

[a] Feed concentration 90 wt% ethanol aqueous solution, 25°C.
[b] PSI = (permeation rate) × (separation factor).

TABLE 2
Effect of $Co(acac)_3$ Content on the Sorption Properties

$Co(acac)_3$ content (wt%)	Ethanol in feed (wt%)	Total sorption (g/100 $g_{membr.}$)	Water sorption (g/100 $g_{membr.}$)	Ethanol sorption (g/100 $g_{membr.}$)	Separation factor	
					α_{sorp}	α_{per}
0	90	6.0	1.72	4.28	3.6	110
1	90	6.3	2.21	4.09	4.9	373
3	90	6.5	2.46	4.04	5.5	370
5	90	6.6	2.47	4.13	5.5	233
7.5	90	7.1	3.26	3.84	7.7	175

the cobalt salt making PC membranes denser, as evidenced by an increasing membranes density.

It was therefore expected that a higher cobalt content would result in a lower permeation flux and a higher separation factor. When complex membranes are applied for gas separation, the results follow the above deductions (18). However, the results shown in Table 1 for pervaporation are completely opposite to the above expectation: a higher cobalt content results in a higher permeation flux and a lower separation factor.

We propose a mechanism to resolve the above contradiction. In pervaporation the liquid feed, which could swell the membrane, is in direct contact with the membrane. A higher cobalt salt content results in a higher degree of swelling due to the high affinity between the cobalt salt and water (solvation effect). And a higher degree of swelling loosens the entanglement of polymer chains and results in a less dense structure. Therefore, although a higher cobalt salt content makes the membrane more dense for gas separation, when the membrane is in contact with water the higher degree of swelling caused by the solvation effect of the cobalt salt makes the membrane less dense. Obviously, the swelling effect dominates in pervaporation, and hence the permeation flux increases and the separation factor decreases with increasing cobalt content in the membrane.

To verify the above mechanism, the effect of cobalt content on the swelling (sorption of liquid) of membranes was investigated experimentally. The results are presented in Table 2. It can be seen that, as expected, the sorption amount does increase with increasing cobalt content, and the increase in the amount of sorption is mainly due to the increase of water sorption. Therefore, the mechanism described in the preceding paragraph seems quite reliable: The swelling of membranes, caused by the solvation effect of the cobalt salt, plays an important role in pervaporation. Further discussion on this point is given below.

Effect of $Co(acac)_3$ Content on the Sorption and Diffusion Properties

According to the solution-diffusion model (19), the permeability (P) of a permeant through a membrane is a product of the solubility (S) and the diffusivity (D). The effects of the cobalt content on the solubility and the diffusivity are discussed in this section.

Sorption experiments were performed to determine the solubility of ethanol and water in PC/$Co(acac)_3$ membranes. The results on the amount of sorption are presented in Table 2, and the water composition in the membrane is depicted in Fig. 2. It can be seen that the water composition in the membrane is higher than that in the liquid feed, indicating that water is preferentially sorbed in the membrane. The preferential sorption of water is related to the cobalt content: higher cobalt content results in higher water composition in the membrane. The dependence of water sorption on the $Co(acac)_3$ content

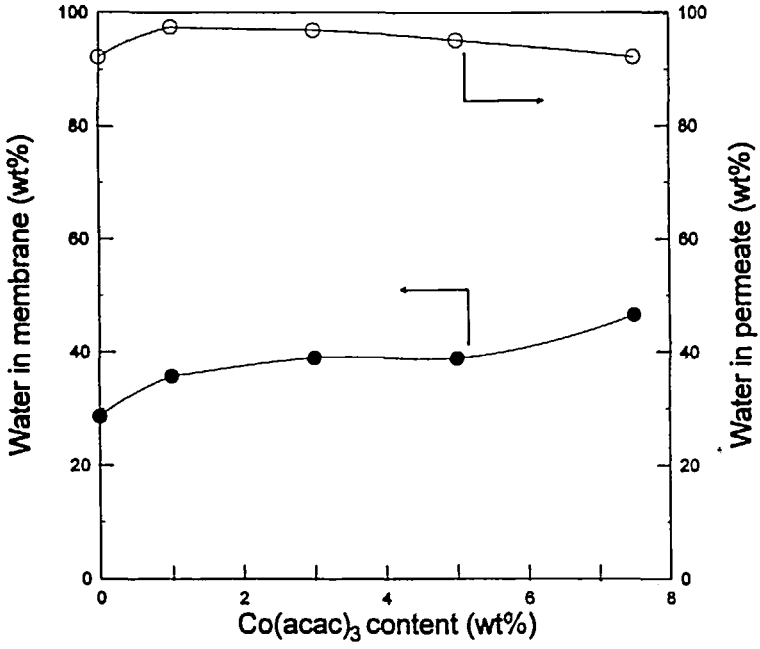

FIG. 2 Effect of $Co(acac)_3$ content on the water concentrations in the permeate and in the membrane.

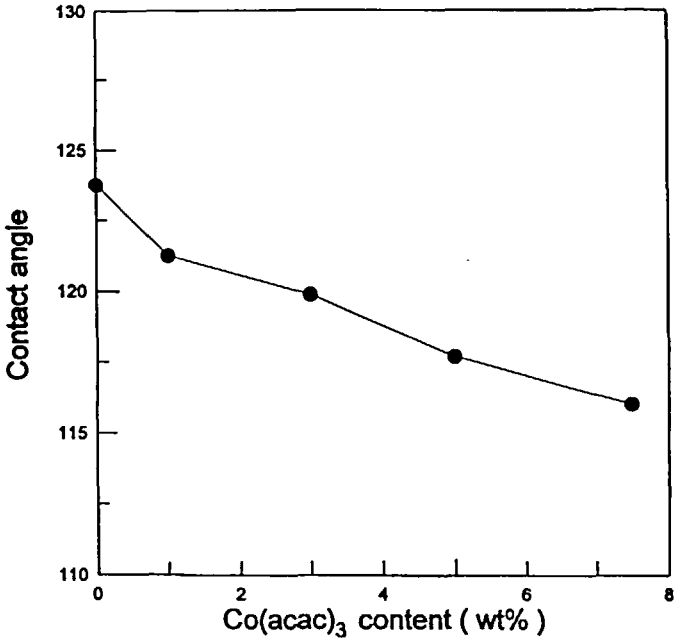

FIG. 3 Effect of $Co(acac)_3$ content on the water contact angle.

was further checked by measuring the water contact angle of membranes with various $Co(acac)_3$ contents. The data are presented in Fig. 3. It can be seen that the water contact angle decreases with increasing $Co(acac)_3$ content in the membrane. Since a lower water contact angle indicates stronger interaction between water and the PC/$Co(acac)_3$ membrane, the data shown in Fig. 3 suggest that the hydrophilicity of the PC membrane increases with an increasing amount of $Co(acac)_3$. The results from the water contact angle experiments agree well with those from the sorption experiments.

On basis of the pervaporation selectivity (Table 1) and the water composition in the permeate (Fig. 2), the PC/$Co(acac)_3$ membranes possess high water permselectivity. Part of the permselectivity stems from the preferential sorption of water discussed in the preceding paragraph. However, by comparing the separation factors from sorption and pervaporation (Table 2), and comparing the water compositions in the membrane and in the permeate, it can be seen that the preferential sorption of water alone is not enough to explain

the high water permselectivity of pervaporation. According to the solution-diffusion model, the permselectivity due to diffusion should also be considered to completely describe the pervaporation process. Additional evidence showing that preferential sorption cannot completely explain the pervaporation performance is that the separation factor decreases but the sorption amount increases with increasing $Co(acac)_3$ content.

The permselectivity due to the diffusivity difference between the permeants originates from the difference in molecular size. Water has a smaller size than ethanol and therefore has a higher diffusivity, which also contributes to the high water permselectivity. The diffusivities of permeants through membranes can be determined on the basis of the solution-diffusion model: $P = D*S$, where P is the permeability, S denotes the solubility, and D stands for the diffusivity. P can be calculated from the permeation flux, and S can be determined from the sorption experiment. With P and S, D can be calculated. The results of the solubility and diffusivity ratios of water to ethanol are depicted in Figs. 4 and 5, respectively. From these two figures it can be seen

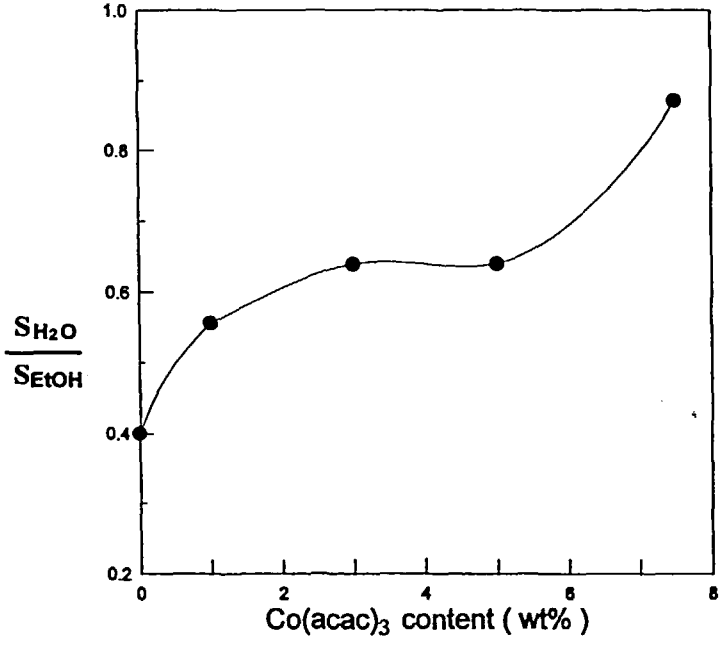

FIG. 4 Effect of $Co(acac)_3$ content on the solubility ratio of water to ethanol.

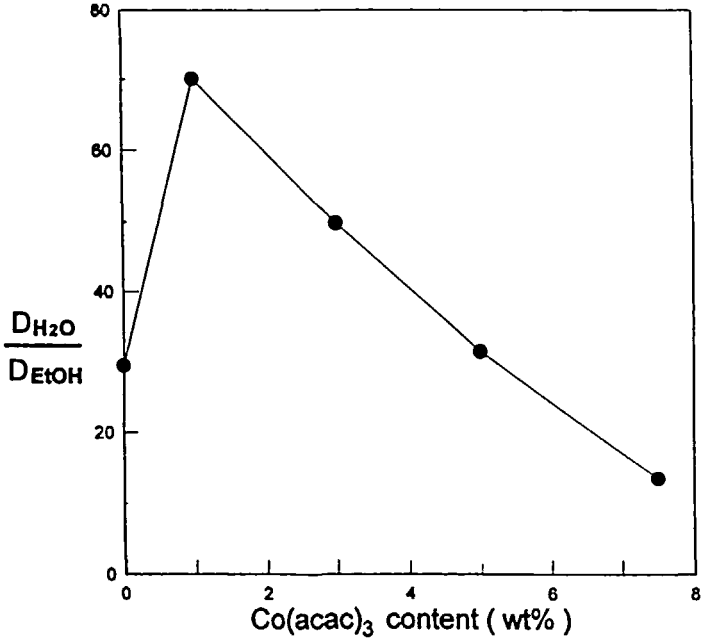

FIG. 5 Effect of $Co(acac)_3$ content on the diffusivity ratio of water to ethanol.

that water is preferentially dissolved into the membrane and diffuses faster through the membrane than ethanol, which therefore results in high water permselectivity.

On basis of Fig. 4, the solubility ratio of water to ethanol increases with an increasing amount of $Co(acac)_3$, which can be accounted for by the high affinity between $Co(acac)_3$ and water (solvation). The diffusivity ratio, shown in Fig. 5, first increases but then decreases with an increasing amount of $Co(acac)_3$. The diffusivity ratio is strongly related to the membrane structure: a denser membrane structure results in a higher diffusivity ratio. The addition of $Co(acac)_3$ makes the polycarbonate membrane denser (18), and therefore results in the increase of diffusivity ratio shown in Fig. 5. However, with the addition of more $Co(acac)_3$, the degree of swelling of membranes becomes higher and results in decrease of diffusivity ratio shown in Fig. 5. Obviously, the effect of diffusivity dominates the behavior of pervaporation because the separation factors of pervaporation (Table 1) follow the same trend as the diffusivity ratio (Fig. 5) but not the trend of the solubility ratio (Fig. 6).

Effect of Feed Composition on Pervaporation Performance

On basis of the above discussion, the permeation flux increases but the separation factor decreases with an added amount of $Co(acac)_3$ due to the swelling effect. The pervaporation separation index (PSI), defined as the product of the permeation flux and the separation factor, was calculated and is presented in Table 1. A maximum PSI value of 61,200 occurs with the addition of 3 wt% $Co(acac)_3$ in the polycarbonate membrane. Compared to the pure PC membrane, the complex membrane possesses a similar permeation flux, but has a separation factor three times higher. It is obvious that the pervaporation of PC membranes can be improved by the addition of $Co(acac)_3$, and the optimal amount to add is about 3 wt%.

The above discussions are based on a feed composition of 90 wt% ethanol. The effect of the feed composition on the pervaporation performance of the PC/$Co(acac)_3$ membrane [3 wt% $Co(acac)_3$] is discussed in what follows. Figure 6 shows the influence of ethanol concentration in the feed on ethanol concentrations in the permeate and in the membrane. It can be seen that ethanol concentration in the permeate is very low and is insensitive to the

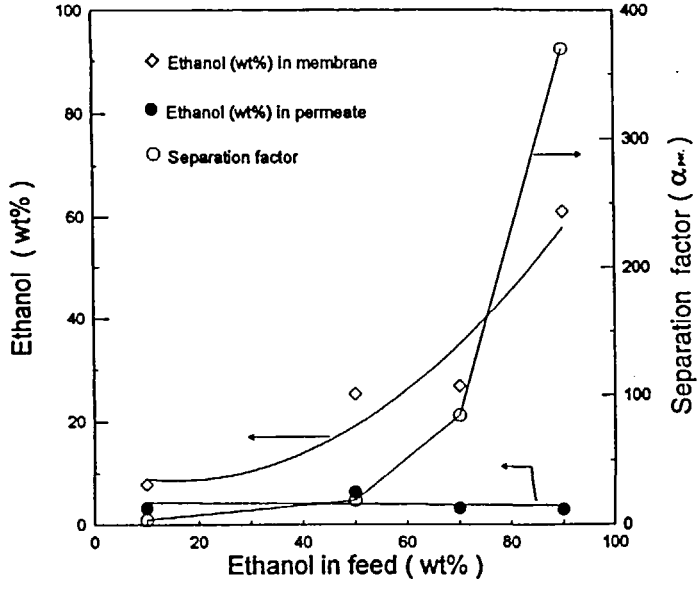

FIG. 6 Effect of the ethanol concentration in the feed on the separation factor and on the concentration of ethanol in the permeate and in the membrane.

feed composition, indicating that the membrane possesses high water permselectivity. The effect of ethanol concentration in the feed on the separation factor is also presented in Fig. 6.

It should be noted that ethanol concentration in the membrane increases with increasing ethanol concentration in the feed. Therefore, it is reasonable to expect that ethanol concentration in the permeate will follow the same trend. However, ethanol concentration in the permeate is insensitive to feed composition. This phenomenon can be explained by considering the swelling effect. Since $Co(acac)_3$ has a strong interaction with water, a higher water concentration (lower ethanol concentration) in the feed results in a higher degree of swelling. On the basis of the above discussion, it is known that a higher ethanol concentration in the feed will make the ethanol concentration in the membrane higher, indicating a higher permeation flux. The diffusivity of ethanol through the membrane is lower, however, because the degree of swelling is lower, indicating a lower permeation flux. The competition between solution and diffusion makes the permeation flux insensitive to feed composition. The above observation again confirms that the effect of swelling on diffusion plays an important role in pervaporation.

CONCLUSION

It is proved in this work that the addition of cobalt(III) acetylacetonate in a polycarbonate membrane can improve the pervaporation performance. By adding 3 wt% $Co(acac)_3$, the resulting complex membrane possesses a permeation flux similar to that of a pure PC membrane, but the separation factor is about three times higher. It was also found that the cobalt salt in the membrane remains stable after a 72-hour immersion in an aqueous ethanol solution.

In addition, it was found that the addition of a small amount of $Co(acac)_3$ (1 wt%) makes the PC membrane denser, and results in a lower permeation flux but a higher permselectivity. However, when more $Co(acac)_3$ is added, the degree of swelling increases due to the strong interaction between the added salt and water (solvation), resulting in a higher permeation flux but a lower permselectivity. It should be stressed that the effect of swelling on the diffusivity of permeates through membranes plays an important role in the pervaporation separation process.

ACKNOWLEDGMENT

The authors thank the National Science Council of the Republic of China for financial support (NSC 85-2216-E- 033-002).

REFERENCES

1. R. C. Binning, R. J. Lee, J. F. Jennings, and E. C. Martin, *Ind. Eng. Chem.*, *53*, 45 (1961).
2. M. Fels and R. Y. Huang, *J. Macromol. Sci.—Phys.*, (1), 89 (1971).
3. P. Aptel, N. Challard, J. Cuny, and J. Neel, *J. Membr. Sci.*, *1*, 271 (1976).
4. R. Y. M. Huang and Y. F. Xu, *Eur. Polym. J.*, *24*(10), 927 (1988).
5. Y. Nagase, S. Mori, and K. Matsui, *J. Appl. Polym. Sci.*, *37*, 1259 (1989).
6. M. Yoshikawa, H. Yokoi, K. Sanui, N. Ogata, and T. Shimidzu, *Polym. J.*, *16*(8), 653 (1984).
7. C. S. Slater, P. J. Hickey, and F. P. Jurici, *Sep. Sci. Technol.*, *25*, 1063 (1990).
8. T. Masuda, B. Z. Tang, and T. Higashimura, *Polym. J.*, *18*, 165 (1986).
9. J. Y. Lai, S. H. Li, and K. R. Lee, *J. Membr. Sci.*, *93*, 273 (1994).
10. J. Y. Lai, R. Y. Chen, and K. R. Lee, *J. Appl. Polym. Sci.*, *47*, 1849 (1993).
11. H. L. Hu, K. R. Lee, and J. Y. Lai, *J. Macromol. Sci.—Pure Appl. Chem.*, *A30*(11), 815 (1993).
12. K. R. Lee, R. Y. Chen, and J. Y. Lai, *J. Membr. Sci.*, *75*, 171 (1992).
13. A. Mochizuki, S. Amiya, Y. Sato, H. Ogawara, and S. Yamashita, *J. Appl. Polym. Sci.*, *40*, 385 (1990).
14. A. Mochizuki, S. Amiya, Y. Sato, H. Ogawara, and S. Yamashita, *Ibid.*, *37*, 3385 (1989).
15. A. Mochizuki, Y. Sato, H. Ogawara, and S. Yamashita, *Ibid.*, *37*, 3375 (1989).
16. A. Mochizuki, S. Amiya, Y. Sato, H. Ogawara, and S. Yamashita, *Ibid.*, *40*, 663 (1990).
17. R. Y. M. Huang, (Ed.), *Pervaporation Membrane Separation Processes*, Elsevier Science Publishers, New York, NY, 1991, Chap. 1.
18. S. H. Chen, J. Y. Lai, R. C. Ruaan, and A. A. Wang, *J. Membr. Sci.*, (123), 197 (1997).
19. J. G. Wijrans and R. W. Baker, *Ibid.*, (79), 101 (1993).

Received by editor June 20, 1997
Revision received January 1998