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Esterification of Carboxylic Acid with Ethanol Accompanied by Pervaporation

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The use of water-permeable membranes for pervaporation in the esterification of carboxylic acid with ethanol was studied. The perfect conversion due to the equilibrium shift was obtained by using an asymmetric polyetherimide membrane for removal of water generated by the esterification.

In the past few years, interest in the application of a membrane reactor to many chemical processes has substantially increased. The use of membrane for separation of a reaction product in a reversible reaction seems to be an attractive method to increase the conversion of reversible reaction resulting in a considerable reduction in the reaction time and the saving of reactants. All of the membranes applied to this type of reactor1-6) have been micro porous membranes for separating the gaseous product including small molecules such as hydrogen, except those in two patents.7,8) Recently, we have reported the use of dense membranes of polymeric materials for removal of water vapor generated by the esterification of oleic acid with ethanol in order to achieve the favorable chemical equilibrium shift.9) The esterification reaction of carboxylic acids with alcohols has been widely studied mainly because of its industrial interest and this reaction has been studied in the liquid phase. It is interesting, therefore, to investigate the esterification accompanied by the liquid permeation.

In this paper, the use of water-permeable membrane for pervaporation in the esterification of oleic acid and acetic acid with ethanol has been studied in order to shift the equilibrium and increase the conversion of the esterification.

The esterification accompanied by pervaporation was carried out using the apparatus depicted in Fig. 1. A mixture of acid (oleic acid or acetic acid) and ethanol with a catalytic amount of p-toluenesulfonic acid was fed to the reaction cell. Total amounts of the mixture were about 100 cm^3 and the molar ratio of ethanol to acid was 2:1 or 3:1. The cell was placed in a thermostated water-bath and the temperature was maintained at 75 °C in the reaction of acetic acid with ethanol and at 60 °C in that of oleic acid with ethanol. The amount of acid was titrated according to the method described previously.9) The membrane for pervaporation was set in the bottom of the reaction cell. The membrane area in contact with the reaction mixture was 19.0 cm^2. Membrane materials are listed in

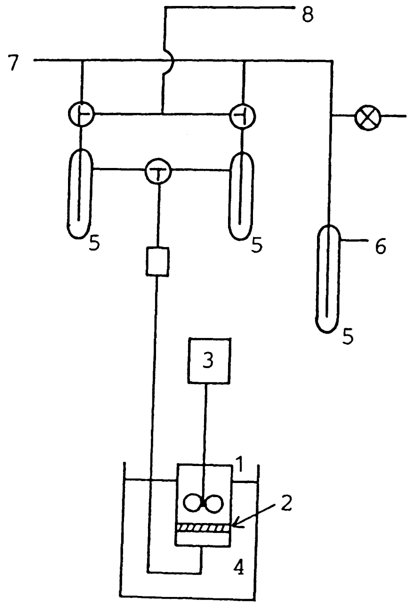

Fig. 1. A schematic diagram of the experimental apparatus: (1) reaction cell, (2) pervaporation membrane, (3) stirring motor, (4) constant temperature bath, (5) cold trap, (6) vacuum pump, (7) Pirani gauge, (8) vent (N_2 gas).

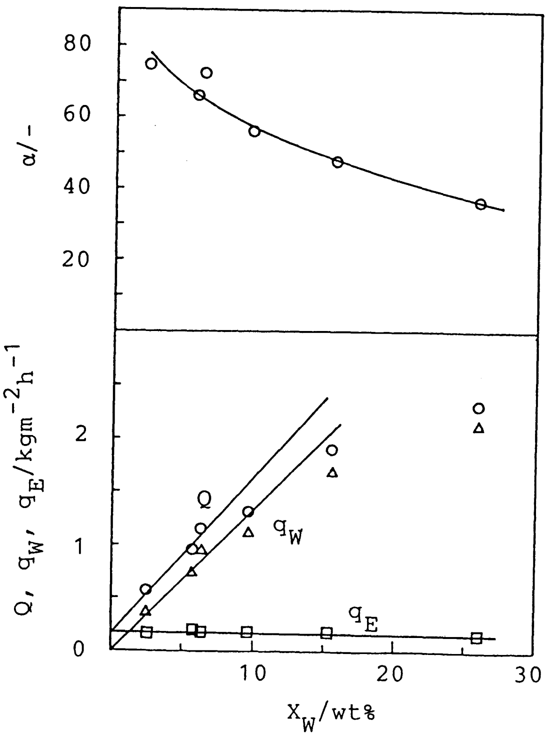

Fig. 2. Effect of feed composition on permeation rates and separation factors of pervaporation of water-ethanol mixtures through an asymmetric PEI membrane at 75 °C.

Table 1. Permeation rate (Q) and separation factor (α) of pervaporation for the water 10 wt%-ethanol 90 wt% mixture at 75 °C

Membrane(μm)	Supplier(Trade Name)	Q / $kg\ m^{-2}\ h^{-1}$	$\alpha_{W/E}$[a]
Polyetherimide(12.5)	General Electric(Ultem 1000)	0.03	570
Asymmetric polyetherimide	this work	1.29	57
Chitosan(39)	Kyowayushi(FLONAC #250)	0.29	36
Perfluorinated ion-exchange membrane(175)	Du Pont(Nafion 117)	2.45	2

a) Defined as concentration ratio $Y_{water}/Y_{ethanol}$ in the permeate divided by the ratio $X_{water}/X_{ethanol}$ in the feed.

Table 1. The pervaporation experiments were carried out by the method described elsewhere.[10)]

Table 1 also shows the pervaporation results for the liquid mixture of water 10 wt% and ethanol 90 wt% at 75 °C. Among the membranes used in the present study polyetherimide(PEI) showed the highest selectivity. PEI is one of engineering polymers offering good mechanical strength and high heat resistance. Although PEI seems to be useful in the application to the separation of the reaction mixture generated by the esterification because of high selectivity and high-temperature stability, the disadvantage of the polymer is the low permeation rate. Thus, we have prepared an asymmetric PEI membrane by inversion precipitation as described in German patent[11)] in order to achieve an improvement in the permeation rate. The asymmetric membrane was prepared by casting a polymer solution containing 15 wt% PEI on a glass plate and immersion in an acetone bath at room temperature. The composition of the casting solution was as follows; PEI 15 wt%, dichloromethane 55 wt%, 1,1,2,2-tetrachloroethane 5 wt%, xylene 18 wt%, and acetic acid 7 wt%. The membrane was dried for one day at 50 °C. As shown in Table 1 the asymmetric PEI membrane showed higher permeability and furthermore the selectivity remained at the relatively high value, although the asymmetric membrane seems to have pinholes judging from the decrease in selectivity in comparison with the homogeneous PEI membrane.

Figure 2 shows the effect of feed composition (weight percentage of water, X_W) on permeation rates and separation factors of pervaporation of water-ethanol mixtures through an asymmetric PEI membrane. The separation factor decreases with an increase in X_W. Both the total permeation rate (Q) and the partial one of water (q_W) increase with an increase in X_W, while the partial permeation rate of ethanol (q_E) decreases slightly. Thus, in the dilute solutions ($X_W < 20$ wt%) where the esterification reaction was studied, water can permeate selectively through the asymmetric PEI membrane at the higher permeation rate than the homogeneous membranes.

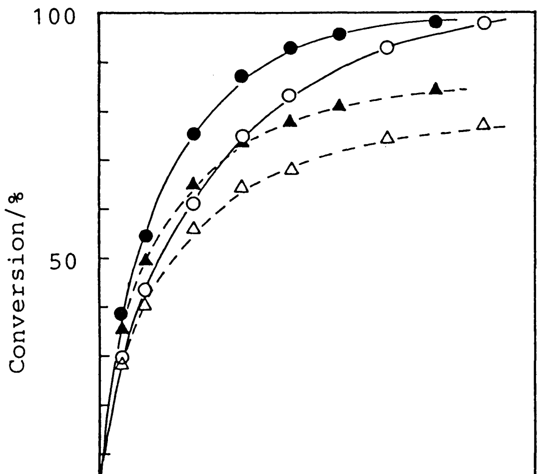

Fig. 3. Effect of membrane separation on the conversion of the esterification of oleic acid with ethanol at the molar ratio of 1:2 (open symbols) and 1:3 (closed symbols) at 75 °C: (△,▲) without pervaporation.

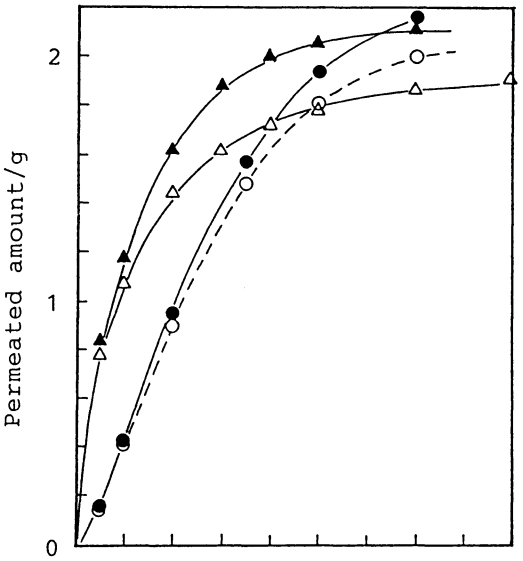

Fig. 4. The permeation behavior of an asymmetric PEI membrane in the esterification of oleic acid with ethanol at the molar ratio of 1:3 at 75 °C: (●) total amount of the permeate, (○) permeated amount of water, (▲) amount of water generated by the esterification, (△) amount of water generated by the esterification without pervaporation.

Figure 3 shows the effect of pervaporation through the asymmetric PEI membrane on the conversion of oleic acid to ethyl ester at two different molar ratios. It is evident that the removal of water by pervaporation shifts the equilibrium in favor of the ester formation. On the other hand, the conversion of the esterification was only slightly affected by pervaporation through the chitosan or perfluorinated ion-exchange membrane. This seems to be due to the low permeation rate of chitosan membrane or due to the very low selectivity of perfluorinated ion-exchange membrane. In the case of the asymmetric PEI membrane, where the permeation rate is high but the selectivity is not so large, a 100% conversion can be obtained due to the equilibrium shift. A conversion greater than the equilibrium value without pervaporation was obtained in about 3 and 4 hours at the molar ratio of 3:1 and 2:1, respectively. The almost perfect conversion was also obtained in the case of the esterification of acetic acid with ethanol. Figure 4 shows the permeation behavior of an asymmetric PEI membrane during the course of the esterification reaction. In the case of the esterification accompanied by pervaporation, amounts of water generated by the esterification rapidly increased with an increase of permeated water in comparison with the case of the esterification without pervaporation. This is because of the equilibrium shift due to removal of water by pervaporation. Figure 4 also shows that there was no appreciable loss of ethanol due to pervaporation. Permeated amounts of ethanol were only 1.1 wt% of initial amounts of ethanol. The comparison between amounts of water generated by the esterification and those of permeated water during the course of reaction shows a large portion of water generated by the esterification was permeated in about 6 hours.

In conclusion, the conversion of the ester formation can be increased beyond the equilibrium value by using the pervaporation through the asymmetric membrane in the formation of liquid esters and this enables a considerable reduction in the reaction time and the saving of reactants.

References

1) T. Kameyama, M. Dokiya, M. Fujishige, H. Yokokawa, and K. Fukuda, Ind. Eng. Chem. Fundam., 20, 97(1981).
2) O. Shinji, M. Misono, and Y. Yoneda, Bull. Chem. Soc. Jpn., 55, 2760(1982).
3) N. Itoh, Y. Shindo, K. Haraya, K. Obata, T. Hakuta, and H. Yoshitome, Int. J. Hydrogen Energy, 9, 835(1984).
4) N. Itoh, Y. Shindo, K. Haraya, K. Obata, T. Hakuta, and H. Yoshitome, Int. Chem. Eng., 25, 138(1985).
5) K. Mohan and R. Govind, AIChE J., 32, 2083(1986).
6) Y-M. Sun and S-J. Khang, Ind. Eng. Chem. Res., 27, 1136(1988).
7) J. F. Jennings and R. C. Binning, U. S. Patent 2956070(1960).
8) G. K. Pearce, Eur. Pat. Appl. EP 210055(1987).
9) H. Kita, K. Tanaka, K. Okamoto, and M. Yamamoto, Chem. Lett., 1987, 2053.
10) K. Okamoto, A. Butsuen, S. Tsuru, S. Nishioka, K. Tanaka, H. Kita, and S. Asakawa, Polym. J., 19, 747(1987).
11) K.-V. Peinemann, Ger. Pat. Appl. P3420373.7 (1984).

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