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Studies on Syntheses and Permeabilities of Special Polymer Membranes. 68. Analysis of Permeation and Separation Characteristics and New Technique for Separation of Aqueous Alcoholic Solutions through Alginic Acid Membranes

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Abstract

Permeation and separation characteristics of methanol/water and ethanol/water mixtures through an alginic acid membrane by a pervaporation method were investigated under various conditions. The permeation and separation characteristics for these aqueous alcoholic solutions were significantly different. To elucidate these different characteristics, a new combined evaporation and vapor permeation membrane separation technique, named "evapomeation," was developed. The permeation and separation mechanisms for these two aqueous alcoholic solutions through the alginic acid membrane in pervaporation are discussed. Also, the permeation and separation characteristics for ethanol/water mixtures obtained by the evapomeation method are compared with those of pervaporation.

INTRODUCTION

Recently, the effective use of biomass has developed as an important problem because of the crisis of such fossil resources as coal and petroleum. Membrane separation techniques have been used for the separation and concentration of aqueous alcoholic solutions obtained from biomass instead of a distillation method because these techniques do not require large quantities of energy. In the membrane separation techniques, the pervaporation method is very advantageous for the separation of organic liquid mixtures, e.g., azeotropic mixtures, mixtures with very close boiling points, and structural isomers (*1*).

The permeation and separation characteristics of aqueous methanol and ethanol solutions through an alginic acid membrane by pervaporation were first studied under various conditions. There is a very significant difference between the permeation and separation characteristics for these aqueous alcoholic solutions. In pervaporation the feed liquid mixtures, in general, is kept in the upstream side of the membrane and the downstream side is vacuumed. Separation through the membrane in this method results by differences of the solubility of the permeating molecules into the polymer membrane in the dissolution process, the diffusivity of these molecules through the polymer membrane in the diffusion process, and the volatility of these molecules from the polymer membrane on the downstream side in the evaporation process (*1*). The difference of the permeation and separation characteristics for aqueous methanol and ethanol solutions is dependent on a separation mechanism for the permeating molecules through the alginic acid membrane.

In order to clarify the difference of these separation mechanisms, a new membrane separation technique is proposed, named "evapomeation." The separation mechanisms for aqueous methanol and ethanol solutions through the alginic acid membrane are discussed based on the results from the pervaporation and evapomeation methods. Also, the permeation and separation characteristics for aqueous ethanol solutions through the alginic acid membrane obtained by the pervaporation and evapomeation methods are compared and discussed.

EXPERIMENTAL

Materials

Sodium alginate (produced by Kimitsu Chemical Industry Co.) was employed as a membrane material. All reagents used in this study were supplied by commercial sources.

Preparation of Membrane

The casting solution, aqueous sodium alginate solution (0.5 wt%), was prepared by dissolving sodium alginate in water at 25°C. The alginic acid membranes were prepared by pouring the casting solution onto a rimmed glass plate and allowing the casting solvent (water) to evaporate at 60°C in an oven until a dried sodium alginate membrane was obtained. The membrane was then immersed in 1 *N* HCl for 24 h at 25°C, washed repeatedly with pure water, and dried at 25°C.

The dried alginic acid membrane had a thickness of 3 μm.

Apparatus and Measurements

The permeation apparatus for the pervaporation method was conventional. The principal scheme of this method is shown in Fig. 1. The feed liquid mixture was kept in the upstream side of the membrane, and the downstream side of the membrane was vacuumed. The permeation and separation of the permeating species through the membrane are dependent on the solubility, diffusivity, and volatility of these species.

The pervaporation and evapomeation experiments were carried out at 40°C under a reduced pressure of 10^{-2} torr.

The permeation under pressure was carried out using a conventional ultrafiltration cell (*2*) at 40°C and 5 kg/cm^2.

The degree of swelling of the membrane for each feed was determined by the following equation:

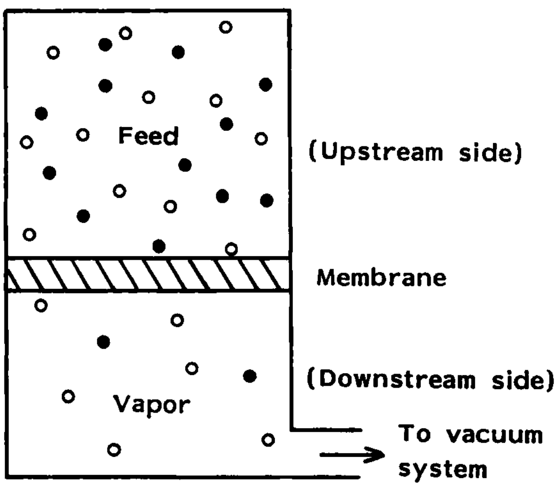

FIG. 1. Principal scheme of the pervaporation method.

$$\text{Degree of swelling} = \frac{\text{weight of membrane swollen with feed}}{\text{weight of dry membrane}}$$

The composition of the solution adsorbed in the membrane was measured by using the sytem shown in Fig. 2. After the swelling of the membrane was preequilibrated with a certain feed, a desired amount of the swollen membrane was placed in a container. The system in Fig. 2 was vacuumed, and the container with the swollen membrane was heated. Then the liquid adsorbed in the membrane was completely evaporated, trapped in the U-tube, and analyzed by gas chromatography (Shimadzu GC-4CPTF).

The permeation rate was determined by weighing the permeate. The compositions of the feed and permeate were determined by gas chromatography.

The separation factor, α, was calculated by

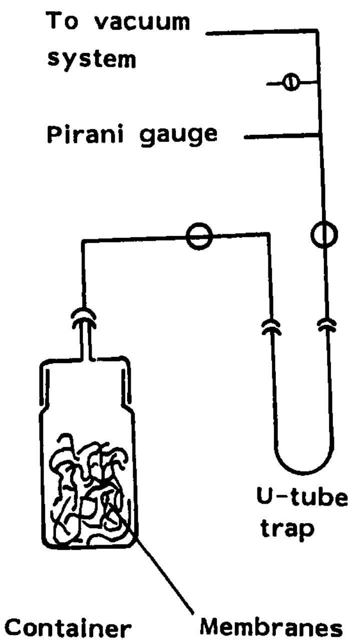

FIG. 2. Diagram of the apparatus to determine the composition of solution adsorbed inside the membrane.

$$\alpha = \frac{Y_{H_2O}/Y_{EtOH}}{X_{H_2O}/X_{EtOH}}$$

where X_{H_2O}, X_{EtOH}, Y_{H_2O}, and Y_{EtOH} denote the weight fractions of water and ethanol in the feed solution and in the permeate, respectively.

RESULTS AND DISCUSSION

Permeation and Separation Characteristics by Pervaporation

The permeation and separation characteristics for various aqueous methanol solutions through the alginic acid membrane by the pervaporation method are shown in Fig. 3. As can be seen, methanol was predominantly premeated through the alginic acid membrane for all feed solutions and concentrated in the permeate. On the other hand, the permeation rate increased with an increase of methanol concentration in the feed. Figure 3 also includes the relation between the feed composition and the degree of swelling of the membrane. A decrease of the degree of swelling of the membrane with an increase of the methanol concentration in the feed implies that the membrane becomes denser due to shrinkage. However, the permeation rate became higher as the methanol content in the feed increased. These results are explained as follows. When the methanol content in the feed is small, the diffusion of the permeating molecules through the alginic acid membrane is difficult because the interaction between the permeating molecules and the alginic acid membrane is very strong. Consequently, the permeation rate is smaller. On the other hand, when this interaction is weak, the permeation rate becomes higher.

The compositions of solutions adsorbed in the alginic acid membrane from the feed and the permeations under pressure of aqueous methanol solutions were investigated in order to reveal a separation mechanism for aqueous methanol solutions through the alginic acid membrane by the pervaporation method. Figure 4 shows the effect of feed composition on the compositions of solutions adsorbed in the alginic acid membrane and on those in the permeate through the membrane by permeation under pressure. These results suggest that water molecules are preferentially adsorbed into the alginic acid membrane. This is caused by the hydrophilicity of the alginic acid membrane. The dashed line in Fig. 4

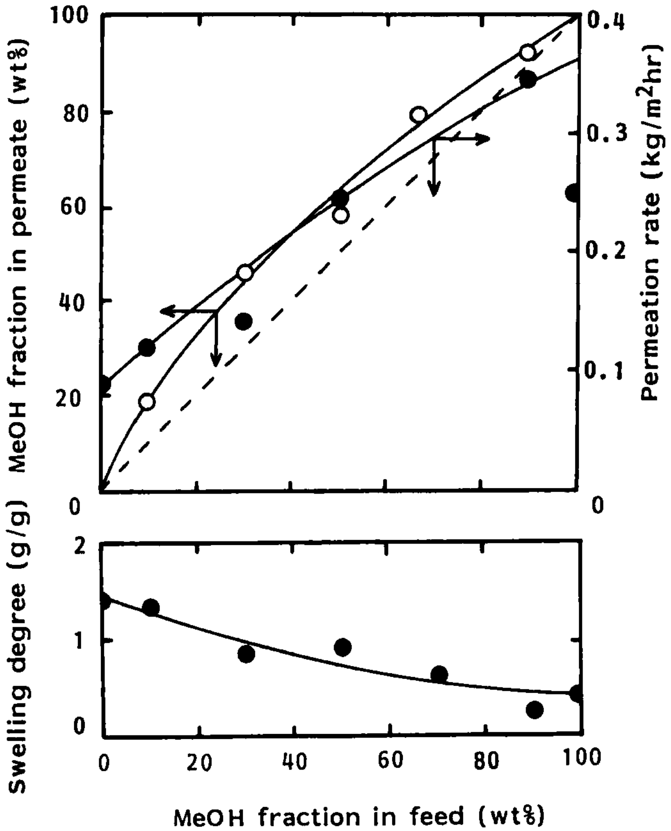

FIG. 3. Permeation and separation characteristics for aqueous methanol solutions through the alginic acid membrane, and the degree of swelling of the membrane by the feed solutions in the prevaporation method.

shows nonseparation composition. The compositions in the permeate by permeation under pressure are close to this dashed line. This fact suggests that aqueous methanol solutions are poorly separated by permeation under pressure, and that separation in the diffusion process of the permeating molecules through the alginic acid membrane by pervaporation hardly occurs.

From these results the mechanism for the permeation and separation of aqueous methanol solution through the alginic acid membrane by pervaporation is considered to be as follows. The water molecules are predominantly dissolved into the alginic acid membrane, but the mixture

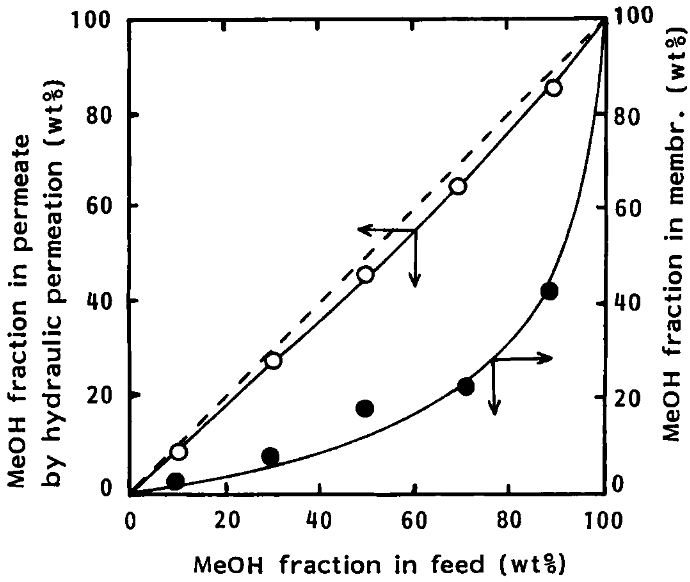

FIG. 4. Effect of feed composition of aqueous methanol solutions on the methanol concentrations in the permeate through the alginic acid membrane in the permeation under pressure and adsorbed inside the membrane.

of water and methanol adsorbed in the membrane are not separated in the diffusion process through the membrane. This mixture, which is diffused on the membrane surface of the downstream side, is evaporated. In this evaporation process the methanol molecules are predominantly evaporated due to the specific volatility effect. Consequently, the methanol molecules are preferentially permeated through the hydrophilic alginic acid membrane by pervaporation.

The effects of ethanol concentration in the feed on the permeation rate and in the permeate through the alginic acid membrane are shown in Fig. 5. As can be seen, the permeation and separation characteristics are significantly influenced by the feed composition. In the permeation of an aqueous ethanol solution of less than about 45 wt%, the ethanol in the feed was selectively permeated and concentrated in the permeate. In the case of more than about 45 wt% ethanol content, water is easily permeated. Consequently, an equisorptic composition appears at about 45 wt% but an azeotropic point at 95.6 wt% disappears. Kopeček et al. (*3*) found that there is an equisorptic composition in separation experiments for a binary mixture system of organic solvents when using a porous

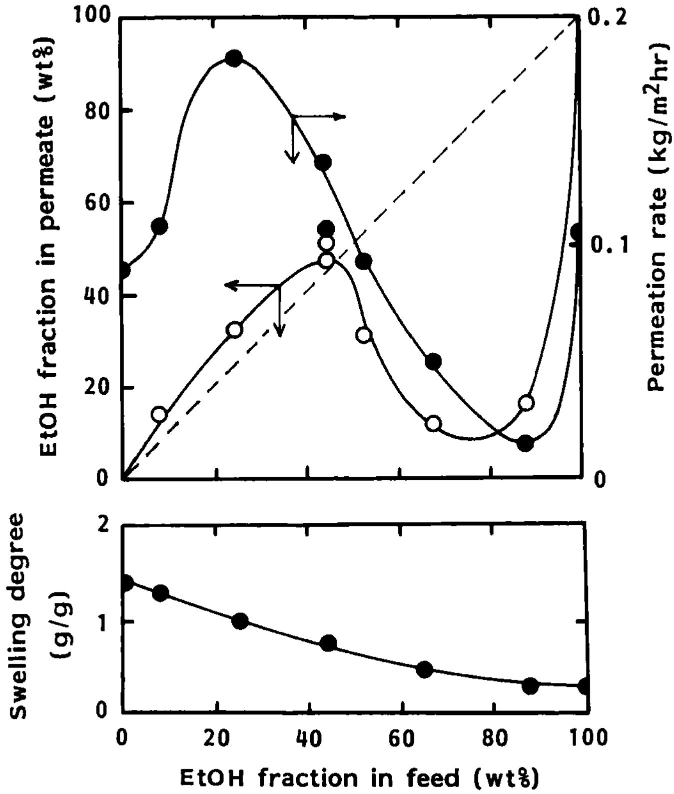

FIG. 5. Permeation and separation characteristics for aqueous ethanol solutions through the alginic acid membrane, and the degree of swelling of the membrane by the feed solutions in the pervaporation method.

cellulose acetate membrane in a reverse osmosis process. They reported that equisorptic compositions are obviously functions of the chemical nature of the membrane materials and the feed solution. Separation does not entirely occur at this composition. The appearance of an equisorptic composition is unfavorable in the membrane separation technique, but the disappearance of the azeotropic point is favorable. Also, when the ethanol content in the feed was lower or higher, preferential permeation of ethanol or water occurred. These facts are advantageous for the separation of mixtures of ethanol and water.

Figure 5 also includes the relationship between the degree of swelling of the membrane and the feed composition. The permeation rate is dependent on the degree of swelling of the membrane when the ethanol content in the feed is more than 25 wt% but not when it is less than 25 wt%.

The effect of the feed composition of aqueous ethanol solutions on the ethanol concentration adsorbed into the membrane and permeation under pressure is shown in Fig. 6. These results are approximately similar to those for aqueous methanol solutions as shown in Fig. 3. That is, these results imply that the water molecules are preferentially dissolved into the alginic acid membrane but that separation cannot be performed in the diffusion process through the membrane. From the results in Figs. 3 to 6, it is shown that the permeation and separation mechanisms for aqueous ethanol solutions through the alginic acid membrane are significantly different from those for aqueous methanol solutions. When the content of ethanol in the feed is lower than 45 wt%, the water molecules are preferentially dissolved into the membrane, but the water and ethanol molecules move to the opposite side of the membrane without separation in the diffusion process through the membrane. These molecules are then evaporated in the downstream side. The ethanol molecules are evap-

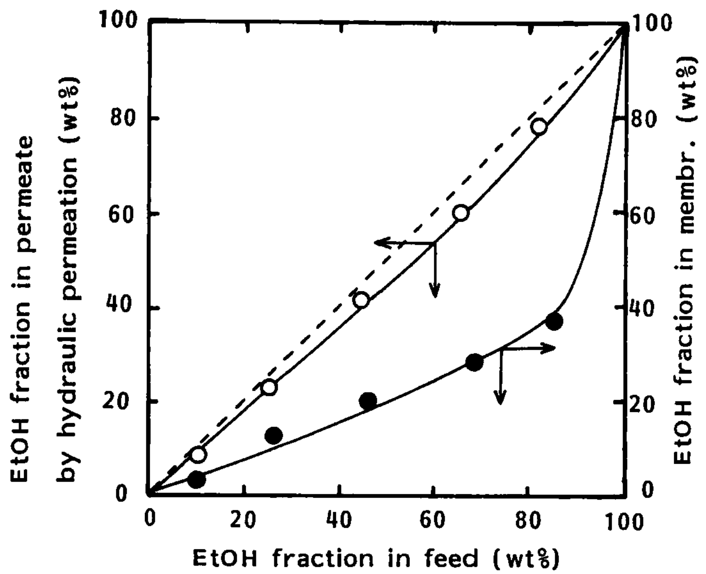

FIG. 6. Effect of feed composition of aqueous ethanol solutions on the ethanol concentrations in the permeate through the alginic acid membrane in the permeation under pressure and adsorbed inside the membrane.

orated easier than the water molecules. Therefore, the ethanol molecules are selectively permeated and concentrated in the permeate when the ethanol content in the feed is lower.

In the case of a higher ethanol content in the feed, the separation of aqueous ethanol solutions cannot be explained by such a mechanism. A new membrane separation technique was designed to reveal the separation mechanism for aqueous solutions with a higher ethanol content through the alginic acid membrane by the pervaporation method.

New Membrane Separation Technique

The principal scheme of the new membrane separation technique is shown in Fig. 7. In this system, when the permeating side is vacuumed, the feed solution is vaporized. The vaporized molecules contact the

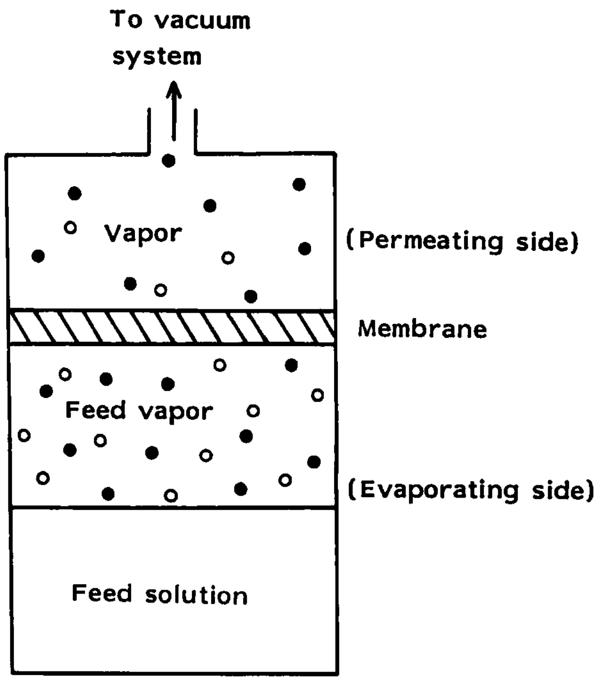

FIG. 7. Principal scheme of the evapomeation method.

membrane, dissolve into the membrane, diffuse through the membrane, and evaporate from the membrane. This method consists of the evaporation process of the feed solution and the permeation process of the evaporated molecules. Therefore, we named this membrane separation technique "evapomeation." This method has characteristics which prevent swelling or shrinking of the membrane because the membrane is not directly contacted by the feed solution, which will improve the weak points of the pervaporation method. That is, in pervaporation the chemical and physical functions of the membrane are not retained due to swelling or shrinking of the membrane due to the feed mixtures, and consequently the membrane performance is low. In the case of evapomeation, however, since swelling or shrinking of the membrane can be controlled, membrane performance for the separation of organic liquid mixtures should be significantly improved.

The permeation and separation characteristics for aqueous ethanol solutions through the alginic acid membrane by the evapomeation method are shown in Fig. 8. The composition in the permeate suggests that the water molecules are preferentially permeated. This result is

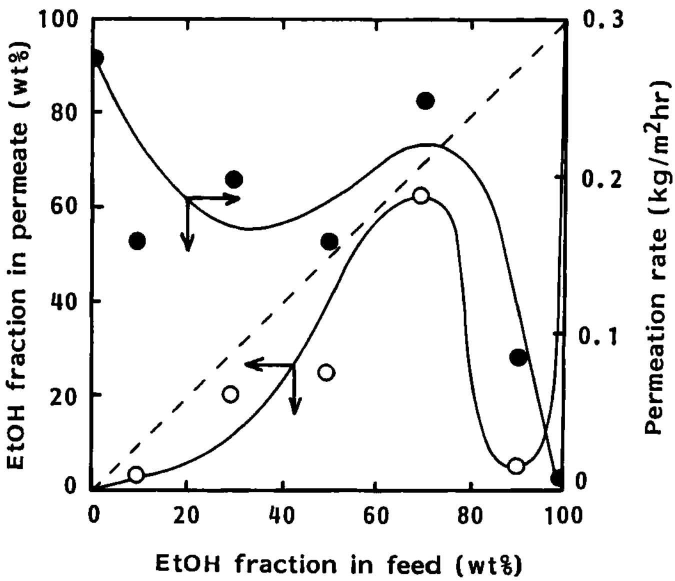

FIG. 8. Permeation and separation characteristics for aqueous ethanol solutions through the alginic acid membrane by the evapomeation method.

attributed to the hydrophilicity of the alginic acid membrane. The permeation rate decreases with an increase of ethanol content in the feed. This decrease of permeation rate is due to the difference of the intereaction between the vaporized permeating molecules and the alginic acid membrane.

Membrane Model

In order to explain the separation mechanism for aqueous alcohol solutions through the alginic acid membrane by the pervaporation method, the membrane model shown in Fig. 9 is proposed for the pervaporation process. The membrane consists of three layers: swelling layer, boundary layer, and dry layer. The existence of these three layers could not be experimentally observed. However, the assumption of three layers helps in understanding the separation mechanism. The dissolution of permeating molecules into the swelling layer, the diffusion of these molecules through the swelling layer, and the separation through the dry layer can be explained by the experimental results of the adsorption of permeating molecules into the membrane, the permeation under pressure, and the evapomeation, respectively. Also, the evaporation of permeating molecules occurs in the boundary layer between the swelling layer and the dry layer, and the separation in this boundary layer is due to the specific volatility of the permeating molecules.

If this membrane model is used, the separation mechanism for higher ethanol content in the feed through the alginic acid membrane by the pervaporation method, which could be not explained previously, can be easily understood. That is, the water molecules are selectively adsorbed into the swelling layer, and the adsorbed molecules are diffused without separation through the swelling layer. Then the permeating molecules are

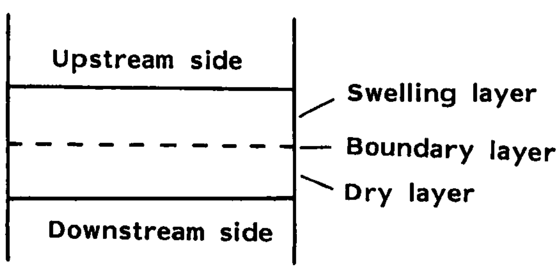

FIG. 9. Membrane model in pervaporation.

TABLE 1
Comparison of the Permeation Rates and Separation Factors for Aqueous Ethanol Solutions by the Evapomeation and Pervaporation Methods through the Alginic Acid Membrane

Aqueous ethanol solution in feed (wt%)	Evapomeation		Pervaporation	
	Permeation rate ($g/m^2 \cdot h$)	Separation factor (α)	Permeation rate ($g/m^2 \cdot h$)	Separation factor (α)
0	270	1	92	1
10	180	4.5	110	0.63
30	200	5.5	180	0.67
50	180	5.8	110	0.85
70	250	7.3	52	16
90	81	295	16	32
96	7.5	1940	48	8.8
100	2.4	1	110	1

evaporated into the boundary layer, and the evaporated molecules are permeated through the dry layer. As can be seen from the results in the evapomeation experiments of aqueous ethanol solutions in Fig. 8, the water molecules are preferentially permeated through the dry layer. This dry layer plays an important role in the permeation of higher ethanol content in pervaporation, and consequently the water molecules are preferentially permeated under such conditions. Also, the remarkable decrease of the permeation rate for aqueous ethanol solutions of more than 25 wt% ethanol content in pervaporation in Fig. 5 is dependent on the existence of this dry layer.

Table 1 summarizes the permeation rates and separation factors for aqueous ethanol solutions through the alginic acid membrane by the evapomeation and pervaporation technique. Both the permeation rate and separation factor in the evapomeation method are greater than those for pervaporation. In particular, the separation factor at the azeotropic composition has a very high value. These results suggest that the evapomeation method is excellent as a membrane separation technique.

REFERENCES

1. For example: C. Y. Choo, "Membrane Permeation," *Adv. Pet. Chem. Refining*, etd. by Mcketta, Vol. *6* (1962); S. T. Hwang and K. Kammermeyer, *Technique of Chemistry, Vol.*

VII, Membranes in Separations, Wiley-Interscience, New York, (1976), Chap. VII; S. Yamada, *Membrane, 6*, 168 (1981).
2. T. Uragami and M. Sugihara, *Angew. Makromol. Chem., 57*, 123 (1977).
3. J. Kopeček and S. Sourirajan, *Can. Chem. J., 47*, 3467 (1969).

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