Permeation and separation characteristics of ethanol–water mixtures through chitosan derivative membranes by pervaporation and evapomeation

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This paper deals with permeation and separation characteristics of aqueous ethanol solutions through some chitosan derivative membranes such as chitosan, chitosan acetate and crosslinked chitosan membranes by pervaporation and evapomeation methods. The evapomeation method was found to be better than the pervaporation method for the permeation and separation of aqueous ethanol solutions. Separation factors for aqueous ethanol solutions containing more than 90 wt% of ethanol through a chitosan acetate membrane were about ten times that through a chitosan membrane. Also, the separation factor of a chitosan membrane crosslinked with glutaraldehyde was infinity for a feed of less than 70 wt% of ethanol and was about 20 times the chitosan membrane at 90 wt% of ethanol. Permeation rates of the crosslinked chitosan membrane were greater than those of the chitosan membrane. The permeation and separation characteristics for aqueous ethanol solutions are discussed from the viewpoints of the structure of chitosan derivative membranes and the permeation mechanism through the membrane.

(Keywords: chitosan derivative; membrane; aqueous ethanol solution; separation; pervaporation; evapomeation)

INTRODUCTION

We have found that there is a significant difference between the permeation and separation characteristics for aqueous methanol solution and those for aqueous ethanol solution through an alginic acid membrane by the pervaporation method[1]. In order to reveal the permeation and separation characteristics for these aqueous alcoholic solutions, we proposed a new membrane separation technique, which was named evapomeation[1,2]. The evapomeation method is the membrane separation technique that amends some faults of the pervaporation method while keeping its several advantages. Namely, because organic feed mixtures are not directly in contact with the membrane in contrast to the vaporized molecules in the evapomeation method, the swelling or shrinking of the membrane due to the feed mixture can be prevented and the chemical and physical functionalities which were part of the membrane design can be retained. Consequently, when the evapomeation technique is applied to the separation of organic liquid mixtures through the polymer membranes, an improvement of membrane performance is normally expected. In previous papers[1,2], the permeation and separation characteristics for aqueous alcoholic solutions through the alginic acid and chitosan membranes by the pervaporation and evapomeation methods have been reported. The separation characteristics for aqueous alcoholic solutions through these membranes in the evapomeation method were better than those in the case of pervaporation.

In the chitosan membrane of the pervaporation, increasing the water concentration in aqueous ethanol solution increased the degree of swelling of the membrane. The permeation rate was increased by an increase of swelling of the membrane but the separation characteristic was decreased[2]. On the other hand, the degree of swelling of the chitosan membrane by the feed vapour in the evapomeation was prevented. However, the permeation rate was decreased and the separation factor was increased[2]. The permeation and separation characteristics for aqueous ethanol solutions through the chitosan membrane were not sufficient in either the pervaporation and evapomeation methods. Therefore, it is necessary to modify the chitosan membrane to improve the membrane performance for the separation of aqueous ethanol solutions in pervaporation and evapomeation.

For the research described in this paper, some chitosan derivative membranes were prepared in order to improve the membrane performance for the separation of ethanol–water mixtures through the chitosan membrane. The permeation and separation characteristics of aqueous ethanol solutions through these chitosan derivative membranes using the pervaporation and evapomeation methods will be discussed in some detail.

EXPERIMENTAL

Materials

Chitosan (produced by the bioscience laboratory of Katokichi Co. Ltd, Kannonji, Kagawa, Japan) with a degree of deacetylation of 99.1% and an average molecular weight of 5×10^4–1×10^5 was used as a membrane substance. Acetic acid used for the preparation of the chitosan membrane, glutaraldehyde used as a crosslinking reagent of the chitosan membrane, ethanol used as one component in the feed mixtures and other reagents used in this study were supplied by commercial sources.

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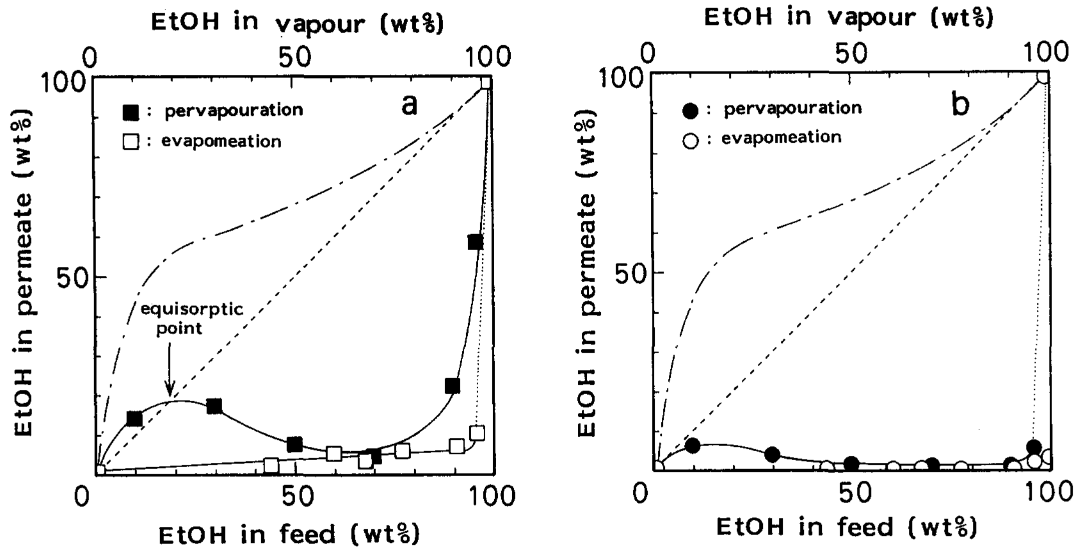

Figure 1 Relationship between the compositions of ethanol in the feed and the permeate, (a) chitosan membrane and (b) GAC membrane by the pervaporation and evapomeation methods. Dashed line indicates an equilibrium curve of vapour–liquid

Preparation of membrane

The casting solution was prepared by dissolving chitosan (2 g) in 1 M CH_3COOH (200 ml) at 25°C. Chitosan acetate salt membranes (CAS membranes) were made by pouring the casting solution onto a rimmed glass plate and allowing the casting solvent to evaporate in an oven at 60°C. The chitosan membranes were prepared by immersing the CAS membranes into 1 M NaOH for 24 h at 25°C, washing repeatedly with pure water to remove completely NaOH and drying at 25°C under vacuum. The chitosan membranes crosslinked with glutaraldehyde (GAC membranes) were prepared by immersing the chitosan membranes into 0.4 wt% glutaraldehyde solution (50 ml) containing 0.5 M H_2SO_4 (5 ml) for 15 min at 25°C, washing repeatedly with pure water and drying at 25°C under vacuum. The CAS, chitosan and GAC membranes had a thickness of about 20 μm.

Apparatus and measurements

Permeation experiments were done using apparatus for pervaporation and evapomeation which has been described previously[1,2]. Both experiments were carried out at 40°C under the reduced pressure of 10^{-2} T. The determinations of the permeation rate, compositions of the feed solution and permeate, degree of the swelling of the membrane, and compositions of solution adsorbed in the membrane were carried out as described previously[1,2].

The separation factor, $\alpha^{H_2O}_{EtOH}$, in the pervaporation method was calculated by the following equation:

$$\alpha^{H_2O}_{EtOH} = (Y_{H_2O}/Y_{EtOH})/(X_{H_2O}/X_{EtOH})$$

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

The separation factor, $\alpha^{H_2O}_{EtOH}$, in the evapomeation method was computed from the equation:

$$\alpha^{H_2O}_{EtOH} = (Y_{H_2O}/Y_{EtOH})/(V_{H_2O}/V_{EtOH})$$

where V_{H_2O} and V_{EtOH} are weight fractions of water and ethanol vapours from the feed mixture, Y_{H_2O} and Y_{EtOH} are weight fractions of water and ethanol in the permeate.

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

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

RESULTS AND DISCUSSION

The separation characteristics of ethanol–water mixtures through the chitosan membrane and the GAC membrane by the pervaporation and evapomeation methods are compared in *Figure 1*. The chitosan and GAC membranes predominantly permeate water both in pervaporation and evapomeation. Also, azeotropic compositions, namely 95.6 wt% ethanol in the feed solution, were not observed in either membranes or methods. In the chitosan membrane by pervaporation shown in *Figure 1a*, an equisorptic composition implies that the separation cannot be entirely obtained through the membrane[3]. An appearance of the equisorptic point is attributed to a remarkable swelling of the chitosan membrane due to the feed mixture. The chitosan membrane in pervaporation selectively permeates ethanol in the feed solution with low ethanol concentration.

It is well known[4] that the permeation and separation in the pervaporation method are governed by a dissolution of permeating molecules into the polymer membrane, diffusion of these molecules through the polymer membrane and evaporation of these molecules from the polymer membrane. A selective permeation of ethanol in the feed with low ethanol concentration is due to the fact that the specific volatility of ethanol gives a greater effect on separation in the evaporation process than in separation during the diffusion process. However, the equisorptic point disappears in the GAC membrane for pervaporation in *Figure 1b*. This fact suggests that the swelling of the membrane, due to the aqueous solution with low ethanol concentration, is significantly prevented by crosslinking the chitosan membrane with glutaraldehyde.

On the other hand, both chitosan and GAC membranes in evapomeation do not have an equisorptic point, the separation characteristics for evapomeation through these membranes are superior to those in the case of pervaporation in all feed compositions. Higher separation characteristics in the evapomeation method are attributable to the fact that the dissolution of permeating species as a monomolecular water vapour into the membrane and diffusion of the monomolecular vapour through the membrane are enhanced. In particular, the separation characteristics for the GAC membrane in evapomeation are very high. This is dependent on the fact that the solubility of water vapour in the GAC membrane and diffusivity of these vapours through the GAC membrane are high, and in addition that a denser membrane is formed by crosslinking the chitosan membrane with glutaraldehyde. It was confirmed that the separation characteristics for aqueous solutions with low ethanol concentration are improved by crosslinking the chitosan membrane with glutaraldehyde.

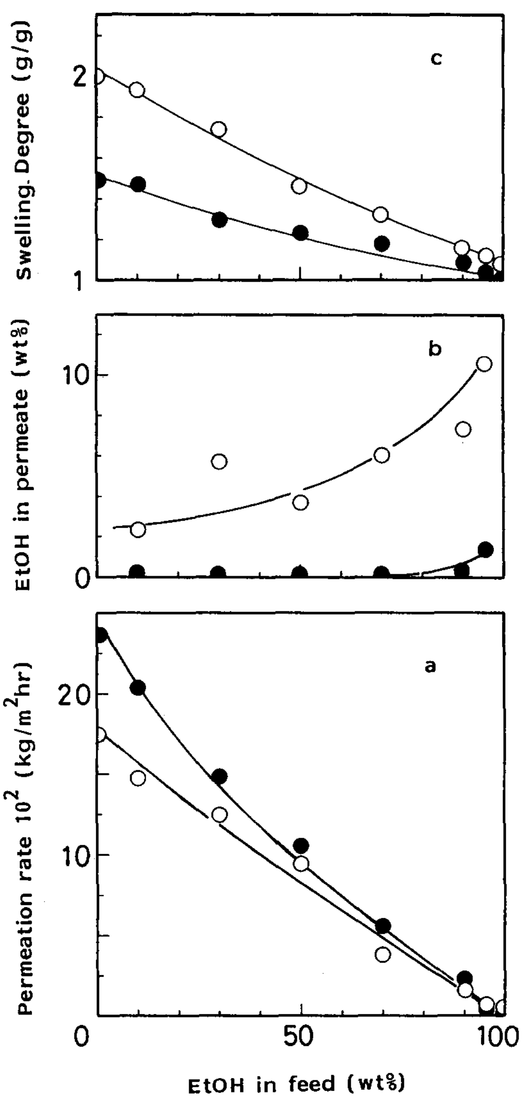

Figure 2 Effect of feed composition on (a) permeation rate; (b) composition in the permeate in evapomeation; and (c) degree of swelling of the membrane. ○, chitosan membrane; ●, GAC membrane

The effect of feed composition of aqueous ethanol solution on the permeation rate, compositions in the permeate by evapomeation and degree of swelling of the chitosan and GAC membranes is shown in *Figure 2*. The degree of swelling of the GAC membranes is lower than that of the chitosan membranes as shown in *Figure 2c*. However, the permeation rates through the GAC membranes are greater than those for the chitosan membranes as shown in *Figure 2a*. This tendency increases with the decrease of ethanol concentration in the feed mixture. Also as can be seen from *Figure 2b*, there are significant differences between the compositions in the permeate for the chitosan and GAC membranes. The separation characteristics of the GAC membrane are higher than those of the chitosan membrane.

The fact that the GAC membrane has higher permeation rates and separation characteristics than those for the chitosan membrane may be interpreted as follows. When the polymer membrane is crosslinked, in general, the resulting membrane becomes denser, and the separation characteristics of this membrane increase but the permeation rate decreases. However, the GAC membrane increases both the permeation rate and separation characteristics. If the chitosan membrane is crosslinked with glutaraldehyde without the swelling, the crosslinked membrane shows general permeation and separation characteristics. In this study, the chitosan membrane is crosslinked in an aqueous solution with glutaraldehyde. Therefore, the chitosan membrane is swollen in aqueous solution and is then crosslinked with glutaraldehyde. Consequently, the dense GAC membrane with high hydrophilicity is formed. Higher permeation rate and separation characteristics for the GAC membrane depend on both the dense structure and high hydrophilicity of the GAC membrane.

The permeation rates and separation factors for the chitosan derivative membranes by the evapomeation method are summarized in *Table 1*. When the ethanol concentration in the feed is less than 70 wt%, separation factor for the CAS membrane is not appreciable. This is

Table 1 Permeation rates (PR) and separation factors of the chitosan derivative membranes by evapomeation

	Chitosan membrane		CAS membrane		GAC membrane	
EtOH in feed (vapour) (wt%)	PR (kg/m^2 h) × 10^3	$\alpha^{H_2O}_{EtOH}$	PR (kg/m^2 h) × 10^3	$\alpha^{H_2O}_{EtOH}$	PR (kg/m^2 h) × 10^3	$\alpha^{H_2O}_{EtOH}$
0	176	–		–	237	–
10 (43.9)	148	5 (33)			204	219 (1542)
30 (60.4)	126	7 (25)			149	∞
50 (67.7)	96	26 (56)			106	∞
70 (77.3)	39	37 (53)	116	4 (5)	55	∞
90 (90.8)	18	114 (124)	16	916 (1002)	25	2557 (2797)
95.6 (95.6)	7	202 (202)	2	2556 (2556)	4	2208 (2208)
100	6	–		–	3	–

attributed to an important increase of the degree of swelling of the CAS membrane for feed compositions rich in the water vapour, because the CAS membrane is soluble in water. As the ethanol content in the feed becomes higher than 90 wt%, the CAS membrane is not swollen, and instead, shrinks and consequently becomes denser. The separation factors for 90 and 95.6 wt% of feed composition are 1002 and 2556, respectively. These values are about ten times greater than the separation factors at the same feed compositions for the chitosan membrane.

In addition, there are no large differences between the permeation rates of the CAS and chitosan membranes. In the GAC membranes, when the ethanol concentrations

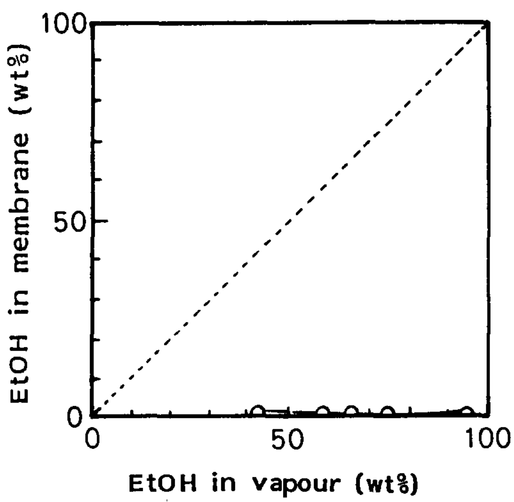

Figure 3 Effect of feed vapour composition from aqueous ethanol solution on the vapour composition adsorbed inside the GAC membrane

in the feed are 30 to 70 wt%, the separation factors are infinite. This means that the GAC membrane permeates only water from the feed mixtures with 30 to 70 wt% of ethanol concentration. The result shown in *Figure 3* supports the fact that the GAC membrane has such a high separation factor. *Figure 3* shows the relationship between the composition of vapour adsorbed inside the membrane and the vapour composition vaporized from the feed of aqueous ethanol solution. As can be seen from this figure, the GAC membrane predominantly adsorbs water in all feed compositions. This result is attributed to the higher hydrophilicity of the GAC membrane. The fact that water molecules are selectively dissolved into the GAC membrane and also that these molecules with smaller molecular size can easily diffuse through the GAC membrane significantly influences the high permeation rate and separation factor.

In *Table 1*, the permeation rates for these feed compositions are also greater than those for the chitosan membrane. The separation factors for 90 and 95.6 wt% of feed composition are about 20 and 10 times greater, respectively, than those for the chitosan membrane. Higher permeation rates and separation factors of the GAC membrane can be considered to be very interesting features of membrane performance.

In *Table 2*, the permeation and separation characteristics for aqueous ethanol solution through water selective polymer membranes in pervaporation and evapomeation are summarized. The separation factors for the chitosan derivative membranes such as chitosan, CAS, GAC membranes in pervaporation are relatively higher than those for other polymer membranes. However, the permeation rates of the chitosan derivative membranes are smaller. In evapomeation, the separation factors for these derivative membranes are greater. It is

Table 2 Permeation and separation characteristics for aqueous ethanol solution through some polymer membranes in pervaporation and evapomeation

Membrane	Feed[a] (wt%)	Temperature (°C)	Permeation rate ($kg/cm^2 \cdot h$)	Separation factor ($\alpha^{H_2O}_{EtOH}$)	Ref.
Cellophane	75.6	60	6.0	5	5
Cellulose acetate	95.6	60	0.2	5.9	6
Polytetrafluoroethylene–g–polyvinylpyrrolidone	95.6	25	2.2	2.9	7
Nafion–H^+–$(CH_2)_2NH^+$	95.6	70	5.0	2.5	8
Polyacrylonitrile–polyvinylpyrrolidone blend	95.6	20	2.2	3.2	9
Poly(maleimide co-acrylonitrile)	95	15	0.036	44.8	10
Poly(acrylic acid co-acrylonitrile)	81.5	15	0.013	876	11
Polystyrene	95.6	40	0.005	101	12
Polyvinylchloride	95.6	40	0.003	63	13
Alginic acid	95.6	40	0.048	8.8	1
Chitosan	70	40	0.012	31	2
	95.6	40	0.065	17	
CAS	70	40	0.272	4	
	95.6	40	0.074	20	
GAC	70	40	0.043	182	
	95.6	40	0.033	390	
Polystyrene[b]	95.6	40	0.003	1516	12
Polyvinylchloride[b]	95.6	40	0.002	203	13
Alginic acid[b]	95.6	40	0.007	1940	1
Chitosan[b]	70	40	0.039	37	
	95.6	40	0.007	202	2
CAS[b]	70	40	0.116	5	
	95.6	40	0.002	2556	
GAC[b]	70	40	0.055	∞	
	95.6	40	0.004	2208	

[a] Concentration of aqueous ethanol solution
[b] Evapomeation

necessary to improve the permeation rate further. In future, if an ultrathin membrane is prepared from the chitosan derivatives, an appearance of the chitosan derivative membranes with both high permeation rate and high separation characteristics will be expected.

REFERENCES

1. Uragami, T. and Saito, M. *Sep. Sci. Technol.* 1989, **24**, 541
2. Uragami, T., Saito, M. and Takigawa, K. *Makromol. Chem., Rapid Commun.* 1988, **9**, 361
3. Kopeček, J. and Sourirajan, S. *Can. Chem. J.* 1969, **47**, 3467
4. Yamada, S. *Membrane* 1981, **6**, 168
5. Heisler, E. G., Hunter, A. S., Sicilians, J. and Treadway, R. H. *Science* 1956, **124**, 77
6. Aptel, P., Cunny, J., Josefowicz, J., Morel, G. and Neel, J. *J. Appl. Polym. Sci.* 1974, **18**, 351
7. Aptel, P., Challard, N., Cunny, J. and Neel, J. *J. Membr. Sci.* 1982, **11**, 3
8. Ishikawa, T. *Chem. Eng.* 1984, **29**, 19
9. Ngnyen, Q. T., Balnc, L. L. and Neel, J. *J. Membr. Sci.* 1985, **22**, 245
10. Yoshikawa, M., Yokoi, H., Sanui, K. and Ogata, N. *J. Polym. Sci., Polym. Chem. Edn* 1984, **22**, 2159
11. Yoshikawa, M., Yokoshi, H., Sanui, K. and Ogata, N. *J. Polym. Sci., Polym. Lett. Edn* 1984, **22**, 473
12. Uragami, T. and Morikawa, T. *Makromol. Chem.* 1989, **190**, 329
13. Uragami, T., Morikawa, T. and Okuno, H. *Polymer* 1989, **30**, 329