Pervaporation Properties of Carboxymethylcellulose Membranes with Different Degree of Substitution

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1. Introduction

Recently, there has been increased interest in the use of various polymer membranes for the selective separation of organic liquid mixtures by pervaporation separation techniques because of their high separation efficiency and permeability.

It has been known that these separation techniques depend on the facts that certain polymer membranes permit easier passage of one liquid than the others. In a pervaporation separation process, it is desirable to have a polymer membrane which combines good permeation rates and a high selectivity for organic liquid mixtures and it is essential to choose the right polymer membrane as well as the optimum operating condition. Therefore, membranes of the composite type such as the G.F.T. membrane[1] have been developed and tested for their pervaporation capabilities. Furthermore, these newly developed composite membranes exhibit excellent performance in the removal of water from organic aqueous solutions such as ethanol, iso-propanol, and n-propanol[2,3].

However, there are only few reports on preparing a composite membrane based on carboxymethylcellulose(CMC) for pervaporation. It has been reported that CMC dense membranes were highly water permselective for pervaporation in alcohol-water mixtures[4]. In this work, we prepared a composite membrane based on CMC with various degrees of substitution(DS) in order to develop a new dehydration composite membrane having high selectivity and permeability.

New dehydration composite membranes were produced by casting CMC polymer solutions on dense nonwoven fabrics. And then, we investigated practical pervaporation performances of alcohol aqueous solutions through the CMC composite membranes.

2. Experimental

2.1 Materials

Carboxymethylcellulose, sodium salt(CMC-Na$^+$)samples of 0.65, 0.73, 0.82, and 1.06 degree of substitution(DS) and molecular weight 210,000~250,000 were obtained from Korean ginseng products Co.,Ltd (Korea). Polyester nonwoven fabrics (MF-135k, kanai Juyo, Japan) were used as porous supports.

2.2 Membrane preparation

CMC dense membranes were prepared by casting aqueous solutions(2~5wt%) on glass plates using solution casting method. The composite membranes were prepared by casting CMC solution on the dense polyester nonwoven fabrics, and then the membranes were dried in an oven. The thickness of separation layer for composite membrane was controlled by adjusting the concentration of the casting solution. The thickness of separation layer was about 50~60μm.

2.3 Pervaporation experiments

Pervaporation experiments have been performed with a laboratory test cell[5] and a pervaporation module unit[**Fig.1**].

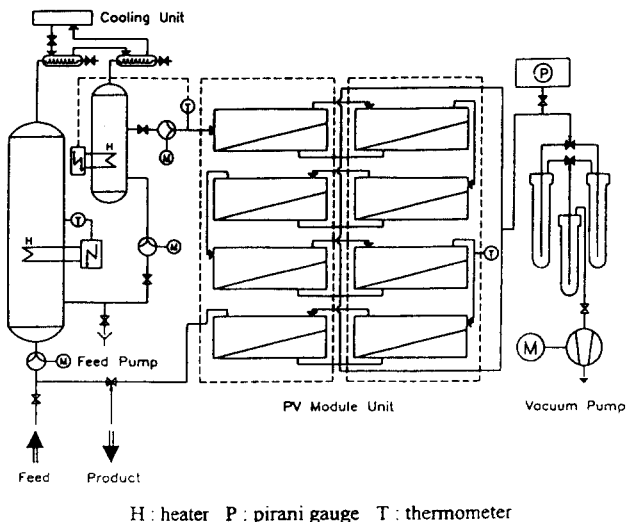H : heater P : pirani gauge T : thermometer

Fig. 1 Pervaporation process unit of the plate and frame module.

The laboratory test cell contains a standard separation cell with a total membrane area of 19.63cm². The volume of the feed vessel is 1ℓ. The pervaporation module unit contains a plate and frame type with a membrane area of 2260cm² and a feed volume of 10ℓ.

2.4 Membrane evaluations

Pervaporation separation performance is usually characterized by permeation rate (flux, J_t), separation factor(selectivity, α), and pervaporation separation index(PSI). The feed as well as the permeate is analyzed using gas chromatography equipped with a thermal conductivity detector. Total fluxes J_t(kg/m²·h) are obtained by weighting the condensed permeate. The separation factor(α) is defined as follows :

$$\alpha = (Y_1/Y_2)/(X_1/X_2) \qquad (1)$$

where Y_i is the weight fraction of the permeate and X_i is that of the feed; 1 and 2 denote water and the organic solvent, respectively.

A pervaporation separation index(PSI) can be defined, which is a new measure of the separation ability of a membrane, as the product of a separation factor(α) and a permeation rate (J_t)

$$PSI = J_t \times \alpha \qquad (2)$$

3. Results and Discussion

Carboxymethylcellulose, sodium salt(CMC-Na⁺) showed good film forming properties, and although water soluble, it was insoluble in the organic solvent-water mixtures and could be evaluated as a membrane without crosslinking. The pervaporation performance data for CMC dense membranes with various degrees of substitution in 80 and 85wt% iso-propanol aqueous solutions at 60℃ are shown in **Table 1**.

The water permeate of various CMC membranes was much higher than the iso-propanol permeate because of the polar and hydrophilic nature of the membranes. The water content in the permeate was almost above 99wt% when the feed iso-propanol concentration was higher than 80wt%.

Table 1 Pervaporation properties of CMC dense membranes with various degrees of substitution

iso-Propanol in feed (℃)	DS[a]	Permeation rate(kg/m²·h)	Separation factor(α)	PSI[b] (kg/m²·h)	%H2O in permeate
80wt% (60)	0.65	0.596	782	466	99.49
	0.73	0.604	650	393	99.39
	0.82	0.940	632	594	99.37
	1.06	1.158	1600	1853	99.75
85wt% (60)	0.65	0.263	11326	2979	99.95
	0.73	0.297	11319	3362	99.95
	0.82	0.423	8847	3742	99.94
	1.06	0.496	35398	17557	99.98

(a) Degree of substitution : the average number of hydroxyl groups substituted per anhydroglucose unit in cellulose.

(b) Pervaporation separation index.

The results of pervaporation experiments for CMC membrane with 1.06 DS show that the permeation rate as well as separation factor are better than those of other membranes. Therefore, we prepared a composite membrane based on CMC with 1.06 DS in order to increase the removal of water from organic liquid mixture. The dependence of pervaporation experiments was not determined for all degree of substitution, but such dependence for the CMC membrane with 1.06 DS was carried out in iso-propanol aqueous solution.

Fig.2 shows temperature dependence for permeation rate and separation factor of CMC composite membrane with 1.06 DS in iso-propanol aqueous solution. As can be seen, an Arrhenius linear relationship is observed between the permeation rate and temperature. The pervaporation activation energies are 21.5 and 43.6 kJ/mol for 85 and 90wt% iso-propanol aqueous solutions, respectively.

Fig.3 shows the effect of feed iso-propanol concentration on the permeation rate and separation factor of CMC composite membrane with 1.06 DS at 60℃. The separation factor and the permeation rate were 1285~8982 and 0.10~1.45 kg/m²·h, respectively. The highest value of pervaporation separation index(PSI) which means the best pervaporation performance was 3233 kg/m²·h for the 90wt% iso-propanol aqueous solutions at 60℃.
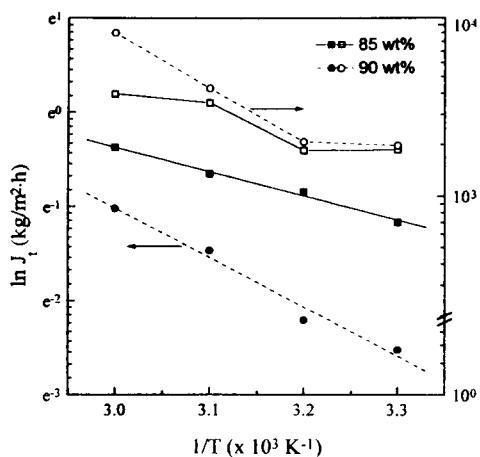
Fig.2 Temperature dependence of the permeation rate(J_t) and separation factor(α) for the CMC composite membrane with 1.06 DS at different iso-propanol concentrations.
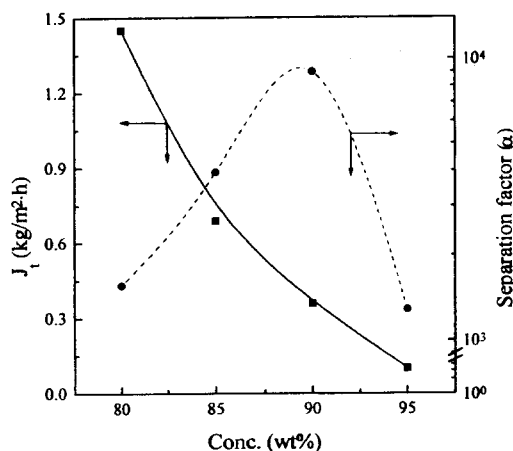
Fig.3 Effect of feed concentration for the CMC composite membrane with 1.06 DS in iso-propanol aqueous solution at 60℃.

4. Conclusion

We prepared a composite membrane based on CMC with 1.06 DS in order to develop a new dehydration composite membrane having high selectivity and permeability.

The separation factor and the permeation rate for the CMC composite membrane in iso-propanol aqueous solutions were 1285~8982 and 0.10~1.45 kg/m'·h, respectively. These experimental results indicated that the new CMC composite membrane with 1.06 DS would be very effective to apply on a pervaporation module unit for the removal of water from the water/iso-propanol mixture systems.

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