

Pervaporation of Methanol/Methyl *tert*-Butyl Ether Mixtures Through Agarose/Hydroxyethylcellulose Blended Membranes

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ABSTRACT: In this study, we investigated methanol (MeOH)/methyl *tert*-butyl ether (MTBE) separation with hydroxyethylcellulose (HEC)/agarose blended membranes by applying a pervaporation technique. The membranes permeated MeOH in preference to MTBE from MeOH/MTBE mixtures. From pervaporation and sorption data, the

permselectivity of HEC/agarose blended membrane was dominantly due to solubility selectivity. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3408–3411, 2002

Key words: membranes; polysaccharides; separation techniques; blends

INTRODUCTION

Pervaporation is perceived as a potential method for separating liquid mixtures, such as in the dehydration of organics, the removal of organics from water, and organic/organic separations, and as an alternative to distillation and rectification processes.¹ Among liquid mixtures, especially organic/organic mixtures, methanol (MeOH)/methyl *tert*-butyl ether (MTBE) is one of the most interesting and important to be separated by pervaporation. MTBE has been adopted as an octane enhancer² in connection with environmental pollution.³ MTBE is produced by the reaction of MeOH and isobutene (2-methyl-1-propene); however, MeOH forms an azeotrope with MTBE at a composition of 14.3 wt % MeOH. From this, the separation of MeOH/MTBE mixtures by pervaporation is a challenging subject in pervaporation studies. More than a few articles have reported on the pervaporation of MeOH/MTBE mixtures with synthetic polymeric membranes.^{4–16}

From these previous studies,^{4–16} one can deduce that polar hydrophilic polymers might be candidate materials, giving MeOH permselective membranes. To this end, we adopted agarose (Aga) as a membrane material for the pervaporation of MeOH/MTBE mixtures. Aga is a linear polymer of alternating D-galactose and 3,6-anhydro-L-galactose from red algae, and it is one of the most abundant natural polymers (Scheme 1). However, it has not been used as a membrane material, excepting as a material for gel filtration, gel electrophoresis, and matrices for immobilizing biologically active molecules, and so forth.¹⁷ To

this end, membranes were prepared from Aga, and their pervaporation of MeOH/MTBE mixtures was investigated.¹⁸ The Aga membrane gave high permselectivity toward MeOH, whereas its flux was not always enough for application. To improve the performance of the Aga membrane, hydroxyethylcellulose (HEC) was adopted as an hydrophilic polymeric material, HEC/Aga blended membranes were prepared, and their pervaporation of MeOH/MTBE mixtures was investigated.

EXPERIMENTAL

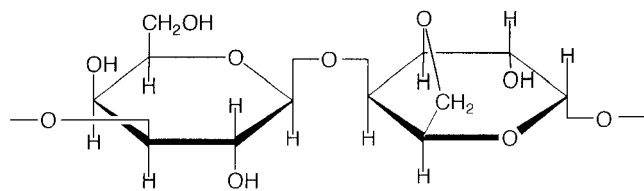
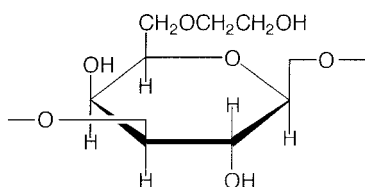
Materials

Aga (standard low m_r) was purchased from Bio-Rad Laboratories (Hercules, CA) and was used without further purification. HEC SP-600 (Daicel Chemical Industries, Ltd., Tokyo, Japan) was employed as HEC. MeOH and sodium azide were used without purification. MTBE was kindly provided by Idemitsu Petrochemical Co. Ltd. (Tokyo, Japan). Deionized water was also used.

Membrane preparation

We describe a typical membrane preparation process using that for the HEC/Aga-050 membrane, in which the weight ratio of HEC to Aga was 0.50. Aga (0.40 g) and HEC (0.20 g) were dissolved in 39.40 g of water. Sodium azide (6 mg) was added as a fungicide. The aqueous HEC/Aga solution thus obtained was poured onto a tray (14 cm long × 15 cm wide) and was allowed to stand at ambient temperature.¹⁹ The obtained HEC/Aga gel was sandwiched between two porous Teflon sheets, and both outsides were covered with a few sheets of filter papers. The HEC/Aga gel

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**Agarose****HEC****Scheme 1**

thus covered was allowed to evaporate water at ambient temperature under a compression of a constant pressure of 104 g/cm². Other membranes were prepared in a manner similar to that mentioned previously, with differing amounts of HEC and water. For the HEC/Aga-025 membrane, 0.10 g of HEC and 39.50 g of water was used, and 0.30 g of HEC and 39.30 g of water was used for the HEC/Aga-075 membrane. The

thickness of the membranes used in this study was around 24 μm.

Pervaporation

Permeation of the MeOH/MTBE mixtures was performed by an ordinary pervaporation technique.²⁰ The membrane area in contact with the liquid feed was 17.3 cm². The downstream pressure applied was kept around 267 Pa (2.0 mmHg). Pervaporation experiments were carried out at a constant temperature of 30°C.

Separation analysis was carried out on a Shimadzu GC-8APT gas chromatograph (Shimadzu Co., Kyoto, Japan) equipped with a 3.0 m long column packed with poly(ethylene glycol) 6000 (Shimalite TPA) (Shimadzu Co., Kyoto, Japan).

The separation factor (α) is defined as

$$\alpha = (Y_{\text{MeOH}}/Y_{\text{MTBE}})/(X_{\text{MeOH}}/X_{\text{MTBE}})$$

where Y_i is the weight fraction in the permeate and X_i is the weight fraction in the feed.

Sorption

The sorption of the HEC/Aga-025 membrane was measured as described previously.²¹ The solubility selectivity (S_s) is defined as

$$S_s = (Z_{\text{MeOH}}/Z_{\text{MTBE}})/(X_{\text{MeOH}}/X_{\text{MTBE}})$$

TABLE I
Results of the Pervaporation of MeOH/MTBE Mixtures Through HEC/Aga Membranes^a

Membrane	X_{MeOH}	Y_{MeOH}	α	J/g m ⁻² h ⁻¹
HEC/Aga-025	0.09399	0.99999 ^b	964,000	2.31
	0.30290	0.99998	115,000	15.2
	0.51770	0.99999 ^b	93,200	46.7
	0.71922	0.99939	640	167
	0.90610	0.99902	106	470
HEC/Aga-050	0.09231	0.98933	912	1.25
	0.31164	0.99995	48,000	8.53
	0.52404	0.99990	9,080	59.0
	0.71179	0.99935	623	148
	0.89166	0.99933	181	218
HEC/Aga-075	0.10255	0.94354	146	11.2
	0.31376	0.96170	54.9	25.4
	0.51364	0.98992	93.0	73.4
	0.70345	0.99672	128	273
	0.90126	0.99738	41.7	854
Aga ^c	0.09579	0.99999 ^b	944,000	0.674
	0.30340	0.99999 ^b	230,000	19.7
	0.51746	0.99999 ^b	46,600	48.3
	0.72016	0.99987	2,990	114
	0.92097	0.99952	477	280

^a Downstream pressure = 267 Pa (2.0 mmHg); operating temperature = 30°C.

^b MTBE was hardly observed.

^c Cited from ref. 18.

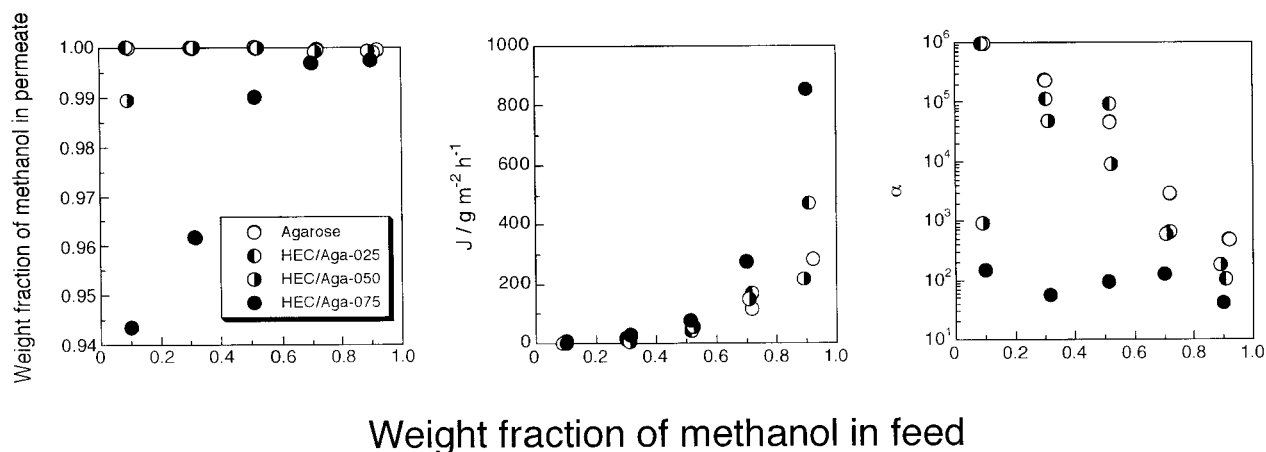


Figure 1 Effect of feed composition on the separation, total flux (J), and α in the pervaporation of MeOH/MTBE mixtures through HEC/Aga membranes (downstream pressure = 267 Pa (2.00 mmHg); operating temperature = 30°C).

where Z_i is the weight fraction in the membrane and X_i is the weight fraction in the solution after equilibrium was reached.

RESULTS AND DISCUSSION

Pervaporation

The pervaporation results of MeOH/MTBE separation through three kinds of HEC/Aga blended membranes are given in Table I together with those of the Aga membrane.¹⁸ These pervaporation results are also visually shown in Figure 1. The pervaporation performance was plotted as a function of the weight fraction of MeOH in feed. As expected, the HEC/Aga blended membranes also permeated MeOH in preference to MTBE like the Aga membrane. As for the permeates at the weight fractions of MeOH in feed of 0.1 and 0.5 for the HEC/Aga-025 membrane, MTBE was hardly detected in the permeate like those in feeds of 0.1 to 0.5 for the Aga membrane. In this case, we calculated α assuming that the weight fraction of MTBE in the permeate was, at the highest, 1×10^{-5} because the lowest limit of the detection of MTBE in this study was a weight fraction of MTBE of around 1×10^{-5} .

In this study, we aimed to obtain modified Aga membranes that gave higher flux values than the Aga membrane previously reported.¹⁸ As expected, an increase in the flux value was attained by the addition of the hydrophilic polymeric material HEC to Aga; an enhancement of flux was especially observed in the HEC/Aga-075 membrane, whereas permselectivity toward MeOH was decreased, as is often observed in membrane separation. The weight fractions of MeOH in the permeate for the HEC/Aga-075 membrane was over 0.944, as can be seen in Figure 1.

Sorption

To elucidate the factor that governs the permselectivity, we investigated the sorption experiments. The HEC/Aga-025 membrane, which gave relatively high permselectivity among the three kinds of HEC/Aga membranes, was adopted as the sample membrane for the sorption experiments. The composition of the liquid mixture sorbed in the HEC/Aga-025 membrane and the total amount sorbed in the membrane are plotted against feed composition in Figure 2. As ex-

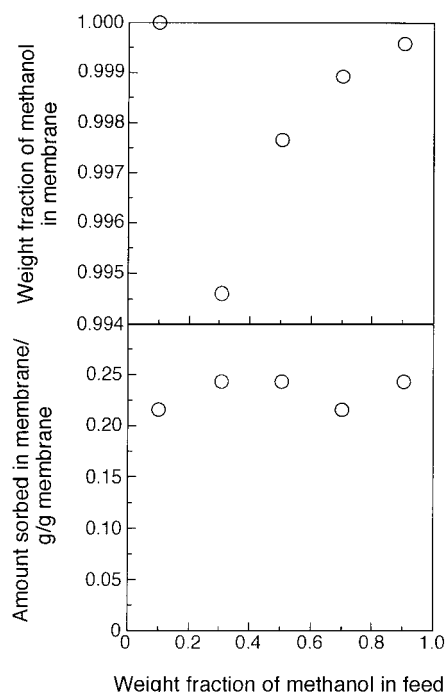


Figure 2 Effect of feed concentration on the composition of solution in the membrane and on the total sorption for the HEC/Aga-025 membrane at 30°C.

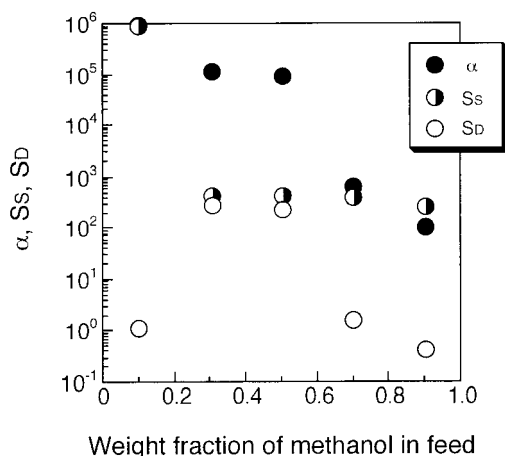


Figure 3 Effect of feed composition on α , S_S , and S_D of the HEC/Aga-025 membrane (downstream pressure = 267 Pa (2.0 mmHg); operating temperature = 30°C).

pected from the pervaporation results given in Figure 1, MeOH was greatly sorbed in the HEC/Aga-025 membrane. As for the weight fraction of MeOH in a solution composition of 0.1, MTBE was hardly detected. In this case, we calculated S_S assuming that the weight fraction of MTBE in the membrane was, at the highest, 1×10^{-5} , as mentioned in the previous section.

S_S was calculated with the sorption data. When the solution-diffusion theory is obeyed, diffusivity selectivity ($S_D = D_{\text{MeOH}}/D_{\text{MTBE}}$, where D_{MeOH} and D_{MTBE} are the diffusion coefficients of MeOH and MTBE, respectively) can be estimated from α and S_S ($S_S = S_{\text{MeOH}}/S_{\text{MTBE}}$, where S_{MeOH} and S_{MTBE} are the solubility coefficients of MeOH and MTBE, respectively) thus obtained.²² α , S_S , and S_D for the HEC/Aga-025 membrane are shown in Figure 3, as a function of the weight fraction of MeOH in feed (solution). From the amount sorbed in the membrane, as given in Figure 2, it might be said that the state of the membrane in contact with downstream side during the pervaporation experiment, which played an important role for permselectivity, was different from that of the sorption experiment.^{23,24} Therefore, S_S and S_D obtained in this study were apparent values, and true S_S should be higher than those obtained from sorption experiments. Diffusivity selectivities should be, at the highest, those given in Figure 3, and true diffusivity selectivities might be lower than those. The results in Fig-

ure 3, however, led to the conclusion that the S_S was the dominant factor for the determination of the permselectivity toward MeOH. However, it is hard to conclude that this was ascribed to adding HEC to Aga, even though the presence of HEC in the membrane, especially, in HEC/Aga-075 membrane, contributed to the enhancement of flux values.

CONCLUSIONS

The membranes prepared from HEC and Aga permeated MeOH from MeOH/MTBE mixtures by pervaporation. The addition of HEC to Aga membrane led to an increase in flux value. From the pervaporation and sorption data, the permselectivity of HEC/Aga blended membrane was dominantly determined by S_S .

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