An Analysis of Pervaporation of MTBE/Methanol Mixtures through the Cellulose Acetate and Triacetate Membranes

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INTRODUCTION

Methyl *tert*-butyl ether (MTBE) is produced by a reaction of methanol with isobutylene. It is often desired to add methanol excessively in order to improve the conversion. Excess concentration of methanol up to about 20 % of the stoichiometric amount is generally used to achieve high conversions. However, the use of excess methanol causes a purification problem because methanol forms a minimum-boiling azeotrope with MTBE at a composition of 14.3 wt.% methanol at 760 mmHg. Thus pervaporation has been employed mainly in order to break the azeotrope.[1,2] In this study, we investigate how methanol and MTBE permeate through membranes of cellulose acetates with two different acetyl values.

EXPERIMENTAL

Cellulose acetates(CA) with the degree of substitution of 2.45 were obtained from Eastman with degree of substitution 2.45 and cellulose triacetates(CTA) from Fluka. The membranes were prepared as follows. About 1g of polymer was dissolved in 30ml of DMF for cellulose acetate and in methylene chloride for cellulose triacetate, respectively. The solution was cast on a glass plate, then the solution is allowed to evaporate at 70°C for CTA and 25°C in glove box for CTA for 1 day, respectively. Finally, the membrane was removed from the glass plate and was dried in a vacuum oven at 100°C for 3 days.

Pervaporation experiments were carried out at 40°C unless otherwise specified. The compositions in the permeate were analyzed by gas chromatography. To evaluate the Flory interaction parameters, χ, equilibrium sorption experiments were performed at 40°C. The total sorption was calculated from the difference of wet weight (after equilibrium sorption) and dry weight of the membranes. Diffusion coiefficients of MTBE and methanol at zero concentration were determined by inverse gas chromatography[3].

RESULTS AND DISCUSSION

Figure 1 shows that the flux increased with the degree of acetylation while the selectivity decreased. This phenomenon is, of course, due to the bulky structure of cellulose triacetate which gives more space for permeates to pass through. As seen in table 1, χ_{13} is lower than χ_{23} for both membranes. This difference indicates that methanol will sorbe preferentially onto membranes. The absolute value and the difference between χ_{13} and χ_{23} for cellulose triacetate are smaller than for cellulose acetate. These facts explain that celluloce triacetate has the higher flux and lower selectivity than cellulose acetate as shown in figure 1. Diffusion coefficients of two permeates in both membranes can be considered from two points of view. First, the diffusion coefficients of methanol at 40°C in both membranes were larger than those of MTBE since the molecular dimension of methanol is smaller than that of MTBE. Secondly, the diffusion coefficients of permeates in cellulose triacetate are larger than in cellulose acetate due to its bulkier structure. This comparison reasonably explain the pervaporation data.

REFERENCES

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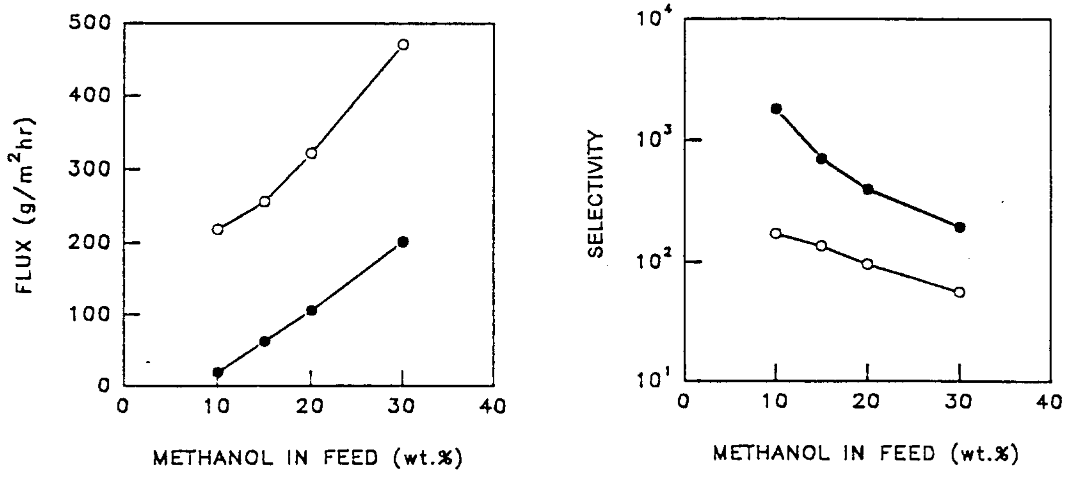
Table 1. Diffusion coefficients[a] of methanol and MTBE and Flory interaction parameters between pure liquid and membranes

Membrane	D_1	D_2	χ_{13}	χ_{23}
CA	7.01	2.59	1.18	2.79
CTA	9.33	4.73	1.13	1.31

[a] 10^{-11} (cm^2/sec)

Note: subscripts 1, 2, and 3 denote methanol, MTBE, and membranes, respectively



(a) (b)

Fig. 1. The pervaporation flux (a) and the selectivity (b) of MTBE/methanol mixtures through the cellulose acetate (•) and triacetate (o) membranes .