SEPARATION OF BUTANOL FROM BUTANOL-OLEYL ALCOHOL MIXTURE BY PERVAPORATION WITH POLY(DIMETHYLSILOXANE) HOLLOW-FIBER MEMBRANE

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Pervaporation of butanol-oleyl alcohol mixture through a poly(dimethylsiloxane) hollow-fiber membrane was carried out at various temperatures, pressures on the permeate side and concentrations of butanol in the feed solution. The butanol flux increased with increasing temperature and with increasing concentration of butanol in the feed solution. The butanol flux was analyzed by the solution-diffusion model modified with a term for the swelling effect of butanol on the membrane. The oleyl alcohol flux was irrelevant to the change in temperature and pressure on the permeate side, and could be explained by the solution-diffusion model.

The separation factors of butanol ranged from 19 to 270 below $2.5 \times 10^3 \text{ mol} \cdot \text{m}^{-3}$ of butanol concentration in the feed solution in the range of 323–353 K. The separation factor increased with increasing temperature and concentration of butanol in the feed solution.

Introduction

Recently, the production of butanol via acetone-butanol fermentation from biomass has become of interest as a promising source of liquid fuel and chemicals. In conventional operation of such a fermentation, however, the butanol concentration is about 2wt% in broth and the production rate is severely suppressed owing to the product inhibition to the microorganism. To increase the production rate of butanol, a continuous separation of butanol from aqueous solution in broth is industrially required.

Until now, pervaporation using the ethanol-permselective membrane has been used to separate ethanol from water-ethanol mixture produced in a fermentation system.⁹⁾ However, a direct application of pervaporation for butanol-water mixture seems not to be feasible because the commercially available membranes⁵⁾ permeate water in preference to butanol. As a development of butanol-selective membrane, Matsumura *et al.*⁷⁾ proposed a technique for separating butanol from the fermentation broth using an oleyl alcohol-impregnated polypropylene membrane. In long-term operation, however, fouling of the membrane may occur owing to solid impurity or microbial cell debris present in the broth.

Recently, an extractive fermentation system with oleyl alcohol as extractive solvent has been pro-

posed for butanol production with *Clostridium acetobutylicum*.²⁾ Butanol separation from butanol-oleyl alcohol mixture (denoted as BOM) by the pervaporation technique is expected to be advantageous in preventing the fouling of the membrane as BOM does not include solid particles.

The authors¹⁰⁾ previously examined butanol separation from BOM by pervaporation using a flat sheet membrane made from poly(dimethylsiloxane) (denoted as PDMS) and found that pervaporation was effective in the separation of butanol.

In the present study, we first obtain experimental data on the respective fluxes of butanol and oleyl alcohol through a hollow-fiber membrane made from PDMS. Secondly, we clarify the mechanism of pervaporation by examining the effect of operating conditions on the fluxes of alcohols and the separation factor.

1. Experimental

1.1 Materials

In the previous work with flat sheet membranes, the authors¹⁰⁾ found that the butanol flux from butanol-oleyl alcohol mixture through a poly(dimethylsiloxane) membrane was superior to that through other synthetic polymer membranes made from polypropylene or polyester.

In the present study, a PDMS hollow-fiber membrane module was used to secure a large permeating area of the membrane for pervaporation

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of butanol from BOM. The module was supplied by Nagayanagi Kogyo Co. Its specifications are shown in Table 1.

Butanol (special grade) and oleyl alcohol (special grade) were purchased from Wako Pure Chemical Industries Co.

1.2 Pervaporation by the hollow-fiber membrane

Figure 1 is a schematic diagram of an apparatus for pervaporation experiments using the hollow-fiber membrane module. Feed solutions were prepared at prescribed compositions of butanol and oleyl alcohol. The mole fractions of butanol in the feed solution, X_B , were 0.05 to 0.8. The feed solution was circulated by a peristaltic pump between a reservoir of the feed solution (volume: 0.5 dm^3) and the shell side of the hollow-fiber module (*i.e.*, the outside of the membrane) at a constant flow rate of $1.5 \text{ dm}^3 \cdot \text{h}^{-1}$, and the inside of the hollow fibers was kept at reduced pressure. The feed solution permeated from the outside to the inside of the hollow-fiber membrane by pervaporation. The operation time of pervaporation was 1 to 3 h and the change in composition of the feed solution was less than 10% of initial composition during the operation.

To collect the permeate inside the membrane, the permeate side of the module was connected to a cold trap in a methanol bath which was kept at 243 K by a dip-type cooler (LC-260; Advantec Toyo Co.). The module was thermostated at prescribed temperatures ($T = 323, 338$ and 353 K) in an incubator. The pressure on the permeate side, P_2 , was maintained at 0.04 or 1.07 kPa by regulating valve 8-2 (see Fig. 1) connected to a vacuum pump (Minivac PD-102; Yamato Scientific Co.). The pressure was measured by a manometer (New S Type Rotary Macleod Vacuum Gage; Okano Co.).

1.3 Analysis

A quantitative analysis of butanol in the permeate solution collected in the cold trap was carried out using a gas chromatograph (Model GC-8A; Shimadzu Co.) with a flame-ionization detector (column temperature: 473 K, injection temperature: 493 K, carrier gas: N_2) and a $3 \text{ mm} \phi \times 2 \text{ m}$ stainless steel column packed with 80–100 mesh Chromosorb 101 (Gasukuro Kogyo Co.). The amount of oleyl alcohol in the permeate solution, W_O , was calculated by subtracting the weight of butanol, W_B , from the total weight of the permeate solution collected in the trap, W_T , as follows.

$$W_O = W_T - W_B \quad (1)$$

The respective fluxes of butanol and oleyl alcohol were determined by the following equation.

$$J_i = \frac{W_i}{M_i \cdot A \cdot t} \quad (i = B, O) \quad (2)$$

Table 1. Specifications of PDMS hollow-fiber membrane module

Length of a module [mm]	200
Volume of the shell side of a module [cm^3]	90
Number of hollow fibers [—]	4500
Length of a hollow fiber [mm]	150
Inner diameter of a hollow fiber [μm]	200
Membrane thickness [μm]	60
Effective area of the membrane [m^2]	0.56

1 Reservoir of feed solution	6 Trap
2 Feed pump	7 Manometer
3 Hollow-fiber membrane module	8 Valve
4 Incubator	9 Vacuum pump
5 Cooling bath	

Fig. 1. Schematic diagram of apparatus for pervaporation by hollow-fiber module

The separation factor, α , is defined as

$$\alpha = \frac{Y_B/X_B}{Y_O/X_O} \quad (3)$$

where X_i and Y_i ($i = B, O$) are mole fractions of i component in the feed and permeate solutions, respectively.

When the butanol concentration in the feed solution, C_{FB} , was higher than $2.5 \times 10^3 \text{ mol} \cdot \text{m}^{-3}$, W_O was very small ($W_O/W_B < 0.01$). By considering the precision of experimental data of W_O , the oleyl alcohol flux was analyzed within the C_{FB} range of $0\text{--}2.5 \times 10^3 \text{ mol} \cdot \text{m}^{-3}$.

2. Theoretical Analysis

In the pervaporation of BOM, butanol permeates through the membrane and vaporizes on the membrane surface on the permeate side, but oleyl alcohol does not vaporize owing to its high boiling point (450 K at 1.7 kPa). Oleyl alcohol permeates through the membrane and descends as liquid along the membrane surface on the permeate side. These

situations are depicted in Fig. 2.

To derive the transport equations, the following assumptions are made.

1) The butanol flux is analyzed on the basis of the solution-diffusion model.⁶⁾

2) Butanol vaporizes on the membrane surface on the permeate side, and equilibrium is established between the butanol concentration in the membrane and the pressure of butanol in the gas phase on the permeate side.

3) The membrane matrix is swollen by butanol and the diffusion coefficient of butanol, D_B , is expressed by a function of butanol concentration.

4) The oleyl alcohol flux is analyzed on the basis of the solution-diffusion model.⁶⁾

5) Butanol dissolves into oleyl alcohol that descends in liquid film along the membrane surface on the permeate side as liquid.

6) Oleyl alcohol does not swell the membrane matrix.

From assumption 1), the butanol flux at steady state is represented as follows.

$$J_B = -D_B \frac{dC_{mB}}{dx} = -D_B \cdot K_B \frac{dC_B}{dx} \quad (4)$$

and the boundary conditions are given as

$$C_B = C_{FB} \quad \text{at } x=0 \quad (5a)$$

$$C_B = C_{PB} \quad \text{at } x=\delta \quad (5b)$$

The dependency of D_B on butanol concentration is expressed by an exponential formula proposed by Rogers *et al.*⁸⁾ as follows.

$$D_B = D_B^0 \cdot \exp(b \cdot C_B) \quad (6)$$

where b is the swelling parameter.

Substituting Eq. (6) into Eq. (4) and integrating Eq. (4) with the boundary conditions yields Eq. (7).

$$J_B = \frac{D_B^0 \cdot K_B}{\delta \cdot b} \{ \exp(b \cdot C_{FB}) - \exp(b \cdot C_{PB}) \} \quad (7)$$

Considering the equilibrium between the butanol in the membrane and that in the gas phase at the membrane surface on the permeate side, C_{PB} is expressed by the following equation proposed by Kataoka *et al.*⁴⁾

$$C_{PB} = \frac{C_{mT} \cdot P_2 \cdot Y_B}{K_B \cdot P_v} \exp \left\{ \frac{v(P_v - P_1)}{R \cdot T} \right\} \quad (8)$$

From assumption 4), the oleyl alcohol flux at steady state is expressed as follows:

$$J_O = -D_O \frac{dC_{mO}}{dx} = -D_O \cdot K_O \frac{dC_O}{dx} \quad (9)$$

and the boundary conditions are given as

Fig. 2. Model of butanol and oleyl alcohol permeation through membrane

Fig. 3. Relation between mole fraction of butanol in feed solution and that in permeate solution

$$C_O = C_{FO} \quad \text{at } x=0 \quad (10a)$$

$$C_O = C_{PO} \quad \text{at } x=\delta \quad (10b)$$

Integrating Eq. (9) with the boundary conditions yields Eq. (11).

$$J_O = \frac{D_O \cdot K_O}{\delta} (C_{FO} - C_{PO}) \quad (11)$$

3. Results and Discussion

3.1 The relation between the mole fraction of butanol in the feed and permeate solutions

Figure 3 indicates the relations between the butanol mole fraction in the feed solution, X_B , and that in the

permeate solution, Y_B , at respective temperatures of 323, 338 and 353 K, and at respective pressures on the permeate side of 0.04 and 1.07 kPa.

As shown in Fig. 3, the permeate composition curves stay above the diagonals. This means that butanol was concentrated in the permeate to a considerable extent.

3.2 The flux of butanol through hollow-fiber membrane

Figure 4 shows the effect of the butanol concentration in the feed solution, C_{FB} , on the butanol flux, J_B . J_B increased with increasing C_{FB} and temperature, respectively. No significant difference was observed between the values of J_B at the two pressures on the permeate side in the range of experimental conditions.

Let us consider the butanol flux according to the solution-diffusion model with the swelling effect.

Under experimental conditions, we have

$P_v = 24$ kPa (at 353 K), $P_1 = 101$ kPa,

$P_2 = 1.07$ kPa, $v = 0.9-3 \times 10^{-4} \text{ m}^3 \cdot \text{mol}^{-1}$ and

$T = 353$ K

Then, the right-hand side of Eq. (8) becomes nearly zero because

$$\exp\left\{\frac{v(P_v - P_1)}{R \cdot T}\right\} \simeq 1 \quad \text{and} \quad \left(\frac{P_2 \cdot Y_B}{P_v}\right) \simeq 0$$

Thus, Eq. (7) can be reduced as follows.

$$J_B = \frac{D_B^0 \cdot K_B}{\delta \cdot b} \left\{ \exp(b \cdot C_{FB}) - 1 \right\} \quad (12)$$

The values of $D_B^0 \cdot K_B$ and b in Eq. (12) were evaluated by fitting the experimental values to the calculated ones using a least-squares method. The calculated values are shown as the curves in Fig. 4. The evaluated values of $D_B^0 \cdot K_B$ and b are summarized in Table 2.

Yoshikawa *et al.*⁽¹¹⁾ reported that the values of swelling parameters of ethanol for poly(4-vinylpyridine-co-acrylonitrile) membranes were $2.67-6.14 \times 10^{-4} \text{ m}^3 \cdot \text{mol}^{-1}$ and Brun *et al.*⁽¹⁾ reported that the value of the swelling parameter of benzene for poly(acrylonitrile-co-butadiene) membrane was $5.0 \times 10^{-4} \text{ m}^3 \cdot \text{mol}^{-1}$. In the present study, the values of the swelling parameter were $1.7-1.8 \times 10^{-4} \text{ m}^3 \cdot \text{mol}^{-1}$, indicating that the butanol-PDMS membrane interaction is fairly small compared with the above solvent-membrane systems.

3.3 The flux of oleyl alcohol through hollow-fiber membrane

Figure 5 shows the relation between the oleyl alcohol flux, J_O , and the oleyl alcohol concentration in the feed solution, C_{FO} . As seen from Fig. 5, J_O increased with increasing C_{FO} as a whole. No significant difference was observed among data for variations in temperature and pressure on the permeate side.

Fig. 4. Effect of butanol concentration in feed solution on butanol flux

Table 2. Permeation coefficients and swelling parameters

	T [K]		
	323	338	353
$D_B^0 \cdot K_B \times 10^9$ [$\text{m}^2 \cdot \text{h}^{-1}$]	3.2	5.4	8.5
$b \times 10^4$ [$\text{m}^3 \cdot \text{mol}^{-1}$]	1.7	1.8	1.7

Fig. 5. Relation between oleyl alcohol concentration in feed solution and oleyl alcohol flux

The experimental data with respect to J_O are analyzed by the solution-diffusion model as follows.

Oleyl alcohol descends in a liquid state along the membrane surface on the permeate side without vaporization as shown in Fig. 2.

At steady state, the concentration of oleyl alcohol on the membrane surface on the permeate side, C_{PO} , may depend upon the concentration of dissolved

butanol in oleyl alcohol. The concentration of dissolved butanol in oleyl alcohol might be balanced dynamically to that of butanol in the membrane surface and the pressure of butanol in the vapor phase on the permeate side.

To estimate C_{PO} , the assumptions are made that C_{PO} and the solute permeability of oleyl alcohol, $D_O \cdot K_O$, are independent of the variations in temperature and pressure. The solid line in Fig. 5 was obtained by fitting Eq. (11) to experimental values of J_O using a least-squares method. From the slope and the intercept on the abscissa, the values of $D_O \cdot K_O$ and C_{PO} were evaluated as $5.3 \times 10^{-10} \text{ m}^2 \cdot \text{h}^{-1}$ and $2.3 \times 10^3 \text{ mol} \cdot \text{m}^{-3}$, respectively. $D_O \cdot K_O$ was 1/6–1/15 as much as $D_B^0 \cdot K_B$ in Table 2. The mole fraction of butanol in liquid oleyl alcohol was evaluated as 0.56, corresponding to $C_{PO} = 2.3 \times 10^3 \text{ mol} \cdot \text{m}^{-3}$. This suggests that liquid oleyl alcohol descending as liquid on the permeate side contains a relatively high amount of butanol.

3.4 The effect of butanol concentration in feed solution on separation factor

At steady state, the following relation holds.

$$Y_B/Y_O = J_B/J_O \quad (13)$$

Substituting Eq. (13) into Eq. (3), the separation factor is expressed as follows.

$$\alpha = \frac{X_O}{X_B} \cdot \frac{J_B}{J_O} \quad (14)$$

The evaluated values of α using Eq. (14) and experimental data are plotted in Fig. 6 against C_{FB} below $2.5 \times 10^3 \text{ mol} \cdot \text{m}^{-3}$ at various temperatures and pressures on the permeate side.

The values of α ranged from 19 to 270. α increased with increasing C_{FB} and temperature, while α was independent of pressure on the permeate side. The larger values of α were obtained at higher temperature. The temperature dependency of α was attributed to the results that J_B increased with increasing temperature and that J_O did not change with temperature.

The calculated values of α from Eqs. (11), (12) and (14) are shown by the curves in Fig. 6. The calculated values were close to the experimental ones.

The relationship between α and C_{FB} in Fig. 6 can be practically valid for extractive fermentation by considering that the butanol concentration in BOM is at most $2\text{--}3 \times 10^2 \text{ mol} \cdot \text{m}^{-3}$ under operating conditions.

Let us estimate the capacity of the pervaporation system combined with extractive fermentation using the module tested in the present work.

In extractive fermentation with *C. acetobutylicum* IAM 19012,²⁾ C_{FB} is kept at $2 \times 10^2 \text{ mol} \cdot \text{m}^{-3}$ by feeding to fresh oleyl alcohol, so that the microorgan-

Fig. 6. Relation between butanol concentration in feed solution and separation factor

ism can actively grow without butanol inhibition. In the case of $C_{FB} = 2 \times 10^2 \text{ mol} \cdot \text{m}^{-3}$, J_B is $2.3 \times 10^{-3} \text{ kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ at 353 K and the feed solution is concentrated to one-twenty-ninth by considering the partition coefficient of 3.7 between water and oleyl alcohol phases. As the butanol productivity of *C. acetobutylicum* is about $0.5 \text{ kg} \cdot \text{m}^{-3} \cdot \text{h}^{-1}$,²⁾ the fermentor volume is calculated to be 1.3–2.6 dm³ at the range of 323–353 K, based on the membrane surface area of 0.56 m² of the module (see Table 1).

With regard to the butanol separation from BOM obtained from the extractive fermentation, Iwata *et al.*³⁾ employed a flash-vaporation operation. However, this operation seems to be unsuitable for the butanol separation unit combined with a continuous system of extractive fermentation in spite of its high efficiency of butanol separation. In contrast, the separation process using a membrane with a large surface area provides a simple and compact separation unit, in which the extracting solvent on the feed side can be easily returned to a fermentor because the reduced-pressure (permeate) side is separated by the membrane. Thus, the membrane separation of butanol-oleyl alcohol mixture by pervaporation appears to be a promising means in a continuous process for production of butanol by the extractive fermentation.

Conclusion

Pervaporation of butanol-oleyl alcohol mixture through poly(dimethylsiloxane) hollow-fiber membranes was carried out and the following findings were obtained.

1) The flux of butanol through the membrane increased with increasing butanol concentration in the

feed solution and with increasing temperature. The permeability of butanol was analyzed by the modified solution-diffusion model with the swelling effect.

2) The oleyl alcohol flux was irrelevant to either temperature or pressure on the permeate side, and the flux could be explained by the solution-diffusion model.

3) The separation factors varied from 19 to 270 below $2.5 \times 10^3 \text{ mol} \cdot \text{m}^{-3}$ of butanol concentration in the range of 323–353 K.

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Nomenclature

A	= effective membrane area	$[\text{m}^2]$
b	= swelling parameter in Eq. (6)	$[\text{m}^3 \cdot \text{mol}^{-1}]$
C	= concentration of alcohol in the solution	$[\text{mol} \cdot \text{m}^{-3}]$
C_m	= concentration of alcohol in the membrane	$[\text{mol} \cdot \text{m}^{-3}]$
D	= diffusion coefficient	$[\text{m}^2 \cdot \text{h}^{-1}]$
D^0	= diffusion coefficient without swelling	$[\text{m}^2 \cdot \text{h}^{-1}]$
J	= flux of alcohol	$[\text{mol} \cdot \text{m}^2 \cdot \text{h}^{-1}]$
K	= partition coefficient	$[-]$
M	= molecular weight	$[\text{kg} \cdot \text{mol}^{-1}]$
P_v	= saturated vapor pressure of butanol	$[\text{Pa}]$
P_1	= pressure on the feed side	$[\text{Pa}]$
P_2	= pressure on the permeate side	$[\text{Pa}]$
R	= gas constant	$[\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}]$
T	= temperature	$[\text{K}]$
t	= operating time	$[\text{h}]$
v	= molar volume	$[\text{m}^3 \cdot \text{mol}^{-1}]$
W	= weight of alcohol collected in a cold trap	$[\text{kg}]$
X	= mole fraction of alcohol in the feed solution	$[-]$
x	= distance across the membrane	$[\text{m}]$
Y	= mole fraction of alcohol in the permeate	

	collected in a cold trap	$[-]$
α	= separation factor	$[-]$
δ	= membrane thickness	$[\text{m}]$

<Subscript>

B	= butanol
F	= feed side
i	= i component (butanol or oleyl alcohol)
O	= oleyl alcohol
P	= permeate side
T	= total amount

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