

## Pervaporation of Esters with Hydrophobic Membrane

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**Abstract**—Surface-modified alumina membrane ( $\text{Al}_2\text{O}_3$ ) was used for ester flavor recovery by pervaporation. This study focused on the permeation characteristics of ester compounds (ethyl acetate, EA; ethyl propionate, EP; ethyl butyrate, EB) through tube-type hydrophobic membrane. Experiments were performed to evaluate the effects of the feed concentration (0.15-0.60 wt%) and temperature (30-50 °C) on separation of EA, EP, and EB from aqueous solutions. It was found that the permeation flux increased with increasing feed ester concentration and operating temperature. The fluxes of EA, EP, and EB at 0.60wt% feed concentration and 40 °C were 254, 343, and 377  $\text{g/m}^2$  hr, which was much higher than those of polymer membranes. It was reported that the permeate flux of EA with PDMS was 1.1-58  $\text{g/m}^2\text{Phr}$  at feed concentration of 90-4,800 ppm and 45 °C. The separation factors for the 0.15-0.60 wt% feed solution of EA, EP, and EB at 40 °C were in the range of 66.9-78.9, 106.5-97.3, and 120.5-122.8, respectively. Due to the high separation factor, phase separation occurred in permeate stream because the ester concentration in permeate was much above the saturation limit.

Key words: Surface-modified Membrane, Pervaporation, Ethyl Acetate, Ethyl Propionate, Ethyl Butyrate, Flux, Separation Factor

### INTRODUCTION

The economical and efficient recovery of flavor compounds and the concentration of foods such as fruit juices continue to be a research field for the food, biotechnology and cosmetics industries [Baudot and Marin, 1999; Heath and Pharm, 1978]. In many cases, the processing of foods and beverage results in some loss of their original flavor. Fruit juices were routinely concentrated for economic reasons (reduced transport and storage costs), and the classical concentration processing caused the losses of the initial aromatic compounds. Flavor concentrates are widely used as food additives to enhance the overall flavor of foodstuff or to compensate for the loss of aromas during food processing [Charalambous and Inglett, 1978; Ho et al., 1995]. Natural flavor compounds are preferable to chemically synthesized ones by consumers due to their higher public acceptance.

Several efforts have been made to develop new technologies such as cryoconcentration and membrane process that would more satisfactorily conserve the original qualities of flavor. The recovery of organic compounds from dilute organic-water mixtures can be accomplished very effectively with the membrane technique [Joao et al., 1993; Won et al., 1996]. Membrane processes such as pervaporation, vapor permeation, reverse osmosis, membrane distillation and osmotic distillation have the potential to recover the flavor compounds. Advantages of membrane process in biotechnology can be attributed to the absence of thermal or pressure stresses and chemical alterations. Among biotechnological processes, the recovery of aroma compounds is the area, which is increasing interest in pervaporation. Rajagopalan and Cheryan [Rajagopalan and Cheryan, 1995] reported the pervaporation of a model flavor compound of

grapes, and Baudot and Marin [Baudot and Marin, 1997] carried out experiments with two dairy aroma compounds diluted in model aqueous solutions through GFT silicate-filled silicone composite membrane and GKSS PEBA homogeneous membrane.

Performance of pervaporation is dependent not only upon the characteristics of membrane materials but also upon the operating parameters such as feed concentration, temperature, permeate pressure and feed flow rate. The present paper is focused on the permeation characteristics of hydrophobic membrane towards aqueous dilute solutions of ethyl acetate (EA), ethyl propionate (EP) and ethyl butyrate (EB). These esters represent the model flavor compounds with fruit smell: ethyl acetate is ethereal, ethyl propionate has a sweet and fruity odor, and ethyl butyrate is associated with pineapple.

### THEORY

The diffusive mass transport of dilute compounds like aroma or flavors in biological fermentation products through pervaporation membrane can be described as Eq. (1). The mass flux of compound *i* becomes [Baudot et al., 1999; Beaumelle and Marin, 1994]:

$$J_i = K_i (f_i^{\text{feed}} - f_i^{\text{permeate}}) \quad (1)$$

where,  $J_i$  is the permeate flux of compound *i*,  $K_i$  is the apparent mass transfer coefficient, and  $f_i$  is fugacity. The fugacity of component *i* in the feed and in permeate can be expressed as follows:

$$f_i^{\text{feed}} = \gamma_i x_i^{\text{feed}} p_i(T^{\text{feed}}) \quad (2)$$

$$f_i^{\text{permeate}} = y_i p_T \quad (3)$$

where,  $p_i^o$  is the vapor pressure of compound *i*,  $\gamma_i$  is activity coefficient, and  $p_T$  is total pressure. The mass transfer coefficient ( $K_i$ ) includes sorption to, diffusion through, and desorption from the mem-

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brane. It is equivalent to the relation between the permeability coefficient ( $P_i$ ) and the thickness of the active layer of the membrane ( $l$ ) as shown in Eq. (4).

$$K_i = \frac{P_i}{l} \quad (4)$$

$$P_i = S_i D_i \quad (5)$$

where the permeability coefficient ( $P_i$ ) is equal to the product of the solubility coefficient of the permeant in the membrane ( $S_i$ ) and the diffusion coefficient ( $D_i$ ) of the permeant in the membrane. The sorption often results in non-linear sorption isotherm due to interactions between the components and membrane material. However, in the case of dilute aqueous solutions in hydrophobic membranes, these interactions are often small, resulting in linear sorption [Olsson and Trägårdh, 2001]. And, the diffusion coefficient of permeant is generally concentration dependent.

The performance of pervaporation [Howell et al., 1993] is usually represented with the separation factor  $\alpha_i$ . The separation factor  $\alpha_i$  for a given compound  $i$  is defined as the following.

$$\alpha_i = \frac{w_i^{\text{permeate}}}{1 - w_i^{\text{permeate}}} \bigg/ \frac{w_i^{\text{feed}}}{1 - w_i^{\text{feed}}} \quad (6)$$

where,  $w_i$  is the weight fraction of the compound  $i$  in the feed ( $w_i^{\text{feed}}$ ) and in the permeate ( $w_i^{\text{permeate}}$ ).

In pervaporation, temperature is an important process parameter. According to the solution-diffusion mechanism, the effect of temperature can be expressed by an Arrhenius type function.

$$J_i = A \exp\left(-\frac{E_{ai}}{RT}\right) \quad (7)$$

where  $A$  is the pre-exponential factor,  $E_{ai}$  the activation energy of the compound  $i$ ,  $R$  the gas constant, and  $T$  the absolute temperature.

The activation energy included in the exponential function can be dissociated into two parts [Feng and Huang, 1996; Yeom et al., 1996]:

$$E_{ai} + \Delta H_{\text{sorption},i} + E_{\text{diffusion},i} \quad (8)$$

where,  $\Delta H_{\text{sorption},i}$  is the enthalpy of dissolution of component  $i$  to be sorbed into the membrane and  $E_{\text{diffusion},i}$  is the activation energy required for the permeating molecules to diffuse through the membrane. It can be seen from Eqs. (7) and (8) that temperature can influence the transport in the membrane for the sorption and the diffusion step inside the membrane.

## MATERIALS AND METHOD

Ethyl acetate, ethyl propionate, and ethyl butyrate (Aldrich) were dissolved in de-ionized water (Milli-Q UF plus) to prepare the model solutions. The physical properties of the esters are given in Table 1.

**Table 1. Physical properties of ester compounds**

Compounds	Formula	Molecular weight (g/mol)	Molar volume (cm <sup>3</sup> /mol)	Boiling point (°C)	Water solubility at 25 °C (g/cm <sup>3</sup> )
Ethyl acetate	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	88.10	97.7	77	0.084
Ethyl propionate	C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	102.13	114.6	99	0.024
Ethyl butyrate	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	116.16	132.2	121	0.006

The tube-type alumina membrane (Al<sub>2</sub>O<sub>3</sub>) was obtained from Dongsu Co. (Korea) and used as a substrate. The surface was modified with silane coupling agent (perfluoro-alkylsilane). The surface-modified membrane showed super-hydrophobicity, and the water drop contact angle on the surface-modified membrane was about 162°. When the water drop contact angle on plate is over 90°, the surface is called hydrophobic [Mulder, 1991]. Inside and outside diameter of the membrane were 6.48 mm and 8.0 mm, respectively, and the effective membrane area was 18 cm<sup>2</sup>.

An aqueous-ester feed solution of known composition was stirred in the feed tank. The temperature of feed mixture was kept constant by a water bath. The membrane driving force was generated by a downstream vacuum pump. The downstream pressure was controlled by a vent valve and kept at 10 mmHg. Permeate was condensed and collected in cold trap positioned between the membrane cell and vacuum pump. The ester concentration in condensed permeate was analyzed by gas chromatography (Shimadzu GC-14B) equipped with a column of Porapak Q. For low water-soluble feed components, the collected permeate was diluted with an excess of ethanol in order to produce a single-phase sample for GC analysis.

Pervaporation (PV) experiments were carried out at temperatures of 30, 40, and 50 °C. The feed volume (1,000 ml) was greater than the pervaporation volume (10 ml) to avoid variations of feed concentration.

## RESULTS AND DISCUSSION

### 1. Effect of Ester Concentrations in Feed

#### 1-1. Permeation Fluxes of the Esters (EA, EP, and EB)

The permeate fluxes of the ester feed concentration of 0.15-0.60 wt% were measured at 30 °C, 40 °C, and 50 °C. The permeation fluxes of the esters (EA, EP, EB) were calculated from the total permeation rate and permeate composition. Measured fluxes of esters, ester concentrations in permeate stream, water fluxes, and total fluxes at 40 °C were plotted against the ester feed concentrations in Figs. 1, 2, 3, and 4, respectively.

It was shown that the permeation fluxes of esters (Fig. 1) increased linearly as feed concentration increased, while the permeation flux of the water was not affected by ester concentration in the feed (Fig. 3). The fluxes described in Eq. (1) can be expressed as follows.

$$J_i = K_i [C_i x_i^{\text{feed}} \frac{P_i^{\text{feed}}}{P_i} - C_2] \quad (9)$$

At a given temperature, the permeation flux of ester is a function of  $K_i$ , saturation pressure of ester ( $P_i^{\text{feed}}$ ), and molar fraction of ester ( $x_i^{\text{feed}}$ ). As described by Eq. (4) and (5),  $K_i$  increases with the feed concentration owing to the increasing solubility coefficient ( $S_i$ ) and diffusion coefficient ( $D_i$ ). As expected from Eq. (9), ester flux increased relatively linearly with increasing molar fraction in feed ( $x_i^{\text{feed}}$ ). In case of water flux, however, it might be inferred from Eq.

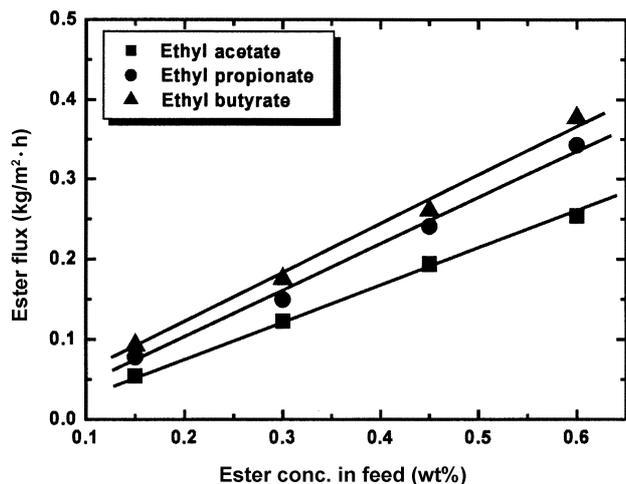


Fig. 1. Ester fluxes as a function of feed concentrations (EA, EP, EB) at 40 °C.

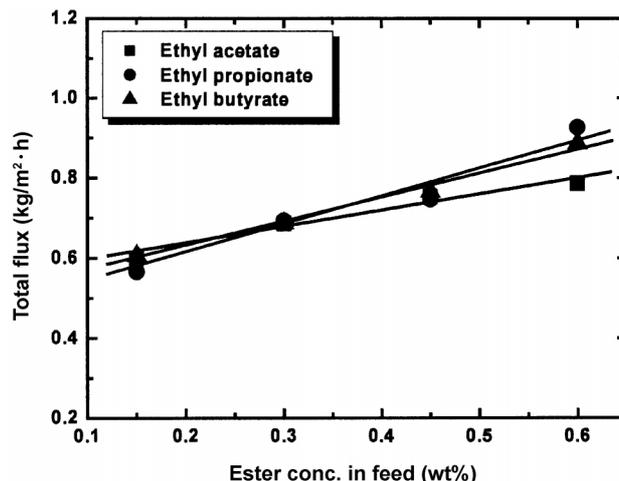


Fig. 3. Total fluxes as a function of feed concentrations (EA, EP, EB) at 40 °C.

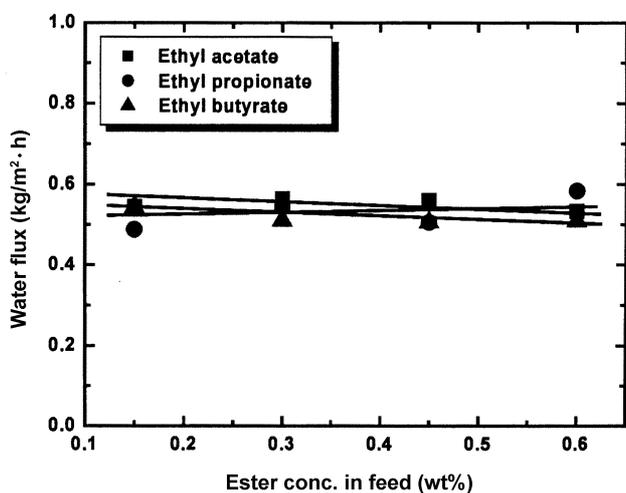


Fig. 2. Water fluxes as a function of feed concentrations (EA, EP, EB) at 40 °C.

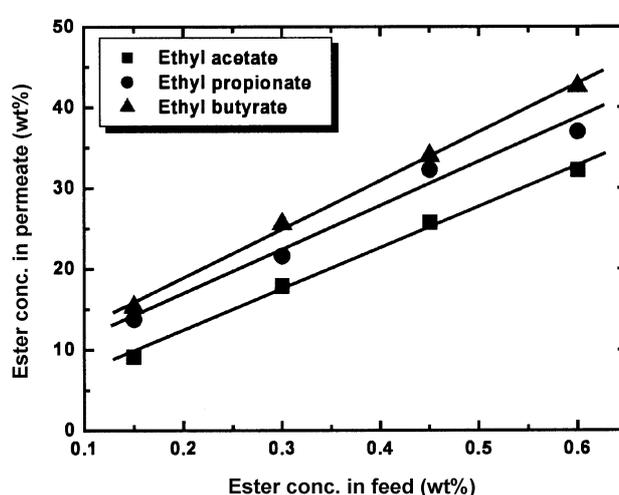


Fig. 4. Ester concentrations in permeate as a function of feed concentrations (EA, EP, EB) at 40 °C.

(9) that water flux at a given temperature did not depend on ester concentration in feed (Fig. 2) because the molar fraction of water in feed ( $x_i^{feed}$ ) remained virtually constant in the range of dilute ester concentration. That is why the permeation flux of water was not affected by ester concentration. The total flux increased with increasing ester concentration in feed due to the high flux of ester (Fig. 3). This tendency was the same as Baker's and Beaumelle's [Beaumelle and Marin, 1994; Baker et al., 1997]. Owing to the high hydrophobicity of the membrane surface, the membrane sorbed ester molecules more significantly in the solution with a higher ester content. Compared to the permeation flux of water, the permeation flux of ester was more strongly affected by the feed ester concentration.

The fluxes of EA, EP, and EB at feed concentration of 0.60 wt% and 40 °C were 254, 343, and 377 g/m<sup>2</sup>·hr. In case of pervaporation with PDMS at feed concentration of 90-4,800 ppm and 45 °C, it was reported that the permeate flux of EA was 1.1-58 g/m<sup>2</sup>·hr [Baudot and Marin, 1997]. Compared to PDMS, the surface-modified membrane studied in this study showed much higher flux of esters.

#### 1-2. Ester Concentrations in Permeate

Ester (EA, EP, and EB) concentrations in permeate increased almost linearly with increasing ester concentrations in the feed as shown in Fig. 4. The ester concentration in permeate increased in the order of EB>EP>EA as well as ester flux, even though molecular weight and molar volume of EB are greater than EP and EA (Table 1). This may be attributed to the lowest solubility of EB in water, since the low solubility relates to the high hydrophobicity. Due to the lowest solubility, EB has highest affinity to the hydrophobic surface of the membrane. This is as would be expected, since organic species have a stronger affinity to the organophilic membrane than water-soluble solutes. Although the concentration of esters (EA, EP, and EB) was only 0.15-0.60 wt% in the feed, EA, EP, and EB in permeate were concentrated up to 9.13-32.26, 13.79-37.0, and 15.33-42.57 wt%, respectively. Phase separation occurred in permeate stream because the ester concentration in permeate was much above the saturation limit (Table 1).

#### 1-3. Separation Factor

Fig. 5 shows the corresponding separation factor for the separa-

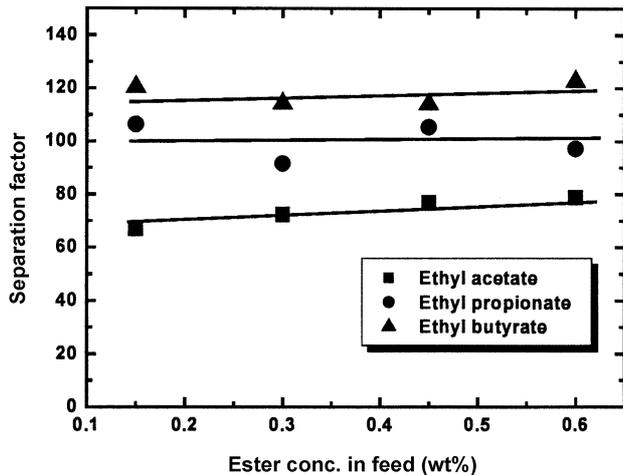


Fig. 5. Effect of feed concentrations (EA, EP, EB) on separation factor at 40 °C.

Table 2. Vapor pressures of the aroma compounds

Compounds	Vapor pressure (mmHg)		
	30 °C	40 °C	50 °C
Ethyl acetate	120.1	189.9	287.7
Ethyl propionate	48.48	79.25	124.9
Ethyl butyrate	21.72	36.80	59.99
Water	31.87	55.40	92.64

Sources : Perry's, Chemical Engineer's Hand book, 1984.

Table 3. Activation energy of permeation for ester compounds and water

		Ethyl acetate	Ethyl propionate	Ethyl butyrate
Ea	Ester	30.0±7.6	30.6±1.7	34.1±1.7
(kJ/mol)	Water	43.9±1.0	44.3±1.1	45.7±1.2

tion of esters from aqueous solution. As the feed ester concentration increased from 0.15 to 0.60 wt%, the separation factor of EA at 40 °C increased from 66.9 to 78.9. However, the separation factors

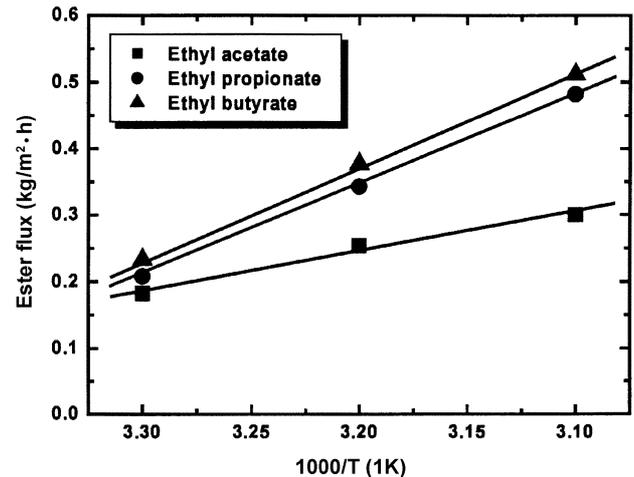


Fig. 6. Arrhenius plots of ester fluxes (EA, EP, EB) through surface-modified membrane.

of EP and EB were not much affected by feed concentration, which was in the range of 106.5-97.3 and 120.5-122.8, respectively. As shown in Table 4, the separation factors of PDMS membrane are higher than those of this study; separation factor of EA with PDMS GFT is 85.0-145.0; PDMS GFTz 254.0; PDMS DC 368.0. Those of EP and EB with PDMS are 79.0-171.2 and 96-196.3, respectively.

## 2. Effect of Temperature

The temperature effect on the pervaporation process was investigated. The feed temperature was varied from 30 to 50 °C. The flux can be fitted to an Arrhenius type of expression, according to Eq. (7), to account for their temperature dependences. Fig. 6 shows that Arrhenius law was valid for pervaporation of mixtures. The curves  $\ln(J)=f(1/T)$ , plotted for different esters (EA, EP, and EB), are straight lines. Their slopes give the activation energy of pervaporation. As expected, it was observed that all ester compound and water fluxes increased exponentially with temperature.

### 2-1. Activation Energy

The average values of activation energy of esters and water permeation are shown in Table 3. Eq. (8) can be modified to Eq. (10) because the enthalpy change due to phase change in pervaporation influences the permeation behavior [Feng and Huang, 1996; Song

Table 4. Comparison of polymer membranes with surface modified membrane

Flavor	Membrane	Condition	Flavor flux (g/m <sup>2</sup> h)	Separation factor ( $\alpha$ )	Enrichment factor ( $\beta$ )
Ethyl acetate	PDMS GFT <sup>a</sup>	90-4,800 ppm, 25 °C	1.1-5.8		85.0-14.5.0
	PDMS GFTz <sup>a</sup>	100 ppm, 30 °C	1.3		254.0
	PDMS DC <sup>a</sup>	100 ppm, 30 °C	1.0		368.0
	This study	0.15-0.60 wt%, 30-50 °C	31.9-380.3	56.0-95.0	48.5-62.8
Ethyl propionate	PDMS <sup>a</sup>	5,000 ppm, 35 °C	35.0	134.0	
	This study	0.15-0.60 wt%, 30-50 °C	53.7-482.2	75.0-113.8	55.3-92.5
Ethyl butyrate	PDMS <sup>b</sup>	300 ppm, 30-50 °C	15.2-18.7		79.0-171.2
	POMS <sup>b</sup>	300 ppm, 30-50 °C	15.9-20.9		96.0-196.3
	This study	0.15-0.60 wt%, 30-50 °C	55.0-511.7	89.1-131.4	60.0-102.2

<sup>a</sup>Sources : Rajagopalan and Cheryan, 1995.

<sup>b</sup>Sources : Sampranpiboon et al., 2000.

et al., 2002]. However, it should be noted that Eq. (10) applies when the downstream-side permeate pressure is sufficiently low as compared to the vapor pressure over the feed liquid.

$$E_p = E_a - \Delta H_v \quad (10)$$

For EB and water permeation through a hydrophobic alumina membrane, the  $E_a$  values are 34.1 and 45.7 kJ/mol for EB and water, respectively, whereas their corresponding  $E_p$  values are 2.2 and 5.1 kJ/mol. The negative value of  $E_p$  for EB means that the increasing rate of ester flux reduces with increasing temperature. Activation energy of penetrant increased as the penetrant size increased in the order: EA < EP < EB. Activation energy ( $E_a$ ) is the sum of the activation energy of diffusion ( $E_d$ ) and the enthalpy of sorption ( $\Delta H$ ). While  $E_d$  is generally positive,  $\Delta H$  is usually negative for the exothermic sorption process. When the positive  $E_d$  dominates over the negative  $\Delta H$ , positive value of  $E_a$  occurs, indicating that the membrane permeability coefficient increases with increasing temperature [Feng and Huang, 1996]. In this study, the activation energy ( $E_p$ ) of esters was negative and that of water was positive values. The ester flux decreased and water flux increased with increasing temperature, which shows the activation energy of sorption ( $\Delta H$ ) dominates over diffusion. The activation energy of EB was greater than EA and EP, which means that permeation flux of EB was most sensitive to the temperature change.

## 2-2. Ester Fluxes

The surface-modified membrane here exhibited its selectivity to ester molecules (EA, EP, and EB) over water. It might be expected from Eq. (9) that vapor pressure ( $p^*$ ) increases with increasing temperature, resulting in the increase of flux ( $J$ ). The fluxes of EB increased with increasing temperature, which represented that the increasing rate of EB fluxes at 50 °C was greater than that at 30 °C and 40 °C as shown in Fig. 7. Therefore, it was expected that the slope of concentration curve of EB in permeate at 50 °C would be steepest. However, the slope at 50 °C was of the least steep (Fig. 8). It might be attributed to the fact of unchanged water flux at 50 °C contrary to the decrease in water flux at 30 °C and 40 °C as shown in Fig. 7.

## 2-3. Permeate Concentrations

EB in permeate was concentrated up to 15.2-44.2 wt% at 30 °C

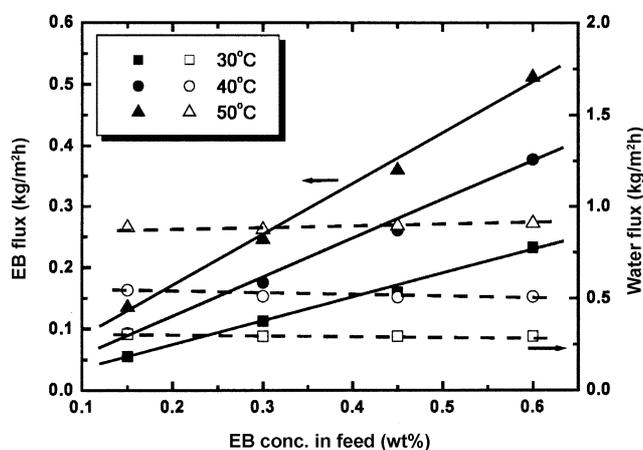


Fig. 7. EB and water flux in permeate as a function of concentrations of EB in feed.

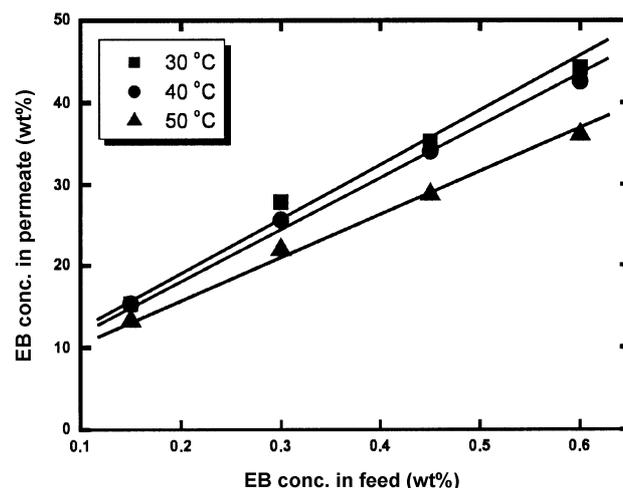


Fig. 8. Concentrations of EB in permeate as a function of feed temperature and concentrations of EB in feed.

for EB concentration of 0.15-0.60 wt% in feed. Since the concentration of EB in permeate was much higher than solubility, the phase separation occurred. As shown in Fig. 8, the concentration of EB in permeate decreased with increasing temperature. This result might be explained by the negative value of  $E_p$  for ester as described above. All esters (EA, EP, and EB) exhibited similar behavior regarding permeate concentration with feed temperature. Although EB has a rather high boiling point, 122 °C, indicating low equilibrium partial pressure, EB showed higher concentration in permeate than EA and EP at same conditions (temperature and feed concentration). Ethyl acetate was the aroma compound which was the least enriched in the process, EA < EP < EB, although EB can be characterized as low boiler if compared to water. This result indicates that EB has highest affinity to the hydrophobic membrane.

It is thus of great importance to know the temperature dependence of the different ester compounds, which are to be enriched with the pervaporation process. If these are known, the feed temperature can be chosen in such a way that relative ester composition obtained in permeate is the one desired.

With polymer membranes, an increase in feed temperature normally results in increased permeation rates of the water than that of organic species, since the organic feed component was plasticizing and swelling the polymer membrane at the elevated feed temperatures, which would allow for higher water permeation rates and result in lower selectivity [Ren and Jiang, 1998; Baudot et al., 1999; Choi et al., 1999]. However, the surface-modified membrane tested in this experiment did not show a decrease in selectivity. This means that the membrane, contrary to polymer membranes, did not swell significantly by esters (EA, EP, and EB) in the experimental range.

## CONCLUSION

The surface-modified alumina membrane showed high hydrophobicity. The membrane tested in this study showed much higher flux than that of polymer membranes, and showed higher selectivity to esters (EA, EP, and EB). The fluxes of EA, EP, and EB at feed concentration of 0.60 wt% and 40 °C were 254, 343, and 377 g/m<sup>2</sup>·hr. It was reported that the permeate flux of EA with PDMS was

1.1-58 g/m<sup>2</sup>·hr at feed concentration of 90-4,800 ppm and 45 °C. The separation factors for the 0.15-0.60 wt% feed solution of EA, EP, and EB at 40 °C were in the range of 66.9-78.9, 106.5-97.3, and 120.5-122.8, respectively. Phase separation occurred in permeate stream because the ester concentration in permeate was much above the saturation limit.

The surface-modified alumina membrane used in this study, which shows much higher flux than polymer membranes, may be a very promising membrane for recovery of flavor compounds from dilute aqueous solution.

### ACKNOWLEDGMENT

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### NOMENCLATURE

J	: permeate flux [kg/m <sup>2</sup> h]
K	: apparent mass transfer coefficient [mol/m <sup>2</sup> ·pa·s]
f	: fugacity of component i [pa]
P	: permeability coefficient [mol/m·pa·s]
p	: vapor pressure [pa]
l	: thickness of the active layer of the membrane [m]
S	: solubility coefficient of the permeant in the membrane [mol/m <sup>2</sup> ·pa]
D	: diffusion coefficient of the permeant in the membrane [mol/m <sup>2</sup> ·pa]
E	: activation energy [kJ/mol]
ΔH	: enthalpy of dissolution [kJ/mol]
R	: gas constant [Kj/mol·°K]
A	: pre-exponential factor [kg/m <sup>2</sup> h]
T	: absolute temperature [°K]
C	: constant [-]

### Greek Letters

α <sub>i</sub>	: separation factor
w <sub>i</sub>	: weight fraction component i
β <sub>i</sub>	: enrichment factor
γ	: activity coefficient

### Superscripts

feed	: in the feed
permeate	: in the permeate

### Subscripts

i	: concerns compound i
j	: concerns compound j

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