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Pervaporation of Flavors with Hydrophobic Membrane

Kun-Ho Song and Kwang-Rae Lee†

Department of Chemical Engineering, Kangwon National University, Chuncheon 200-701, Korea

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Abstract−Using a pervaporation process, a surface-modified hydrophobic membrane was used for recovery of esters which are volatile organic flavor compounds; ethyl acetate (EA), propyl acetate (PA), and butyl acetate (BA). A surface-modified tube-type membrane was used to evaluate the effects of the feed concentration (0.15-0.60 wt%) and feed temperature (30-50 °C) on the separation of EA, PA, and BA from dilute aqueous solutions. The permeation flux increased with the increasing feed ester concentration and operating temperature. EA, PA, and BA in the permeate were concentrated up to 9.13-32.26, 11.44-34.95, and 14.96-36.37 wt%, respectively. The enrichment factors for the 0.15-0.60 wt% feed solution of EA and BA were in the range of 48.5-62.8 and 97.7-101.5, respectively. Phase separation occurred in the permeate stream because the ester concentration in the permeate was above the saturation limit. This meant that selectivity of the membrane was high enough for the recovery of esters from dilute aqueous solution, even though the enrichment factor of the membrane was lower than that of non-porous PDMS membrane. The fluxes of EA, PA, and BA at 0.60 wt% (6,000 ppm) feed concentration and 40 °C were 254, 296, and 318 $g/m^2\cdot hr$, which are much higher than those obtained with polymer membranes. In the case of non-porous PDMS at feed concentrations of 90-4,800 ppm and at 45 °C, it was reported that the permeate flux of EA was 1.1-5.8 $g/m^2\cdot h$. Compared to non-porous PDMS, the surface-modified membrane investigated in this study showed a much higher flux and enough selectivity of esters.

Key words: Pervaporation, Esters, Flux, Enrichment Factor

INTRODUCTION

Pervaporation has been widely investigated as a technique for separation of liquid mixtures and recovery of organic compounds from dilute solutions. The research has focused on applications in wastewater treatment, in the pharmaceutical industry, and for the recovery of the products from fermentation broth in bioreactors and for aroma recovery. Aroma compounds are of various chemical groups such as alcohols, aldehydes, esters, etc.

Natural flavor/aroma recovery has received much attention in the food, biotechnology and cosmetic industries [Baudot and Marin, 1999; Heath and Pharm, 1999; Chang et al., 1998], since natural aroma compounds are preferred by consumers than chemically synthesized ones. In the addition to preference for “natural” aroma, fruit juices are routinely processed to be concentrated for economic reasons (reduced transport and storage costs). Because the processing of foods and beverage results in some loss of their original flavor, flavor concentrates are widely used to compensate for the loss of aromas during food processing, and used as food additives to enhance the overall flavor of foodstuff [Charalambous and Inglett, 1978; Ho et al., 1995].

Pervaporation is characterized by the imposition of a membrane layer between a liquid and a gaseous phase, with mass transfer to the gas side which occurs selectively across the membrane. Since different species permeate through the membrane at different rates, a substance at a low concentration in the feed stream can be highly enriched in the permeate. Pervaporation technology has the potential to recover the flavor compounds and satisfactorily conserve the original qualities of flavor. Rajagopalan and Cheryan [1995] reported the pervaporation of a model flavor compound of grapes, and Baudot and Marin [1997] carried out pervaporation experiments with two dairy aroma compounds diluted in model aqueous solutions through GFT silicate-filled silicone composite membrane and GKSS PEBA homogeneous membrane.

In this study, flavor model solutions of ethyl acetate (EA), propyl acetate (PA), and butyl acetate (BA) were prepared. These esters represent the model aroma compounds with fruit smell; ethyl acetate is ethereal, propyl acetate has a sweet and fruity odor, and butyl acetate is associated with the flavor of pineapple. The surface of micro-porous alumina substrate was modified to hydrophobic, and the performance of the surface-modified membrane in pervaporation process was investigated at 40 °C and various feed concentrations.

THEORY

The permeation flux of a dilute compound i through pervaporation membrane can be described by Eq. (1) [Baudot et al., 1999; Beaumelle and Marin, 1994];

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

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 the permeate can be expressed as follows:

$$f_i^{feed} = \gamma_i x_i^{feed} p_i^o(T^{feed}) \tag{2}$$

$$f_i^{permeate} = y_i p_T \tag{3}$$

The mass transfer coefficient (K_i) includes the sorption to, diffusion through, and desorption from the membrane. It is equivalent to the relation between the permeability coefficient (p_i) and the thickness of the active layer of the membrane (*l*).

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† To whom correspondence should be addressed.
E-mail: krlee@kangwon.ac.kr

The enrichment factor β_i for a given compound i is usually defined as the following:

$$\beta_i = \frac{w_i^{permeate}}{w_i^{feed}} \tag{4}$$

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

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

$$J_i = A\exp\left(-\frac{E_{ai}}{RT}\right) \tag{5}$$

where, A is the pre-exponential factor, E_{ai} the activation energy for permeation 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 [Olsson and Trägåardh, 2001; Song et al., 2002].

$$E_{ai} = \Delta H_{sorption,\,i} + E_{diffusion,\,i} \tag{6}$$

where, $\Delta H_{sorption,\,i}$ is the enthalpy of dissolution for feed molecules of component i to be sorbed into the membrane and $E_{diffusion,\,i}$ is the activation energy required for the molecules to diffuse through the membrane.

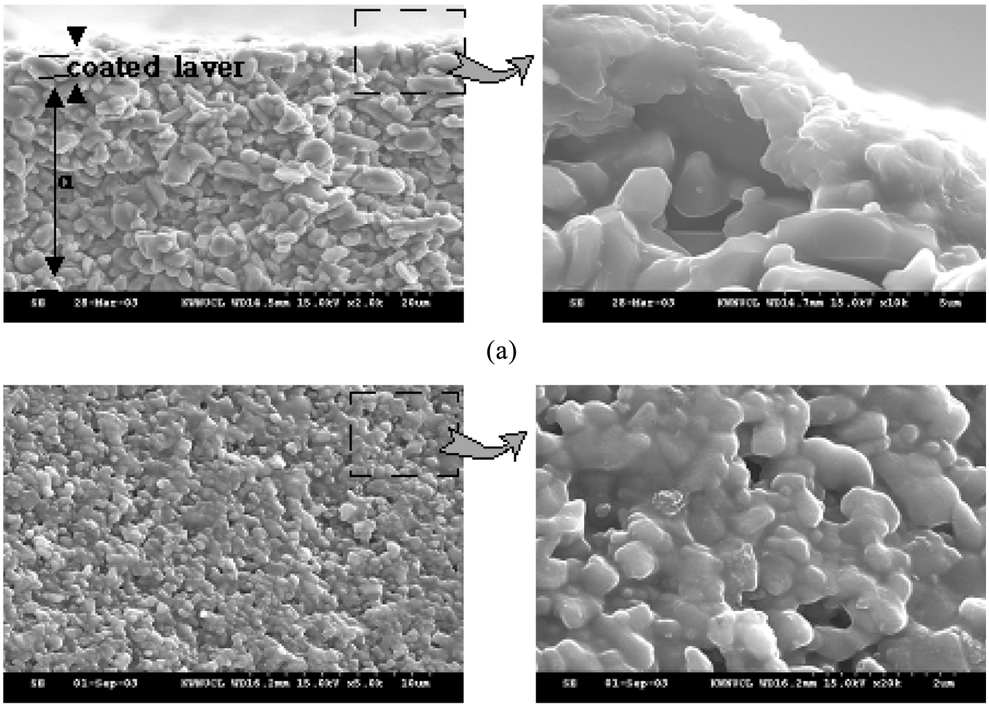
MATERIAL AND METHOD

1. Materials

The tube-type alumina membrane (Al_2O_3) used as a substrate (pore diameter of 0.1 mm) was obtained from Dongsu Co. (Korea). The inside and outside diameters of the membrane are 6.48 mm and 8.0 mm, respectively, and the effective membrane area is 18 cm^2. The surface of tube-type alumina substrate was modified with silane coupling agent (perfluoro-alkylsilane). The procedure and chemicals for surface modification of substrate were illustrated in previous report [Song, 2003]. SEM photographs of the surface-modified membrane were shown in Fig. 1. The membrane showed super-hydrophobic and the water drop contact angle on the surface-modified alumina membrane was about 162°. The model solutions for permeation experiment were prepared by dissolving esters (EA, PA, and BA; Aldrich) in de-ionized water (Milli-Q UF plus). The physical properties of the esters are given in Table 1.

2. Apparatus

One end of the tube-type membrane, which was outside surface-modified, was blocked and the other end was connected to a



(a)

(b)

Fig. 1. SEM photographs of the surface-modified membrane with FASs : (a) cross-section, (b) surface.

Table 1. Physical properties of EA, PA and BA

Compounds	Formula	Molecular weight (g/mol)	Molar volume (cm^3/mol)	Water solubility at 25 °C (g/cm^3)
Ethyl acetate (EA)	$C_4H_8O_2$	88.10	97.7	0.084
Propyl acetate (PA)	$C_5H_{10}O_2$	102.13	115.6	0.016
Butyl acetate (BA)	$C_6H_{12}O_2$	116.16	132.6	0.007

cold trap. The membrane was placed in the solution of feed tank. The temperature of feed solution was kept constant by means of a thermostatic bath. The species in feed solution were sorbed on the outside surface of the tube-type membrane. The sorbed substance permeates through the membrane at different rates, and a substance at low concentration in the feed stream can be highly enriched in the permeate. 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 vapor was condensed and collected in a cold trap positioned between the membrane cell and the vacuum pump. The ester concentration in condensed permeate was determined by a gas chromatography (GC-14B Shimadzu) 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 40 °C. The feed volume (1,000 ml) largely exceeds the PV volume (10 ml) to avoid variations of feed concentration.

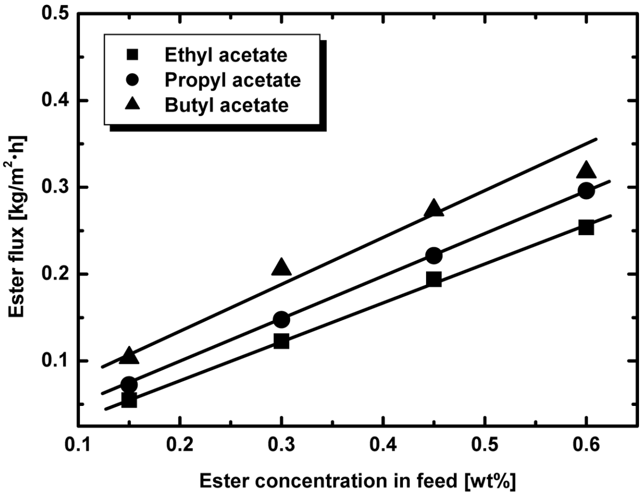


Fig. 2. Ester fluxes as a function of feed concentrations (EA, PA, BA) at 40 °C.

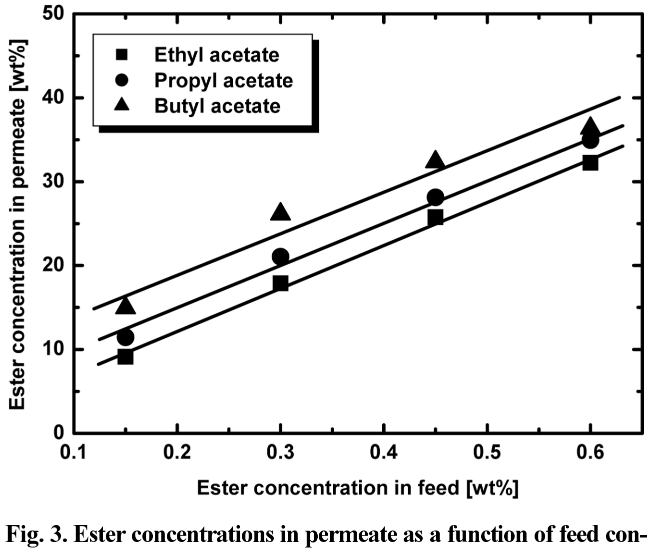


Fig. 3. Ester concentrations in permeate as a function of feed concentrations (EA, PA, BA) at 40 °C.

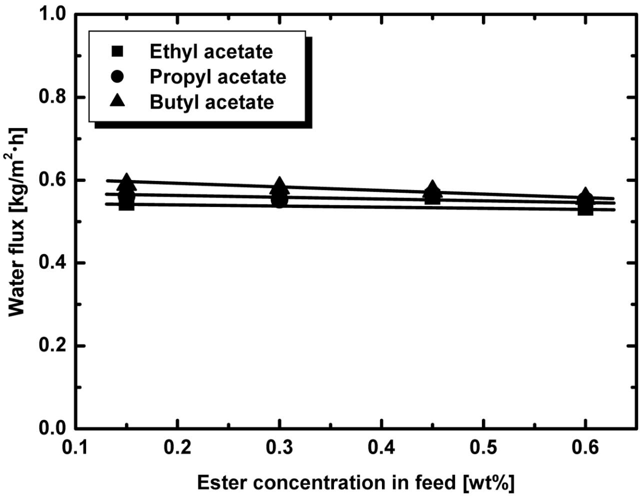


Fig. 4. Water fluxes as a function of feed concentrations (EA, PA, BA) at 40 °C.

RESULTS AND DISCUSSION

1. Effect of Ester Concentrations in the Feed

1-1. Permeation Fluxes of EA, PA, and BA

Water fluxes, fluxes of esters and ester concentrations in permeate at 40 °C were measured in the range of ester feed concentration of 0.15-0.60 wt% (1,500-6,000 ppm) and were plotted against the ester feed concentration in Figs. 2, 3 and 4, respectively.

The permeation fluxes of esters (Fig. 2 increased linearly as feed concentration increased. However, permeation flux of water slightly decreased with increasing ester concentration in the feed (Fig. 4). The permeation fluxes can be expressed by Eq. (1).

$$J_i=K_i[C_1 x_i^{feed} p_i^{o}(T^{feed})-C_2] \qquad (7)$$

These experimental results are well explained by Eq. (1). The permeation flux of esters at a given temperature is a function of K_i, saturation pressure of ester (P_i^o), and molar fraction of esters (x_i^{feed}). As expected from Eq. (7), ester flux increased relatively linearly with increasing molar fraction in feed (x_i^{feed}). In the case of water flux, however, the presence in the feed of a small-sized rather hydrophobic compound leads to an increased resistance to water transport and thus, to a slight decrease of water flux [Baker et al., 1997] as shown in Fig. 4. The presence of ester (EA, PA, BA) induced a decrease in water flux, even at a low concentration in the feed side. Such a behavior has already been observed when pervaporating organic volatiles diluted in water [Sampranpiboon et al., 2000; Won et al., 1996]. When filled with very non-polar molecules, the membrane becomes impenetrable to water. That is why the permeation flux of the water was slightly affected by ester concentration. Compared to the permeation flux of water, the permeation fluxes of esters were more strongly affected by the feed ester concentration. Owing to the high hydrophobicity of the membrane surface, the membrane sorbed esters more significantly in the solution with a higher ester content.

At a feed concentration of 0.60 wt% and 40 °C, the fluxes of EA, PA, and BA were 254, 296, and 318 g/m²·h. In the case of pervaporation with non-porous PDMS at feed concentration of 90-4,800

Table 2. Comparison of polymer membranes with the surface-modified membrane

Flavor	Membrane	Condition	Flavor flux (g/m^{2}h)	Enrichment factor (β)
Ethyl acetate	PDMS GFT*	90-4,800 ppm, 25 °C	1.1-5.8	85.0-145.0
	PDMS DC*	100 ppm, 30 °C	1.0	368.0
	This study	0.15-0.60 wt% (6,000 ppm), 30-50 °C	31.9-380.3	48.5-62.8
Butyl acetate	PDMS GFT*	10-15 ppm, 5 °C	-	112.0
	This study	0.15-0.6 0wt% (6,000 ppm), 30-50 °C	103.7-317.6	97.7-101.5

*Sources: Rajagopalan and Cheryan, 1995.

ppm and 45 °C, it was reported that the permeate flux of EA was 1.1-5.8 g/m^2·h [Baudot and Marin, 1997]. The membrane investigated in this study showed much higher flux of esters than PDMS (Table 2). Showing higher flux is one of the promising characteristics of the surface-modified membrane investigated in this study.

1-2. Ester Concentrations in the Permeate

The concentration of ester (EA, PA, BA) in the permeate increased almost linearly with increasing ester concentration in feed, as shown in Fig. 3. Even though the molecular weight and molar volume of BA are greater than those of PA and EA (Table 1), the ester concentrations in the permeate increased in the order of BA>PA>EA as well as ester fluxes. This may be attributed to the lowest solubility of BA in water since the low solubility relates to the high hydrophobicity. In another words, BA has the highest affinity to the hydrophobic surface of membrane due to the lowest solubility. The hydrophobic membrane worked best for less water-soluble feed components (even those with boiling points greater than that of water), as would be expected, since the esters have stronger affinity to the organophilic surface of membrane than water. The good performance of the membrane tested in this study might be attributed to an enhancement of the ester transport rather than the reduced permeability of water owing to the hydrophobicity of the membrane surface. Very dilute solution of ester (only 0.15-0.60 wt%) in the feed was concentrated up to 9.13-32.26, 11.44-34.95, and 14.96-36.37 wt%, respectively. In the permeate, phase separation occurred as the ester concentration in the permeate was much above the saturation limit (Table 1).

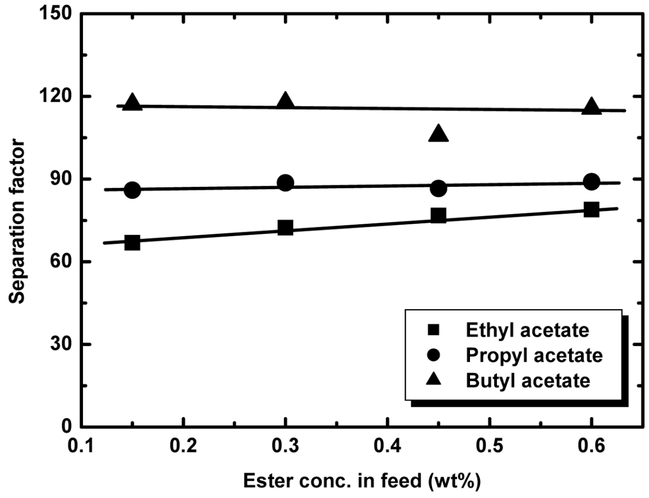


Fig. 5. Effect of feed concentrations (EA, PA, BA) on separation factor at 40 °C.

1-3. Enrichment Factor (β)

In the range of ester feed concentration of 0.15-0.60 wt%, the corresponding enrichment factor for aqueous-ester solution is shown in Fig. 5. The enrichment factors for the 0.15-0.60 wt% feed solution of EA and BA were in the range of 48.5-62.8 and 97.7-101.5, respectively, as shown in Table 2. The enriching factors of non-porous PDMS polymer membrane for the feed solution of EA and BA were 85.0-145 and 112.0, respectively. The enrichment factors of non-porous PDMS polymer membrane were much higher than those of the surface-modified membrane. However, the ester concentration in permeate was much above the saturation limit, which resulted in the phase separation. Therefore, the surface-modified membrane here exhibited high enough selectivity to recover ester molecules (EA, PA, BA) from aqueous solution.

2. Activation Energy for the Permeation

In the range of temperature of 30 to 50 °C, the flux can be fitted to an Arrhenius type of expression. The plot ln(J)=f(1/T) is a straight line whose slope gives the activation energy of pervaporation. The average values of activation energy of esters and water permeation are shown in Table 3. Eq. (6) can be modified to Eq. (8) because the enthalpy change due to phase change in pervaporation influences the permeation behavior [Olsson and Trägåardh, 2001; Yeom et al., 1996].

$$E_p=E_a-\Delta H_v \tag{8}$$

The E_a values for BA and water permeation through the surface-modified membrane were 37.5 and 26.6 kJ/mol, respectively, whereas their corresponding E_p values were 1.6 and −14 kJ/mol. The positive value of E_p for BA means that the increasing rate of ester flux increases with increasing temperature. The penetrant activation energy increased as the penetrant size increased from EA to PA and BA. Activation energy (E_a) is the sum of the activation energy of diffusion (E_D) and the enthalpy of sorption (ΔH) as shown in Eq. (7). While E_D is generally positive, ΔH is usually negative for the exothermic sorption process. When the positive E_D dominates over the negative ΔH, a positive value of E_a occurs, indicating that the membrane permeability coefficient increases with increasing temperature [Feng and Huang, 1996]. As the activation energy (E_p)

Table 3. Activation energy of permeation for EA, PA, BA and water

		Ethyl acetate (EA)	Propyl acetate (PA)	Butyl acetate (BA)
E_a	Ester	30.0±7.6	34.0±1.7	37.5±1.7
(kJ/mol)	Water	24.9±1.0	26.2±1.1	26.6±1.2

of ester was positive and that of water was negative in this study, the ester flux increased and water flux decreased with increasing temperature, which shows that the activation energy of diffusion dominates over enthalpy of sorption (ΔH). The activation energy of BA was greater than EA and PA, which indicated that the permeation flux of BA was the most sensitive to the feed temperature change.

CONCLUSIONS

The membrane used in this study showed high hydrophobicity and higher flux of esters. The permeation flux and permeate concentration increased almost linearly with ester concentration in the feed. The fluxes of EA, PA, and BA at feed concentration of 0.60 wt% (6,000 ppm) and at 40 °C were 254, 296, and 318 $g/m^2 \cdot h$. It was reported that the permeate flux of EA through non-porous PDMS polymer membrane at feed concentration of 90-4,800 ppm and 45 °C was 1.1-5.8 $g/m^2 \cdot h$. The membrane investigated in this study showed much higher flux than non-porous PDMS. The membrane has lower selectivity to esters than non-porous PDMS. However, selectivity of the membrane is high enough for the recovery of esters, because the ester concentration in the permeate was much above the saturation limit which results in phase separation. Higher flux as well as proper selectivity to esters is a prominent characteristic for the application to flavor recovery processes.

ACKNOWLEDGMENT

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NOMENCLATURE

A : pre-exponential factor [$mol/m^2 \cdot h$]
C : constant [-]
E : activation energy [kJ/mol]
f : fugacity of component i [pa]
J : permeate flux [$mol/m^2 \cdot h$]
K : apparent mass transfer coefficient [$mol/m^2 \cdot Pa \cdot h$]
p : permeability coefficient [$mol/m \cdot Pa \cdot h$]
R : gas constant [$kJ/mol \cdot {}^{o}K$]
T : absolute temperature [^{o}K]

Greek Letters

α_i : separation factor [-]
β_i : enrichment factor [-]
γ : activity coefficient [-]
ΔH : enthalpy of dissolution [kJ/mol]
w_i : weight fraction of component i [kg/kg]

Subscripts

i : concerns compound i
j : concerns compound j

Superscripts

feed : in the feed
permeate : in the permeate

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