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Recovery of Esters from Dilute Aqueous Solutions by Vapor Permeation

Kun-Ho Song and Kwang-Rae Lee†

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

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Abstract−The vapor permeation characteristics of ester compounds (ethyl acetate, EA; ethyl propionate, EP; and ethyl butyrate, EB) through a tube-type surface-modified alumina-silane hydrophobic membrane were investigated. Experiments were performed to evaluate the effects of the feed concentration (0.15-0.60 wt%) and temperature (30-50 °C) on the 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 0.60 wt% feed concentration and 40 °C were 282, 506, 742 $g/m^2 \cdot h$, which were much higher than those of PDMS polymer membrane. The separation factors for the 0.15-0.60 wt% feed solutions of EA, EP, and EB at 40 °C were in the range of 28.1-93.9, 145.3-162.6, and 260.4-268.8, respectively. Phase separation occurred in the permeate when collected in a cold trap, because the concentration of the ester in the permeate was much higher than its solubility.

Key words: Surface-Modified Membrane, Vapor Permeation, Ethyl Acetate, Ethyl Propionate, Ethyl Butyrate, Separation Factor

INTRODUCTION

Since membrane processes generally have low capital investment as well as low energy consumption and operating cost, there are a number of industrial applications covering many existing and emerging uses in the chemical, environmental, water treatment, food, beverage, dairy, medical, and electronic industries.

Membrane technology is of great interest in many applications, such as wastewater treatment [Kim et al., 2001], the harvesting of organic substances from fermentation broths, and the recovery of valuable organic compounds from bioreactors. Vapor permeation (VP), in particular, has been reported as an emerging technology for recovery of organic compounds from dilute organic-water mixtures [Crespo and Böddeker, 1993; Won et al., 1996].

Aroma 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]. The consumer prefers natural aroma compounds to chemically synthesized ones. The processing of foods and beverage causes the loss of their original aroma. If this loss includes an important aroma compound, the effect is perceived as serious quality loss in the final product. The existing typical separation and purification processes such as distillation, adsorption and solvent extraction often deteriorate the aroma quality and may cause undesirable changes in the flavor profiles and thus lower its market value [Rajagopalan and Cheryan, 1995; Schäfer et al., 1999]. In addition, such processes use toxic solvents or involve elaborate purification steps to remove solvent residues from the final product.

In the present study, vapor permeation was investigated for the recovery of ester compound from dilute ester-water mixtures; a hydrophobic membrane was prepared and the permeation characteristics of ethyl acetate (EA), ethyl propionate (EP) and ethyl butyrate (EB) through the hydrophobic membrane were investigated. These esters represent the model aroma compounds with fruit smell: ethyl acetate is ethereal, ethyl propionate has a sweet and fruity odor, and ethyl butyrate is associated with the flavor of pineapple.

THEORY

The separation factor α_i of the vapor permeation for a given compound i is usually defined as follows [Howell et al., 1993]:

$$\alpha_i = \frac{w_i^{permeate}}{1-w_i^{permeate}} / \frac{w_i^{feed}}{1-w_i^{feed}} \tag{1}$$

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

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

$$J_i = A\exp\left(-\frac{E_{ai}}{RT}\right) \tag{2}$$

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].

$$E_{ai} = \Delta H_{sorption,\,i} + E_{diffusion,\,i} \tag{3}$$

where, $\Delta H_{sorption,\,i}$ is the enthalpy of dissolution of component i to be sorbed into the membrane, and $E_{diffusion,\,i}$ is the activation energy required for the permeating molecules to diffuse through the membrane. It can be seen from Eq. (2) that the temperature can influence the flux through the membrane in both the sorption and diffusion step.

EXPERIMENTAL

1. Materials and Apparatus

EA, EP, and EB were purchased from Aldrich Co. The model

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

Table 1. Physical properties of ester compounds [Lide, 1993]

Compounds	Formula	Molecular weight (g/mol)	Molar volume (cm^3/mol)	Boiling point (°C)	Water solubility at 25 °C (g/cm^3)
Ethyl acetate	$C_4H_8O_2$	88.10	97.7	77	0.084
Ethyl propionate	$C_5H_{10}O_2$	102.13	114.6	99	0.024
Ethyl butyrate	$C_6H_{12}O_2$	116.16	132.2	121	0.006

Table 2. Vapor pressures of the aroma compounds [Lide, 1993]

Compounds	Vapor pressure (Pa)		
	30 °C	40 °C	50 °C
Ethyl acetate	16,012	25,318	38,357
Ethyl propionate	6,463	10,566	16,652
Ethyl butylate	2,896	4,906	7,998
Water	4,249	7,386	12,351

solutions of ethyl acetate (EA), ethyl propionate (EP), and ethyl butyrate (EB) were prepared at the given concentrations by dissolving them in deionized water (Milli-Q UF plus). The physical properties of the esters are given in Tables 1 and 2.

The feed solution of a known composition was first charged to a feed tank, and the temperature of the feed mixture was kept constant by means of a thermostatic bath. The liquid mixture was partially vaporized. The vapor reached equilibrium with the liquid phase at a given temperature. The outside surface-modified tube-type membrane was placed into the vapor phase. One end of the membrane was blocked and the other end was connected to a cold trap. The vapor in the feed tank was sorbed on the outside surface of the tube-type membrane, and permeated into the inside of the membrane. The driving force for the material transport through the membrane was generated by a downstream vacuum pump. The downstream (i.e., tube inside) pressure was controlled by a vent valve and kept at 1.33 kPa. Permeated vapor was condensed and collected in a cold trap positioned between the membrane cell and the vacuum pump. The ester concentration in the condensed permeate was determined by gas chromatography (Shimadzu GC-14B) equipped with a column of Porapak Q. The permeate, which was condensed and collected in the cold trap, was phase-separated, because the concentration of the ester in the permeate was higher than its solubility. The permeate was diluted with an excess of ethanol in order to produce a single-phase sample for the GC analysis.

Vapor permeation (VP) experiments were carried out at temperatures of 30, 40, and 50 °C. The feed volume (1,000 ml) largely exceeds the vapor permeation volume (10 ml) to avoid variations of feed concentration.

2. Surface Modification of an Alumina Substrate

The tube-type alumina membrane (Al_2O_3) used as a substrate (pore diameter of 0.1 μm) was obtained from Dongsu Co. (Korea). The inside and outside diameters of the membrane are 6.48 mm and 8.0 mm respectively, with an effective membrane surface area of 18 cm^2. The surface of a substrate was grafted with a fluorinated silane ($C_6F_{13}C_2H_4SiCl_3$; FA). The fluorinated silane (FA) has linear hydrophobic tails and functional groups. By these functional groups, the silane is coupled together with the oxide material of the substrate. Grafting occurs with a succession of condensation reactions between the -OH groups of the substrate and the Si-Cl of the silane. The grafting solution of FA was prepared at a concentration of 0.1-1.0 wt% with chloroform and hexadecane mixture (wt. ratio 3 : 1). The substrate membrane was completely immersed in solution under a dry nitrogen atmosphere. Prior to immersing of the substrate membrane in solution, both ends of the tube-type substrate were closed up with Teflon plugs in order to prepare an outside surface-modified membrane. Grafting rate can be controlled by grafting time and reaction temperature. After the grafting was completed, the grafted substrate was washed repeatedly with deionized water to remove the residual coating solution.

The analysis of ESCA showed that the fluorinated silane was chemically bonded to alumina substrate. The water drop contact angle on the surface-modified membrane was about 162°, which meant that the membrane surface showed super-hydrophobicity. When the water drop contact angle exceeds 90°, the surface is called hydrophobic [Mulder, 1991]. When esters (EA, PA, and BA) were dropped, however, on the surface of the un-coated alumina substrate, those drops wetted the membrane surface and soaked into the membrane. The surface-modified membrane was tested by the bubble-point method, in order to measure the pressure needed to blow air through a surface-modified membrane. The bubble-point pressure was 353 kPa. As the bubble-point pressure (353 kPa) was much higher than the tube inside pressure (1.33 kPa) of this vapor permeation experiment, the modified membrane might be regarded as nonporous in the range of this experiment.

RESULTS AND DISCUSSION

1. Effect of Ester Concentrations in the Feed

1-1. Permeation Flux of the Ester

The permeate flux of the feed concentration of 0.15-0.60 wt%

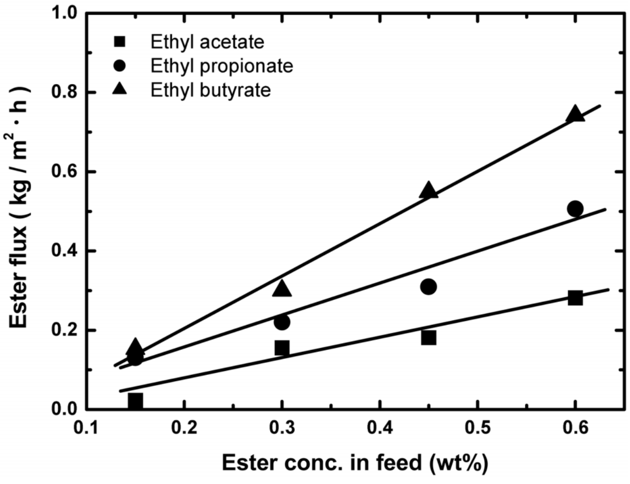

Fig. 1. Ester fluxes as a function of feed concentrations (EA, EP, EB) at 40 °C.

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

It was shown that the permeation flux of esters increased linearly with ester concentration in the feed (Fig. 1), while the permeation flux of water was slightly decreased (Fig. 3). Due to the high fluxes of esters, the total flux was increased with an increasing ester concentration in the feed. Compared to the permeation flux of water, the permeation flux of esters was more strongly affected by the feed concentration. Owing to the high hydrophobicity of the membrane surface, the membrane sorbed ester molecules more significantly. The flux of EA, EP, and EB at 0.60 wt% feed concentration and at 40 °C were 282, 506, and 742 g/m^2·h. In the case of pervaporation with PDMS at feed concentration of 0.009-0.48 wt% and at 45 °C, it was reported that the permeate flux of EA was 1.1-58 g/m^2·h [Baudot and Marin, 1997]. Compared to PDMS, the surface-modified hydrophobic membrane of this study showed much higher flux of esters.

1-2. Ester Concentrations in the Permeate

The ester concentrations in the permeate increased almost linearly with an increasing concentration in the feed as shown in Fig. 2. The ester concentration in the permeate increased in the order of EB>EP>EA as well as the ester flux, even though the molecular weight and molar volume of EB are greater than EP and EA (Table 1). It 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 the highest affinity to the hydrophobic surface of membrane. The hydrophobic membrane worked best for less water-soluble components (even those with boiling points greater than that of water), as would be expected, since esters 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 the permeate were concentrated up to 4.05-36.18, 18.34-49.54, and 25.08-61.87 wt%, respectively. Since the ester concentration in the permeate was much

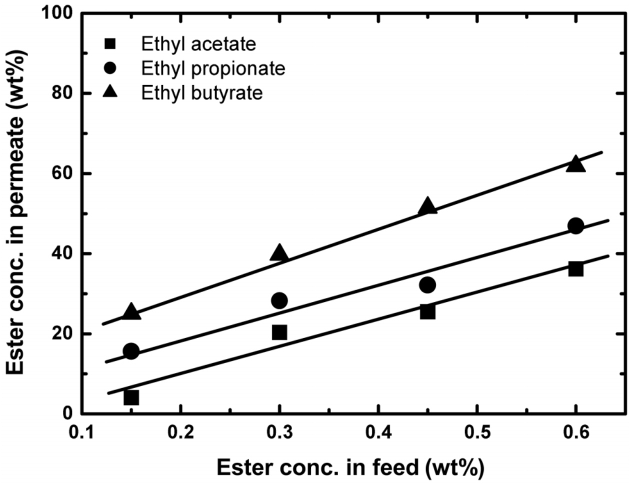

Fig. 2. Ester conc. in the permeate as a function of feed concentrations (EA, EP, EB) at 40 °C.

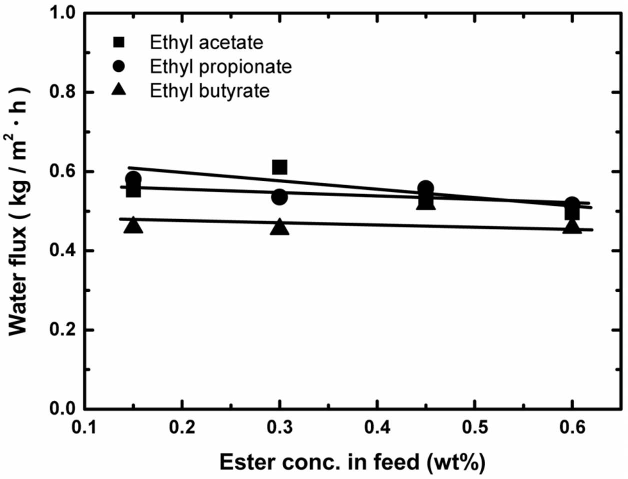

Fig. 3. Water fluxes as a function of feed concentrations (EA, EP, EB) at 40 °C.

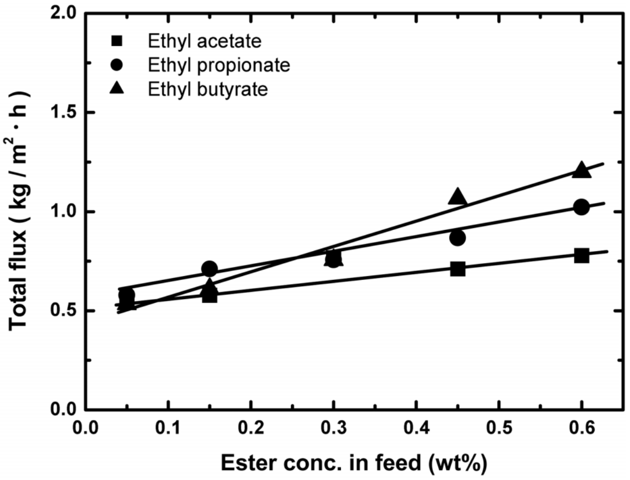

Fig. 4. Total fluxes as a function of feed concentrations (EA, EP, EB) at 40 °C.

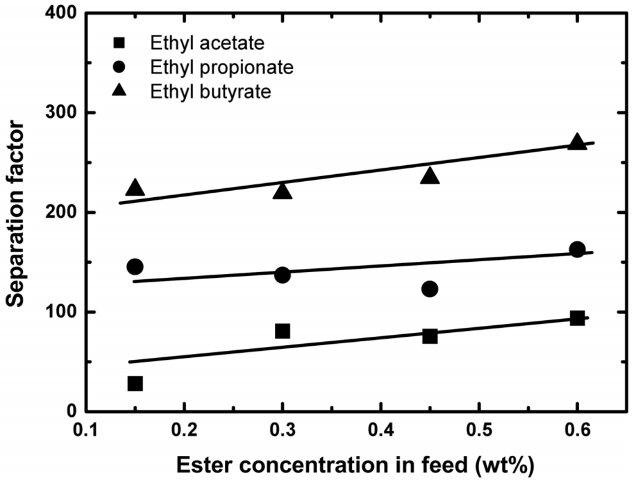

Fig. 5. Effect of feed concentration (EA, EP, EB) on the separation factor of the vapor permeation at 40 °C.

above the saturation limit (Table 1), the phase separation occurred in the permeate stream.

1-3. Separation Factor

As the feed ester concentration increased from 0.15-0.60 wt%, the increase in esters flux was more significant than that of the water flux, resulting in an increase of the separation factor. 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 28.1-93.9, 145.3-162.6, and 260.4-268.8, respectively. The corresponding separation factor for the separation of aqueous ester solutions is shown in Fig. 5.

The high selectivity of the membrane tested in this study is to be attributed to a real enhancement of the ester transport rather than significantly lowering the water permeability owing to the hydrophobicity of the membrane surface.

2. Effect of Temperature

The feed temperature range tested in this study was from 30 to 50 °C. The temperature effect on the flux can be fitted to an Arrhenius type expression, according to Eq. (2). The curve ln(J)=f(1/T), plotted for different ester concentrations, is a straight line (Fig. 6), which means that the Arrhenius law is valid for vapor permeation of the ester solution. The slopes give the activation energy of vapor permeation.

2-1. Activation Energy

The activation energies (E_a) for the permeation of EA, EP, and EB were 19.68, 34.42, and 51.18 kJ/mol, respectively. The penetrant activation energy increased as the penetrant size increased from EA to EP and EB. The average values of the activation energy of ester and of water permeation are shown in Table 3. Activation energy (E_a) is the sum of the activation energy of diffusion ($E_{diffusion}$) and the enthalpy of sorption ΔH. While $E_{diffusion}$ is generally positive, ΔH is usually negative for the exothermic sorption process. When the positive $E_{diffusion}$ dominates over the negative ΔH, a positive value of E_a occurs, indicating that the membrane permeability coefficient increases with an increasing temperature [Feng and Huang, 1996]. In this study, the activation energy (E_a) of esters and water was positive, and the ester and water fluxes increased with an increasing temperature, which shows that the activation energy of diffusion ($E_{diffusion}$) dominates over sorption. The activation energy of EB was greater than EA and EP, which means that the permeation flux of EB was the most sensitive to the feed temperature change.

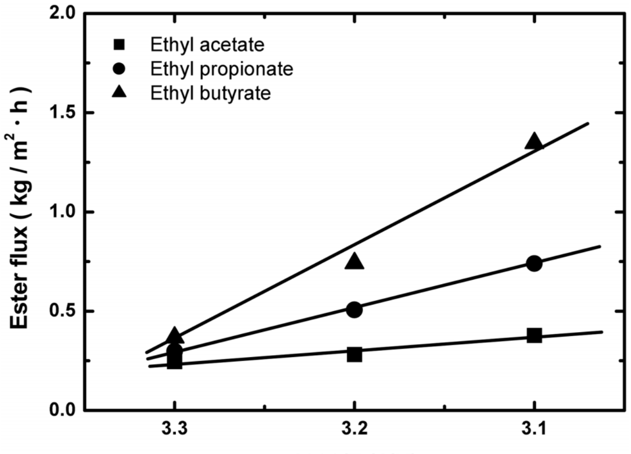

Fig. 6. Arrhenius plots of ester fluxes (EA, EP, EB) through the surface-modified membrane at 40 °C.

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

		Ethyl acetate	Ethyl propionate	Ethyl butylate
Ea (kJ/mol)	Ester	19.68±3.1	34.42±2.6	51.18±2.1
	Water	16.96±2.8	32.52±3.3	32.02±5.3

2-2. Ester Fluxes

The membrane used here exhibited an affinity to ester molecules (EA, EP, EB) over water. As shown in Fig. 7, the fluxes of EB increased with increasing temperature. It was, therefore, expected that the slope of the EB flux at 50 °C would be the steepest. Regardless of temperature, however, the slopes EB concentration in the permeate were almost equal (Fig. 8). This fact might be attributed to the simultaneous increase of water and EB flux with an increasing

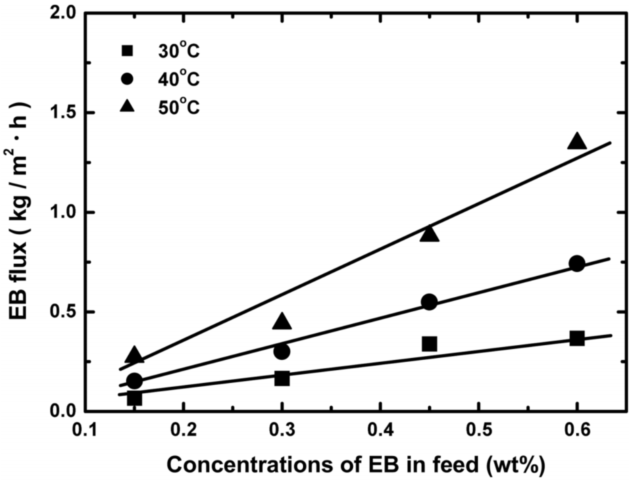

Fig. 7. EB flux in the permeate as a function of concentrations of EB in feed and feed temperature (30, 40, 50 °C).

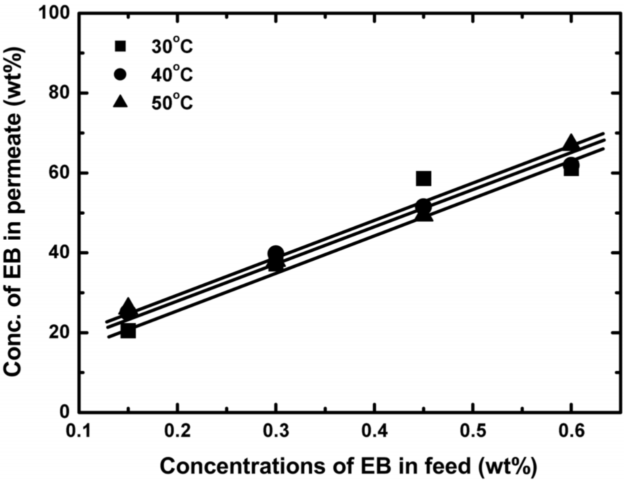

Fig. 8. Concentrations of EB in the permeate as a function of concentrations of EB in feed and feed temperature (30, 40, 50 °C).

temperature.

2-3. Permeate Concentrations

EB in the permeate was concentrated up to 20.50-61.12 wt% at 30 °C, and 26.04-67.0 wt% at 50 °C for feed concentration of 0.15-0.60 wt%. Since the EB concentration in the permeate was much higher than its solubility, phase separation occurred. As shown in Fig. 7, the concentration of EB in the permeate increased with an increasing temperature. All esters (EA, EP, and EB) exhibited a similar behavior regarding the permeate concentration with a feed temperature. Although EB has a rather high boiling point, 122 °C, indicating a low equilibrium partial pressure, EB showed a higher concentration in the permeate than EA and EP at the same temperature and feed concentration. Ethyl acetate (EA) was the least enriched aroma compound in the process (EA<EP<EB), although EB can be characterized as low boiler if compared to EA and EP. This result means that EB has the highest affinity for the hydrophobic membrane.

In the pervaporation process with a polymer membrane, the organic feed component was plasticizing and swelling of the polymer membrane at the elevated feed temperatures. Plasticizing and swelling allow for higher water permeation rates and result in lower selectivity [Ren and Jiang, 1998; Baudot et al., 1999; Yeom et al., 1996]. However, the surface-modified membrane tested in the present research experiment did not show the decrease in selectivity. Contrary to polymer membranes, the membrane did not swell significantly by esters (EA, EP, and EB) being present in the solutions.

CONCLUSION

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 28.1-93.9, 145.3-162.6, and 260.4-268.8, respectively. Since the ester concentration in the permeate exceeded the saturation limit, phase separation occurred in the permeate stream. The membrane showed a high hydrophobicity. The fluxes and permeate concentrations increased almost linearly with an increasing feed concentration. The membrane tested in this study showed higher fluxes than polymer membranes, and showed a higher selectivity to esters (EA, EP, and EB).

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NOMENCLATURE

J_i : permeation flux [kg/m^{2}h]
E_{ai} : activation energy of component i in permeation [kJ/mol]
$E_{diffusion}$: activation energy for diffusion
ΔH : enthalpy of dissolution [kJ/mol]
R : gas constant
A : pre-exponential factor [kg/m^{2}h]
T : absolute temperature [°K]

Greek Letters

α_i : separation factor
w_i : weight fraction of component i

Subscripts

i : concerns compound i
j : concerns compound j

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