

Esterification of Acetic Acid and Isobutanol in a Pervaporation Membrane Reactor Using Different Membranes

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ABSTRACT: In this study the ester-permeable polydimethylsiloxane (PDMS) and the water-permeable poly(vinyl alcohol) membranes prepared in our laboratory and the commercial Nafion 117, PERVAP 1201, and PERVAP 2216 membranes were used in the esterification of acetic acid with isobutanol catalyzed by Dowex 50W-X8 in a pervaporation membrane reactor process in order to shift the equilibrium by removal of relevant product from the reaction mixture. The effects of membrane type, the ratio of membrane area to reaction volume, and temperature were investigated. PERVAP 1201 membranes provided a higher water flux and higher selectivity than other hydrophilic membranes, but the highest fluxes were obtained using PDMS membrane, which selectively permeated isobutyl acetate compared to the other components. Increase in temperature and ratio of membrane area to reaction volume increased the conversion.

1. INTRODUCTION

A membrane is a physical barrier which prevents or reduces the mass transfer in certain levels.¹ Membranes have been known as separation agents for over a hundred years, but it has been in the last 50 years that they became available with wide range applications.² In a pervaporation-aided membrane reactor, the membrane inside the reactor functions according to the pervaporation principle. In pervaporation, the membrane is brought into contact with the liquid mixture; liquid permeates through the membrane and vaporizes thereafter.³ Permeate is condensed and then removed. Since the membrane inside the reactor permits selective permeation of a product component from the reaction medium, it is possible to enhance the conversion of a thermodynamically or kinetically limited reaction by shifting the reaction to the desired direction.^{4–7}

Esterification reactions are commercially important.⁸ In industrial esterification reactions one of the products is removed by energy-intensive distillation or inefficient vacuum stripping processes.⁷ Pervaporation is a more energy-efficient process than distillation⁹ and has a compact design.¹⁰ Zhu and Chen achieved almost complete reaction with pervaporation in their work for the esterification of acetic acid with *n*-butanol.⁴ Won et al. separated the water from reaction media using asymmetric poly(vinyl alcohol) (PVA) membranes they prepared and also commercial Nafion 117 and Nafion NE 450 membranes in a pervaporation system to produce racemic ibuprofen by lipase-catalyzed esterification reaction.¹¹ They reported that PVA membranes were more effective in enantioselectivity and, generally, the pervaporation-coupled esterification process increased the reaction rate and the enantiomeric ratio.¹¹ In another study, hydrophilic PERVAP 1000 and a catalyst-coated version of PERVAP 1000 membranes were used in pervaporation-assisted ethanol–acetic acid esterification in the presence of Amberlyst 15 and 35 catalysts.¹² The catalytic membrane showed transport and acidic (catalytic) properties that were similar to those of the commercial membrane and catalyst, respectively, and increased the conversion up to 60% in 8 h, at 60 °C.¹² In another work, Krupiczka and Koszorz studied the esterification of acetic acid

with ethanol, coupled with pervaporation, using hydrophilic PERVAP 1005 membranes, and they proposed that the activity-based model is a better method for predicting concentration profiles than the concentration model.¹³ PERVAP 1005 membranes were also successfully employed in the pervaporation-coupled esterification of acetic acid with benzyl alcohol with a flux of 0.54 kg/m²·h, 96% selectivity in water, and 99% conversion.¹⁴ Zeolite/polyelectrolyte multilayer pervaporation membranes having higher thermal stability and acid resistance were prepared to remove water preferentially from the esterification of lactic acid with ethanol, catalyzed by *p*-toluenesulfonic acid, and improved reaction yields were obtained.¹⁵ The commercial polymeric membrane PERVAP 2201 was successfully applied to the esterification of acetic acid with isopropanol catalyzed by Amberlyst 15 coupled with a pervaporation unit for the selective removal of water; and higher conversions with high selectivity values were obtained.¹⁶

The aim of this work is the production of isobutyl acetate (iBAc) via esterification by an energy-efficient and environmentally friendly pervaporation membrane reactor (PVMR) process. Isobutyl acetate, C₆H₁₂O₂, is used in cosmetics, aroma, and paint industries.^{17,18} It is conventionally synthesized by direct esterification of acetic acid (AsAc) with isobutanol (iBOH). The final purification of isobutyl acetate by traditional technologies involves techniques such as azeotropic and extractive distillation or reactive distillation.^{18–20} Esterifications are the main class of reactions that have been studied in PVMR and the most frequent configuration to carry out esterification reactions coupled with pervaporation consist of a batch reactor.^{21,22} In several recent studies of a pervaporation–esterification membrane reactor, water-selective hydrophilic membranes have been employed, whereas ester-removing hydrophobic membranes were not investigated much because of limited availability of hydrophobic

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Table 1. Useful Information about the Commercial Membranes Used^{25–27}

	PERVAP 1201	PERVAP 2216	Nafion 117
main application	for volatile neutral organics and reaction mixtures	for volatile neutral organics and their mixtures, EtOH from fermentation processes	proton conductor for proton exchange membrane fuel cells, superacid catalyst for fine chemical production
base polymer	PVA highly cross-linked	PVA cross-linked	tetrafluoroethylene-based fluoropolymer-copolymer
acetic acid limitation, wt %	≤50%	≤10%	N/A
isobutanol limitation	N/A	N/A	N/A
water limitation, wt %	≤50%	≤40%	N/A
isobutyl acetate limitation	no limitation	no limitation	N/A
max. operating temperature, °C	95	100	175 (anhydrous systems), 220 (aqueous systems)
thickness, μm	2	0.5–5	177.8

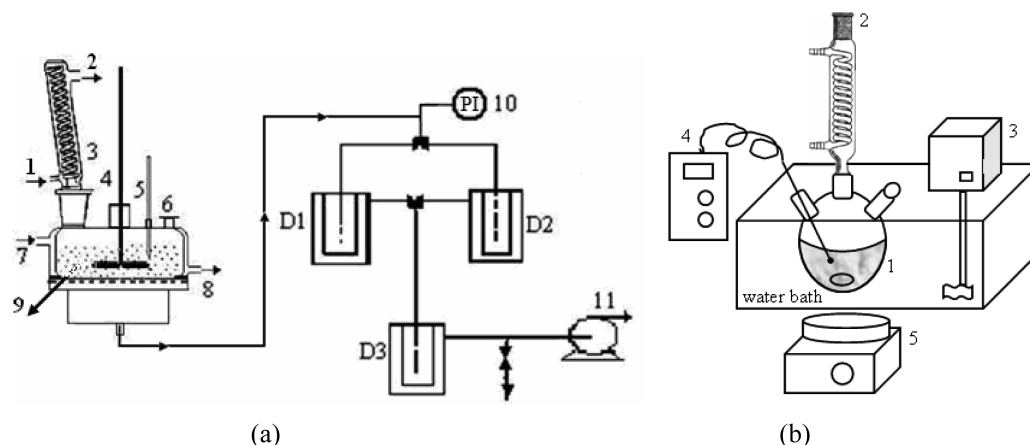


Figure 1. (a) Pervaporation membrane reactor: 1–2, Cold water inlet–outlet to reflux condenser; 3, reflux condenser, 4, agitator; 5, thermocouple; 6, sample collection; 7–8, hot water inlet–outlet to jacket of membrane reactor cell; 9, membrane; 10, vacuum meter; 11, vacuum pump; D1, D2, D3, Dewar flask. (b) Simple batch reactor assembly: 1, reactor flask; 2, reflux condenser; 3, thermostat; 4, thermocouple; 5, magnetic stirrer.^{29,30}

membranes that are sufficiently selective to the ester compounds.²³ In this study, both hydrophobic and hydrophilic membranes were used in PVMR. Hydrophilic (water-permeable) membranes involve PVA, PERVAP 1201, PERVAP 2216, and Nafion 117. Polydimethylsiloxane (PDMS) is used as a hydrophobic (ester-permeable) membrane. The ester-permeable PDMS membrane and the water-permeable PVA membranes prepared in our laboratory and the commercial Nafion 117, PERVAP 1201, and PERVAP 2216 membranes were used in order to shift the equilibrium by removal of relevant product from the reaction mixture. The effects of membrane type, the ratio of membrane area to reaction volume, and temperature were investigated. In addition, pervaporation performance of the membranes employed was evaluated using the flux and selectivity data.²⁴

2. EXPERIMENTAL SECTION

2.1. Materials and Membrane Preparation. PDMS prepolymer and its cross-linker (RTV 615 A and RTV 615 B, respectively) were purchased from General Electric (GE). The molecular mass and hydrolysis degree of poly(vinyl alcohol) (PVA) purchased from Fluka Co. were 72 kg/mol and 99%, respectively. Tartaric acid (Tac) used as a cross-linking agent for PVA, PERVAP 1201, and PERVAP 2216 membranes and Nafion 117 membrane were purchased from J.T. Baker, Sulzer

Chemtech, and Sigma-Aldrich, respectively. Table 1 gives detailed information^{25–27} about hydrophilic commercial membranes used. Isobutanol and acetic acid of HPLC grade were purchased from J.T. Baker. Materials were used without further purification. Wet ion-exchange resin Dowex 50W-X8 was purchased from Acros Organics and was dried for 2 days in an oven at 90 °C prior to use.

A description of the preparation of PVA membranes cross-linked with Tac and PDMS membranes was given previously^{28,29} but a short summary is given below. PVA in granular form was dissolved in water by stirring at low speed for 6 h at 90 °C. The content of PVA in solution was 10 wt %. A certain amount of aqueous solution containing 10 wt % Tac was added into the PVA solution to obtain 20 wt % Tac content in the membrane, and the mixture obtained was stirred at low speed for 1 h. The polymer solution was cast on Plexiglass plates, and the solvent was evaporated overnight in an oven kept at 50 °C. Then the peeled off membranes were cross-linked for 1 h at 150 °C. After cooling, membranes were placed in a water bath, and after 24 h, they were dried at 105 °C for 2 h. The thickness of the resulting membranes was about 100 μm. For the preparation of PDMS membranes, the polymer and its cross-linking agent (RTV 615A+B) were mixed. The content of the cross-linker agent in the mixture was 10 wt %. The solution was cast onto Plexiglass plates, after it was free of air bubbles achieved by means of a degassing

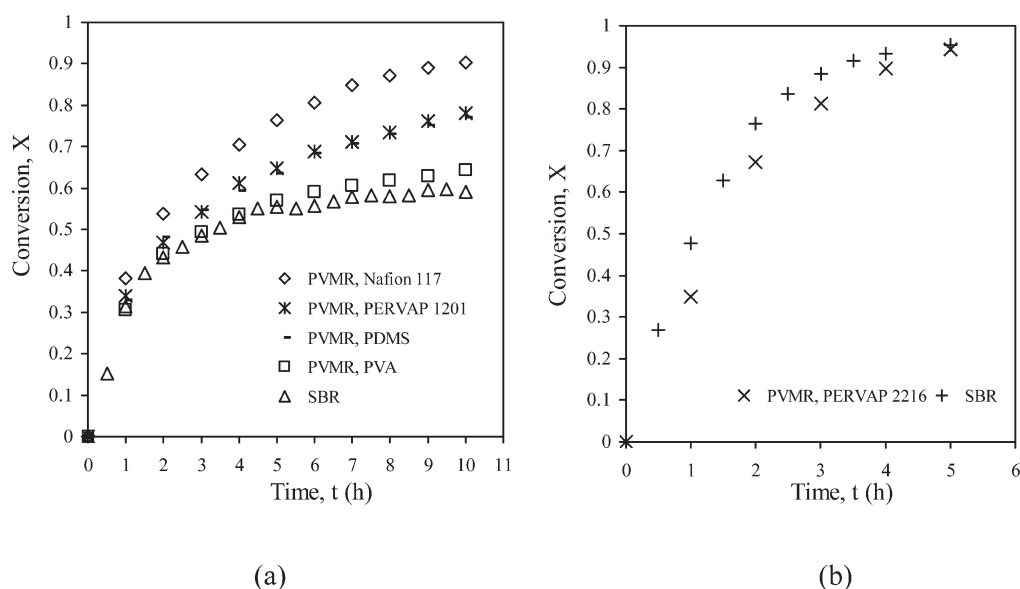


Figure 2. Effect of different membrane types on conversion and the comparison between PVMR and SBR systems for initial molar ratios of (a) $M = 1:1$ and (b) $M = 8:1$ ($C = 16.67$ g/L, $T = 70$ °C, $S/V = 0.1325$ cm⁻¹; catalyst: Dowex 50W-X8).

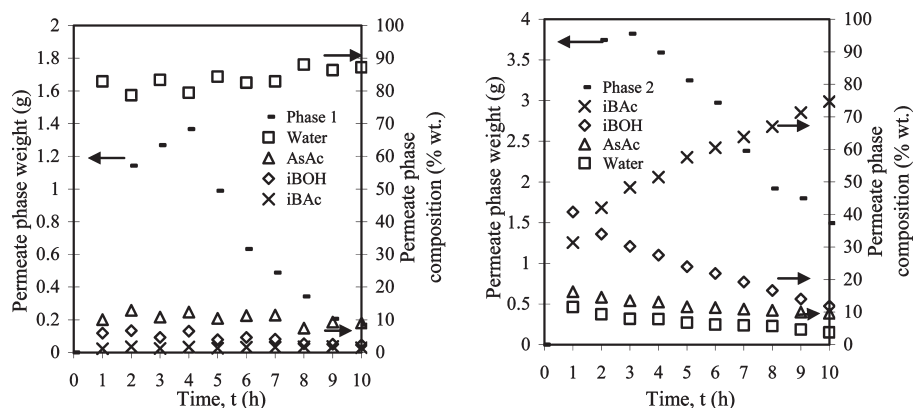


Figure 3. Phase compositions and phase weights of the permeate obtained by Nafion 117 membrane ($C = 16.67$ g/L, $M = 1:1$, $T = 70$ °C, $S/V = 0.1325$ cm⁻¹; catalyst: Dowex 50W-X8).

treatment under vacuum for 0.5 h. The membranes were cross-linked on the plates at 100 °C for 1 h. The thickness of the resulting membranes was about 200 μ m.

2.2. PVMR and Simple Batch Reactor Experiments. The schematic representation of PVMR and simple batch reactor (SBR) assembly are given in (a) and (b), respectively, of Figure 1.^{29,30} The initial mole ratio of the reactants (alcohol/carboxylic acid) at the reaction temperature of 70 °C was 1:1 for all membranes, but because of working media concentration limitation of PERVAP 2216 membrane, the initial molar ratio of the reactants (M) was taken as 8:1 (isobutanol/acetic acid). Dowex 50W-X8 ion-exchange resin was used as the catalyst and its content in the reaction mixtures was 16.67 g/L.

PVMR experiments were performed in batch mode. Isobutanol was placed in the reactor together with the catalyst and heated up to the reaction temperature. Acetic acid was heated separately to the reaction temperature and then added to the reactor. A heat-jacketed membrane cell was used to keep the temperature constant. During the PVMR runs, product samples were taken from both the reaction mixture and the collec-

tion tubes every hour and analyzed by gas chromatography. The pressure at the downstream side was reduced to read zero on the millibar scale using a Vacuubrand RZ-5 vacuum pump. The pressure was measured by a Vacuubrand DVR-2 digital vacuum meter. The uncertainty in the measurement of the digital vacuum meter is $\leq 1.0 \pm 0.10$ mbar. The effective membrane area to initial reaction volume ratio (S/V) was 0.1325 cm⁻¹.

SBR kinetic reactions were carried out in a glass reaction flask fitted with a reflux condenser to prevent product losses. The reaction flask was kept in a water bath with a thermostat. The temperature of the reaction mixture was measured by a thermocouple. The mixture was mixed using a magnetic stirrer having a speed of 1000 rpm. The same procedure was followed in preparation of the reactants and catalysts as in PVMR experiments. The total volume of the reaction mixture was 0.3 L. The analysis of the permeate and the samples withdrawn from the reaction mixture was performed on a Shimadzu model GC-9A model gas chromatograph fitted with a Porapak T 80/100 column with dimensions of 6 ft \times 1/8 in. and equipped with a thermal conductivity detector. The oven temperature was at

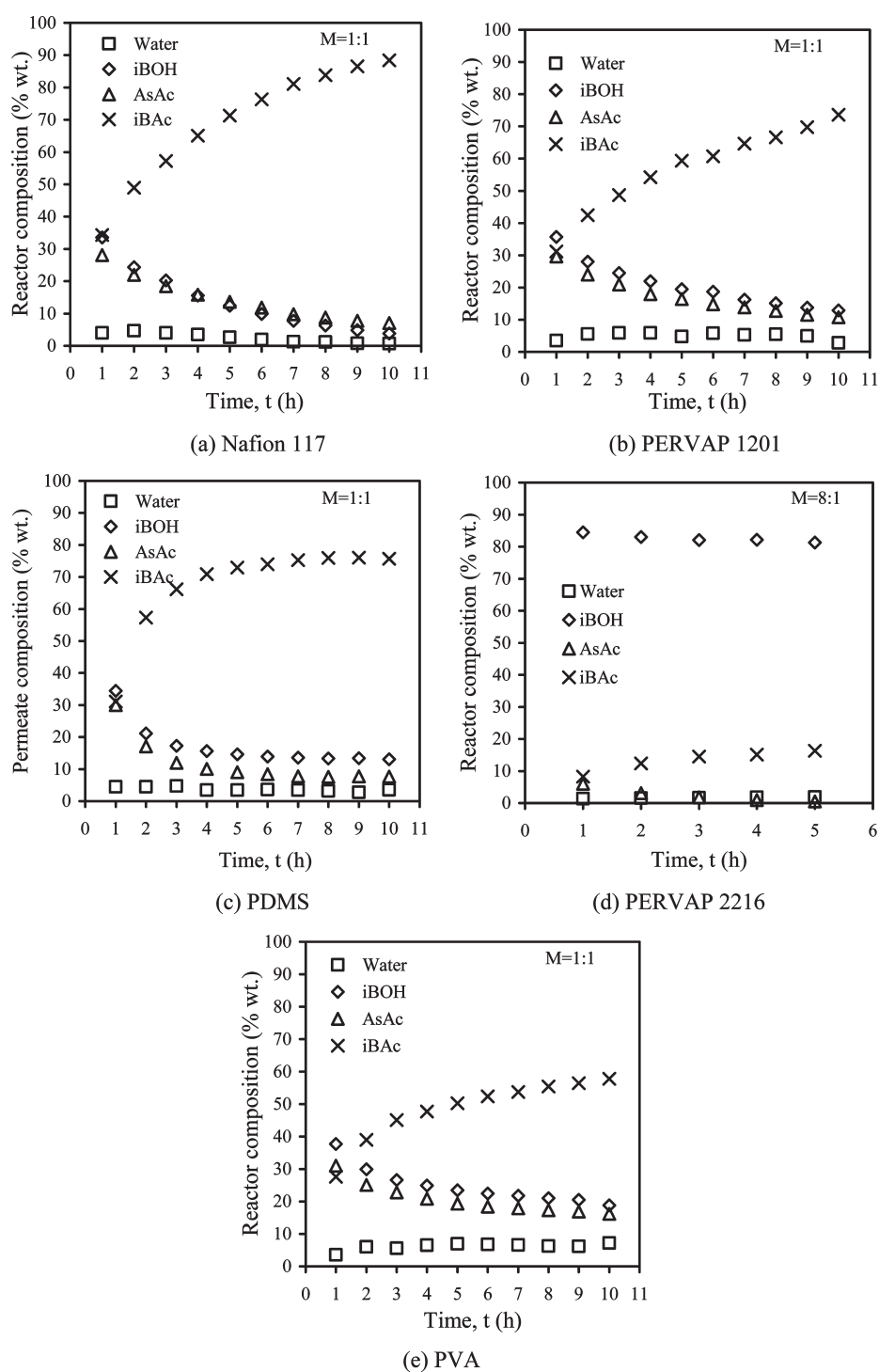


Figure 4. Reactor compositions of PVMR using hydrophilic membranes and the composition of permeate obtained from PVMR experiments using PDMS membrane ($C = 16.67$ g/L, $T = 70$ °C, $S/V = 0.1325$ cm⁻¹; catalyst: Dowex 50W-X8).

200 °C. The conversion of the esterification reaction was determined by acetic acid measurement. The conversions are calculated from eq 1, where N_{A0} is the initial molar amount of acetic acid and N_A is the molar amount of acetic acid at any reaction time. The reproducibilities of conversions and fluxes were within $\pm 2\%$.

$$X = \frac{N_{A0} - N_A}{N_{A0}} \quad (1)$$

3. RESULTS AND DISCUSSION

3.1. Effect of the Membrane Type. The effect of the membrane type on conversion is given in Figure 2 plotted by using the experimental data obtained from SBR and PVMR experiments. The concentration (C) of the Dowex 50W-X8 catalyst and the temperature (T) were taken as 16.67 g/L and 70 °C, respectively. The initial molar ratios of reactants (M) were

1:1 for PDMS, PVA, PERVAP 1201, and Nafion 117 membranes, whereas it was 8:1 (alcohol/carboxylic acid) for PERVAP 2216 membrane because of the working media concentration limitation of PERVAP 2216 membrane. Each membrane has unique properties (e.g., membrane thickness, polymeric structure, and cross-linking degree) affecting the pervaporation transport. Therefore, the data given in Figure 2 cannot be used to compare the membranes studied. But, the experimental results of these membranes can give information about the performance of each membrane in a pervaporation–esterification membrane reactor. Figure 2 shows that conversions obtained by using different membranes decrease in the following order: $X_{\text{PERVAP 2216}} > X_{\text{Nafion 117}} > X_{\text{PERVAP 1201}} \approx X_{\text{PDMS}} > X_{\text{PVA}}$. Higher conversions were obtained in the PVMR system because of the equilibrium shift caused by the membranes. As can be seen from Figure 2b, SBR conversions at $M = 8:1$ exceed PVMR conversions because of the slow removal rate of water at the studied S/V ratio of 0.1325 cm^{-1} . The increase in the S/V ratio, which is the factor that directly influences the pervaporation kinetics, enables a fast removal of the desired product and leads to a faster conversion.

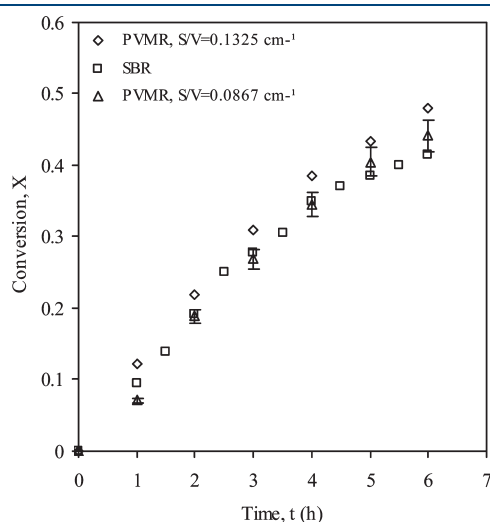


Figure 5. Effect of the ratio of membrane area to reaction volume on conversion, and the comparison between systems with PVMR and SBR ($C = 16.67 \text{ g/L}$, $M = 1:1$, $T = 50^\circ\text{C}$; catalyst: Dowex 50W-X8; membrane: PDMS).

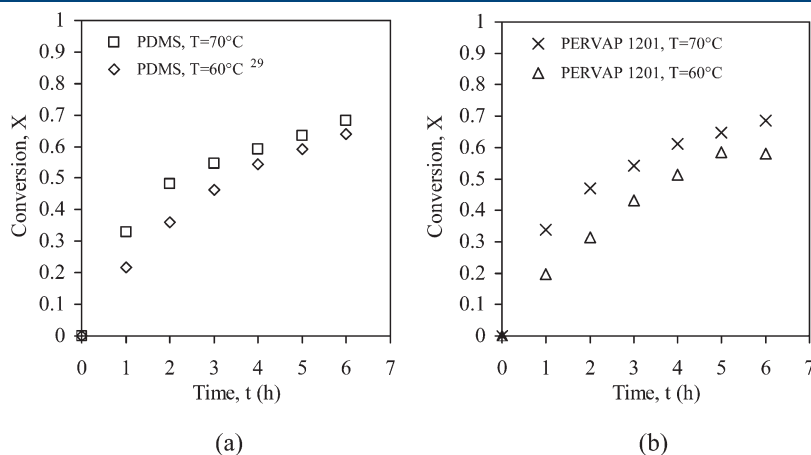


Figure 6. Effect of the temperature on conversion in PVMR using (a) PDMS membrane and (b) PERVAP 1201 membrane ($C = 16.67 \text{ g/L}$, $M = 1:1$, $S/V = 0.1325 \text{ cm}^{-1}$; catalyst: Dowex 50W-X8).

The conversions achieved by Nafion 117 membranes were calculated by analyzing both phases, as permeate obtained by this membrane consisted of two immiscible phases. In Figure 3, the phase compositions and phase weights of the permeate obtained by Nafion 117 membrane are given. Nafion 117 membrane absorbs water in terms of a widely accepted cluster-network model³¹ in which the connected cylindrical channels play a role in the molecular transport. Small water molecules can easily pass through these hydrophilic ionic channels in Nafion 117 membrane. Because of the plasticization effect of water on the polymer, the larger molecules could pass more readily with the increasing water concentration in the reaction mixture. As a result, the permeate consisted of the other reaction components as well as water. Because the concentrations of components in the permeate were higher than their solubility limits, the permeate underwent a phase separation under the experimental conditions studied. For an industrial application point of view the organic phase can be recycled to the distillation column for reprocessing, whereas the aqueous phase can be recycled to the PVMR unit for further conversion. Considering the process economics due to the additional phase separation needed in the case of Nafion 117 membrane and inefficient use of reactor space with an extra separation step to recover the unreacted compound in the case of PERVAP 2216 membrane, the usage of Nafion 117 and PERVAP 2216 membranes seems to be inconvenient. PDMS and PERVAP 1201 membranes gave higher conversions than PVA membrane in PVMR experiments. This is mainly because of the capacity of eliminating the related product from the reaction system.

Figure 4 shows the reactor compositions of hydrophilic membranes and the permeate composition of PDMS membrane. It is seen that the reactor fraction of iBAc for hydrophilic membranes increases with the reaction time, whereas the acetic acid and isobutanol fraction decrease. The initial increase in water fraction indicates that water removal rate by pervaporation is lower than the reaction rate for hydrophilic membranes. Similar to the flux results (Figure 7) of the membranes used, the water and/or iBAc (product) content decreased in the reaction mixture after an increase at the beginning of the reaction. The performance of PVMR is limited by the performance of the membrane used. Higher iBAc fractions obtained with the membranes giving higher conversions, except for PERVAP 2216 membrane whose initial molar reactant ratio, M was 8:1.

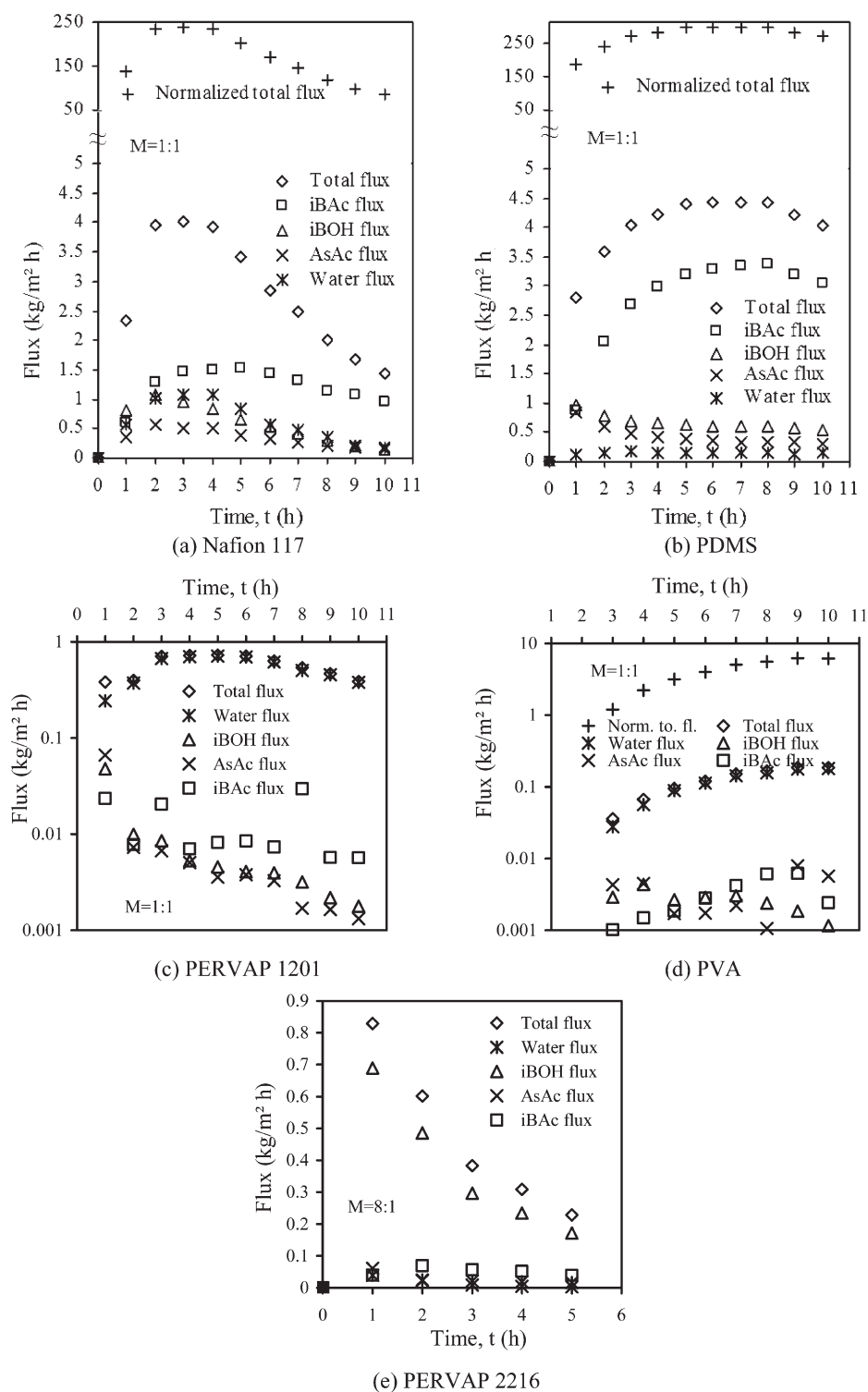


Figure 7. Total and partial fluxes as a function of reaction time for PVMR using (a) Nafion 117, (b) PDMS, (c) PERVAP 1201, (d) PVA, (e) PERVAP 2216 ($C = 16.67$ g/L, $T = 70$ °C, $S/V = 0.1325$ cm⁻¹; catalyst: Dowex 50W-X8).

For hydrophobic PDMS membrane, the permeate compositions of the reaction components reached an equilibrium after the seventh hour of the process.

3.2. Effects of the Ratio of Membrane Area to Reaction Volume and the Temperature. The effects of the ratio of membrane area to reaction volume (S/V) and the temperature (T) on conversion are given in Figures 5 and 6, plotted by using

the experimental data obtained from SBR and PVMR experiments with Dowex 50W-X8 catalyst. The concentration of Dowex 50W-X8 was taken as 16.67 g/L for all the experiments. The studied ratios of membrane area to reaction volume (S/V) were 0.0867 and 0.1325 cm⁻¹ at 50 °C. The effect of temperature was studied for 60 and 70 °C by using PDMS and PERVAP 1201 membranes.

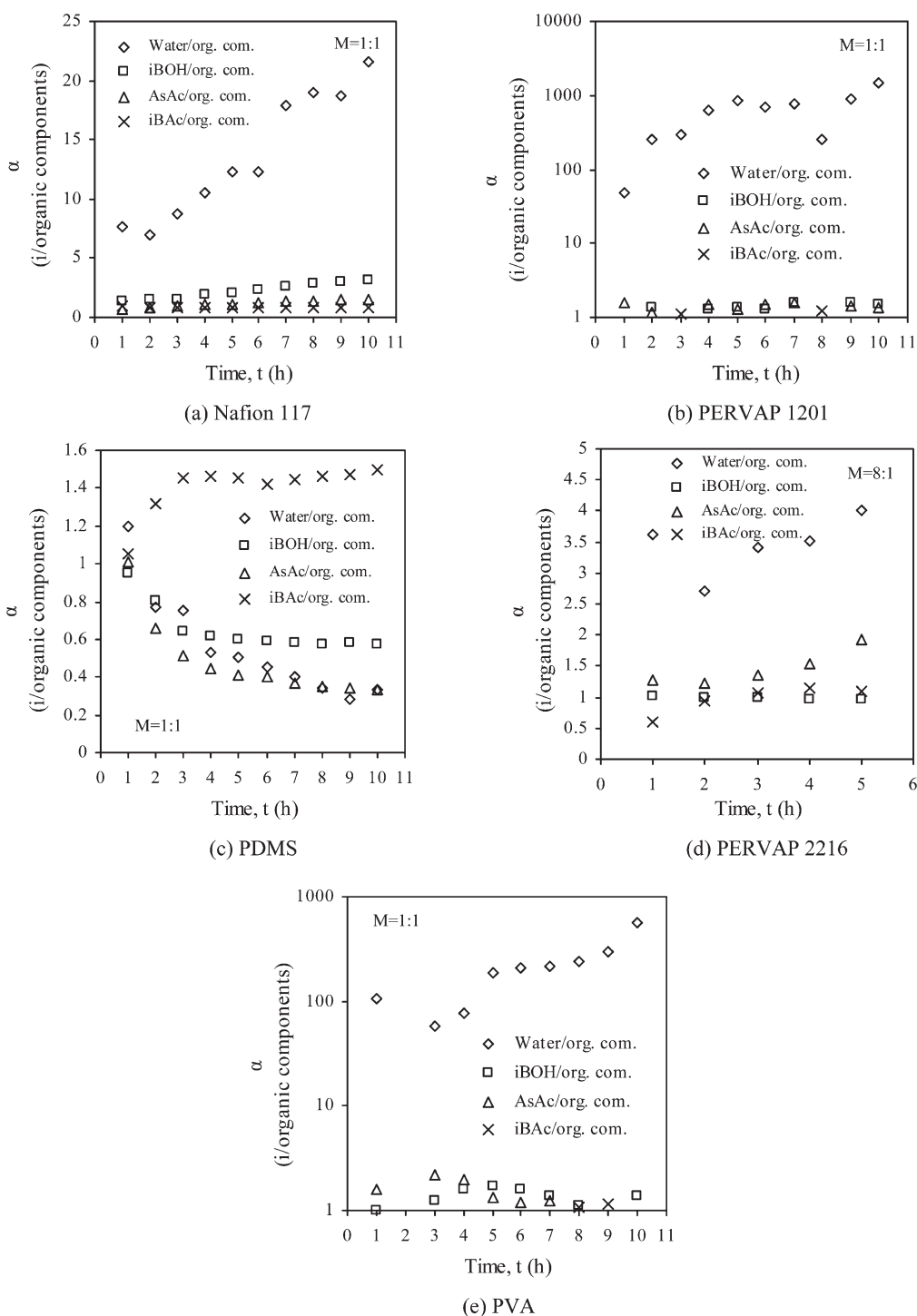


Figure 8. Selectivities as a function of reaction time for PVMR experiments using (a) Nafion 117, (b) PERVAP 1201, (c) PDMS, (d) PERVAP 2216, (e) PVA ($C = 16.67$ g/L, $T = 70$ °C, $S/V = 0.1325$ cm⁻¹; catalyst: Dowex 50W-X8).

As can be seen from Figure 5, the S/V ratio directly affects the pervaporation kinetics.³² The conversion of acetic acid increased because of increased removal of iBAc, whereas its production rate was the same at various S/V ratios, as the ratio of membrane area to reaction volume increased. Because of the fact that the reaction mixture could contact the membrane surface more fully, increased forward reaction was favored because of a lower accumulation of iBAc in the reactor. In addition, higher conversions

were obtained in the PVMR system. The effect of the temperature for 60 and 70 °C by using PDMS and PERVAP 1201 membranes at the initial mole ratio of isobutanol to acetic acid of 1:1 is given in Figure 6.

Temperature has a dual effect on both reaction kinetics and membrane structure.^{29,32,33} The production rates of the products are higher at higher temperature. The diffusion of the permeants are facilitated, as the thermal motion of the polymer chains

increases with increasing of the temperature.³⁴ It is seen in Figure 6 that an increase in temperature leads further enhancement in reaction conversion in the case of PERVAP 1201 membrane. PDMS membrane with a more elastic structure relative to PERVAP 1201 membrane with rigid PVA base gives higher fluxes but lower selectivity values (leading to limited conversion) with temperature increase. Thus, the conversion enhancement was higher in PERVAP 1201 membranes with temperature increase compared to PDMS because of the lower selectivity of this membrane. Additionally, higher conversions were obtained in the PVMR system.

3.3. Evaluation of the Pervaporation Performance. The flux data and the calculated selectivities were used to evaluate the pervaporation performance in PVMR experiments. The fluxes (J) obtained from PVMR experiments are expressed as

$$J = \frac{W}{St} \quad (2)$$

where W , S , and t represent the permeate amount, the effective membrane area, and the reaction time, respectively. Partial fluxes of components (J') are obtained by multiplying the fluxes by the weight fraction of the relevant component in permeate.

$$J' = J y_i \quad (3)$$

The total flux values of PDMS, PVA, and Nafion 117 membranes were normalized by using eq 4 for 3 μm membrane, where l is the thickness of the related membrane:

$$J = \frac{W}{St} \frac{l}{3} \quad (4)$$

Total and partial fluxes of components and normalized total flux values of PDMS, PVA, and Nafion 117 membranes calculated from eqs 2, 3, and 4 versus reaction time for PVMR using different membranes are given in Figure 7. A log scale is used in Figure 7 for PERVAP 1201 and PVA membranes. In the case of Nafion 117 membrane, because permeate consisted of two immiscible phases, flux calculations were done by weighing both of the two permeate phases after gas chromatography analysis and the phase separation by means of a separating funnel.

The total and partial fluxes of components given in Figure 7a–e are mainly affected by the membrane type used. Hydrophilic PVA and PERVAP 1201 membranes give partial flux results in the following order: $J_{\text{water}} > J_{\text{iBOH}} \approx J_{\text{AsAc}} \approx J_{\text{iBAC}} \approx 0$. However, hydrophobic PDMS gives $J_{\text{iBAC}} > J_{\text{iBOH}} > J_{\text{AsAc}} > J_{\text{water}}$. Nafion 117, which has hydrophobic backbone and hydrophilic ionic domain,³⁵ gives closer partial flux values in the following order: $J_{\text{iBAC}} > J_{\text{water}} > J_{\text{iBOH}} > J_{\text{AsAc}}$. The flux results are consistent with the components' polarities with respect to the membrane type used. The importance of polarity of the species in determining the separation characteristics was cited in the literature.³⁶ Higher removal of the product (iBAC or water) than the others increases the conversion. Because of working media concentration limitation of PERVAP 2216 membrane, the initial molar ratio of reactants (M) was taken as 8:1 (isobutanol/acetic acid). Thus, flux data obtained from PERVAP 2216 is rated according to this feed composition as $J_{\text{iBOH}} > J_{\text{iBAC}} > J_{\text{water}} > J_{\text{AsAc}}$. Also, total fluxes of the membranes decrease in the following order: $J_{\text{PDMS}} > J_{\text{Nafion}_117} > J_{\text{PERVAP}_2216} > J_{\text{PERVAP}_1201} > J_{\text{PVA}}$. Polymer structure, cross-linking degree, and effective membrane thickness are the main parameters affecting the flux ratios obtained by different

Table 2. Experimental Results of PVMR Process at $t = 6$ h for Different Ratios of Membrane Area to Reaction Volume a and Temperature^b

		S/V (cm^{-1})		T ($^{\circ}\text{C}$)	
		0.0867	0.1325	60	70
PDMS	J ($\text{kg}/\text{m}^2 \cdot \text{h}$)	1.565	1.786	4.270 ²⁹	4.429
	$\alpha_{\text{iBAC}/\text{organic_components}}$	1.757	1.636	1.526 ²⁹	1.421
PERVAP 1201	J ($\text{kg}/\text{m}^2 \cdot \text{h}$)			0.321	0.712
	$\alpha_{\text{water}/\text{organic_components}}$			749.9	686.5

^a Experimental conditions: $C = 16.67$ g/L, $M = 1:1$, $T = 50$ $^{\circ}\text{C}$; catalyst: Dowex 50W-X8. ^b Experimental conditions: $C = 16.67$ g/L, $M = 1:1$, $S/V = 0.1325$ cm^{-1} ; catalyst: Dowex 50W-X8.

membranes. In Figure 7a–e, total and partial fluxes decreased because of the lesser water and/or iBAC (product) content in the reaction mixture after an increase at the beginning of the reaction. The reaction proceeds until a maximum product concentration is reached. After that point, product removal from the reaction mixture is faster than its production rate. Therefore, as the product content decreases in the reaction medium, the fluxes decrease.^{4,16} In the case of PVA membrane the maximum product concentration is reached at the ninth hour of the process.

The selectivities (α) are calculated from the equation below, where x_i, x_j and y_i, y_j are the weight fractions of components in the feed and permeate, respectively, considering “ i ” as the referred component and “ j ” as the organic components' total (iBOH + AsAc + iBAC).

$$\alpha_{ij} = \frac{y_i/y_j}{x_i/x_j} \quad (5)$$

Selectivities of components versus reaction time for PVMR with different membranes are given in Figure 8. A log scale is used in Figure 8 for PERVAP 1201 and PVA membranes. Hydrophilic membranes showed high water selectivities. This result is consistent with the polarity of water. PERVAP 1201 membrane, having a high cross-linking degree, showed the highest water selectivity among the hydrophilic membranes. The water selectivities of hydrophilic membranes increased generally, as reaction time is longer. These increases could be related to the increasing production of water in the reactor side. From Figure 8c, it can be seen that the selectivity of iBAC with respect to total organic components for PDMS membrane was the highest, which is consistent with the flux data showing the preferential permeation of iBAC through the membrane. The iBOH selectivities for PDMS and Nafion 117, which has both polar and nonpolar groups,³⁷ were generally higher than AsAc ($\alpha_{\text{iBOH}} > \alpha_{\text{AsAc}}$). This result is consistent with the lesser polarity of iBOH.

Table 2 summarizes the experimental pervaporation results of PVMR processes at $t = 6$ h for different temperatures and the ratios of membrane area to reaction volume. Fluxes increased with increasing the S/V and T because S/V and T have a positive effect on the PVMR process. Selectivities, on the other hand, decreased because of plasticization effect of the membrane selective component.

4. CONCLUSION

In this study, a PVMR study of isobutyl acetate production by the esterification of isobutanol and acetic acid was performed using different membranes with Dowex 50W-X8 catalyst. The

increasing of the temperature and the ratio of membrane area to reaction volume increased the conversion. Pervaporation performance of the PVMR system was evaluated by means of flux and selectivity data. PERVAP 1201 membranes provided a higher water flux and higher selectivity than other hydrophilic membranes. It has been found that the highest fluxes were obtained using PDMS membrane and that PDMS membrane selectively permeated iBac compared to the other components. Fluxes and selectivities are consistent with the polarities of components. In conclusion, PVMR results show that the hydrophobic and hydrophilic membranes can be used to remove selectively the isobutyl acetate or water formed in the esterification reaction with relatively higher conversions and reasonable pervaporation fluxes. The selective removal of the water by using hydrophilic membranes shifts the equilibrium to higher yields of the ester product formed by esterification, and then it can be recovered using a hydrophobic membrane. Improvement of PDMS membranes with higher selectivities and improved resistance offer a potential for the application in pervaporation–esterification membrane reactors. Also, this study is a useful reference in the membrane selection for pervaporation-aided esterification membrane reactors.

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NOMENCLATURE

AsAc	acetic acid
α	selectivity
C	catalyst concentration, g/L
D1,D2,D3	Dewar flasks
GC	gas chromatograph
GE	General Electric
iBac	isobutyl acetate
iBOH	isobutanol
J	pervaporation flux, kg/m ² ·h
J'	Partial pervaporation flux, kg/m ² h
l	membrane thickness, μ m
M	initial molar ratio of reactants
N _A	molar amount of acetic acid at any reaction time
N _{A0}	initial molar amount of acetic acid
norm. to. fl.	normalized total flux
org. comp.	organic components
PI	vacuum meter
PDMS	polydimethylsiloxane
PVA	poly(vinyl alcohol)
PVMR	pervaporation membrane reactor
RTV	room temperature vulcanization
S	effective membrane area, m ²
SBR	simple batch reactor
S/V	ratio of membrane area to initial reaction volume, cm ⁻¹
t	time, h

T	temperature, °C
W	permeate amount, kg
X	AsAc conversion
x	feed fraction (wt)
y	permeate fraction (wt)

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