Pervaporation of butanol/water mixtures using siloxane polymer/ceramic composite membranes

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ABSTRACT

In this study, siloxane polymers were coated on a prepared alumina ceramic support layer (γ-Al_2O_3/α-Al_2O_3). A layer of rubbery polydimethylsiloxane (PDMS) was deposited on the γ-Al_2O_3 surface and a secondary coating of phenyltrimethoxysilane (PhTMS) was added to enhance membrane hydrophobicity. The role of the double ceramic support layers was discussed, using simple analytic calculations. PDMS/ceramic and PhTMS/PDMS/ceramic composite membranes were used to separate butanol from a butanol/water mixture using pervaporation. Effects of the secondary PhTMS coating were investigated with respect to butanol concentration, temperature, and flow rate of feed solution. The PhTMS/PDMS/ceramic composite membrane showed promising potential to improve butanol recovery from the fermentation broth but the trade-off is total flux reduction.

Keywords: Alumina ceramic membrane; Butanol; Pervaporation; Phenyltrimethoxysilane; Polydimetylsiloxane

1. Introduction

Due to depletion of the supply of economic crude oil, attention is being paid to utilization of renewable energy resources. While recovery of biofuels from the acetone–butanol–ethanol (ABE) fermentation may generate industrial resuscitation, biofuel research has turned, in part, to the recovery of butanol from biomass, which is as effective as ethanol as a fuel [1–4]. However, butanol fermentation yields a lower concentration than that of ethanol produced by yeast culture and butanol toxicity to microorganisms impedes the productivity [5,6]. Although technological development for energy-

efficient separation of butanol from a butanol/water mixture is of great necessity [7], research on this subject is still in a burgeoning stage. The lower recovery ratio of butanol (as well as ethanol) from fermentation broth makes the use of distillation-based thermal processes uneconomical [8]. In the past, several techniques were reviewed to recover biofuels, including adsorption, chemical recovery, gas stripping, liquid–liquid extraction, membrane distillation, reverse osmosis, pervaporation and salt induced phase separation [9,10]. Among them, pervaporation is currently considered as the potentially best technology to recover biofuels because of noticeable capacity of separating specific organic materials from water, when process efficiency is the main concern in distillation, extraction, and sorption [2].

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Structural modification of polymer pervaporation membranes using advanced materials is currently an active research area [11–13]. Compared to distillation, pervaporation is a very energy-efficient process because of much lower temperature requirements than those of thermal processes. During the butanol pervaporation process, butanol is sorbed into the membrane on the feed side, diffused through the membrane, and desorbed into the vapor phase on the permeate side [14,15]. At the end of the process, condensation is required to liquefy the butanol vapor into the solution phase. The performance of the pervaporation membrane can be enhanced by improving both sorption and diffusion capabilities for specific solutes of interest and also by optimizing operational conditions [16].

Cross-linked polydimethylsiloxane (PDMS) is known to be a good material to prepare organic selective membranes, especially when supported/composited membranes using micro-porous ceramic materials/fillers [12,17–21]. As ceramic materials have the ability to resist thermal and mechanical stresses and withstand harsh chemicals [22,23], they were widely used for processes of food engineering and bio-energy generation research [24,25]. If a composite membrane, i.e., a thin active layer supported on a porous substance, is formed, it is possible to increase flux without loosing the intrinsic selectivity [26]. Several studies have described separation of butanol from fermentation broth or their mixture with water using pervaporation with silicon rubber (PDMS) membranes [27–33]. However, specific studies on the butanol recovery using siloxane composite membranes are rare in the literature.

In this study, we made an alumina (ceramic) support layer to optimize total flux [26] and prepared a siloxane polymer/ceramic composite membranes to investigate the separation capability of butanol from a butanol/water mixture using pervaporation. To increase butanol sorption capability on the membrane surface, (glassy) phenyltrimethoxysilane (PhTMS) was additionally coated on the surface of the (rubbery) PDMS/ceramic composite membrane and its performance was compared with that of the PDMS/ceramic composite membrane. We systematically studied effects of operational conditions such as butanol concentration, temperature, and flow rate of feed solution on the pervaporation performance of PDMS and PhTMS active layers on aluminum ceramic supports. In addition, the role of the ceramic support layer on the separation factor is explained using a simple mathematical model.

2. Materials and method

2.1. Ceramic support layer

To prepare siloxane polymer-coated membranes, we made (double) ceramic support layers as follows.

First, we put 10 g of aluminum oxide powder (α-Al_2O_3, A-16SG, 99%, Alcoa) and 1.5 mL of deionized water in a mortar, vigorously ground the mixture, and compressed 3.5 g of the mixture in a stainless steel mold for 2 min at pressure 52.8 kN. The compressed alumina disk was dried at a room temperature (25 °C) and put into a furnace for sintering. An α-Al_2O_3 (ceramic) support layer formed after 30 h in the furnace at temperature 1260 °C, which from room temperature increased 1 °C/min. Because the α-alumina support layer has pore sizes below 1 μm, direct coating of a PDMS solution on its surface may lead to serious leakage of the coating solution. To avoid this situation, we added a second support layer (γ-Al_2O_3) on top of the α-alumina support before the PDMS coating. To form a γ-Al_2O_3 on the α-Al_2O_3 ceramic surface (for later coating of the PDMS solution), we dip-coated the α-Al_2O_3 disk in a solution of boehmite sols and polyvinylalcohol (PVA, molecular weight (MW) = 35,000) for 2 s, dried it at 40 °C and 60% humidity for 24 h, and calcinated it in the furnace at 600 °C for 3 h. For the calcination, we increased the furnace temperature 0.5 °C per minute from room temperature. This γ-Al_2O_3 dip-coating process, followed by the calcination at 600 °C, was repeated one more time (total two coatings) to generate a more homogeneous and potentially crack-free γ-Al_2O_3 layer than that of the single γ-Al_2O_3 coating. We prepared several γ-Al_2O_3/α-Al_2O_3 disks to form PDMS and PhTMS/PDMS active layers for pervaporation experiments.

2.2. Active layer coating

We dissolved PDMS prepolymer (Dow Corning, DC 184, Dow Chemical) and crosslinker with a 10:1 weight ratio in an *n*-hexane solution to prepare a 3 wt.% PDMS solution. γ-Al_2O_3/α-Al_2O_3 ceramic disks were soaked in the 30 wt.% PDMS solution and dried in a vacuum oven at 100 °C for 6 h. Stable PDMS active layers were formed on the surface of γ-Al_2O_3-coated α-Al_2O_3 ceramic disks. Then we prepared a solution of 3 wt.% of (glassy) PhTMS (MW = 198.3, 97%, Aldrich Chemical Co.), ethanol (30.78 ml), water (1.05 ml), and 10 mL hydrochloric acid (0.2 ml); and coated a PDMS membrane with the solution to make PhTMS/PDMS/γ-Al_2O_3/α-Al_2O_3 composite membranes. In this paper, we refer to PDMS/γ-Al_2O_3/α-Al_2O_3 and PhTMS/PDMS/γ-Al_2O_3/α-Al_2O_3 composite membranes as PDMS and PhTMS membranes, respectively, for simplicity. After the active layer coating processes, the prepared membranes have surface areas of 3.87 cm².

2.3. Pervaporation tests

A schematic of the pervaporation unit for this study is shown in Fig. 1. In the feed tank (a), we prepared 1 L of butanol solution (of 1–5 wt.% to water)
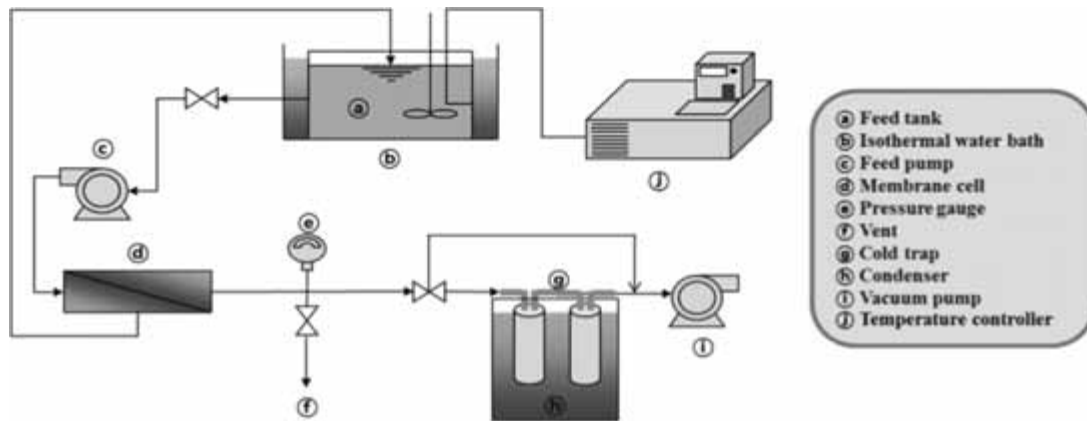
Fig. 1. Schematic representation of pervaporation setup.

and maintained a uniform concentration by stirring the solution using a magnetic bar. The temperature of the feed solution was kept constant by using an isothermal water bath (b) as a temperature reservoir. The feed butanol solution was introduced to the membrane cell (d) using a feed pump (c), and the retentate (brine) stream was returned to the feed tank. (During the pervaporation process, the recirculation of the retentate stream only minimally changed the feed concentration.) The permeate vapor condensed as it passed through the liquid nitrogen trap (g) in the condenser (h). The pressure of the permeate vapor was kept below 300 Pa (= 0.003 atm) using a vacuum pump (i) as measured using a pressure gauge (e). All pervaporation experiments were conducted for 2 h after the system reached a steady state (within an hour). During the process, feed temperature was maintained constant using the temperature controller (j). After the permeate was collected in the cold trap, the permeate flux J was calculated as

$$J = \frac{Q}{A_m t}$$ (1)

where Q is the weight of the collected butanol permeate (grams) passing through the membranes of effective surface area of A_m (3.87 cm^2) during the elapsed time t (hour). After the system reached equilibrium, the initial time for steady-state pervaporation was set to 0. Butanol concentrations in the feed and permeate were measured using gas chromatography (GC, ACME 6000, Yong Lin Instrument Co. Ltd.). The performance of this butanol pervaporation is estimated using separation factor α defined as the weight ratio of butanol to water in permeate divided by that in feed, i.e.,

$$\alpha = \frac{Y_{BuOH}/Y_{H_2O}}{X_{BuOH}/X_{H_2O}}$$ (2)

where X and Y are weight fractions in the feed and permeate streams, respectively, and the subscripts indicate butanol (BuOH) and water (H$_2$O) [26,34]. For the binary mixture of butanol and water, a sum of weight fractions of butanol and water is equal to one, i.e.,

$$Y_{BuOH} + Y_{H_2O} = X_{BuOH} + X_{H_2O} = 1.$$

3. Results and discussion

3.1. Characterization of ceramic composite membranes

Physical and chemical characteristics of PDMS and PhTMS membranes were investigated as follows. Contact angles were measured to investigate surface hydrophobicity of the γ-Al$_2$O$_3$/α-Al$_2$O$_3$ support, PDMS, and PhTMS layers. A field emission-type scanning electron microscope (FE-SEM, Carl Zeiss model: LEOSPRA 55) was used to determine top morphology of these surfaces, and X-ray photo-electron spectroscopy (XPS, KAlpha Thermo Electron) was used to measure chemical bonding energies of the PDMS and PhTMS surface layers.

3.2. Contact angle (CA)

Fig. 2 shows water contact angle (CA) measurements on the γ-Al$_2$O$_3$/α-Al$_2$O$_3$ ceramic support (38.69°), PDMS (109.26°), and PhTMS (116.00°) at 25 °C. CA on the PDMS surface is within the standard range of 105°–110° [35–37]. As the results indicate, a phenyl functional group of PhTMS, bonded to Si ions, seems to enhance CA. In general, a higher CA indicates stronger surface tension
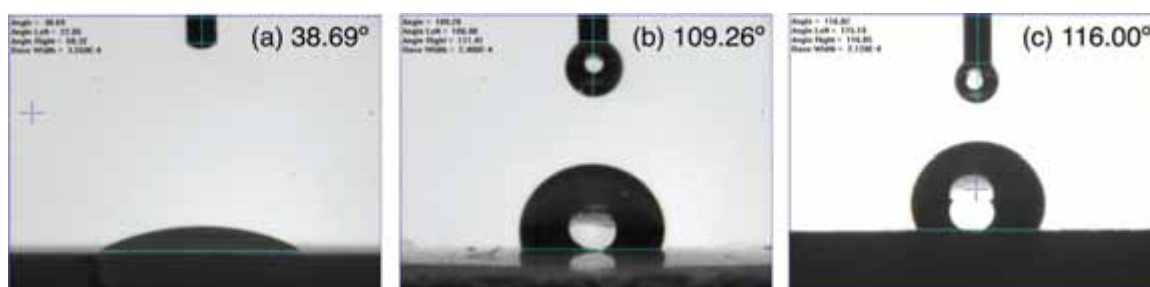
Fig. 2. Contact angles on (a) the ceramic support, (b) PDMS-coated, and (c) PhTMS/PDMS-coated membrane surfaces.

as well as hydrophobicity. Surface tensions of PDMS and PhTMS are reported as 24 mN/m and 33.2 mN/m, respectively, which indirectly support our CA measurement results [38–40]. Because the CA of PhTMS is higher than that of PDMS, the PhTMS membrane was expected to have a higher selectivity of butanol over water (see next section).

3.3. FE-SEM analysis

To confirm that the composite membranes were properly prepared with mechanical stability for pervaporation experiments, we used an FE-SEM imaging technique to visualize layers on the ceramic support. Fig. 3 shows micro-structures of cross-sectional surfaces of (a) (bare) α-Al$_2$O$_3$ ceramic support, (b) γ-Al$_2$O$_3$ coating layer, and (c) PDMS membrane. The α-Al$_2$O$_3$ layer of Fig. 3(a) shows a micro-granular porous structure with pore size smaller than 1 μm (visually estimated). Fig. 3(b) shows that the intermediate γ-Al$_2$O$_3$ layer was properly formed on the α-Al$_2$O$_3$ support with thickness about 5 μm, on which the PDMS active layer of 30 μm thickness was formed as shown in Fig. 3(c). In Fig. 3(b), the interface between the γ-Al$_2$O$_3$ and PDMS coating layer is quite smooth without noticeable variation in thickness where the top (dark) gray portion indicates the empty spaces. As our objective for the of γ-Al$_2$O$_3$ coating on the α-Al$_2$O$_3$ ceramic support is to

provide a uniform micro-porous surface with smaller pore sizes (than those of α-Al$_2$O$_3$) to avoid leakage of PDMS solution during the preparation process, Fig. 3(c) confirms the successful coating of PDMS on the intermediate layer. The active layer thickness of PDMS prepared in this study (30 μm) is within the same order as other researchers' work: 25 μm [41] and 24–110 μm [26]. The PhTMS coating on the PDMS surface was too thin to visualize its thickness using the FE-SEM imaging technique.

3.4. XPS analysis

XPS spectrum was measured to investigate Si-bonding on the top surfaces of the PDMS and PhTMS membranes, as shown in Fig. 4. PDMS Si-bonding energy with carbon and oxygen were measured as 100.30 eV (Si–C) and 101.73 eV (Si–O). As expected, the backbone chain of the Si–O bonding is stronger than that of the Si–C branches. PhTMS Si-bonding energy with carbon and oxygen were measured as 100.56 eV (Si–C) and 102.07 eV (Si–O), respectively. The bonding energy of PhTMS Si–O (102.07 eV) is higher than that of PDMS Si-O (101.73 eV), which implies that the rigid phenyl groups were successfully formed on the PDMS membrane surfaced, contributing to selectivity of butanol over water through the enhanced hydrophobicity (as indicated in the CA measurement section).

Fig. 3. FE-SEM images of (a) the ceramic support (scale bar = 1 μm), (b) γ-Al$_2$O$_3$ intermediate layer (scale bar = 1 μm), and (c) PDMS-coated membrane surfaces (scale bar = 10 μm).
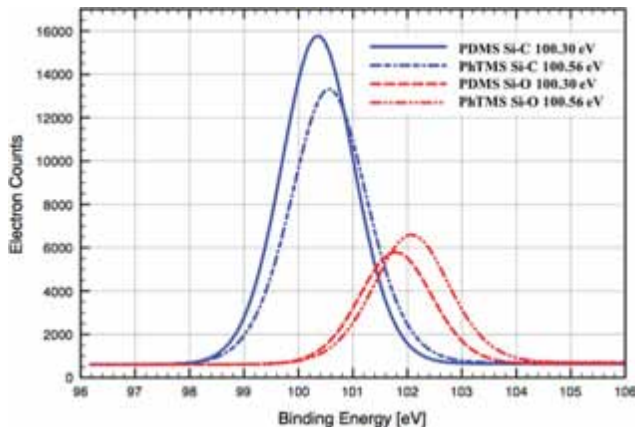
Fig. 4. XPS high-resolution spectra of composite membrane surfaces.

3.5. Pervaporation performance

Membrane performance for the butanol separation from the butanol/water mixture using pervaporation (of the PDMS and PhTMS membranes) was evaluated in terms of butanol concentration, temperature, and flow rate of the feed stream. Data shown in each graph of Figs. 5–7 are averages of three experiments. Overall, total fluxes and separation factors for various experimental conditions (described below) range from 200 to 900 g/m^2 h and 10–30, respectively. Takegami et al. [18] prepared PDMS membranes to separate ethanol from an ethanol/water mixture, of which performance was represented as total flux of 30–100 g/m^2 h and separation factors

below 10. Hong and Hong [41] used a PDMS/ceramic composite membrane for pervaporation of IPA/water mixtures, resulting in a separation factor between 4 and 16. Huang and Meagher [26] used thin-film silicalite-filled silicone composite membranes for pervaporative recovery of *n*-butanol from aqueous solutions and acetone–butanol–ethanol fermentation broth; and reported a total flux of about 200–900 g/m^2 h and a butanol separation factor of about 50 during pervaporation of the ABE fermentation broth at 70 $^{\circ}$C. In addition, when cross-linked polyvinyl alcohol membranes were prepared and used for pervaporative separation of water–acetic acid mixtures, total fluxes ranged from 50 to 250 g/m^2 h [42]. From this brief literature review, we indicate that the overall performances of our PDMS and PhTMS membranes are within the standard rages in terms of flux and separation factor. Specific analyses of pervaporation performance in terms of operating conditions are as follows.

3.6. Effect of butanol concentration

To investigate effects of butanol concentration on the flux, permeate concentration, and separation factor, we maintained the feed temperature at 30 $^{\circ}$C and flow rate at 0.6 L/min. Fig. 5(a) and (b) indicate that the total flux and the permeate concentration linearly increased as the feed concentration increased from 1.0 wt.% to 5.0 wt.%, which can be easily understood using the solution–diffusion model [43,44], indicating that the solute flux is proportional to the concentration gradient across the membrane. As an expected result of the additional coating, the PhTMS membrane provided lower
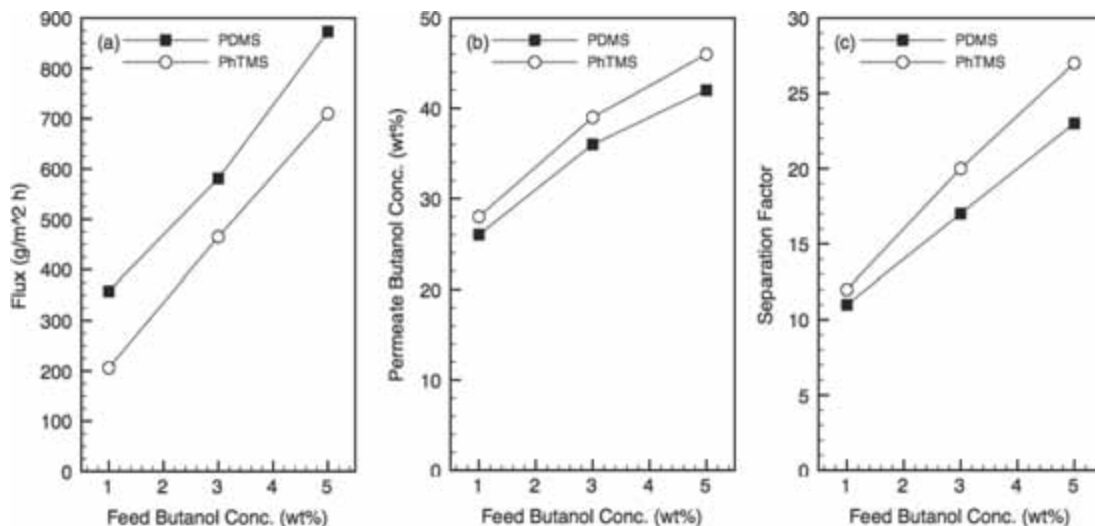

Fig. 5. Effect of butanol feed concentration on pervaporation performance with PDMS/ceramic and PhTMS/PDMS/ceramic composite membranes: (a) total flux, (b) permeate butanol concentration, and (c) separation factor. The feed temperature was 30 $^{\circ}$C and the flow rate was 0.6 L/min.

flux and higher permeate concentration than those of the PDMS membrane [44]. This can be explained by increases in hydraulic resistance and hydrophobicity (as also verified using CA measurement shown in Fig. 2) of the PhTMS layer on top of the PDMS membrane. The cross-linked polymer structure of the PhTMS membrane surfaces with strong hydrophobicity absorb butanol molecules preferentially to water molecules [45]. As shown in Fig. 5(c), the separation factor of the PhTMS membrane was higher than that of PDMS membrane, and the difference seems to increase linearly with the feed concentration. Analysis of this trend is as follows. The definition of the separation factor equation (2) can be written as

$$\alpha = \frac{y}{1-y}\frac{1-x}{x} \tag{3}$$

where we denoted for simplicity $x(= X_{BuOH})$ and $y(= Y_{BuOH})$ for butanol concentrations (weight fraction between 0 and 1) in feed and permeate solutions. Differentiation of equation (3) with respect to x provides

$$\frac{d\alpha}{dx} = \frac{\beta x(1-x) - y(1-y)}{x^2(1-y)^2} \tag{4}$$

where $\beta \equiv dy/dx$ is assumed to be constant for small x. Eq. (4) indicates that the sign of $d\alpha/dx$, i.e., slope of α versus x plot, can be either positive or negative in terms of y varying with x. For low x between 0.01 and 0.05 as used in this study, the permeate fraction can be approximated as $y = \beta x + y_0$, where y_0 can be estimated at the minimum feed fraction (in our case, $x = 0.01$). We let the numerator of Eq. (4) equal to zero to find the local extrema of the separation factor using the linear relationship between y and x, which yields

$$y^2 = \beta x^2 + y_0 \approx y_0 \tag{5}$$

where the term including β is neglected for the following reasons. From Fig. 5(c) we approximate $y_0 \approx 0.25$ and $\beta \approx 5$ because of the fact that as the feed fraction (x) increases from 0.01 to 0.05, the permeate fraction (y) changes roughly from 0.25 to 0.45. The maximum value of βx^2 is then $5 \times 0.05^2 = 0.0125$, which is much smaller than y_0. Substitution of these values into Eq. (5) gives $y \approx 0.5$, which indicates that as the permeate butanol fraction reaches about 50%, the slope of $d\alpha/dx$ changes its sign. Because the permeate butanol fraction in Fig. 5 does not exceed 50%, the corresponding feed fraction x must be larger than our maximum value, 0.05 (5%).

As the presence of the extrema is mathematically proved in this study, the phenomenological explanation is as follows. For low feed concentrations and low temperatures during pervaporation processes (such as our experiments), capillary condensation of water in the porous support layer is very probable, and membrane swelling or plasticization may not play a significant role in controlling butanol and water transport. The capillary condensation provides extra resistance to water permeation so that, as a consequence, the butanol transport is enhanced over the water transport while the feed concentration increases by a few percent [41]. This trend does not occur if the porous ceramic support is absent. For high feed fraction, the capillary condensation is suppressed by membrane swelling or plasticization so that the separation factor decreases with respect to the feed fraction.

3.7. Effect of feed temperature

Effects of feed temperature on the pervaporation performance were investigated by changing the temperature from 20 °C to 40 °C at the feed concentration of 3.0 wt.% and flow rate 0.6 mL/min, as shown in Fig. 6. The toxicity of butanol to fermentating microorganisms limits the butanol feed concentration as much as 5%. We arbitrarily set 3 wt.% of feed butanol as a reference concentration in this study [5,6]. Fig. 6(a) and (b) indicate that the total flux and permeate concentration through both PhTMS and PDMS membranes increase monotonously with respect to the temperature. The free volume of these siloxane polymer layers may increase with respect to temperature, provide less hydraulic resistance, and hence generate higher flux due to enhanced transport of both butanol and water molecules [46]. We think that the nonlinearity of the total fluxes at 30 °C through the PDMS membrane is due to decreased capillary condensation of water molecules in the highly hydrophobic ceramic layer. In other words, at 20 °C, this condensation seems to disturb water transport to the permeate side [41]. The strong hydrophobicity of the PhTMS membrane seems less sensitive to the feed temperature in terms of capillary condensation. The total flux through the PhTMS(glassy)/PDMS(rubbery)/ceramic composite membrane linearly increases with respect to temperature, indicating that the higher butanol permeation suppresses the condensation effects over the entire range of temperatures. It is desirable to analyze the temperature effect on total flux using the Arrhenius equation [47,48], but in our case the monotonous increase of flux with respect to the temperature within the narrow range (20–40 °C) only indirectly supports the Arrhenius relationship, which can be qualitatively expressed from the solution–diffusion model [43]:
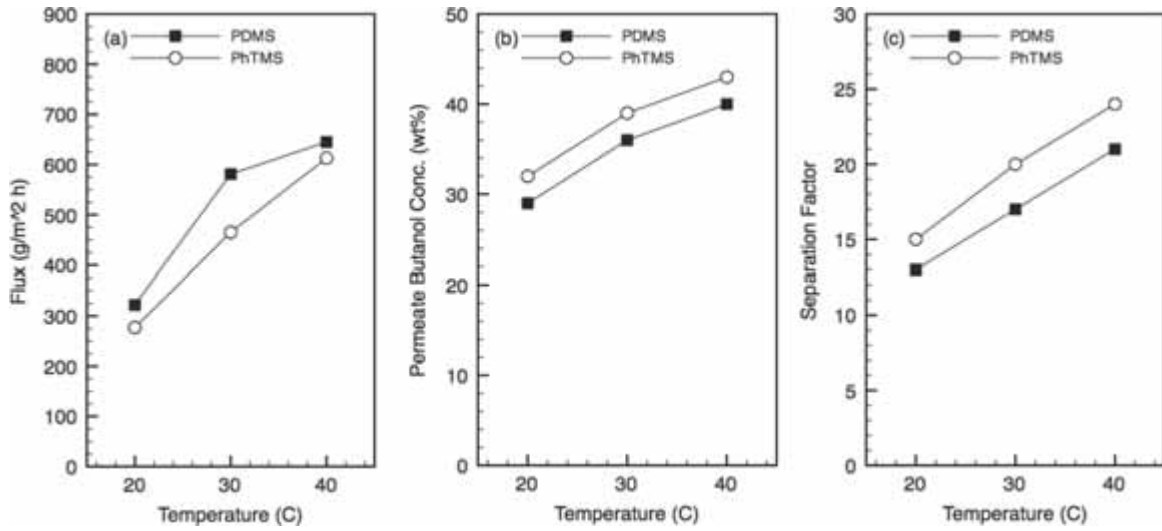
Fig. 6. Effect of feed temperature on pervaporation performance with PDMS/ceramic and PhTMS/PDMS/ceramic composite membranes: (a) total flux, (b) permeate butanol concentration, and (c) separation factor. The feed butanol concentration was 3 wt.% and the flow rate was 0.6 L/min.

$$\frac{J}{J_0} = \exp\left[-\frac{E_p}{RT}\right] \qquad (6)$$

where J_0 represents a reference flux value, Ep is the activation energy of the order of O (10) kJ/mol, R = 8.314 J/mol K is the universal gas constant, and T (K) is the absolute temperature. Because $RT \cong 2.5$ kJ/mol near standard temperature ($T \cong 300$ K), the exponent of Eq. (6) is greater than 1. Since we changed the feed temperature from 20 °C to 40 °C, we represent the temperature as $T = T_0 + \Delta T$ where T_0 = 293.5 K and ΔT =0, 20, and 40 K. The Taylor expansion of Eq. (6) with respect to ΔT yields

$$\frac{J}{J_0} = e^{-\varepsilon_p}\left[1 + \frac{\varepsilon_p \Delta T}{T_0} - \frac{1}{2}\left(\frac{\varepsilon_p \Delta T}{T_0}\right)^2 + \cdots\right] \qquad (7)$$

where ε_p = E_p/RT is the dimensionless activation energy. Eq. (7) explains the linear relationship between J and small temperature change ΔT from T_0 as shown in Fig. 6(a). The PDMS membrane provides higher total flux and lower permeate butanol concentration than that of the PhTMS membrane. As the feed temperature increases, diffusion of butanol in polymer membranes is enhanced and results in higher permeate concentration as shown in Fig. 6(a). Fig. 6(c) indicates that the trade-off of the flux reduction due to additional PhTMS coating on the PDMS/ceramic composite is the enhanced separation factor. Both composite membranes show the increasing trend of the separation factor with respect to the feed temperature.

3.8. Effect of feed flow rate

As the flow rate increases, the total flux, permeate butanol concentration, and separation factor increase monotonously as shown in Fig. 7(a)–(c). In general, concentration polarization of butanol on composite membrane surfaces contributes to reduction of the effective driving force by increasing the boundary layer resistance. The shear rate (s⁻¹), i.e., the crossflow velocity gradient normal to the membrane surface, is linearly proportional to the crossflow rate (m³/s). As the shear rate increases, a higher velocity gradient sweeps more butanol molecules downstream, diminishing the butanol concentration polarization and the boundary layer resistance. Therefore, transport of both water and butanol through composite membranes is enhanced with respect to the crossflow rate [49]. The increases in the separation factor in Fig. 7(c) can be understood in a similar way. The fast flow rate assimilates the boundary layer to the bulk phase in terms of butanol concentration so that the driving force for evaporation inside the membrane is maintained close to the maximum, effectively increasing permeate concentration. For operations with slow flow rates, lower butanol concentration on the membrane surface than that of the bulk phase reduces the effective driving force as explained by the solution-diffusion model. Similar to previous results, the PDMS membrane provides higher flux and lower
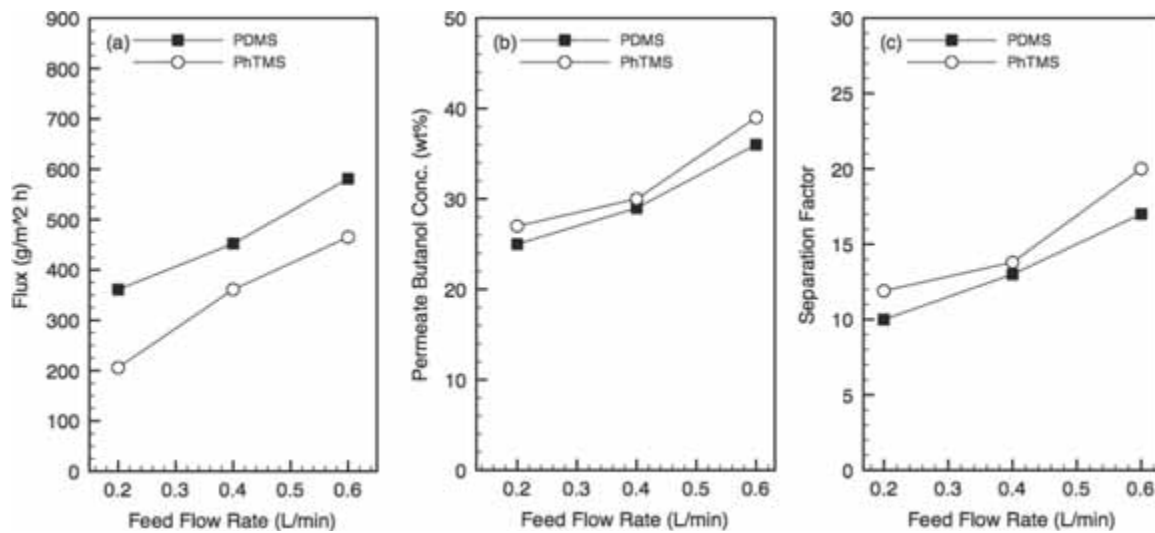
Fig. 7. Effect of feed flow rate on pervaporation performance with PDMS/ceramic and PhTMS/PDMS/ceramic composite membranes: (a) Total flux, (b) Permeate butanol concentration, and (c) Separation factor. The feed butanol concentration was 3 wt.% and the feed temperature was 30 °C.

permeate butanol concentration and separation factor than those of the PhTMS membrane.

3.9. Summary

As the main purpose of this paper is to enhance butanol separation, this section summarizes how the PhTMS on the PDMS surface influences the pervaporation performance as shown in Figs. 5–7. The rigid and glassy properties of the PhTMS top layer provides additional hydraulic resistance, which reduces the total flux through the PhTMS membrane compared to that through a PDMS membrane. The strong hydrophobicity of the PhTMS, as measured using the CA, enhances the butanol selectivity during the pervaporation process, but the trade-off is the total flux decline [50]. In addition to the hydrophobicity analysis, one can compare solubility parameters [(MPa)$^{1/2}$] of PDMS (8.10), PhTMS (9.00), butanol (11.00), and water (47.90) [51]. The affinity between two chemical species increases as deviation of two solubility parameters decreases. In terms of the solubility parameter difference, butanol is preferred by PhTMS to PDMS surfaces as the composite membranes effectively repel water molecules. Recently, a silica-filled poly[1-(trimethylsilyl)-1-propyne] (PTMSP) membrane was prepared for pervaporation for an ethanol/water mixture [52] and for aqueous ethanol and butanol mixtures [53]. Polyvinylidene fluoride (PVDF) was used to support the PTMSP active layer and the addition of hydrophobic silica particles enhanced the flux with the trade-off of the separation factor. The open, irregular, and hydrophobic surface structure of the PVDF support

contributed to the larger flux in comparison to commercial membranes. For pervaporation of butanol/water mixture, Claes et al. [53] obtained an excellent flux of 9.5 LMH and separation factor exceeding 100, showing promising performance of PTMSP/PVDF membranes for pervaporation. However, direct comparison is out of the scope of this study in terms of active polymer material and supporting layers. To the best of our knowledge, comparative analysis on PDMS and PhTMS membrane performance of butanol/water separation are still very rare. In our study, total flux and separation factor are much higher than the reported values. However, direct comparison is not possible since our purpose is butanol/water separation.

4. Conclusions

In this study, we prepared ceramic composite membranes with rubbery PDMS and glassy PhTMS coatings. The prepared composite membranes were used for butanol pervaporation, performance of which was tested in terms of butanol concentration, temperature, and flow rate of the feed butanol/water mixture. The water contact angle measurements indicate that the ceramic support is hydrophilic; and the glassy PhTMS coating provides the highest contact angle, followed by the rubbery PDMS layer. FE-SEM micro-image analysis showed that the formed ceramic support layer has a homogeneous porous structure, and the PDMS layer is stable when coated on the top of the support layer. XPS analysis verified the presence of a rigid phenyl on the surface of the PhTMS coated layer. Pervaporation

experiments indicated that the total flux, permeate butanol concentration, and separation factor increase with increasing feed butanol concentration, temperature, and feed flow rate. In general, the PhTMS membrane has lower total flux and higher selectivity (in terms of permeate butanol concentration and separation factor) due to enhanced hydrophobicity. The extrema of the separation factor with respect to the feed fraction is mathematically proved by calculating $d\alpha/dx$, and its presence at low feed fraction is explained by the condensing ceramic support. This paper showed the potential of a PhTMS-coated PDMS membrane to increase separation by taking advantage of the highly hydrophobic nature of PhTMS and the highly permeable property of PDMS to enhance butanol selectivity. The performance of pervaporation can be further enhanced by optimizing coating processes of PDMS and PhTMS layers on top of the ceramic support.

Acknowledgements

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