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Pervaporation of Organic Compounds from Aqueous Mixtures Using Polydimethylsiloxane-Containing Block Copolymer Membranes

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*Pervaporation of aqueous mixtures of ethanol, acetone, butanol, isobutanol, and furfural through polystyrene-*b*-polydimethylsiloxane-*b*-polystyrene (SDS) triblock copolymer membranes is reported. These mixtures are important for biofuel production from lignocellulosic feedstocks. Feedstock depolymerization results in the formation of furfural which must be removed before fermentation. Ethanol, butanol, isobutanol, and acetone are important fermentation biofuels. The membrane selectivity of SDS is about unity over a wide range of concentrations of aqueous ethanol mixtures, similar to the membrane selectivity of crosslinked polydimethylsiloxane (PDMS). The permeabilities of butanol, isobutanol, and furfural are larger than those of ethanol and acetone. The volatile organic compound permeability through SDS is similar to or higher than that through PDMS across a broad range of temperatures and feed concentrations is found. More selective and permeable membranes are needed to lower the cost of biofuel purification. The SDS membranes developed are but one step toward improved membranes.* © 2015 American Institute of Chemical Engineers *AICHE J*, 61: 2789–2794, 2015

Keywords: membrane materials, membrane separations, polymer properties, separation techniques

Introduction

Pervaporation is a membrane-based separation process in which a liquid feed mixture contacts one side of a membrane and a vacuum is applied to the opposite side. The pervaporative flux of a given species through a dense, nonporous membrane is driven by the resulting gradient in chemical potential. Volatile species are thermodynamically favored to permeate. The compounds in the liquid mixture permeate at different rates due to differences in membrane sorption, diffusion within the membrane, and thermodynamic driving forces.^{1,2}

Pervaporation is a particularly attractive method of separation for processes in biofuels production.³ In the production of biofuels from lignocellulose, cellulose and hemicellulose must be depolymerized to a product called hydrolysate, with sugars being a desirable end product.^{4–6} The reactions employed in depolymerization are complex and result in numerous side products, such as furfural.^{7,8} The sugars produced by depolymerization are converted by fermentation to useful fuel chemicals such as ethanol, butanol, isobutanol, and acetone.^{9–11} In fact, pervaporation can be useful in both the depolymerization

and fermentation processes. These volatile organic compounds (VOCs)—furfural, ethanol, butanol, isobutanol, and acetone—are inhibitory to fermentation. Furfural can be removed from hydrolysate by pervaporation. *In situ* pervaporation is a particularly attractive option for improving fermentation productivity, as it does not interfere with fermenting cells' activity, and has the potential to enable continuous biofuel production.^{12,13}

Traditional methods for removing VOCs, such as distillation, are not viable for *in situ* biofuel separation during fermentation due to harsh treatment conditions. Pervaporation is compatible with mild feed conditions—separation can be performed on a feed which is at pressures near 1 atm and temperatures near 35°C—a necessity when removing VOCs from a sensitive mixture such as a hydrolysate or fermentation broth.¹²

We performed pervaporation using a microphase separated polystyrene-block-polydimethylsiloxane-block-polystyrene (SDS) copolymer membrane. These membranes contain co-continuous polystyrene (PS) and polydimethylsiloxane (PDMS) domains. The PDMS domains are rubbery and have good permeation properties for VOCs.¹⁴ The PS domains are glassy and provide the membrane with structural integrity.¹⁵ We compare the efficacy of SDS membranes with modern VOC-selective pervaporation membranes based on crosslinked PDMS.

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This article is part of a series of investigations using block copolymers for separations in biofuels production. Previously, our group has reported on using SDS block copolymer membranes for the removal of inhibitors from lignocellulosic dilute-acid hydrolysate.¹⁶ We have also detailed the relationship between the segregation strength of SDS and other block copolymers on ethanol permeability in aqueous mixtures.¹⁷ We also have a manuscript in review which reports continuous clostridium fermentation with *in situ* pervaporation of acetone, butanol, and ethanol through SDS membranes.

Solution-Diffusion Pervaporation Model

The separation factor for an aqueous VOC pervaporation, β_{pervap} , is a measure of the enrichment of VOC species i in the permeate compared to water²

$$\beta_{\text{pervap}} = \frac{c_{ip}/c_{wp}}{c_{if}/c_{wf}} = \frac{J_i M_i / J_w M_w}{c_{if}/c_{wf}} \quad (1)$$

where c denotes concentration (g/L), M denotes molecular mass, subscript w denotes water, subscript p denotes permeate, and subscript f denotes feed. For example, c_{ip} denotes the concentration of species i found in the permeate. J_i denotes the molar flux of species i , which can be calculated according to Eq. 2

$$J_i = \frac{P_i}{t_i} (x_i \gamma_i p_i^{\text{sat}} - y_i p_p) = \frac{n_i}{A \Delta \tau} [=] \frac{\text{mol}}{\text{m}^2 \text{s}} \quad (2)$$

where P_i is the permeability of the membrane, t is the membrane thickness, x_i is the feed mole fraction, γ_i is the activity coefficient, p_i^{sat} is the saturated vapor pressure, y_i is the permeate mole fraction, and p_p is the total permeate pressure. In most experimental pervaporations, the product $y_i p_p$ is approximated to zero because of nearly zero permeate vacuum pressure. Experimentally, flux can be calculated by measuring the number of moles permeated n_i per membrane area A per time $\Delta \tau$. The permeabilities determined in our study were independent of feed flow rate (1.5–3 L/min) and membrane thickness (150–200 μm). This indicates that the membrane presents the only mass-transfer limitation to pervaporation. The assumption that the membrane presents the only mass-transfer limitation is implicit in Eq. 2. This assumption is typically valid for pervaporations with dense membranes >100 μm thick with high feed flow rates at low permeate pressures.

The separation factor for evaporation, β_{evap} , is a measure of the enrichment of species i compared to water due to evaporation alone. β_{evap} can be calculated with vapor-liquid equilibrium (VLE) parameters

$$\beta_{\text{evap}} = \frac{p_i/p_w}{x_i/x_w} = \frac{\gamma_i p_i^{\text{sat}}}{\gamma_w p_w^{\text{sat}}} \quad (3)$$

where p_i is the pressure of component i in the gas phase and p_w is the pressure of water in the gas phase. Aqueous binary activity coefficients, γ_i and γ_w , and saturation pressures, p_i^{sat} , were calculated from data and thermodynamic models compiled in Gmehling et al.¹⁸ and Fisher and Gmehling.¹⁹ Antoine equations listed in these references were used to calculate p_i^{sat} . Thermodynamic models—van Laar, nonrandom two-liquid, and Margules—provided by these references were used to calculate γ_i and γ_w . Because we studied dilute binary aqueous VOC mixtures, γ_w was typically calculated to be approximately unity. The separation factor of a pervaporation can be calculated in terms of its effectiveness compared to a simple evaporation

$$\beta_{\text{pervap}} = \alpha_{\text{mem}} \beta_{\text{evap}} = \frac{P_i}{P_w} \beta_{\text{evap}} \quad (4)$$

where P_w is the permeability of water. The membrane selectivity, α_{mem} , is a measure of the enrichment of species i compared to water due to permeation through the membrane alone. It is the truest measure of the selective effectiveness of a membrane.

Materials and Methods

An SDS block copolymer was synthesized by anionic polymerization as described by Ozcam et al.¹⁷ This polymer has a weight fraction of PDMS of 0.83 ($\phi_{\text{PDMS}} = 0.83$), a number-averaged molecular weight (Mn) of 117 kg/mol, and a polydispersity index of 1.06. This polymer exhibits a cylindrical morphology with PS cylinders arranged on a hexagonal lattice in a matrix of PDMS. The center to center distance between adjacent rows of PS cylinders is 42.7 nm.

Pervaporation was performed in a laboratory bench test unit built by Sulzer Chemtech, Germany and described previously.²⁰ A schematic is displayed in Figure 1. Two membranes could be tested simultaneously in parallel and each membrane had a surface area of 37 cm². The SDS membranes were held inside a circular cell designed for radial flow and restrained with an O-ring.

Two membranes were cast by melt pressing prior to each experiment. Membranes were approximately 160 μm thick, measured at 20 places with a micrometer caliper, and had 25 μm variance.

The temperature of the feed was measured in the piping before and after the membrane module and controlled with a heating jacket around the feed tank to within 1°C of the target temperature. The feed tank has a maximum capacity of approximately 2 L, and 2 L of feed were used whenever possible to minimize feed composition changes. A vacuum was applied using a Welch model 2014 vacuum pump on the permeate side of the membranes, and the permeate pressures were controlled with a valve but set at <2 mbar for all experiments.

All feeds were binary mixtures of one VOC in water. Ethanol (Koptec 190 proof), acetone (Sigma-Aldrich 99.5%), butanol (Sigma-Aldrich anhydrous 99.8%), isobutanol (Fisher Scientific 99.9%), and furfural (Sigma Aldrich 99%) were used as received. When making ethanol-water binary mixtures with standard wt %, we were careful to account for the water present in 190 proof ethanol.

Each time a feed composition or temperature was changed, 30 min were allotted to allow the membranes to reach steady state. After steady state was reached, a feed sample was taken. During the next 30 min to 2 h—depending on flux—a permeate sample from each of the two membranes was collected. The sample was collected by condensation in a cold trap cooled with liquid nitrogen or dry ice. The cold trap was exchanged for a new cold trap and another sample was taken 30 min to 2 h later. Permeate samples were weighed to determine the mass permeated through the membrane during the experiment. High performance liquid chromatography (HPLC), gas chromatography–mass spectrometry (GCMS), or nuclear magnetic resonance spectroscopy (NMR) were used to determine the concentration of the VOCs in the permeate, as described in Refs. 15, 17, and 21.

Results and Discussion

The flux of aqueous ethanol through SDS membranes was calculated by recording the time of pervaporation—typically

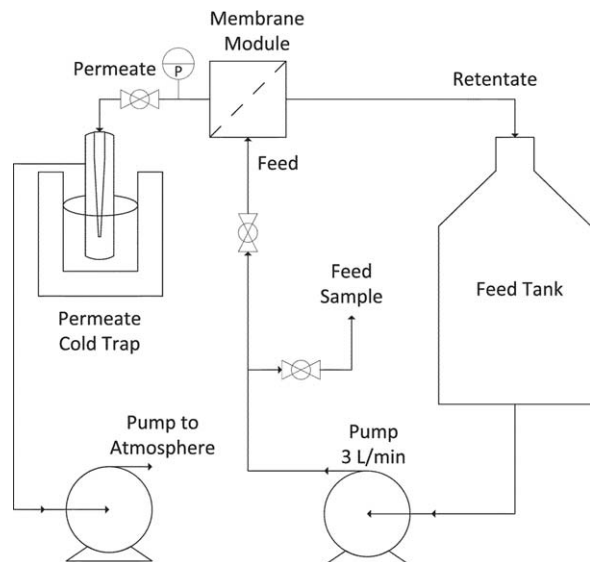


Figure 1. Schematic of the pervaporation apparatus.

Feed was pumped to a membrane module and retentate pumped back into the feed tank and mixed. The permeating species were collected in a cold trap under vacuum.

about an hour—recording the concentration of the feed and permeate, and applying Eq. 2. The data from two membranes used in parallel over two time points is displayed in Figure 2, with the relative standard deviation from these four data points. In Figure 2, the data are normalized to a standard membrane thickness of 50 μm , owing to the variability in thickness (150–200 μm) of the membranes tested. Not surprisingly, increasing temperature results in an increase in total flux through the membrane regardless of feed concentration. Ethanol flux is a strong function of feed concentration, increasing by more than an order of magnitude when

the concentration of ethanol in the feed is changed from 0.5 to 75 wt %. However, there appears to be a break in the trend at a feed concentration of 20 wt % (see Figure 2b). Flux increases rapidly as the feed concentration is increased from 0.5 to 20 wt %. The flux vs. feed concentration slope decreases significantly when the feed concentration exceeds 20 wt %. The trends are approximately linear in each of the two distinct regimes. In contrast, the water flux is independent of feed concentration (see Figure 2c). The chemical potentials of ethanol and water are known to be strong functions of composition. It is worth noting that changes in the driving force for permeation do not affect the flux of water through the membranes.

The permeabilities of ethanol and water were calculated from the data in Figure 2 using Eq. 2, and the results are shown in Figure 3. Ethanol permeability increases as the ethanol concentration in the feed is increased from 3 to 20 wt %. At 40°C, the permeability increases by a factor of about 2, while at 76°C, the permeability increases by a factor of only 1.2. For feed concentrations above 20 wt %, permeabilities at all temperatures are nearly independent of concentration (Figure 3). For example, at 40°C, the ethanol permeability at 75 wt % is only 10% higher than the permeability at 20 wt %. The two regimes identified in the flux data in Figures 2a, b are thus also seen in Figure 3a. Also shown in hollow blue circles in Figure 3a are literature data for crosslinked PDMS at 75°C.² The presence of crosslinks retards the diffusion of permeants in crosslinked PDMS. The presence of rigid and impermeable PS cylinders retards diffusion of permeants in SDS. The data in Figure 2a suggest that the retardation due to crosslinks is more significant than that due to the presence of PS microphases. The dependence of water permeability on feed concentration is shown in Figure 3b. Water permeability is not a sensitive function of feed concentration. Furthermore, water permeability through crosslinked PDMS at 75°C, shown in hollow blue circles, is comparable to that obtained in SDS

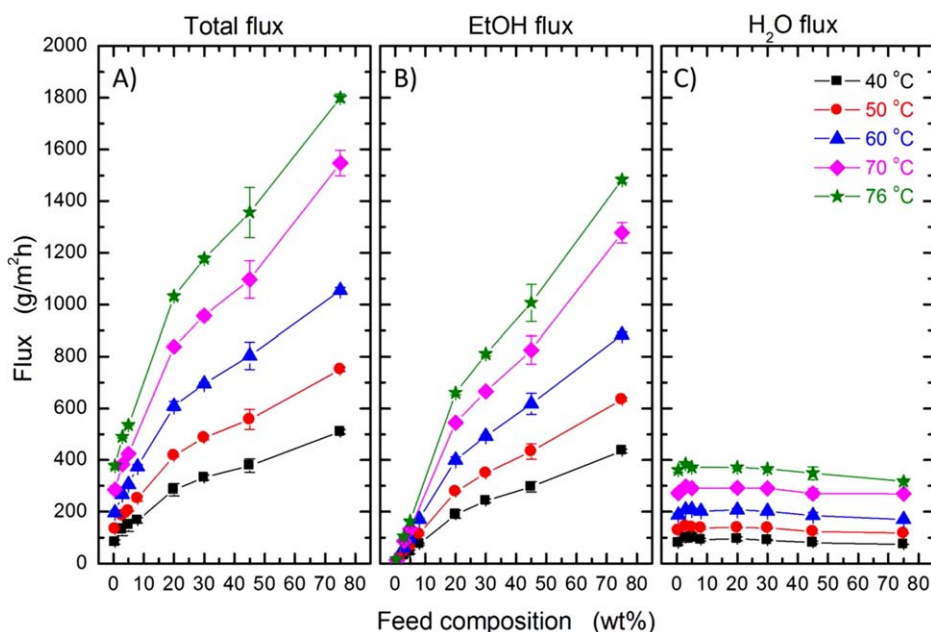


Figure 2. Total (A), ethanol (B), and water (C) fluxes as a function of ethanol feed concentration, 0.5–75 wt %, through SDS membranes at 40°C (■), 50°C (●), 60°C (▲), 70°C (◆), and 76°C (★).

Because the membranes tested had differences in thicknesses, the fluxes have been normalized to 50 μm thickness. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

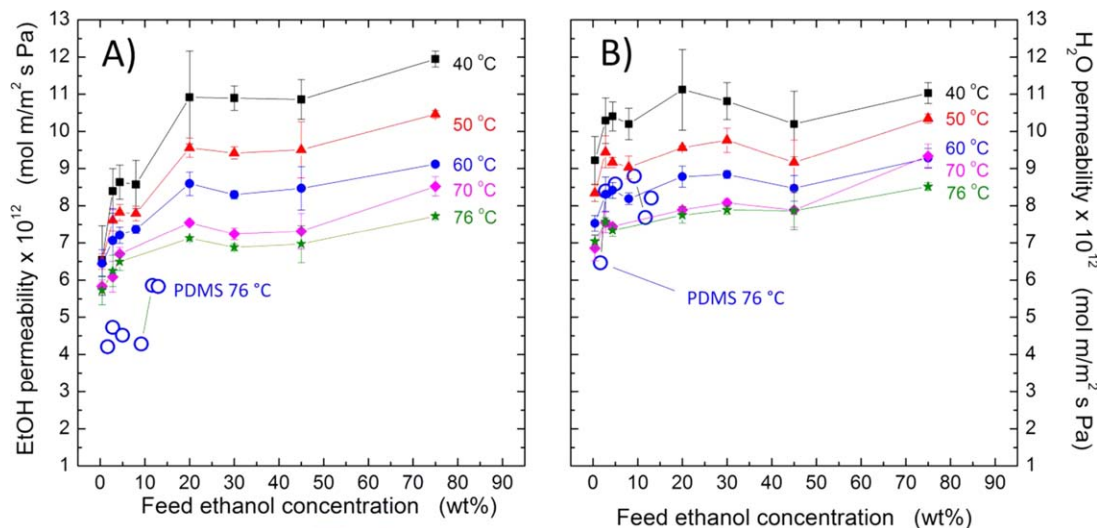


Figure 3. Ethanol (A) and water (B) permeability of SDS membranes as a function of ethanol feed concentration, 0.5–75 wt %, at temperatures 40°C (■), 50°C (●), 60°C (▲), 70°C (◆), and 76°C (★).

The hollow blue circles are data from crosslinked PDMS membranes found in Ref. 2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

membranes. It is perhaps surprising that the permeation of small molecules such as water and ethanol exhibit distinct behaviors in microphase separated block copolymers, as the length scale of the microphase separated structure (42.7 nm) is much larger than the size of the diffusants. Both water and ethanol permeabilities decrease with increasing temperature. Since diffusion coefficients must increase with increasing temperature, ethanol and water solubility in SDS must decrease with increasing temperature and more than offset the increase in diffusion.

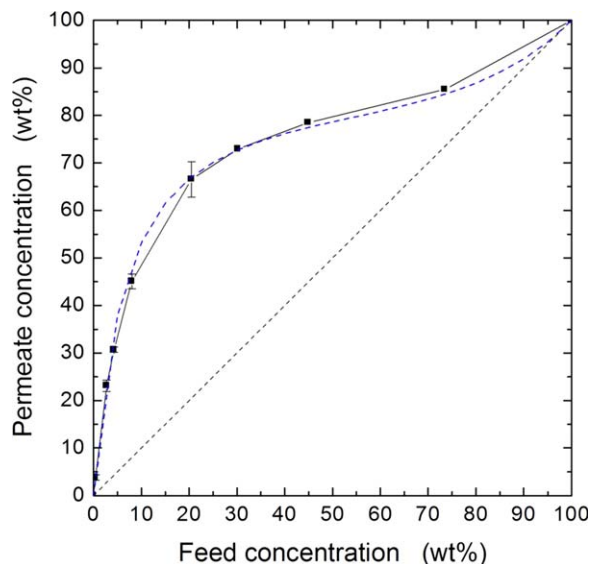


Figure 4. Ethanol concentration in the permeate as a function of ethanol feed concentration for SDS membrane at 40°C (■) and literature values for the vapor-liquid equilibrium (--) for binary aqueous ethanol at 40°C.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The measured dependence of permeate composition on feed concentration for pervaporation through SDS membranes at 40°C is shown in Figure 4. Note that the data in Figure 4 are related to the data in Figures 2 and 3 (see Eq. 2). Also shown in Figure 4 is the composition of the vapor phase at equilibrium with a liquid phase with the same composition as the feed at 40°C, that is, VLE data for aqueous ethanol.¹⁸ The close agreement between the pervaporation results and the VLE curve indicates that the α_{mem} is close to unity (see Eq. 4).

Table 1 reports pervaporation results in terms of permeability (P_i) and membrane selectivity (α_{mem}) of SDS and cross-linked PDMS membranes. Determining these parameters, however, requires accurate VLE modeling. Specifically, it requires accurate values of β_{evap} and partial pressure ($x_i\gamma_iP_i^{\text{sat}}$). We obtained $x_i\gamma_iP_i^{\text{sat}}$ and β_{evap} values from data compiled in Refs. 18 and 19. In most cases, this value was calculated using models such as the van Laar equation in conjunction with the Antoine equation. In other cases, the β_{evap} and $x_i\gamma_iP_i^{\text{sat}}$ values were calculated by direct interpolation of the data compiled in Gmehling et al.¹⁸ These β_{evap} values were typically calculated at two data points with wt % very near to those used in our study and linearly interpolated. In Table 1, we have used footnotes to cite the specific relevant data sets compiled by Gmehling et al.,¹⁸ and we have briefly described the procedures used to obtain each β_{evap} and $x_i\gamma_iP_i^{\text{sat}}$ value.

In Table 1, we report the efficacy of pervaporation as an approach for purifying several VOCs from aqueous mixtures. We compare data obtained from SDS membranes (this work) with literature values obtained from crosslinked PDMS membranes.^{2,22–27} We collected SDS pervaporation data for VOCs other than ethanol using the same procedure as described for ethanol pervaporation. The removal of VOCs from water by pervaporation with PDMS membrane has been widely reported in the literature. However, there are many VOCs, many feed concentrations, and many temperatures from which to choose, giving a large sample space. In Table 1, we choose to cite references with good experimental procedures using precisely the same VOCs, concentrations, and temperatures as our data for the truest feasible comparison. Table 1 includes

Table 1. Feed Conditions, Effectiveness of Separation, and Membrane Properties

	Temp (°C)	Material	Feed (wt %)	Perm (wt %)	β_{pervap}	β_{evap}	α_{mem}	$F_t \times 10^3$ (g m/m ² h)	$J_i M_i t \times 10^3$ (g m/m ² h)	$x_i \gamma_i P_i^{\text{sat}}$ (Pa)	$P_i \times 10^{12}$ (mol m/m ² Pa s)
Ethanol	40	SDS	5	31	8.5	9.4 ^a	0.91	6.4	2.0	1400 ^a	8.6
Ethanol	40	PDMS ²²	5	35	10.2	9.4 ^a	1.08	6.1	2.1	1400 ^a	9.2
Ethanol	50	SDS	5	32	8.9	9.9 ^b	0.90	10.2	3.2	2460 ^b	7.8
Ethanol	50	PDMS ²²	5	35	10.2	9.9 ^b	1.05	8.5	3.0	2460 ^b	7.4
Ethanol	76	SDS	5	32	8.8	10.3 ^c	0.87	27	8.5	8460 ^c	6.5
Ethanol	75	PDMS ²	5	27	6.0	10.2 ^c	0.57	25	7.0	8810 ^c	4.5
Ethanol	76	SDS	3	22	9.0	10.7 ^c	0.83	25	5.4	5270 ^c	6.3
Ethanol	75	PDMS ²	3	20	7.9	10.6 ^c	0.56	23	4.5	5490 ^c	4.7
Acetone	50	SDS	2	42	36	49 ^d	0.73	12.5	5.3	3760 ^d	6.7
Acetone	50	PDMS ²³	2	46	42	49 ^d	0.85	NR	NR	3760 ^d	NR
Butanol	50	SDS	1	33	49	26 ^e	1.87	10.5	3.5	786 ^e	16.5
Butanol	50	PDMS ²⁵	1	37	58	26 ^e	2.23	3.5	1.3	786 ^e	6.2
Isobutanol	50	SDS	1	32	47	36 ^f	1.29	11.5	3.7	1090 ^f	12.7
Isobutanol	50	PDMS ²⁵	1	29	40	36 ^f	1.10	3.65	1.05	1090 ^f	3.6
Furfural	50	SDS	2	44	39	8.6 ^g	4.5	15.3	6.7	406 ^g	47
Furfural	50	PDMS ²⁷	2	55	60	8.6 ^g	6.9	NR	NR	406 ^g	NR

NR—Data not reported (no membrane thickness measured).

^aReference 28, at 40°C. β_{evap} and $x_i \gamma_i P_i^{\text{sat}}$ calculated by Van Laar equations $A_i = 1.4441$, $A_w = 0.9503$.

^bReference 28, at 50°C. β_{evap} and $x_i \gamma_i P_i^{\text{sat}}$ calculated by Van Laar equations $A_i = 1.5176$, $A_w = 0.9576$.

^cReference 29, at 50,700 Pa (~76°C). β_{evap} and $x_i \gamma_i P_i^{\text{sat}}$ calculated by Margules equations $A_i = 1.5871$, $A_w = 0.7941$.

^dReference 30, at 45°C. β_{evap} and $x_i \gamma_i P_i^{\text{sat}}$ calculated by NRTL equations. $A_{i,w} = 917.39$ cal/mol, $A_{w,i} = 910.96$ cal/mol, $\alpha = 0.5916$.

^eReference 19, 50°C. β_{evap} and $x_i \gamma_i P_i^{\text{sat}}$ calculated by NRTL equations. $A_{i,w} = 465.53$ cal/mol, $A_{w,i} = 2451.5$ cal/mol, $\alpha = 0.387$.

^fReference 19, 50°C. β_{evap} and $x_i \gamma_i P_i^{\text{sat}}$ calculated by NRTL equations. $A_{i,w} = 525$ cal/mol, $A_{w,i} = 2334.3$ cal/mol, $\alpha = 0.3931$.

^gReference 31. Data at 7300 Pa (~40.7°C) and 20,000 Pa (~59.7°C) linearly interpolated to 50°C to calculate β_{evap} . From Eq. 3, we calculated $x_i \gamma_i P_i^{\text{sat}}$ assuming $\gamma_w = 1$.

columns for the thickness-normalized total pervaporative flux (F_t) and the thickness-normalized pervaporative flux of the VOC component ($J_i M_i t$). The calculation of F_t is accomplished using only measured parameters—permeate weight, membrane area, membrane thickness, and time. Thus, F_t is often reported or easily calculated. By measuring the permeate VOC concentration, the VOC flux $J_i M_i t$ can be calculated similarly.

Values of F_t and $J_i M_i t$ of aqueous VOC mixtures through SDS vary significantly from one another. The permeability values, P_i , do not vary as significantly from one another because they account for VLE properties. It is interesting to note that α_{mem} for SDS membranes is in the vicinity of unity for ethanol (all temperatures and feed compositions) and acetone. Significantly higher values are obtained for the more hydrophobic VOCs, isobutanol, butanol, and furfural (1.29, 1.87, and 4.5). The permeability of butanol through both SDS and PDMS membranes is significantly higher than that of isobutanol. In most cases, the permeability of VOCs through SDS membranes is larger than that through PDMS membranes, despite the fact that the SDS membranes contain impermeable PS domains. We attribute the higher permeability in SDS membranes to the absence of crosslinks that presumably impede the diffusion of VOCs.

Conclusion

We have completed a comprehensive study of pervaporation of a wide variety of aqueous VOC mixtures through a polystyrene-*b*-PDMS-*b*-polystyrene (SDS) triblock copolymer membrane. The dependence of permeate concentration on feed concentration in the case of ethanol/water mixtures closely follows the VLE curve, indicating that membrane selectivity of SDS membranes is independent of feed concentration. The other VOCs were studied at fixed feed compositions. The permeabilities of larger, more hydrophobic molecules such as butanol, isobutanol, and furfural are larger

than those of smaller, more hydrophobic molecules such as ethanol and acetone. This suggests that permeability is dominated by solubility differences. If differences in diffusion coefficients were dominant, the permeability of smaller molecules would be higher. Our results suggest that SDS membranes present a versatile platform for removing a variety of VOCs from aqueous mixtures. Further efforts to explore the molecular underpinnings of our observations seem warranted.

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