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Pervaporation of oleyl alcohol-modified PDMS membranes: a comparison between the apparent and intrinsic performances for organics + water mixtures

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ABSTRACT

Pervaporation is a promising technology for the removal and recovery of phenol and butanol, which are value-added contaminant from water. The membrane material used in the pervaporation is the key for effective performance. In this study, polydimethylsiloxane (PDMS) and oleyl alcohol (OA)-modified PDMS membranes were prepared by blending and were characterized by X-ray photoelectron spectroscopy (XPS) and swelling experiment. Their effectiveness for the separation of phenol/butanol from water by pervaporation process was evaluated based on apparent and intrinsic separation performances. The result of XPS confirmed a physical blending between PDMS and OA. The addition of OA into PDMS membrane increased the apparent and intrinsic separation performances for phenol + water and butanol + water systems. For PDMS membranes with 5 wt% OA loading, the butanol and phenol fluxes were 69.11 and 10.34 g m^{-2} h^{-1} for 1 wt% butanol and 0.5 wt% phenol solution at 70°C, respectively. This was 43% higher than the unmodified PDMS and due to the affinity of OA to organics. The intrinsic selectivity of membrane to phenol and permeance of phenol were significantly higher than apparent separation factor and phenol flux, which is because the driving force for phenol across membrane was low. With increasing temperature, flux increased. Separation factor for butanol decreased while that for phenol increased, which is related to estimated activation energy. OA-modified PDMS membranes showed a good operation stability at 40°C and are potentially good separation membrane material for organic + water mixtures.

Keywords: Pervaporation; PDMS; Membrane separation

1. Introduction

Most organic compounds are important industrial raw materials, and are potential contaminants in the aquatic environments. Thus, the removal and recovery of organics from water have economic and environmental benefits. Phenol and butanol are two such organics with aromatic ring and alkane structure. Phenol is poisonous to human and valuable in industry [1], while butanol is the second-generation biofuel and should be separated immediately from acetone–butanol–ethanol fermentation system to improve the conversion efficiency [2]. Though adsorption and extraction are considered as effective conventional methods to remove organics from water, they also introduce the additional components.

Pervaporation is a promising physical separation method that is especially suitable for the recovery of organics in water [3]. It is clean and efficient, consumes less energy, and its operation is simple without additional additives. The pervaporation separation of butanol or phenol from water has gained increased research attention recently, and several

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new materials have been introduced for pervaporation separation.

Besides, the evaluation parameters have also been developed. The characterization of membrane separation properties in the pervaporation field has been extended to intrinsic properties such as permeance (or permeability) and selectivity in addition to apparent performances such as flux and separation factor [4,5].

Polydimethylsiloxane (PDMS) has been widely used for pervaporation separation of butanol from water [6,7]. Rozicka [8] investigated pervaporation performances of three commercial PDMS membranes for separating acetone, butanol and ethanol from water, and found that apparent performance for acetone was the most effective with the highest selectivity. However, these membranes became selective towards butanol and nonselective or water selective for acetone–water and ethanol–water mixtures after decoupling the driving force, that is, partial pressure for small molecules across membranes. Wijmans [4] found that PDMS was intrinsically hydrophilic; hence, the good apparent performances of PDMS to ethanol was mainly due to higher driving force for ethanol than water due to large pressure difference across membranes for the former. Consequently, the real affinity of membranes to solvents could be masked by apparent separation performances. Thus, it is important for comparative analysis of the apparent and intrinsic performances of membranes.

PDMS is an inert material without many active groups. Therefore, most PDMS modifications depend on physically blending PDMS with an additional component instead of chemical modification, for example, zeolite is generally added to improve the separation performances [9–12]. However, zeolite particles can precipitate in membrane solution and cause clogging, which requires surface modification of zeolite. Zeolite modified with a coupling agent can increase butanol permeability and selectivity of PDMS to a certain extent [9,11], although the modification process generally prolongs the PDMS membrane preparation. Therefore, novel filler and polymer matrix have been developed, for example, Yin et al. [13] added ZIF-71 to PDMS membrane and found that ZIF-71 could increase butanol intrinsic permeability and selectivity. Similarly, Borisov et al. [14] prepared novel poly[1-(trimethylsilyl)-1-propyne]-based membranes containing elastomeric fillers with increased selectivity. Further, Gao et al. [15] used polymer with intrinsic microporosity for the separation of butanol from water, and obtained high flux. However, PDMS without any modification is one of the most widely used membrane materials for pervaporation separation of butanol from water.

Many studies have investigated the pervaporation separation of butanol from water, and only limited number of studies have focused on that of phenol from water. For example, PDMS [16–19], polyether block amide (PEBA) [3,20,21], and polyurethane (PU) [22–25] have been used in phenol pervaporative recovery from water, though the selectivity of PDMS for phenol unsatisfactory despite being the most commercially used membrane material [26]. In contrast, PEBA exhibited excellent permeability and selectivity for phenol in previous studies, although it is not commercially available [26]. Similarly, despite showing a high separation factor of over 1,000 for separating phenol from water, flux of PU is low at 10 g m^{-2} h^{-1} [23,27]. Consequently, membranes were modified to increase the permeability and selectivity of membranes, for example, β-cyclodextrin [28] and β-cyclodextrin-modified ZSM-5 [29] were introduced into PU membranes, resulting in increased flux and separation factor. Ding et al. [3] incorporated ZIF-8 into PEBA membranes, which showed higher flux and separation factor than the unmodified one. Modified PDMS membranes are less used in the recovery of phenol from water, because its application in butanol–water separation seems to be more promising. Additionally, the intrinsic separation performances including permeability and selectivity have not been investigated in detail.

In summary, PDMS is a promising medium for pervaporation separation of butanol or phenol from water at industrial scale. However, effective modification of PDMS is necessary to increase its performance. A potential PDMS modification method could be the addition of some organic modifier that can dissolve in membrane solution, although only limited studies have focused on the membranes modified by organic modifier. For example, Das and Ray [30] blended organic modifier dioctyl phthalate with polyvinyl chloride (PVC) membranes and used the modified PVC membranes to separate tetrahydrofuran from water. They found that the plasticized PVC membranes showed significantly higher flux than the original one. Uragami et al. [31,32] reported that the modified PDMS membranes containing ionic liquid showed increased selectivity and permeability of benzene. Oleyl alcohol (OA), which is an unbranched-chain aliphatic alcohol with a double bond in alkyl chain, is reported as a good extractant of butanol [33,34] with good stability and low volatility. Due to the electron interaction between double bond and benzene ring, OA is expected to have good affinity for phenol. Thus, OA is used to modify PDMS in this study.

The aims of this study were to characterize PDMS membranes modified using different OA loading and to investigate their pervaporation properties along with the apparent and intrinsic performances.

2. Materials and methods

2.1. Materials

Hydroxyl-terminated PDMS (kinetic viscosity = 20,000 mPa s) was purchased from Juchengzhaoye Co. Ltd. (Guangzhou, China). Phenol (analytical reagent), *n*-butanol (analytical reagent), tetraethoxysilane (TEOS, analytical reagent) as a cross-linking agent, *n*-heptane (analytical reagent) as a solvent, and the catalyst dibutyltin dilaurate (DBTL, analytical reagent) were obtained from Guangfu Fine Chemical Research Institute (Tianjin, China). OA (80%–85%) was purchased from Alfa Aesar (Beijing, China), while polyether sulfone (PES) ultrafiltration membrane (non-woven fabrics supported) was purchased from Pureach Tech Co. Ltd. (Beijing, China). All reagents were used as received without further treatment.

2.2. Membrane preparation

The PDMS membrane was prepared by a casting/solvent evaporation process as described in our previous work [29]. PDMS was dissolved in *n*-heptane by magnetic stirring at 30°C for 20 min. Then, the cross-linking agent TEOS and the catalyst DBTL were added into PDMS/*n*-heptane solution at a mass ratio of 33:60:5:2 (PDMS: *n*-heptane: TEOS: DBTL). The mixture was stirred for another 15 min to react before adding oleyl alcohol with further stirring for 25 min. Finally, the membrane solution was uniformly cast on the PES ultrafiltration membrane. Then, the membrane was kept at room temperature for 10 h for cross-linking reaction, and was dried in a vacuum drying oven at 80°C for 12 h to evaporate the solvent and to promote further cross-linking reaction. The blank PDMS membrane was prepared in similar way, though without adding OA in PDMS. The dense PDMS layers had an average thickness of 250 μm. The molecular structures of PDMS and OA are shown in Fig. 1. PDMS-x% was used to designate PDMS membranes with x% indicating OA loading. x% was maintained at less than 9% because higher loading can induce bleeding of OA on membrane surface.

2.3. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was used to characterize the elemental composition of the membranes using a PHI5000 Versa Probe II instrument (ULVAC-PHI Inc. Japan).

2.4. Swelling experiments

Samples of the membranes were first placed in a vacuum drying oven for 24 h at 60°C, and weighed after the mass remained constant (m_0). Then, they were soaked in 0.5 wt% phenol aqueous solution (or 1 wt% butanol aqueous solution) until the swelling equilibrium was achieved at room temperature. Finally, the samples were taken out and weighed again (m_w), and absorbed liquid was cleaned by a filter paper. Swelling degree (SD) was defined by the following equation:

$$\mathrm{SD} = \frac{m_w - m_0}{m_0} 100\% \tag{1}$$

2.5. Pervaporation experiments

The pervaporation performances of the membranes for phenol (0.5 wt%) or butanol (1 wt%) in aqueous solution were tested using an apparatus obtained from Tiandabeiyang Co. Ltd. (China). The feed was heated and circulated from the feed tank with a volume of 1.5 × 10^{-3} m^3 through the upstream of the membrane cell using a pump with adjustable flow rate.

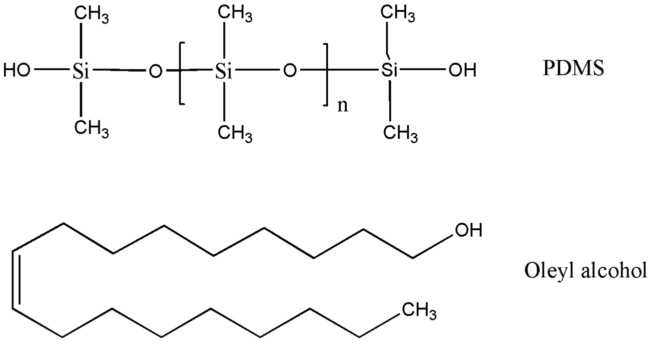

Fig. 1. Chemical structures of PDMS and oleyl alcohol.

A membrane supported by a porous sintered stainless steel at the permeate side was mounted in the pervaporation cell. The feed mixture was maintained at a temperature between 40°C and 70°C using a thermostat. The effective area of the membrane was 2.2 × 10^{-3} m^2. Vacuum on the permeate side was maintained below 200 Pa. Two cold traps were set in parallel allowing the collection of permeate without rupture of the vacuum. The concentrations of permeate and feed mixture were analyzed using the gas chromatograph (GC1120 type, Sunny Optical Technology Company Limited, China) with thermal conductivity detector and the packed column (OV-17, 3 m × 3 mm). When the permeate formed two phases, deionized water was added to dilute the permeate to a transparent solution, which was injected into gas chromatograph. The downstream pipe was wrapped with electrically heated coil to maintain the temperature above 70°C to avoid solidification of phenol on the pipe wall.

The flux (J, g m^{-2} h^{-1}) is defined in Eq. (2) and the partial flux was determined using Eq. (3):

$$J = \frac{Q}{A \times t} \tag{2}$$

$$J_i = J \times C_i \tag{3}$$

where Q (g) is the total mass of permeate collected through the effective area of membrane (A, m^2) during time t (h), C_i is the weight percent of component i at the permeate side.

The separation factor (β) was calculated using Eq. (4) as follows:

$$\beta = \frac{y_{w,i} / y_{w,j}}{x_{w,i} / x_{w,j}} \tag{4}$$

where $y_{w,i}$ and $y_{w,j}$ represent the weight fractions of phenol (or butanol) and water in the downstream permeate, while $x_{w,i}$ and $x_{w,j}$ represent those in the feed mixture, respectively.

Pervaporation separation index (PSI) was defined to evaluate the separation performances of membranes based on both permeation and selectivity, according to Eq. (5) [35]:

$$\mathrm{PSI} = \mathrm{J} \times (\beta - 1) \tag{5}$$

For each composition of membrane, duplicate membrane samples were taken, and at least two samples were analyzed for each feed temperature in triplicates. Their respective average values were used in the analysis.

The permeance was defined according to Eq. (6) to differentiate the effect of driving force and compare the intrinsic properties of different membranes [36].

$$\bar{\mathrm{P}}\mathrm{i} = \frac{Pi}{l} = \frac{J_i}{x_{n,i}\gamma_i p_i^{\mathrm{sat}} - y_{n,i}p^p} \tag{6}$$

where $\bar{\mathrm{P}}\mathrm{i}$ is the permeance used for an anisotropic membrane with an unknown thickness of the dense selective layer, *Pi* is the membrane permeability of the component *i*, *l* is the membrane thickness, $x_{n,i}$ and $y_{n,i}$ are the mole fractions of the component *i* in the feed and permeate, respectively, γ_i is the activity coefficient, p_i^{sat} is the saturated vapor pressure, and p^p is the permeate pressure. p_i^{sat} and γ_i were calculated from ASPEN ONE 7.2.

The partial vapor pressure of each component at the feed side can be expressed in terms of fugacity (f_i) (Eq. (7)). The driving force of component *i* to transport through the membrane was calculated as the difference of its partial vapor pressures at the feed side and permeate side (Eq. (8)). f_i represented driving force of component *i* since the pressure at the permeate side ($y_{n,i}p^p$) was negligible due to the use of vacuum pump.

$$f_i = x_{n,i}\gamma_i p_i^{sat} \tag{7}$$

$$\text{Driving force} = x_{n,i}\gamma_i p_i^{sat} - y_{n,i}p^p \tag{8}$$

Based on the above definition, the intrinsic selectivity was defined as Eq. (9):

$$\alpha = \frac{\overline{\mathrm{P}}\mathrm{i}}{\overline{\mathrm{P}}\mathrm{j}} \tag{9}$$

3. Results and discussion

3.1. XPS characterization

XPS was used to investigate the physical or chemical interaction between OA and PDMS matrix. As shown in Fig. 2, PDMS and 9% OA-modified PDMS show a similar single peak, suggesting that –OH in OA did not react with TEOS. Thus, blending for OA and PDMS was through physical interaction rather than chemical reaction. Because C–OH in OA did not react with Si–O–Et in TEOS, Si–OH in PDMS was easily cross-linked by TEOS.

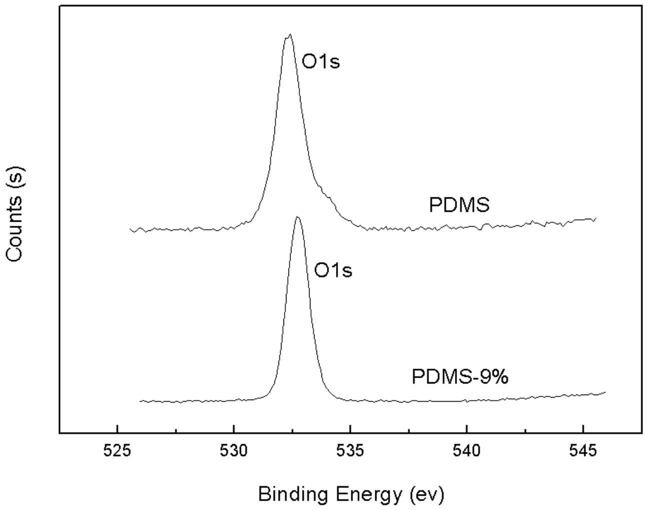

Fig. 2. XPS spectra of PDMS and modified PDMS membranes.

3.2. Swelling properties of membranes

PDMS membranes had diverse sorption characteristics in different solvents (Fig. 3). The membranes had the highest swelling in pure *n*-butanol, followed by 0.5 wt% phenol and 1 wt% butanol feed solution and water. The swelling degree of sample in pure phenol was not tested, because phenol is solid at room temperature. The swelling occurs due to the affinity between polymer and liquid, which can be estimated based on the solubility parameters (δ) [37]. The less difference of δ between PDMS and solvents indicates more affinity and sorption of small molecules to membrane. The solubility parameters of PDMS and OA are 14.9 and 16.4 $J^{1/2}$ $cm^{-3/2}$, while those of phenol, water and *n*-butanol are 29.7, 47.9 and 23.3 $J^{1/2}$ $cm^{-3/2}$, respectively. This explains the swelling trend presented in Fig. 2. Phenol feed solution shows higher swelling than butanol feed solution since phenol size is larger than butanol size (Table 1), resulting in enlargement of the interspace between polymer chains more than water.

1 wt% OA loading restricts the swelling to a certain extent, while higher loading increases it gradually. δ of OA is closer to that of phenol and butanol than PDMS. Higher affinity of OA to solvents can induce higher swelling, though it was not observed under 1% loading due to inflexible OA chain compared with PDMS (Fig. 1). In addition, the plasticization effect of OA was not obvious under low OA content.

3.3. Effects of OA on the apparent and intrinsic pervaporation performances

Apparent separation performances such as partial flux and separation factor are important in industrial application. As evident in Figs. 4(a) and (c), separation factor for both systems was enhanced gradually with increasing OA loading, and this trend was due to the variation of phenol/butanol and water as shown in Figs. 4(b) and (d). Addition of hydrophobic OA impedes the permeation of water, leading to significant reduction in water. In contrast, water flux in phenol + water system was higher than that in butanol + water system due to more swelling of phenol in feed solution

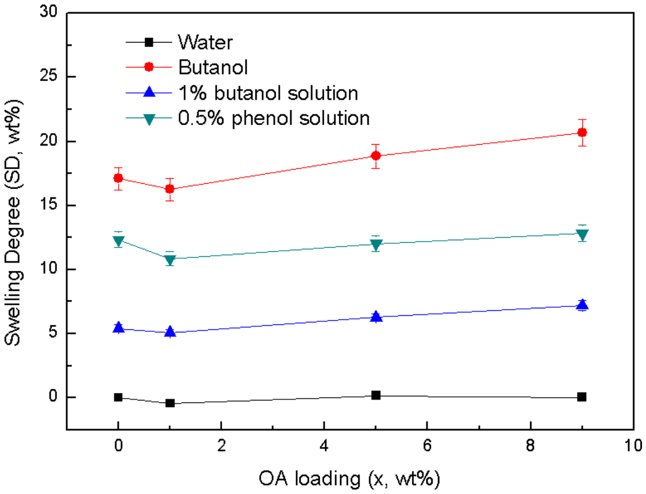

Fig. 3. Swelling degree for PDMS and modified PDMS membranes under different OA loading.

(Fig. 3). The flux of butanol or phenol reached the maximum at 5% loading depending on the facilitating effect of OA. The butanol and phenol fluxes of PDMS-5% were 69.11 and 10.34 g m^{-2} h^{-1}, respectively, which is 43% higher than that of unmodified PDMS. Similarly, water fluxes from butanol + water and phenol + water system decreased by about 30% compared with unmodified PDMS. When OA loading was above 5%, the organics fluxes slightly decreased due to the OA resistance, leading to further reduction in water flux.

Most previous studies on pervaporation compared the different membranes using the apparent performances. However, the investigation of intrinsic performances is also critical for better understanding of the OA roles. Wijmans [4] first suggested that the investigation on pervaporation should decouple the apparent performances from driving force according to Eq. (8) since it can clarify the effect of membrane properties and operating conditions on the overall separation performance and can facilitate the comparison of data. As such, several studies have focused on understanding transport properties of membranes in pervaporation using the intrinsic properties.

Generally, the permeate pressure ($y_{n,i}p^p$) in Eq. (8) for the downstream side is negligible [30,42,43]. Nevertheless, $y_{n,i}p^p$ has significant effect on driving force when fugacity and permeate pressure in Eq. (8) are comparable [19], similar to the scenario in this study, where the low feed concentration was used. Consequently, $y_{n,i}p^p$ was not neglected in the calculation.

Table 1
Physicochemical properties of chemicals used in this study

Materials	Molecular weight (g mol^{-1})	Boiling point (°C)	Solubility parameter (δ) (J$^{1/2}$ cm$^{-3/2}$)[a]	Kinetic diameter (Å)
Phenol	94.11	181.7	29.7	5.1 [38]
Water	18.01	100.0	47.9	2.6 [39]
n-Butanol	74.12	117.7	23.3	5 [40]

[a] Data of solubility parameters are estimated by group contribution method [41].

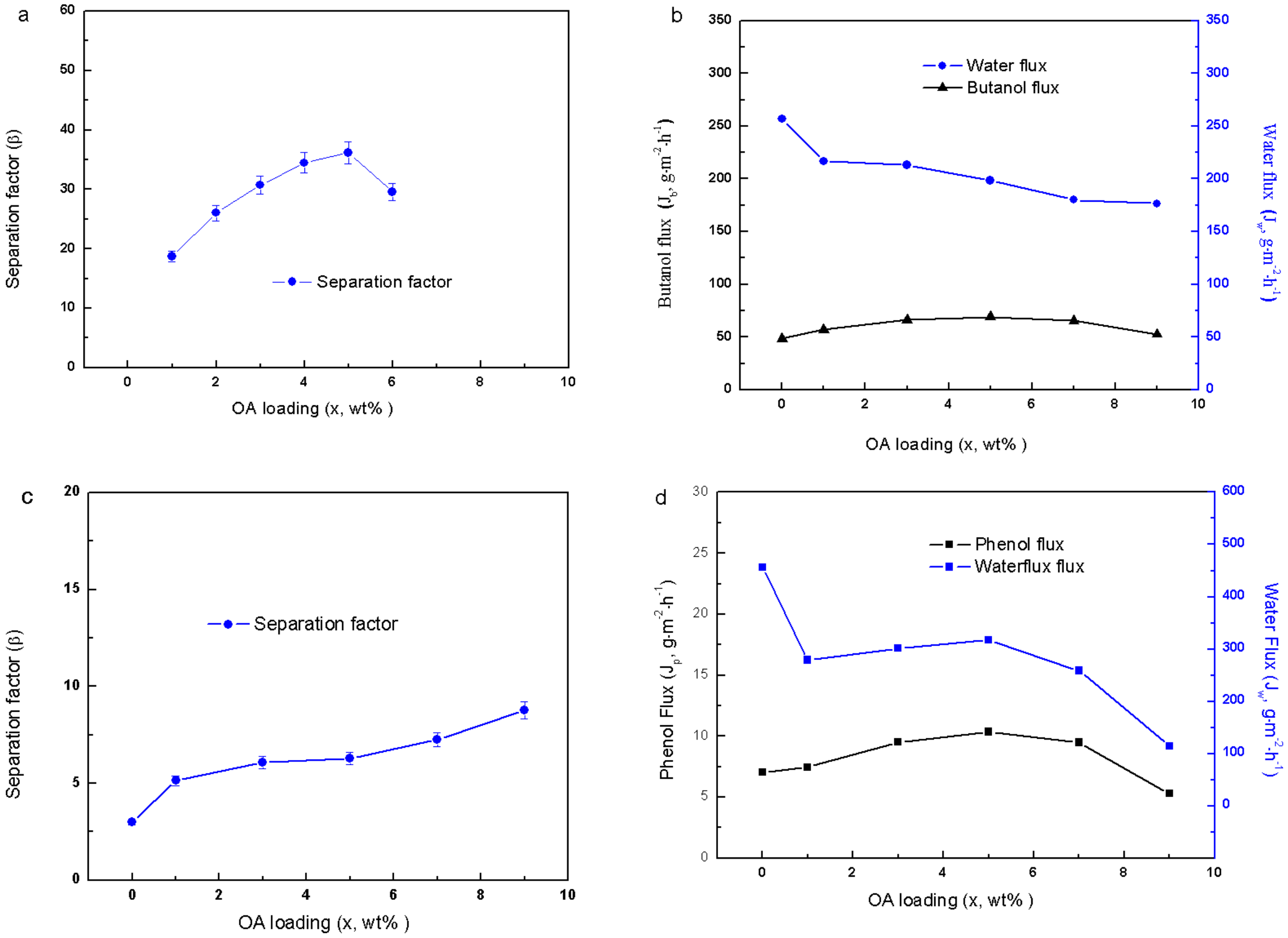

Fig. 4. Effects of OA on apparent pervaporation performances at 70°C: (a) and (b) for butanol (1%) + water system; (c) and (d) for phenol (0.5%) + water system.

Fig. 5 presents the curves for permeance and selectivity based on the macroscopic separation performances in Fig. 4. Since the membranes were tested under the same feed concentration and temperature, fugacity in Eq. (7) was constant, and the permeate pressure $y_{n,i}p^p$ had less effect on the driving force, leading to driving force having almost no dependency on OA loading. As a result, the permeance variation for each solvent molecule shown in Figs. 5(a) and (b) was similar to its corresponding partial flux shown in Figs. 4(b) and (d). Phenol and butanol had significantly different driving force, arising from the diverse products from Eq. (7).

Table 2 lists the permeation parameters of the species. As evident in Table 2, phenol had especially low molar fraction and vapor pressure, which generates significantly lower phenol fugacity than butanol and water. Furthermore, $y_{n,i}p^p$ had limited effect on driving force, because p^p was about 0.1–0.2 kPa in this study. Thus, the driving force of phenol was significantly low, inducing over five times higher phenol permeance compared with water permeance. Similarly, butanol also showed significantly higher permeance than water. It is worthy to note that the diffusion of water mainly depended on driving force across the membrane according to the apparent flux data.

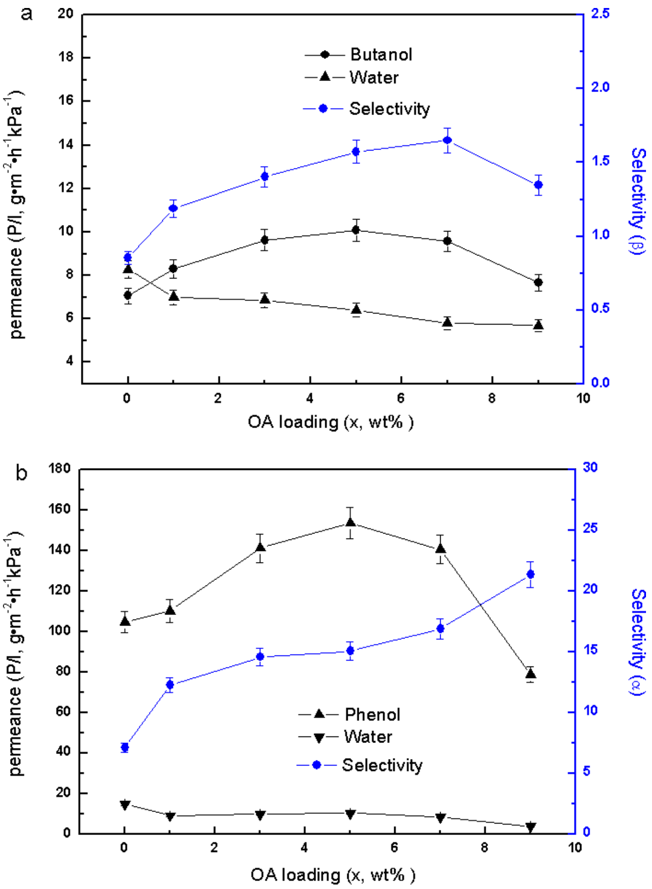

Fig. 5. Effects of OA on intrinsic pervaporation performances at 70°C: (a) for butanol (1%) + water system; (b) for phenol (0.5%) + water system.

In addition, the apparent separation factor over estimates the selectivity of membranes to butanol and minimizes that to phenol. As evident in Fig. 5(a), pure PDMS is water selective in nature with selectivity of 0.85, indicating that the separation efficiency of PDMS is worse than the simple liquid–vapor phase equilibrium without membranes. OA increased selectivity to 1.64 depending on its hydrophobicity (Fig. 5(a)), while the corresponding separation factor was 30 (Fig. 4(a)). For phenol + water system, the separation factor ranged from 3.00 to 8.78, while intrinsic selectivity varied from 7.10 to 21.33, suggesting that PDMS and OA are potentially good separation membrane material and modifier for phenol, respectively. In current research studies, most pervaporation membranes for separating alcohols from water are evaluated based on apparent performances. If the intrinsic separation properties are considered, it may be possible to conduct comprehensive evaluation about the separation performance. Furthermore, the process design and selection could be rearranged according to the intrinsic characteristics of solvents in membranes.

3.4. Effects of temperature on the apparent and intrinsic pervaporation performances

Feed temperature has an influence on the apparent and intrinsic separation properties since it significantly affects the molecular movement and driving force. The apparent performances of unmodified PDMS and PDMS-5% as a function of temperature are shown in Fig. 6. Most studies reported that fluxes have a positive dependence on feed temperature [44–47] due to increased thermal motion of small molecules and polymer, along with the increase of driving force across the membranes. It is important to note the non-Arrhenius relationship in the water flux variation (Fig. 6(d)). The increasing degree of flux tends to decrease. With increasing temperature, the OA droplet expanded its volume, which induced that the gap at the interface between PDMS and OA narrowed and eliminated in some cases. Thus,

Table 2
Permeation parameters of solvents at 70°C

Materials	Weight fraction in feed (wt%)	Molar fraction in feed (mol%)	Activity coefficient	Saturated vapor pressure (kPa)	Feed fugacity (kPa)
Phenol	0.5	0.01	61.220	1.147	0.068
Water[a]	99.5	99.99	1.001	31.164	31.179
n-Butanol	1.0	0.24	210.752	13.314	6.872
Water[b]	99.0	99.76	1.001	31.164	31.132

[a] Water in phenolic feed solution.
[b] Water in butanol feed solution.

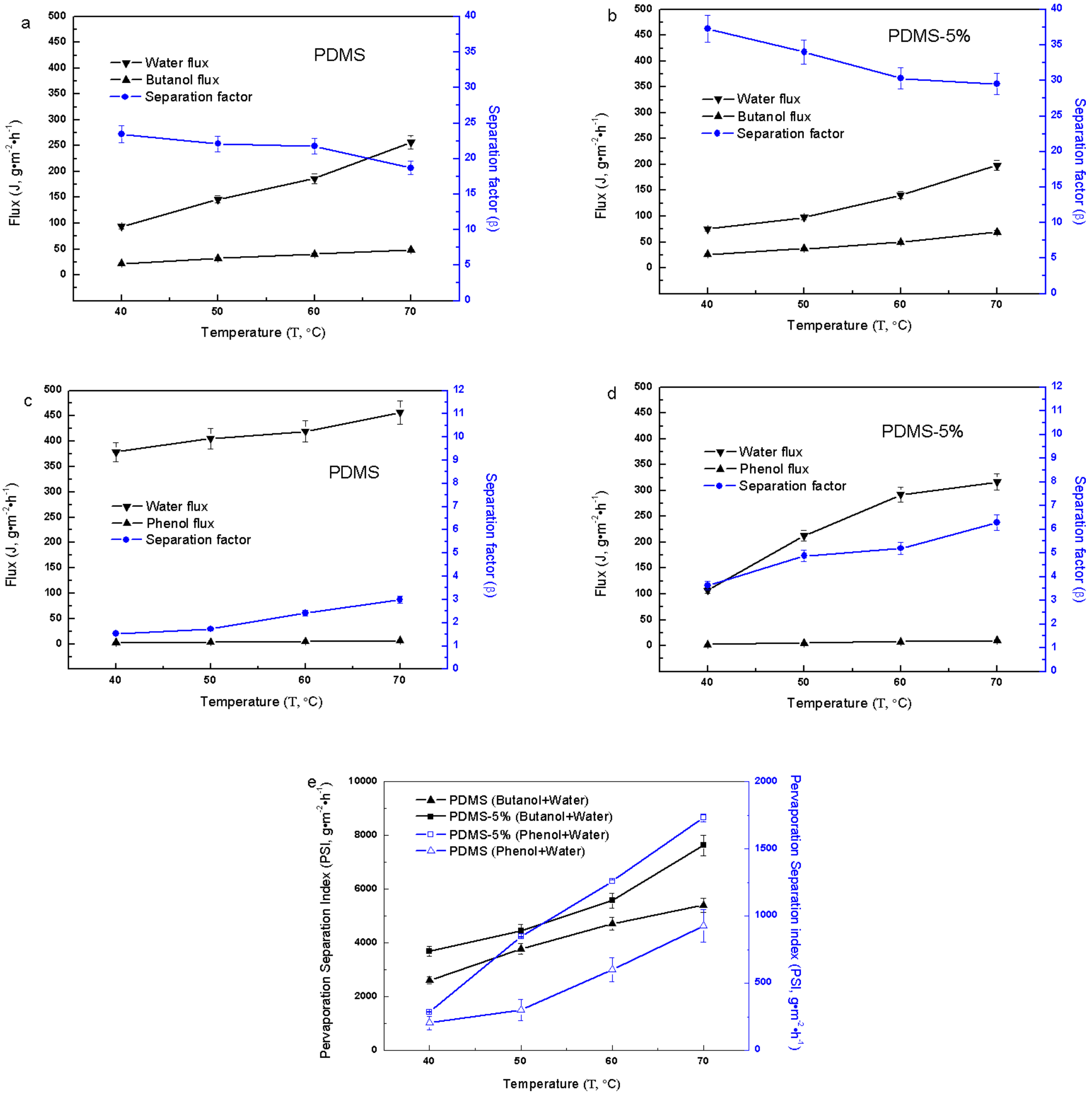

Fig. 6. Effects of feed temperature on flux and separation factor: (a) and (b) for butanol (1%) + water system; (c) and (d) for phenol (0.5%) + water system; (e) PSI.

increase in flux was not as rapid as before with increasing temperature. Furthermore, membranes showed more swelling in phenol solution than butanol solution (Fig. 3), indicating a slightly different trend for the flux for phenol solution, though following Arrhenius relationship.

Furthermore, water flux was restrained after adding 5 wt% OA for the tested temperatures, leading to higher separation factor for the modified PDMS membranes (Figs. 6(b) and (d)) than the unmodified PDMS (Figs. 6(a) and (c)). The comprehensive apparent performances of membranes can be evaluated by PSI. As evident in Fig. 6(e), the modified PDMS membranes performed better than the unmodified ones. PSI of PDMS at 70°C increased by 86.7% for phenol + water and 41.4% for butanol + water system.

The intrinsic performances were calculated based on the data in Fig. 6 and was presented in Table 3. The variation of permeance and selectivity with temperature followed different trends. For butanol + water system, permeances of butanol and water decreased with increasing temperature due to decreased solubility of small molecules as a result of increased diffusion of species at higher temperature. Similar findings have been reported in other studies [5,36,42].

With increasing temperature, the selectivity for butanol + water system decreased, while it increased for phenol + water system. The selectivity decreases with increasing temperature if the permeance of organics decreases more rapidly than that of water and vice versa. Butanol permeance decreased faster than water, which is due to the desorption of more butanol from the membrane than water with increasing temperature. In the phenol + water system, phenol is less volatile than water. Thus, less phenol was desorbed than water. In summary, the intrinsic selectivity for phenol + water system increased with the increasing temperature.

The above temperature dependency of the partial flux (Eq. (10)) and permeance (Eq. (11)) was plotted according to the following Arrhenius equation [42]:

$$J = J_0 \exp(\frac{-E_a}{RT}) \tag{10}$$

$$P = P_0 \exp(\frac{-E_P}{RT}) \tag{11}$$

where J_0 is the pre-exponential factor, R is the universal gas constant, T is the operating temperature, E_a is the apparent activation energies of permeation flux that can reflect the temperature dependency of flux, P_0 is the pre-exponential factor and E_p is the permeance activation energies.

E_a and E_p were calculated from the plots and are presented in Table 4. E_a of water is higher than that of phenol in phenol + water system, while lower than that of butanol in butanol + water system. Thus, the separation factor for phenol showed a positive temperature dependency, while that for butanol presented a descending trend with increasing temperature. The permeance activation energy, E_p, was negative in Table 4 as reported by Ngoc et al. [42]. Feng and Huang [48] defined the difference between E_J and E_p as the molar enthalpy of vaporization ΔH_v, expressed as follows:

$$E_p = E_a - \Delta H_v \tag{12}$$

The value of ΔH_v was estimated and compared with the theoretical value extracted from ASPEN (Tables 4 and 5). Accordingly, it is evident that the estimated ΔH_v values were slightly lower than the corresponding mean theoretical values since the permeate pressure was neglected in Eq. (12).

3.5. Stability of OA-modified membrane

To investigate the stability of membrane performance, three PDMS membranes with 9% OA loading were freshly prepared and used for pervaporation separation using 1 wt% butanol aqueous solution at 40°C, 60°C and 80°C continuously for 12 h. Butanol concentration in feed mixture was monitored at intervals to maintain a constant concentration. Butanol was added to feed tank when butanol concentration was lower. As shown in Fig. 7(a), the total fluxes at 40°C, 60°C and 80°C were relatively constant during

Table 4
Activation energy (kJ mol^{-1}) of solvents

Mixture	Activation energy	PDMS	PDMS-5%OA
Phenol + water	$E_{p\text{-phenol}}$	–19.2	–21.0
System	$E_{p\text{-water}}$	–37.7	–24.7
	$E_{a\text{-phenol}}$	31.5	30.5
	$E_{a\text{-water}}$	5.4	18.5
	$\Delta H_{v\text{-phenol}}$	50.7	51.5
	$\Delta H_{v\text{-water}}$	43.2	43.2
Butanol +water	$E_{p\text{-butanol}}$	–22.8	–17.4
system	$E_{p\text{-water}}$	–14.0	–14.1
	$E_{a\text{-butanol}}$	23.0	28.5
	$E_{a\text{-water}}$	29.2	29.1
	$\Delta H_{v\text{-butanol}}$	45.8	45.9
	$\Delta H_{v\text{-water}}$	43.3	43.3

Table 5
Molar vaporization enthalpy of solvents at different temperatures

Temperature (°C)	ΔH_v of water (kJ mol^{-1})	ΔH_v of phenol (kJ mol^{-1})	ΔH_v of butanol (kJ mol^{-1})
40	46.2	56.4	47.9
50	45.7	55.7	47.1
60	45.1	55.1	46.3
70	44.6	54.5	45.5
Mean value	45.4	55.4	46.7

Table 3
Intrinsic separation performances for butanol + water system and phenol + water [a]

Permeance (g m^{-2} h^{-1}·kPa^{-1})/selectivity	40°C		50°C		60°C		70°C	
	PDMS	PDMS-5% OA	PDMS	PDMS-5% OA	PDMS	PDMS-5% OA	PDMS	PDMS-5% OA
P_{butanol}	15.98	17.73	12.15	13.84	9.00	10.91	7.06	10.07
P_{water}	12.90	10.38	11.99	7.99	9.40	7.10	8.28	6.40
$\alpha_{\text{butanol + water}}$	1.16	1.71	1.01	1.73	0.96	1.54	0.85	1.57
P_{phenol}	255.13	179.81	159.53	246.46	130.08	210.95	105.25	155.98
P_{water}	52.80	14.93	33.42	17.54	21.30	14.82	14.75	10.24
$\alpha_{\text{phenol + water}}$	4.83	12.05	4.77	14.05	6.11	14.23	7.13	15.23

[a] The average confidence interval of the data is higher than 95%.

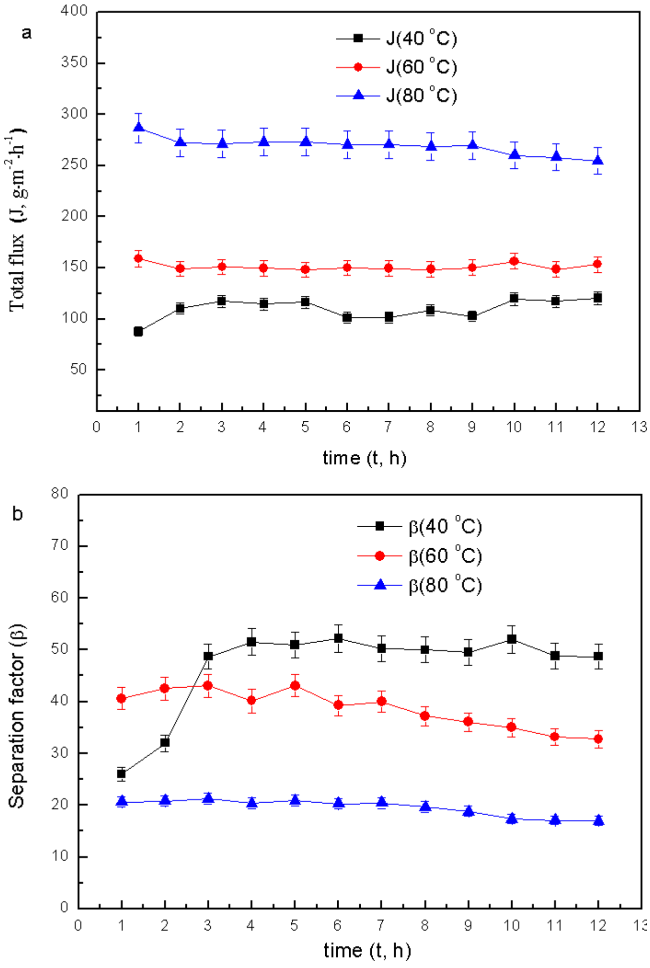

Fig. 7. Effects of operation time on pervaporation performances: (a) total flux, (b) separation factor.

the operational time. A minor decrease in total flux was observed at 80°C when the test lasted over 8 h. Fig. 7(b) indicates that separation factor at 40°C remained stable during the operational time, although mass transfer equilibrium at 40°C was achieved in 2 h for the modified membrane. The separation factors at 60°C and 80°C showed a slight 18% decrease, mainly due to the leakage of OA from PDMS, since the blend between PDMS and OA was physical as suggested by the XPS results. In this study, the pervaporation tests on membranes were finished within 8 h. In addition, at least duplicate samples were used in pervaporation test for each membrane composition. Therefore, the separation performances in this study can be considered reliable. Based on the outcomes of this study, the low operation temperature and OA loading are recommended for industrial application of OA-modified PU membrane. Further research on the chemical modification of OA on PU is needed, since OA is beneficial for the pervaporation separation of phenol and butanol from water.

4. Conclusions

In summary, OA and PDMS present a physical blending without chemical reaction in modified membranes. The addition of OA into PDMS membrane can increase the apparent and intrinsic separation performances for phenol + water and butanol + water systems. For PDMS membranes with 5 wt% OA loading, the butanol and phenol fluxes of PDMS-5% were 69.11 and 10.34 g m^{-2} h^{-1} for 1 wt% butanol and 0.5 wt% phenol solution at 70°C, respectively. This was 43% higher than the unmodified PDMS and due to the affinity of OA to organics. The intrinsic selectivity of membrane to phenol and permeance of phenol were significantly higher than apparent separation factor and phenol flux, which is because the driving force for phenol across membrane is very low. With increasing temperature, flux increased. Separation factor for butanol decreased while that for phenol increased, which was related to estimated activation energy. OA-modified PDMS membranes showed good operation stability at 40°C and are potentially good separation membrane material for organic + water mixtures.

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Symbols

PDMS — Hydroxyl-terminated polydimethylsiloxane
TEOS — Tetraethoxysilane
OA — Oleyl alcohol
DBTL — Dibutyltin dilaurate
XPS — X-ray photoelectron spectroscopy
J — Total flux, g m^{-2} h^{-1}
J_i — Partial flux of i component, g m^{-2} h^{-1}
δ — Solubility parameter, J$^{1/2}$ cm$^{-3/2}$
T — Feed temperature, K
E_a — Apparent activation energy of permeation, kJ mol^{-1}
$\bar{\text{P}}\text{i}$ — Permeance of i component, g m^{-2} h^{-1} kPa^{-1}
f_i — Fugacity of i component, kPa
SD — Swelling degree, %
α — Selectivity
E_p — Permeability activation energies
ΔH_v — Molar enthalpy of vaporization
PSI — Pervaporation separation index, g m^{-2} h^{-1}
β — Separation factor

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