Transmission of butanol isomers in pervaporation based on series resistance model

Chengye Zuo[1,2], Jake Hindley[2], Xiaobin Ding[3], Mark Gronnow[4], Weihong Xing[1,*], Xuebin Ke[2,*]
[1]National Engineering Research Center for Special Separation Membranes, Nanjing Tech University, Nanjing 211816, China
[2]Department of Chemical Engineering, University of Hull, HU6 7RX, United Kingdom
[3]Nanjing Jiusi High-Tech Co., Ltd., Nanjing 211816, Jiangsu, China
[4]Biorenewable Development Centre, University of York, YO19 5SN, United Kingdom
*Corresponding author, E-mail: xingwh@njtech.edu.cn; x.ke@hull.ac.uk

Abstract

Pervaporation (PV) has shown great potential in the separation of butanol aqueous solutions due to their economic and environmental benefits. This work applies polydimethylsiloxane (PDMS) composite membrane to separate four butanol isomers (n-butanol, isobutanol, sec-butanol and tert-butanol) in aqueous solution. Based on physical and chemical properties of butanol isomers, such as solubility, polarity and interaction parameter, we systematically study the transmission difference in the pervaporation process. The influence of feed concentration, temperature and permeate pressure on membrane performance of PDMS composite membrane are investigated. The results show that the contact angles of butanol isomers on the PDMS layer are 51°, 42.7°, 37.7°, 29.1° and the fluxes at 40 °C are 237.6 $g \cdot m^{-2} \cdot h^{-1}$, 245.4 $g \cdot m^{-2} \cdot h^{-1}$, 224.1 $g \cdot m^{-2} \cdot h^{-1}$, 169.4 $g \cdot m^{-2} \cdot h^{-1}$ for n-butanol, isobutanol, sec-butanol, and tert-butanol, respectively. Moreover, the similar compatibility principle is introduced to the series resistance model so the process simulation matches well with the antagonistic effect of water molecules on mass transfer of butanol isomers. The permeation activation energy is negative, indicating that the dissolution dominates the dissolution and diffusion process. In addition, low vacuum is not conducive to the separation of n-butanol from water. The research on isomers separation through pervaporation may pave a way to separate other solvents of similar properties.

Keywords: pervaporation; polydimethylsiloxane; butanol isomers; series resistance model

1. Introduction

The extensive application of new energy sources, including solar, wind, and nuclear energy, are impeded by energy storage infrastructure that provides stable power transmission. Lithium-ion batteries have the highest energy density among currently available energy storage systems, but the maximal energy density of lithium-ion batteries is 2 $MJ \cdot kg^{-1}$, still less than that of liquid fuels (27-47 $MJ \cdot kg^{-1}$) [1]. To alleviate the global shortage of fossil fuels and reduce the solid emissions, people turn the attention to biofuels [2]. Butanol has a high octane number and energy density. While blended with other fuels, it can allow a relatively higher water content in the system and therefore is convenient for transportation and storage [3].

Butanol is always produced by fermentation of biomass and traditional separation includes adsorption [4], extraction [5, 6], salting out [7], and membrane techniques [8]. The adsorption process is impended by the high costs of the adsorbents. The extraction and salting out introduce the third part that causes secondary pollution and increases the difficulty of subsequent separation. By contrast, Pervaporation (PV) is an emerging technique with advanced membrane materials [9]. The membrane materials mainly include water-selective membrane and organic-selective membrane [10, 11]. The organic-selective membrane has obvious technical and economic benefits for the separation of azeotropes or isomers at a low concentration [9, 12]. Among organic-selective membrane materials, polydimethylsiloxane (PDMS) is relative cheap with an alternating O-Si-O unit structure. It is the most promising membrane material for separation and recovery of butanol [13]. The differences of separation system, such as solvent solubility in water, boiling point, molecular structure and inherent properties of the solvent, and operating conditions, inevitably affect the mass transfer.

Many researches investigate some important parameters for the PV process, including molecular size, equilibrium partial vapor pressure (P_i^{sat}), activity factor (γ_i), solubility parameter (δ), and interaction parameter (χ). It partly explains the difference in mass transfer of different components. To separate dimethyl carbonate from methanol, the solubility parameter is crucial for the component to pass through [14]. For the separation of binary, ternary and quaternary acetone/butanol/ethanol (ABE)/water mixed systems, the mass transfer of each solvent is correlated with its equilibrium partial vapor pressure and solubility parameters [15]. In addition, the interaction force among the solvents and that between the components and the membrane cause the permeate differences. The separation factor of acetone is much larger than that of n-butanol and ethanol. For phenol and methanol, the preferential dissolution directly leads to different separation factors of solvents [16]. The solubility parameter is an important prerequisite for the solvent transfer in the composite membrane [17]. In the separation of n-butanol, ethanol, and ethyl acetate from aqueous solution, ethyl acetate has higher selectivity than n-butanol and ethanol due to the better solubility of ethyl acetate in PDMS [18].

Furthermore, much attention is focused on modeling of PV membranes with an emphasis of interface action. The series resistance model is generally used to study the mass transfer of the components in the boundary layer between the liquid feed and the composite membrane. The results show that the resistance of the boundary layer has little effect on transfer process and it can be weakened by increasing flow velocity [19-22]. The study of permeation activation energy shows that dissolution is the dominant step [23, 24]. Therefore, the resistance of the PV process is concentrated in the dissolution process. So far, no systematical studies on the mass transfer state of butanol isomers have been explored. Moreover, due to the similar compatibility principle, the resistance of the boundary layer comes not only from the thickness of the boundary layer but also from the interaction between solvents and water. Therefore, single factors such as solubility parameters or polarity cannot describe the mass transfer of butanol isomers.

In this work, we systematically studied the mass transfer differences (binary and ternary) of butanol isomers in PDMS composite membranes. The preferred selectivity to the pure solvent of butanol isomers is obtained by calculating the interaction parameters, half-time empirical formula and swelling formula. The differences in terms of polarity, solubility parameter, and boiling points between solvents for separation and selectivity are explored by changing the concentration, temperature, and vacuum. This research is a reasonable guidance to separation of butanol isomers and other solvents with similar properties.

2. Experimental Section

2.1 Materials

All of the raw materials and regents (analytical grade) are purchased from commercial vendors and used without further purification: n-butanol (99%, Sinopharm Chemical Co. Ltd., China), isobutanol (99%, Sinopharm Chemical Co. Ltd., China), sec-butanol (99%, Sinopharm Chemical Co. Ltd., China), tert-butanol (Sinopharm Chemical Co. Ltd., China). The physicochemical properties of solvents are shown in Table S1of the support information and their polarity follows the order of n-butanol<isobutanol<sec-butanol<tert-butanol [25]. The commercial PDMS composite membranes are provided by Nanjing Jiusi High-Tech Co., Ltd. This type of membrane consists of PDMS top layer, polyvinylidene fluoride (PVDF) intermediate layer and non-woven fabrics substrate layer. The top layer is 10 μm thickness and mean pore size of intermediate layer is around 76 nm.

2.2. Commercial membrane characterization

Fourier transform infrared spectra (ATR-FTIR, Thermo, Nicolet Nexus 470 spectrometer, USA) are employed to characterize the surface properties of the PDMS membrane in the range of 500-4000 cm^{-1}. The morphology of the membrane materials is observed by field emission scanning electron microscope (FESEM, Hitachi S-4800) using an acceleration voltage of 2 kV. The contact angle is measured on JC2000D contact angle apparatus (Shanghai ZhongChen Digital Technology Apparatus Co. Ltd).

2.3 Swelling experiments

Homogeneous PDMS membranes with the thickness of 2 mm are prepared referring to the reported [26]. The solubility and diffusion rate of butanol isomers in the PDMS homogeneous membrane is measured by weight method. Put the homogeneous membrane in a vacuum drying oven at 60 °C for 24 hours and record the mass (W_d) of the dry membrane. Soak the membranes of known weight and thickness (l) in pure solvents of n-butanol, isobutanol, sec-butanol and tert-butanol, respectively. After a given time (t), take it out and wipe the membrane surface with a dust-free cloth. The mass (W_t) of swollen homogeneous membrane is recorded and then put back into the pure solvent. Repeat until no further weight gain and the final mass (W_s) of the membrane is the swelling limit.

2.4 Pervaporation

The PV device consists of feed tank, water bath, peristaltic pump, membrane module (membrane area of 153.86 cm^2), cold trap, and vacuum pump (Fig. 1). The feed liquid is cross-flowed through the membrane module through the peristaltic pump at a flow rate of 68.4 $L \cdot h^{-1}$ (Reynolds coefficient ≈253.8), and the retentate is cycled to the raw material tank. The permeation side of the membrane is connected to the vacuum system to form the driving force. A glass cold trap is installed between the membrane module and the vacuum pump to collect the permeate at -70 °C. For a high concentration of butanol, the permeate is stratified so the permeate is diluted 10 times before injecting into gas chromatograph for quantitative analysis. All experimental results are repeated three times and have an error of <5 %.

The feed liquid of 1.2 L is preheated for half an hour and then sampled and analyzed after stabilized. Three experiments are performed in parallel and the average value is taken. The concentration of butanol isomers in the feed liquid is 1~3 wt% and the temperature of the feed liquid is 30～60 °C with the vacuum pressure is 0.3 kPa~4 kPa.

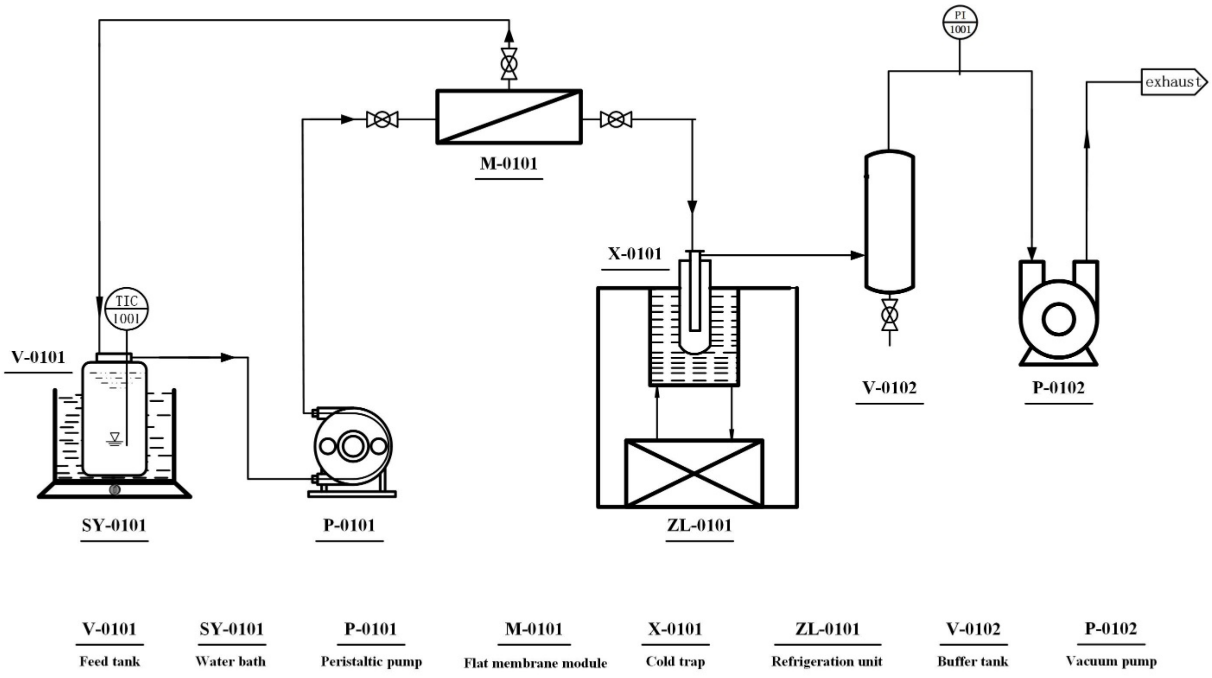


Fig. 1. Experimental device diagram.

2.5 Data analytic methods

Swelling degree (S) of the homogeneous membrane is calculated by *Eq.* (1). Theoretically, when a homogeneous membrane is swelled in different solvents, the diffusion coefficients (D) of the solvents are different. To simplify, we assume that the diffusion coefficient is constant during the dissolution process. Therefore, the half-time empirical formula [14] is used to calculate the diffusion coefficient of butanol isomers in a homogeneous membrane, by *Eq.* (2).

$$\mathrm{S} = \frac{W_s - W_d}{W_d} \qquad (1)$$

$$\mathrm{D} = \frac{0.04919 l^2}{t_{0.5}} \qquad (2)$$

Where W_d and W_s are the weight before and after swelling; l is the thickness and $t_{0.5}$ is the time to achieve solvent uptake $W_t/W_s = 0.5$.

Assuming that the adsorption isotherm of the solvent for the membrane is linear and the solvent diffusion coefficient is independent of the solvent concentration, an ideal selectivity is calculated by *Eq.* (3):

$$\beta_{ideal,i,n} = \frac{S_i D_i}{S_n D_n} \qquad (3)$$

Where i represents isobutanol, sec-butanol or tert-butanol, and n represents n-butanol; S is swelling degree.

The PV performance of PDMS composite membrane is usually expressed in terms of the flux J_i and separation factor α, which are determined by *Eqs.* (4) and (5):

$$J_i = \frac{m_i}{At} \qquad (4)$$

$$\alpha = \frac{y_i/(1-y_i)}{x_i/(1-x_i)} \qquad (5)$$

where m_i is the weight of component i in the permeate (g); A is the effective membrane area (m^2); and t is the permeation time interval for the pervaporation (hours); y_i and x_i are the weight fractions of components in the permeate and feed, respectively

Since changes in flux and separation factor are easily affected by operating conditions, normalizing the flux relative to the permeation driving force will help understand the permeability of the membrane itself to the components. The inherent properties of the membrane can be expressed as permeability P_i and selectivity β, which are determined by *Eqs.* (6) and (7):

$$P_i = \frac{J_i \times l}{x_i^f \gamma_i p_i^{sat} - y_i p_i^P} \qquad (6)$$

$$\beta = \frac{P_i}{P_j} \qquad (7)$$

where l is the membrane thickness (No changes in thickness are involved so it can be ignored); γ_i is the activity of components i, p_i^{sat} is the equilibrium partial pressure of i in the feed, both are calculated by the non-random two-liquid model (NRTL) in Aspen; x_i^f and y_i are mole fraction of i in the feed and permeate, p_i^P is permeation pressure; P_i and P_j are permeability of solvent and water, respectively.

The relationship between the flux and temperature can be described by Arrhenius rule [27], it is obtained by *Eq.* (8):

$$J = J_0 \exp\left(-\frac{E_a}{R_g T}\right) \qquad (8)$$

Where J_0 is the pre-exponential factor; E_a is the apparent activation energy ($J{\cdot}mol^{-1}$); R_g is the gas constant ($J{\cdot}mol^{-1}{\cdot}K^{-1}$); T is the kelvin temperature (K). E_a represents the relationship between flux and temperature, and there is also a relationship between permeability P and driving force Δp, which derived the *Eq.* (9):

$$J = \frac{P}{l}\Delta \mathrm{p} \rightarrow \frac{P}{l} = \frac{J}{\Delta \mathrm{p}} = \frac{P_0}{l}\exp\left(-\frac{E_p}{R_g T}\right) \qquad (9)$$

The permeation activation energy E_p of the influence of temperature on membrane permeability is the slope of the relationship between ln(J/Δp) and 1/T, not lnJ and 1/T. When the pressure on the permeate side is lower than the feed side, the E_p value can be calculated by *Eq.* (10), subtracting the enthalpy of evaporation (ΔH_v) from the apparent activation energy [28]:

$$E_p = E_a - \Delta H_v \qquad (10)$$

Where E_p is the permeation activation energy of each component (J•mol^{-1}); ΔH_v is the heat of vaporization of each component (J•mol^{-1}). This equation expresses the influence of the enthalpy change caused by the phase change on the permeability behavior of the component [29].

The interaction parameter χ is calculated by Flory-Huggins equation [30], by *Eq.* (11):

$$\chi = \frac{V_i}{R_g T}(\delta_2 - \delta_1)^2 \qquad (11)$$

Where δ_1 and δ_2 are the solubility parameters of PDMS and solvent respectively (J$^{1/2}$•cm$^{-3/2}$); V_i is the molar volume of component i (cm^3•mol^{-1}). The smaller the interaction parameter, the stronger the affinity, the higher the solubility of the solvent in PDMS.

The total mass transfer coefficient represents the mass transfer rate of butanol isomers in a certain membrane area in a certain period, K_{ov} is calculated by *Eq.* (12):

$$K_{ov} = \frac{V}{At} In\left(\frac{x_i}{x_{i,t}}\right) \qquad (12)$$

3. Results and Discussion

3.1 Characterization of PDMS selective layer

3.1.1 Surface properties and cross-section morphology of PDMS membrane

The FTIR spectra show the absorption peaks at 2960 cm^{-1} and 2900 cm^{-1} (Fig. 2), which indicates the asymmetric stretching vibration and symmetric stretching vibration of the PDMS side chain (C-H bond), respectively. The peaks near 1410 cm^{-1} and 1260 cm^{-1} are the absorption peaks of Si-C bonds. The peaks at 1080 cm^{-1} and 1010 cm^{-1} indicate the asymmetric stretching vibration of the Si-

O-Si bonds, while 870 cm^{-1} and 781 cm^{-1} peaks are attributed to its symmetric stretching vibration. The results show that the commercial composite membrane conforms to the reported [31]. The cross-sectional morphology of the PDMS composite membrane is observed by a FESEM. The thickness of the functional layer is 10 um and the interface is compatible without any fault (Fig. 2b).

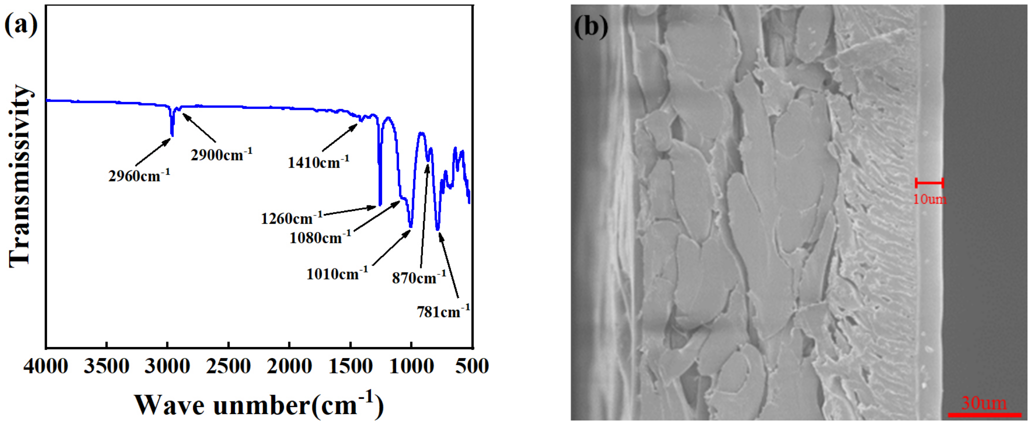
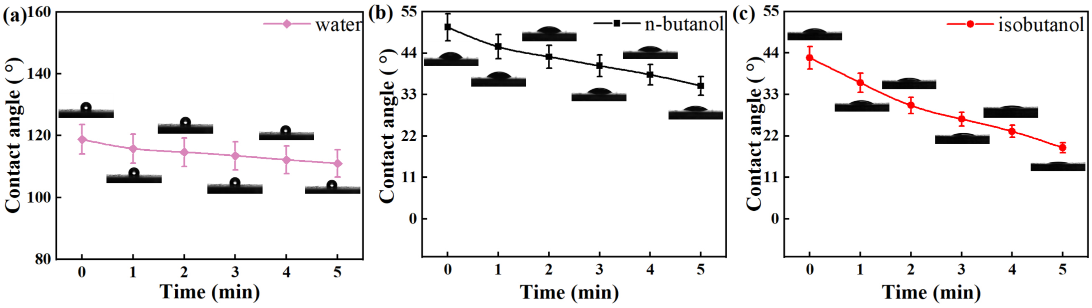


Fig. 2. (a) ATR-FTIR spectra and (b) cross-section morphology of PDMS selective layer.

3.1.2 The affinity of PDMS membrane to butanol isomers and water

The affinity between the PDMS composite membrane and the solvents is measured by the surface dynamic contact angle instrument. Fig. 3 shows that the PDMS layer has a higher hydrophobic angle and a lower affinity butanol angle, indicating that butanols preferentially dissolve in the functional layer. Comparing Fig. 3b-e, it can be found that the contact angle of butanol isomers follows the order of n-butanol>isobutanol>sec-butanol>tert-butanol, consistent with the interaction parameter rule in SI (Table S1).



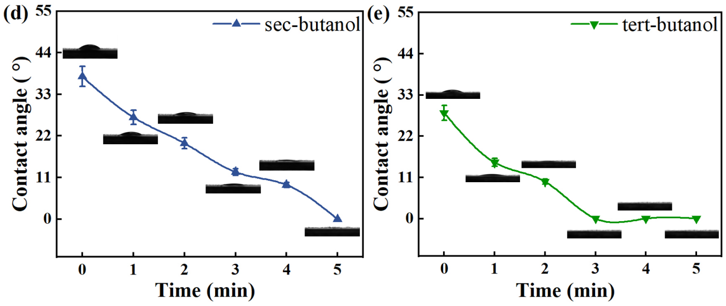


Fig. 3. (a) Water dynamic contact angle and (b-e) butanol dynamic contact angle of the PDMS membranes.

3.1.3 Swelling of pure solvent in PDMS membrane

The process of dissolving the butanol isomers in the PDMS composite membrane is a process of breaking the polymer chain and swelling the membrane, which changes the microstructure of the composite membrane and affects the flux and separation factor of the composite membrane [15]. Fig. 4a depicts the swelling process of pure solvents of n-butanol, isobutanol, sec-butanol, and tert-butanol in the PDMS homogeneous membrane. As the interaction parameters between different solvents and PDMS decrease, the solubility of the solvent in the composite membrane gradually increases. The specific swelling degree is shown in Fig. 4b. As the molecular volume of the component increases and the molecular structure becomes more complex, although the interaction between the solvent and the PDMS layer becomes larger, the time required to reach the swelling equilibrium also becomes longer. This indicates that the molecular structure and molecular volume will affect the diffusion rate of butanol isomers in the PDMS composite membrane.

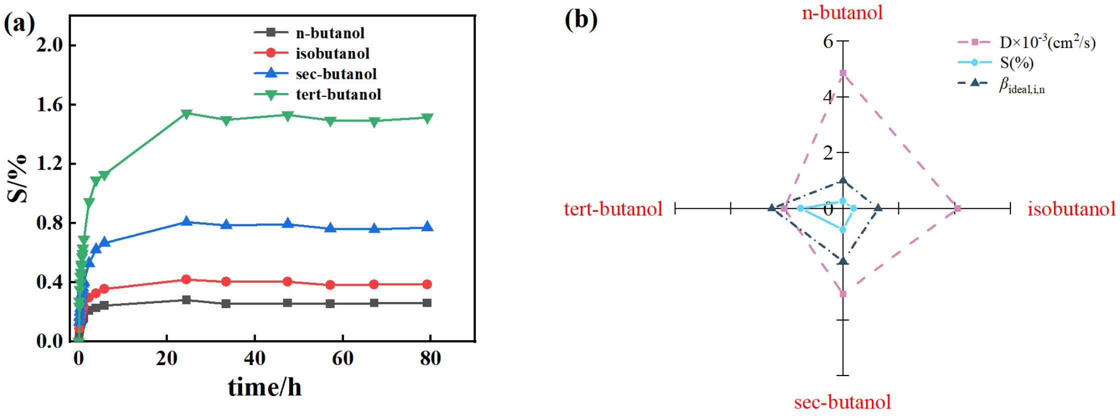


Fig. 4. (a)Swelling degree of PDMS membrane in butanol isomers;(b) Solubility and diffusion of butanol isomers in PDMS.

In order to quantitate the diffusion of butanol isomers, the half-time empirical formula is used to estimate the diffusion coefficient of pure solvent in the PDMS homogeneous membrane. First, the second-order polynomial fitting is performed on the curve of swelling degree with time while its $R^2 \geqslant 0.9$. Through Eq. (2) to obtain the diffusion coefficient of each solvent, as shown in Fig. 4b. The tight cross-linking network in the homogeneous membrane of PDMS makes the molecular structure and volume of the solvent particularly sensitive to the resistance of the diffusion process. Combining the molecular volume and structure of the components (Table S1) and the diffusion coefficient of each component (Fig. 4b), it can be seen that its diffusion coefficient gradually decreases as the component structure becomes more complex and the molecular volume becomes larger. Moreover, the swelling degree of each component has opposite trends. The dynamic swelling of polyethylene (PE) membrane in pure butanol solvent had the similar outcomes [32]. This is due to the differences of solubility and molecular structure of the components.

3.2 PV performance

3.2.1 Effect of feed concentration in binary system

The pervaporation process is jointly controlled by dissolution and diffusion, and therefore, the concentration of the solvent in the feed plays a crucial role. Fig. 5 describes the flux and separation factor of the PDMS composite membrane for the butanol isomer/water binary system with different feed concentrations at 40 °C. For any one type of butanol, as the feed concentration increases, the total flux gradually rises (Fig. 5). The separation factor maintains constant and the order is isobutanol (15.5)>n-butanol (14.9)>sec-butanol (14.4)>tert-butanol (10.6). This result in Fig. 5(b) is contrary to the interaction parameters, and does not comply with "stronger affinity will lead to higher permeation" [15], for reasons which will be discussed later.

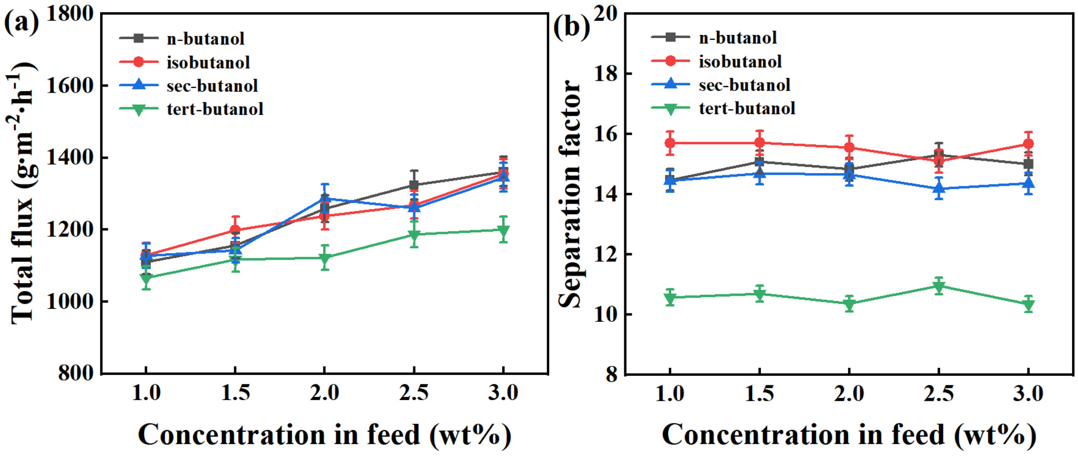


Fig. 5. Effect of feed concentration in butanol/water binary system on (a) total flux and (b) separation factor (feed temperature: 40 °C, Vacuum: 0.3 kPa).

Fig. 6a shows that the water fluxes in the four systems remain unchanged as the feed concentration increases. The sufficient water in the feed results in the solubility of water molecules in the membrane unchanged, as well as the mass transfer force of water molecules. Therefore, the increase in total flux in Fig. 5a is mainly due to the increase of butanol permeation.

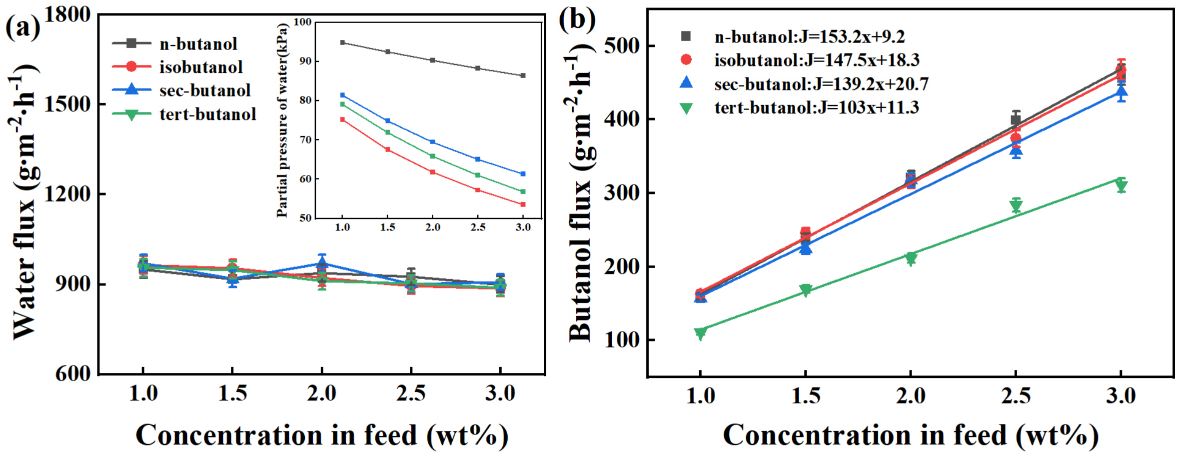


Fig. 6. Effect of butanol isomers (dual system) feed concentration on (a) water flux, partial pressure and (b) butanol flux (feed temperature: 40 °C, Vacuum: 0.3 kPa; the inserted is the correlation between the partial pressure of water and the feed concentration of butanol isomers).

The Fig. 6b shows that the flux of each butanol component increases linearly with the increase of the feed concentration. Therefore, the linear fit of the flux of each butanol with the concentration is performed by the least square method while its $R^2 \geqslant 0.99$. The transmission resistance ($f_{3,i}$) of butanol isomers in the PDMS composite membrane (Figure S2) follows the order of tert-butanol>sec-butanol>isobutanol>n-butanol, consistent with the solvent diffusion coefficient in Fig. 4b.

The permeability and selectivity can better understand the transmission of butanol isomers in the PDMS composite membrane [25]. As shown in Fig. 7, the permeability of butanol isomers increases with the increasing feed concentration of butanol. As a result, the PDMS composite membrane exhibits constant selectivity for the four structures of butanol isomers, which are 3.2, 0.55, 0.74, 0.46 for n-butanol, isobutanol, sec-butanol, and tert-butanol, respectively. It can be seen from Fig. S1b that the partial pressure of butanol increases with the increasing feed concentration of butanol, which makes the P_i^{sat} of the water drop (Fig. 6a). The water flux is unchanged during the separation process but water permeability increases with the increasing feed concentration of butanol isomers. Therefore, it can be concluded that the equilibrium partial pressure of water has little influence on the water flux while feed concentration of butanol changes.

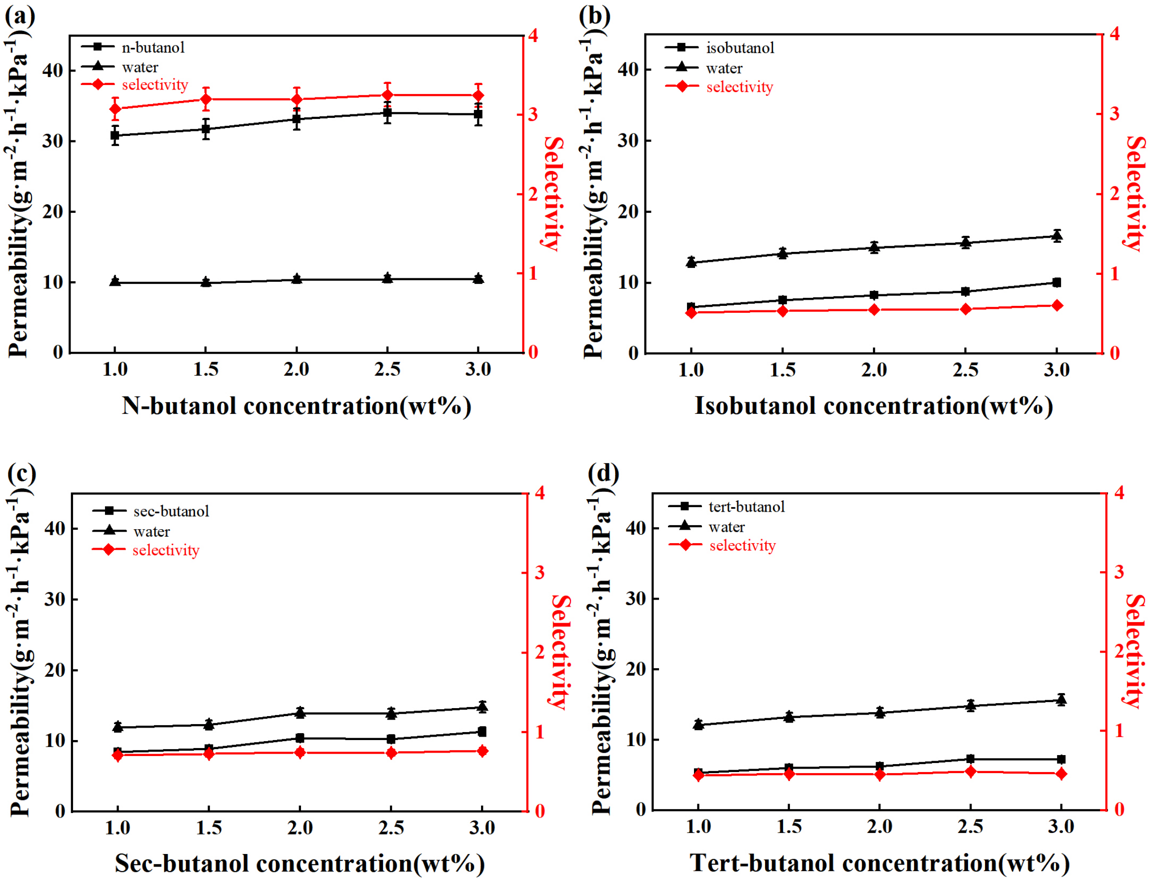


Fig. 7. Effect of feed concentration in butanol/water binary system on permeability and selectivity

(a) n-butanol (b) isobutanol (c) sec-butanol (d) tert-butanol (feed temperature: 40 °C, Vacuum: 0.3 kPa).

It is worth noting that in the same feed concentration, the permeability of n-butanol is the highest, followed by sec-butanol, isobutanol and tert-butanol. Although the flux of isobutanol is higher than that of n-butanol and sec-butanol, the equilibrium partial pressure of isobutanol is much higher than that of other components, resulting in lower permeability of isobutanol than n-butanol and sec-butanol. Therefore, the solvent separation factor of the PDMS composite membrane in Fig. 5b may be dominated by the polarity between the components (shown in Section 2.1). For instance, n-butanol with its smallest polarity can allow it to pass through the PDMS composite membrane at the fastest rate [18]. For tert-butanol, the most polar of the four isomers, it will form large water clusters with water [33], increasing mass transfer resistance. It can be seen from Table S1 that tert-butanol is miscible with water, while n-butanol, isobutanol and sec-butanol are partially miscible with water. Its solubility follows an order of n-butanol <isobutanol <sec-butanol, indicating that the force between water molecules and butanol isomers will produce different mass transfer resistance ($f_{1,i}$), which leads to different separation factors. The polar components have better compatibility and a stronger

interaction with water. In addition, the PDMS composite membrane is a hydrophobic and may also affect the transfer of butanol isomers. The water fluxes in the n-butanol/water and isobutanol/water systems are similar. With the increase of water ratio in the feed of binary system, the permeability of tert-butanol is the lowest, while the permeability of n-butanol is greater than that of isobutanol [38]. This phenomenon shows that the interaction between water and tert-butanol is stronger than that between n-butanol/isobutanol and water. No matter how the water ratio changes, it has little effect on the flux of n-butanol, isobutanol and sec-butanol, but when the water ratio rises to 70 wt%, the flux of tert-butanol drops sharply [32]. By investigating the influence of the concentration of butanol in the feed on the separation of the butanol isomers/water binary system, the interaction parameters cannot be used to predict the separation effect of solvent and water, as the solubility of butanol isomers in water may have a certain impact.

3.2.2 Binary system VS ternary system

Based on the research of the butanol/water binary system, water may have an antagonistic effect on the PV separation process. Therefore, isobutanol, sec-butanol, and tert-butanol are used for comparison. The two-structure butanol (50 wt%/50 wt%) binary system and the two-structure butanol/water (1 wt%/1 wt%/98 wt%) ternary system are studied, as shown in Fig. 8. When isobutanol, sec-butanol and tert-butanol are successively present in the binary mixture, the separation factor of the three structures of butanol is much higher than that of n-butanol. According to the interaction parameters in Table S1, the dissolution resistance ($f_{2,i}$) of butanol isomers in the membrane layer follows the order of tert-butanol<sec-butanol<isobutanol<n-butanol. Therefore, the order for separation factor of butanol binary system is tert-butanol>sec-butanol>isobutanol>n-butanol, which is the same as the $\beta_{ideal,i,n}$ in Fig. 4(b). At this point, the interaction parameter has a decisive effect on the mass transfer of the components. The separation factor and total flux of the binary mixture of n-butanol/tert-butanol are 1.87 and 3825.6 $g\cdot m^{-2}\cdot h^{-1}$, respectively. Compared with the Polyamide/β-cyclodextrin mixed matrix membrane and Polyamide/modified β-cyclodextrin mixed matrix membrane [34, 35], the PDMS membrane has more advantages in separating the binary mixture of n-butanol/tert-butanol.

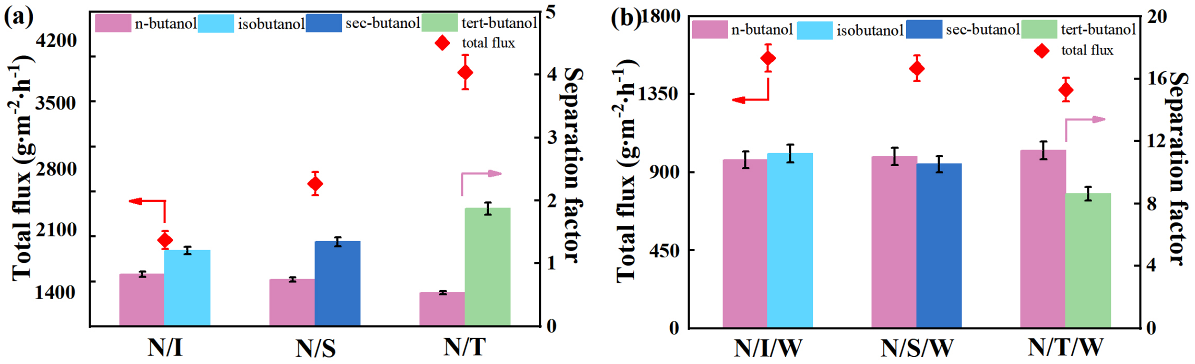


Fig. 8. Total flux and separation factor. (a) Butanol isomers with feed ratio of 1:1; (b) Binary butanol isomers in water with feed ratio of 1:1:98 (feed temperature: 40 °C, Vacuum: 0.3 kPa).

Fig. 8b shows that the separation factors for the ternary system follow an order of isobutanol>n-butanol>sec-butanol>tert-butanol, same as that for the butanol/water binary system. Comparing the total flux in Fig. 8, we can find that with isobutanol, sec-butanol and tert-butanol in the system, the total flux of the binary system is increasing, while the total flux of the ternary system is decreasing. This phenomenon is due to the stronger transmission resistance of water molecules to solvents of high solubility. Therefore, the separation factor of butanol isomers follow the order of polarity. The solubility of n-butanol and isobutanol in water is similar, and the interaction force between isobutanol and the functional layer is greater than that of n-butanol, which results in a greater separation factor of isobutanol than n-butanol. By comparing the binary and ternary systems, the polarity between the solvent and water and the interaction parameters between the solvent and PDMS together determine the separation performance in the pervaporation process.

3.2.3 Influence of feed temperature

Temperature plays an important role in the PV process. It not only affects the thermodynamic process of dissolution, but also the kinetic process of component diffusion in the membrane. Therefore, under the butanol concentration of 2 wt%, the effect of the feed temperature is investigated. The results are shown in Fig. 9. As the temperature increases, the flux of each component increases and the separation factor decreases. The temperature increase promotes mass transfer and the migration of polymer chains, which increases the flux [32]. Moreover, the molecular dynamic diameter of water molecules is smaller than that of butanol isomers, which makes it easier to pass through the preferentially organic-permeable membrane and occupy the permeation channel. So the separation factor is reduced. As the temperature increases, the water molecules show similar fluxes in the four systems (Fig. 9a). The flux of butanol isomers is significantly smaller than the water flux as the pervaporation process is jointly controlled by dissolution and diffusion (Fig. 9b). The higher temperature increases the thermal motion of molecules and weakens the formation of water clusters. The diffusion rate of water molecules in the PDMS layer is greater than that of butanol isomers [36]. As a result, the separation factor gradually decreases with increasing temperature (Fig. 9c).

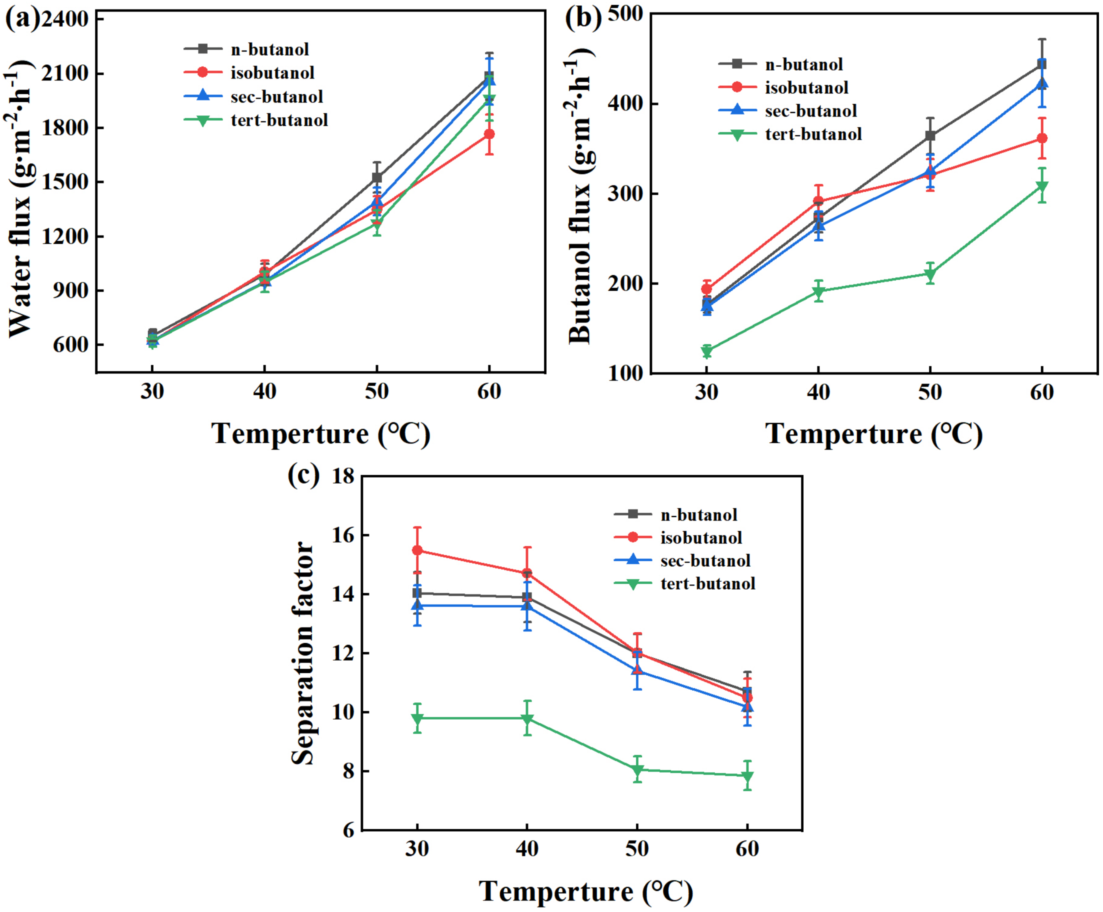


Fig. 9. Effect of feed temperature (binary system) on (a) water flux, (b) butanol flux and (c) separation factor (feed composition: 2 wt% butanol in water, Vacuum: 0.3 kPa).

To observe the energy requirement for mass transfer, the flux of the components corresponding to the feed temperature fits to the Arrhenitz equation (Fig. 10a). The apparent activation energy of butanol isomers is listed in Table 1. The apparent activation energy of tert-butanol is the largest, indicating that higher energy is needed to pass through the PDMS composite membrane [36]. The final osmotic activation energy of each component is calculated by Eq. (10). When the osmotic activation energy is negative, the dissolution process dominates the separation process [24]. The difference in apparent activation energy between butanol isomers may come from the volume difference and the solubility parameters [34, 37]. By comparing with PE membrane, the mass transfer resistance of PDMS composite membrane is lower than that of PE membranes [32].

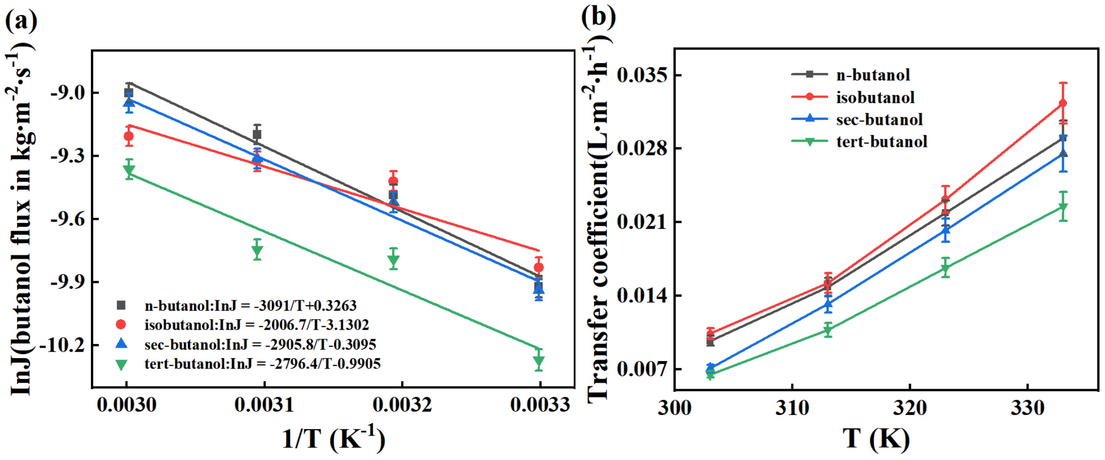


Fig. 10. The relation of temperature and flux to fit the Arrhenius formula (a) and total mass transfer coefficient (b) (feed composition: 2 wt% butanol in water, Vacuum: 0.3 kPa).

According to the Eyring diffusion theory [39], the higher temperature makes the osmotic molecules more active and easier to diffuse and migrate, which improves the thermodynamic process of dissolution. Moreover, the amplitude and frequency of polymer chain movement increase with the rising temperature, which in turn leads to an increase in the free volume of the preferentially organic-permeable membrane for molecular diffusion [34]. Therefore, the increase in free volume reduces the difference in separation factor of butanol /water. The total mass transfer coefficient of each component increases with the rising temperature (Fig. 10b).

Table 1. Activation energy of butanol isomers (feed composition: 2 wt% butanol in water, Vacuum: 0.3 kPa).

Component	ΔH_v/J·mol^{-1}	E_a/J·mol^{-1}	E_p/J·mol^{-1}
N-butanol	43.86	25.7	-18.16
Isobutanol	42.56	16.68	-25.88
Sec-butanol	41.7	24.16	-17.54
Tert-butanol	39.49	23.25	-16.24

3.2.4 Influence of vacuum

In the PV process, the pressure on the permeate side (degree of vacuum) is much lower than the saturated vapor pressure of each component, thus the solvents vaporize instantly. The influence of the osmotic pressure on the mass transfer of butanol isomers is investigated. With the decrease of vacuum (from 0.3 kPa to 4 kPa), the flux of butanol isomers gradually decreases (Fig. 11), which is consistent with the literature [41]. With the decrease of vacuum, the separation factor of n-butanol decreased but the separation factor of tert-butanol rise [42]. The decrease in the degree of vacuum increases the P_i^p

of each component. The saturated vapor pressure of each solvent follows n-butanol<isobutanol<sec-butanol<tert-butanol (Table S1). The difference in the boiling point of the solvents causes the mass transfer driving force between the solvents, and thus leads to the difference in the separation factor. The reduction in vacuum caused the separation factor of n-butanol to drop from 12.1 to 8.9, isobutanol from 14.3 to 13, tert-butanol increased from 9.4 to 10.3, and sec-butanol unchanged (Fig. 11c). When the pressure on the permeate side increased from 0.5 kPa to 3 kPa, the separation factor for the n-butanol/water binary system decreased from 30.5 to 7.4 [43]. When the degree of vacuum is low, the separation of butanol isomers in the water phase has a limiting effect on high-boiling substances, such as n-butanol and isobutanol. As the pressure on the permeate side increases, the flux of each component gradually decreases. Moreover, the separation factor of solvents with a boiling point higher than water decreases, and the solvents with a boiling point similar to water remains unchanged, while the solvents with a boiling point lower than water gradually increases.

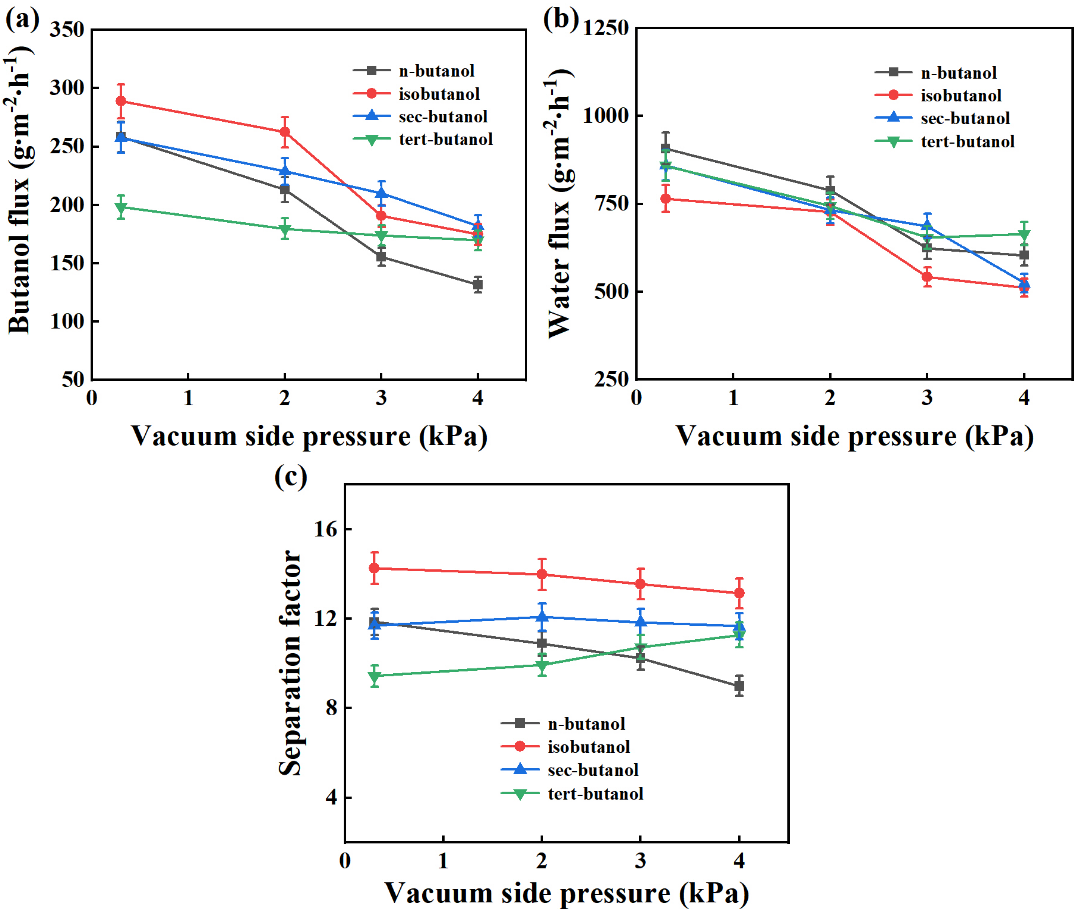


Fig. 11. Effect of vacuum (binary system) on (a) butanol flux, (b) water flux and (c) separation factor (feed composition: 2 wt% butanol in water, feed temperature: 40 °C).

3.2.5 Long-term stability and membrane performance comparison

Fig. 12 shows the variations of total flux and separation factor with the operation time. 10 h long-term test of PDMS commercial composite membrane for separating 2 wt% butanol isomers aqueous solution at 40 °C is performed. It can be observed that the separation factor changed slightly during the 10 h continuous. In addition, the concentration in feed decreased from 2 wt% to 0.3~ 0.5 wt%, indicating that the PDMS composite membrane has stable separation performance.

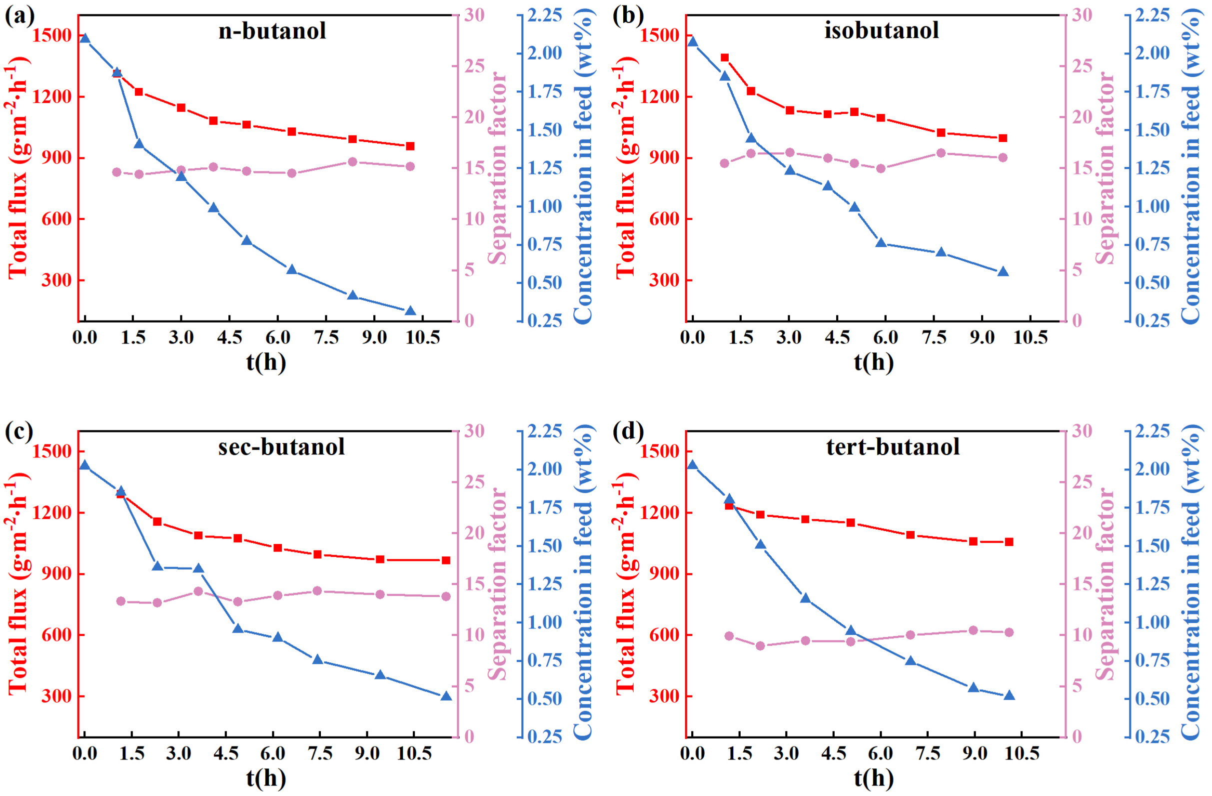


Fig. 12. Long-term PV performance of PDMS commercial composite membrane

(feed composition: 2 wt% butanol in water, feed temperature: 40 °C, Vacuum: 0.3 kPa).

The pervaporation performance of our PDMS composite membrane is compared with those of other PDMS membranes reported in the literature as summarized in Fig. S3 and Table S2 (support information for details). PDMS commercial composite membrane (this study) has a good flux for butanol/water separation, for instance, the flux of isobutanol/water in literature is 193~210 $g \cdot m^{-2} \cdot h^{-1}$, while the flux of the membrane in this study is 1238.1 $g \cdot m^{-2} \cdot h^{-1}$. The pervaporation process shows a great potential in the application of butanol/water separation.

4. Conclusions

The transmission difference of butanol isomers in the PDMS composite membrane is systematically studied. As feed concentration increases, the flux of butanol isomers increases and its order follows tert-butanol <sec-butanol <isobutanol <n-butanol. This is consistent with the theoretical value calculated by the half-time empirical formula. Meanwhile, water flux remains basically unchanged and has little correlation with its partial pressure. Comparing the binary and ternary systems, The PV resistance of butanol isomers is concentrated in three steps which based on the series resistance model: 1) leave the boundary layer; 2) dissolve into the functional layer; 3) diffuse through the functional layer. Moreover, water molecules have an antagonistic effect on the penetration of butanol. The separation of butanol isomers in the aqueous solution should combine polarity and solubility parameters. The separation factors of butanol are n-butanol (14.9), isobutanol (15.5), sec-butanol (14.4), tert-butanol (10.6).

As the temperature rises, the flux of butanol isomers gradually increases while the separation factors decrease. The permeation activation energy of butanol isomers is n-butanol (-18.16 $J\cdot mol^{-1}$), isobutanol (-25.88 $J\cdot mol^{-1}$), sec-butanol (-17.54 $J\cdot mol^{-1}$), tert-butanol (-16.24 $J\cdot mol^{-1}$), and the order is the same as the total mass transfer coefficient. As the pressure on the permeate side increases, the flux of butanol isomers gradually decreases, the separation factor of n-butanol and isobutanol gradually decreases, that of sec-butanol is basically unchanged, and that of tert-butanol gradually rises. This research provides an engineering point of view for PV separation of butanol isomers and have potential to be applied for separating other solvents with similar properties.

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Notes

The authors declare no competing financial interest.

Supplementary data

Supplementary data to this article including physical properties of the components, mass transfer resistance model and membrane performance comparison can be found online at XXX

Nomenclature

A	effective area of the membrane, m^2
D	diffusion coefficient, $cm^2 \cdot s^{-1}$
E_a	apparent activation energy, $J \cdot mol^{-1}$
E_p	permeation activation energy, $J \cdot mol^{-1}$
$f_{1,i}$	boundary layer resistance
$f_{2,i}$	PDMS membrane surface resistance
$f_{3,i}$	PDMS membrane internal resistance
J_0	pre-exponential factor
J_i	flux of component i, $g \cdot m^{-2} \cdot h^{-1}$
K_{ov}	total mass transfer coefficient
l	membrane thickness, um
m_i	weight of component i in the permeate, g
P_i	permeability of component i, $g \cdot m^{-2} \cdot h^{-1} \cdot kPa^{-1}$
$P_i^{\ p}$	permeate pressure of component i, kPa
$P_i^{\ sat}$	equilibrium partial vapor pressure of i in the feed, kPa
R_g	gas constant, $J \cdot mol^{-1} \cdot K^{-1}$
S	swelling degree
t	permeation time interval for the pervaporation, min
T	kelvin temperature, K
$t_{0.5}$	time when M_t/M_s is 0.5
V_i	molar volume of component i, $cm^3 \cdot mol^{-1}$
W_d, W_t, W_s	mass of the dry membrane, mass of membrane after t, Saturated swelling mass of membrane, g
x_i	weight fractions of components in the feed, wt%
$x_i^{\ f}$	mole fraction of i in the feed, mol%
y_i	weight fractions of components in the permeate, wt%

Δp	driving force
ΔH_v	enthalpy of evaporation, $J \cdot mol^{-1}$

Greek

α	separation factor
β, $\beta_{idea,i,n}$	selectivity and ideal selectivity for isobutanol or sec-butanol or tert-butanol and n-butanol
γ_i	activity of components i
χ	interaction parameter
δ_1, δ_2	solubility parameters of PDMS and solvent, $J^{1/2} \cdot cm^{-3/2}$

Subscript

PV	pervaporation
PDMS	polydimethylsiloxane
SI	support information
N	n-butanol
I	isobutanol
S	sec-butanol
T	tert-butanol
W	water

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