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Pervaporation Recovery of Acetone-Butanol from Aqueous Solution and Fermentation Broth Using HTPB-Based Polyurethaneurea Membranes

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In this paper, hydroxyterminated polybutadiene-based polyurethaneurea (HTPB-PU) pervaporation membranes were prepared by phase inversion and used for recovering acetone and *n*-butanol from dilute aqueous solutions. The effects of the operation temperature and feed composition on the pervaporation performance were investigated. The differences of the separation performance between the ternary mixture and binary mixture were also studied through evaluating the permeability coefficient, the swelling degree of the membrane, and the activity coefficient. The results indicated that a complex "coupling effect" occurred in the ternary mixture. The pervaporation performance for the ternary mixture was superior to that for the binary mixture because of the permeant-permeant and permeant-membrane interactions. A high selectivity towards acetone and *n*-butanol was obtained. Acetone and butanol were condensed from 1.5 to 11.9 wt% and 3.0 to 43.5 wt% at 40°C for the ternary mixtures, respectively. Furthermore, potential of the membrane for separation of organics from fermentation was also studied by testing the pervaporaton performance, and acetone and butanol were condensed from 0.5 to 8.7 wt% and 1.1 to 16.4 wt% at 45°C, respectively.

Keywords acetone; butanol; fermentation; pervaporation membrane; polyurethaneurea

INTRODUCTION

Due to extensive oil depletion and its increasing price trend over the past decades, the use of biofuels as a partial replacement for fossil fuels has attracted both academic and industrial attention. Among alternative biofuels, biobutanol is expected to play an important role in the next generation of biofuels (1). Butanol (1-butanol, *n*-butanol) is a clear, low-viscosity, neutral C4 primary alcohol. It has been widely used as solvent for acid-curable lacquers and baking finishes. Similarly to the interest in bioethanol and biodiesel, an important application has emerged for butanol as a renewable energy since it can be used directly as a liquid fuel, and has many chemical and physical features that are particular attractive for application as a biofuel (1,2). Biobutanol can be prepared by fermentation of acetone-butanol (AB), but the fermentation process suffers from product inhibition (acetone/*n*-butanol) and high energy requirements to recover AB from the fermentation broth, which brings about unfavorable economic competition with the petrochemical industry (3,4). Therefore, the in-situ product removal by integrating some separation processes has been proposed, including pervaporation, gas stripping, reverse osmosis, liquid–liquid extraction, and so on (5). Among these processes, pervaporation offers a promising direction as an effective technology (6).

The pervaporation performance depends on the choice of membrane materials. However, very few polymer membranes are available for the separation of AB from an aqueous solution or the fermentation broth. Polyether-block-amide (PEBA) is a copolymer comprised of rigid polyamide and flexible polyether blocks. The membrane of PEBA has been tried to recover butanol from a dilute aqueous solution (7). Other works for removal of butanol from a dilute aqueous solution using several hydrophobic pervaporation membranes have been reported, such as poly(vinylidine difluoride) (PVDF) (8), polydimethylsiloxane (PDMS) (9,10), poly[-1-(trimethylsilyl)-1-propyne] (PTMSP) (11,12), and silicalite/silicone (13,14). However, the prepared membranes either did not exhibit a high selectivity toward AB, or demand a very high cost for the high selectivity toward AB, which restricted the large scale applications. In addition, ionic liquid-PDMS membrane (15) and liquid-trioctylamine membrane (16) have been integrated with fermentation for the recovery of AB, which showed a high selectivity to AB despite the low mass flux. Unfortunately, there have been very few large-scale applications of liquid membrane due to insufficient membrane stability (17).

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Polyurethane copolymers have a unique polymer chain structure and morphology comprising flexible soft segment (polyol) and rigid hard segment (diisocyanate and chain extender, viz. diol, diamine), and the affinity for organics can be increased by the selection of polyol in polyurethane (18). Hydroxyterminated polybutadiene-based polyurethaneurea (HTPB-PU) membranes had been used for the separation of ethanol-water mixture (19,20), furfural-water mixture (21), and gas mixtures (22), and showed fine separation performances. Comparing with the original polyurethane, the higher hydrophobic nature of polybutadiene in HTPB-PU provided advantages for the perselectivity of acetone and butanol from the dilute aqueous solution.

The object of this paper is to evaluate the pervaporation performance of HTPB-PU membrane for separating acetone and *n*-butanol from binary acetone-water (A/W), *n*-butanol-water (B/W), as well as ternary acetone-*n*-butanol-water (A/B/W) at various feed compositions and operation temperatures. In order to investigate the difference of separation performances between ternary and binary mixtures, the permeability coefficient, the swelling degree of the membrane, and the activity coefficient were determined. Furthermore, the separation performance for the fermentation broth was also investigated.

THEORY

In the pervaporation process, permeation is governed by the solubility and diffusivity of each of the components in feed. Thus, it is significant to estimate the permeability coefficients of the penetrating molecules. Based on the solution-diffusion model, the flux of the component i through the membrane can be expressed as:

$$J_i = \frac{D_m C_{i,m}(1 - p_{i,d}/p_i^e)}{l_m} \tag{1}$$

where D_m is the diffusion coefficient in the membrane, $C_{i,m}$ is the permeate concentration in the membrane at the liquid-membrane interface, $p_{i,d}$ is the partial pressure of the component i in downstream, p_i^e is the equilibrium vapor pressure of the component i at the interface between the liquid feed and the membrane, and l_m is the thickness of the membrane. Meanwhile, the equation of overall mass transfer can be expressed as (10):

$$J_i = k_{ov,i}(\gamma_{i,b}C_{i,b} - \gamma_{i,w}C_{i,w}p_{i,d}/p_i^e) \tag{2}$$

where $C_{i,b}$ and $C_{i,w}$ are the concentrations of component i in liquid bulk and at the interface of liquid feed and membrane, respectively. $k_{ov,i}$ is the overall mass transfer coefficient, $\gamma_{i,b}$ and $\gamma_{i,w}$ are the activity coefficient of component i in the liquid bulk and at the interface of the liquid feed and the membrane, respectively. $\gamma_{i,b}$ can be predicted by the effective UNIFAC group-contribution method (23). For a sufficient low downstream pressure on the permeate side, the second term on the right hand of Eq. (2) becomes negligible. Then the overall mass transfer coefficient ($k_{ov,i}$) can be determined from the experimentally measured flux (J_i) as a function of component i concentrations:

$$J_i = k_{ov,i}\gamma_{i,b}C_{i,b} \tag{3}$$

The mass transfer coefficient of the membrane includes sorption to, diffusion through and desorption from the membrane. It could be expressed as:

$$k_{m,i} = \frac{P_i}{l_m} \tag{4}$$

where P_i is the permeability coefficient of solute, $k_{m,i}$ is the membrane mass tranfer coefficient through the membrane. When the feed flow is sufficient, $k_{ov,i}$ is very close to $k_{m,i}$ if the resistance to the mass transport is neglected in the feed boundary layer (24). Combining Eqs. (3) and (4) together generates the following expression for the permeability coefficient:

$$P_i = \frac{l_m J_i}{\gamma_{i,b}C_{i,b}} \tag{5}$$

Equation (5) can be used to calculate the permeability coefficient P_i from the experimentally measured flux J_i, the feed concentration $C_{i,b}$, and the activity coefficient $\gamma_{i,b}$ as well as the membrane thickness l_m.

EXPERIMENTAL

Materials

HTPB (hydroxyl value = 1.08 mmol KOH g^{-1}, Mw = 2000) was bought from Qilu Petrochemical Engineering Co., Ltd. (Shandong, China); Tetrahydrofuran (THF) were purchased from Hangzhou Chemical Agent Co., Ltd. (Hangzhou, China) and used as a solvent. Dibutyltindilaurate (DBTDL, catalyst) and toluene 2,4-diisocyanate (TDI) were purchased from Hangzhou Electronical Group Auxiliary Chemical (Hangzhou, China). 3,3-dichloro-4,4-diaminodiphenymethane (MOCA) was bought from Zhejiang Changxin Chemical Co., Ltd. (Hangzhou, China) and used as a chain-extender.

The organic compounds used in the pervaporation tests were acetone and *n*-butanol, which were purchased from Hangzhou Chemical Agent Co., Ltd. (Hangzhou, China). Their physical-chemical parameters were listed in Table 1.

Membrane Preparation

The synthesis of HTPB-PU was carried out as described in our previous work (25). Prepolyurethane was prepared by a reaction between HTPB and TDI at a mole ratio 2:1 of NCO:OH in dry THF with 0.05 wt% DBTDL as a

TABLE 1
Physical constants of acetone[a], *n*-butanol[a], water[a] and HTPB-PU[b]

Component	M (g/mol)	V_m (10^{-6} m^3/mol)	T_b (°C)	P_v (kPa) at 20°C	δ (10^3/J$^{1/2}$/m$^{3/2}$)
Acetone	58.08	73.3	57	24.61	20.0–20.5
n-Butanol	74.12	91.4	117.7	0.73	23.0–23.6
Water	18.02	18.0	100	2.34	47.9–48.1
HTPB-PU	2000*	–	–	–	20.2–20.6

[a] Derived from Handbook of solubility parameters and other cohension parameters.
[b] The calculated value.
M: molecular weight; V_m: molar volume; T_b: boiling point; P_v: vapour pressure; δ: total solubility parameter. *: average molecular weight.

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catalyst at 30°C for 60 min with strong stirring. Polyurethaneurea was prepared by adding the chain-extender MOCA ($OH:NH_2 = 1:1$) into the prepolyurethane with mechanical stirring for 15 min. After that, the HTPB-PU solution at a solid content of 30 wt% was cast by knife-coating on a clean Teflon plate. The cast film of HTPB-PU about 140 μm thick was left overnight at room temperature for moisture curing, then it was followed by thermal curing at 70°C for 4 h.

FT-IR and DSC Analysis

The chemical structures of HTPB, prepolyurethane and HTPB-PU were characterized by a Bruck Vector22 type Fourier transform infrared (FT-IR) spectrometer. The samples for FT-IR measurement were obtained by spreading a thin film of the solutions of THF on a potassium bromide flake. The solvent was evaporated under vacuum at room temperature. The differential scanning calorimetry (DSC) test of HTPB-PU was performed with a Perkin-Elmer Pyris 1 DSC under N_2 atmosphere at a heating rate of 20°C/min from −150 to 200°C.

Degree of Swelling

The measured HTPB-PU membranes were immersed in water, acetone, butanol, A/W, B/W and A/B/W solutions, and at room temperature, respectively. At regular intervals, the swollen membranes were wiped out carefully with tissue paper to remove superficial liquid and weighted in a tightly closed bottle. The degree of swelling (DS) was calculated using the following equation:

$$DS(\%) = \frac{S_i - S_0}{S_0} \times 100 \tag{6}$$

where S_i and S_0 were the weights of the membrane in wet and dry states, respectively.

Pervaporation Measurement

The pervaporation apparatus used in this study was shown in Fig. 1. The membrane was installed in the cell and the effective area was 42.0 cm^2. The feed solution was continuously circulated from a feed tank to the upstream side of the membrane at the specified temperature by a pump. The downstream pressure was kept at about 0.3 kPa and the permeate was collected by the cold trap.

The performance of the pervaporation process was described by flux (J) and the separation factor (α), which were defined as follows:

$$J = \frac{m}{A \cdot t} \tag{7}$$

$$\alpha = \frac{Y_i/(1 - Y_i)}{X_i/(1 - X_i)} \tag{8}$$

where m, A, and t represented the weight of permeate (g), the effective membrane area (m^2) and the operating time (h), respectively. Furthermore, X and Y are the mass fractions of the organic in the feed and permeate where the subscripts i represents acetone or n-butanol. The weight

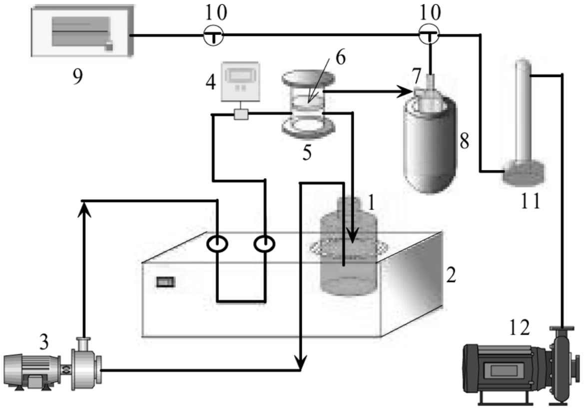

FIG. 1. Schematic diagram of the PVAP experimental equipment: 1-feed tank, 2-digital constant temperature bath, 3-diaphragm pump, 4-electronic thermometer, 5-membrane cell, 6-membrane, 7-permeate collection tube, 8-cold trap, 9-vacuometer, 10-three-way glass stopcock, 11-desiccator, 12-vacuum pump.

fractions of acetone and *n*-butanol were determined by a gas chromatography (Model GC-1890, HP Analytical Instrument Corporation, Shanghai, China).

AB Fermentation

Clostridium acetobutylicum ATCC 824 was bought from American Type Culture Colledtion as spores. The seed liquid was prepared as follows: 2.5 g corn media was soaked in 50 ml water for 20–30 min in a 100 ml screw-capped Erlenmeyer flask which was autoclaved at 121°C for 20 min, followed by cooling to 37°C under oxygen-free nitrogen atmosphere in an anaerobic chamber. Then, the inoculation rate of 5% was added into the Erlenmeyer flask and incubated at 37°C for 18–24 h. Then a 30 mL cell suspension was inoculated to a 400 mL corn media and grew at 37–38°C for 2–3 days. At the end of the fermentation, the concentrations of acetone, butanol, and ethanol in the fermentation broth were about 5 g/l, 11 g/l, and 1 g/l, respectively.

RESULTS AND DISCUSSION

FT-IR and DSC Analysis

The FT-IR spectra of HTPB, HTPB-PU and prepolyurethane were shown in Fig. 2. The strong absorption of the asymmetric–NCO stretch at the 2270 cm^{-1} appeared in the spectrum of prepolyurethane and almost disappeared in that of HTPB-PU. It indicated that the reaction of the chain extent was completed. In prepolyurethane, the peaks of 1738 cm^{-1} (C=O) and 1531 cm^{-1} (N-C) were also observed, which confirmed the forming of the urethane group (−NHCOO−).

The multicomponent copolymers often had a heterogeneous structure owing to the immiscibility of each component. *Tg* obtained by DSC measurements could be used to investigate the heterogeneity of a copolymer. In Fig. 3, two glass-transition temperatures (*Tg*), −75 and 65°C were displayed to reveal that there existed two kinds of incompatible microdomain in the HTPB-PU membrane. The HTPB soft segment was very hydrophobic and the urethane hard segment was very hydrophilic (25), which indicated that the higher *Tg* in the block copolymer membrane was attributed to the urethane component, and the lower *Tg* was from the HTPB component.

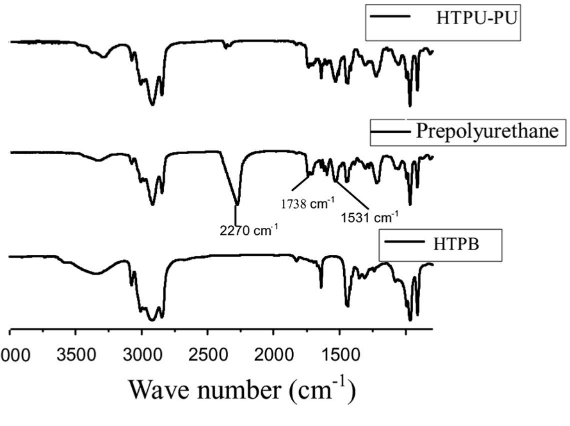

FIG. 2. FTIR spectra of the HTPB, prepolyurethane and HTPB-PU.

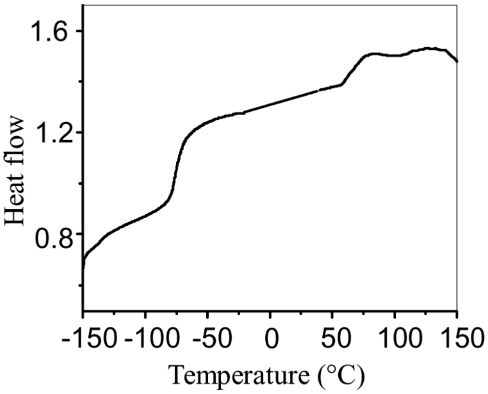

FIG. 3. DSC thermogram of HTPB-PU.

Swelling in Organic Solution

In the pervaporation process, the selectivity of the membrane is dependent on the interaction between the permselective layer of the membrane and the liquid feed. A study on the swelling degree as a function of contacting liquid composition could give an insight into the membrane characteristics in various liquid mixtures. From Fig. 4, it was found that the equilibrium swelling degree of the HTPB-PU membrane in B/W ($DS = 0.99\%$ to 2.29%) was more significant than that in A/W ($DS = 0.39\%$ to 0.69%) (Fig. 4a) with the increase of organic concentration in the feed solution. Comparing lines a–c and a–d in Fig. 4a, the swelling degree of the membrane in the ternary aqueous solution was higher than the algebraic addition of *DS* values in the A/W and B/W solutions, which implied that the sorption capability of the membrane in the ternary solution was enhanced on account of the "plasticizing effects" between the solutes and the membrane (26). Moreover, the swelling degree of the membrane was more obvious in pure acetone and butanol than in pure water (Fig. 4b). The order of the sorption coefficient was: butanol (16.78%) > acetone (14.54%) > water (0.19%). Therefore, the HTPB-PU membrane could be regarded as a suitable candidate for pervaporation separation of AB from aqueous solution.

Effect of Feed Composition

For the pervaporation of a dilute aqueous solution, there is usually a nonlinear relationship of the permeation flux with the feed content due to the complex interaction between the membrane and the feed. Therefore, the influence of feed composition on the pervaporation

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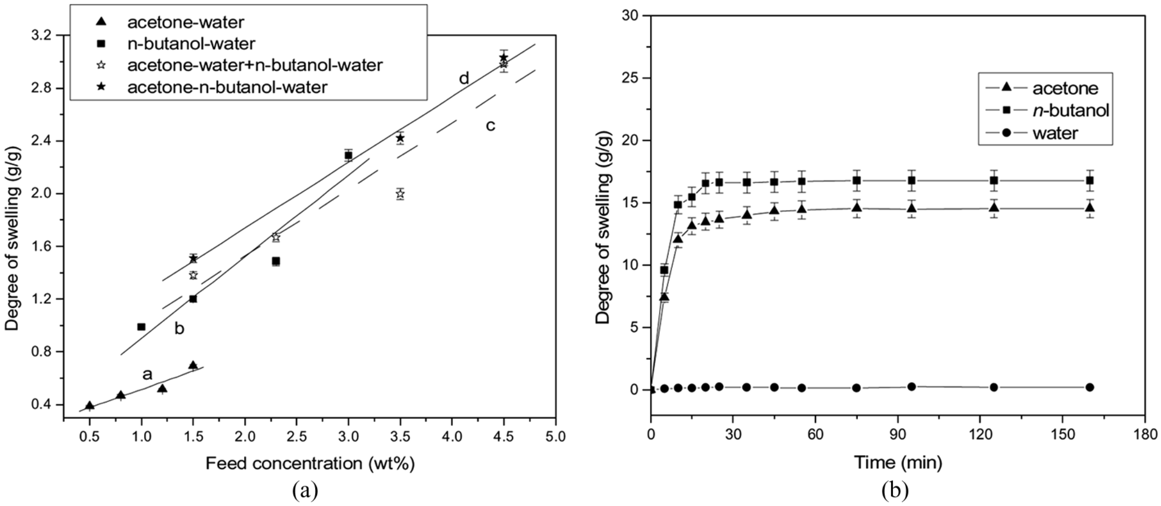

FIG. 4. Degrees of swelling of membrane in different organic concentrations of acetone-water (a, line a–a, ▲), *n*-butanol-water (a, line a–b, ■), acetone-*n*-butanol-water (a, line a–d, ★) mixtures and pure solutions (b). Line a–c (☆) is the algebraic addition value of line a–a (▲) and line a–b (■).

performance for A/W, B/W, and A/B/W dilute aqueous solutions was investigated. The results of Fig. 5(a, b) showed that the fluxes of acetone and butanol through the membrane were enhanced with increasing organic concentration, and the increase of butanol flux was more significant than that of acetone. Though the increase of the acetone concentration in the feed also increased the water flux, the increase of the acetone flux through the

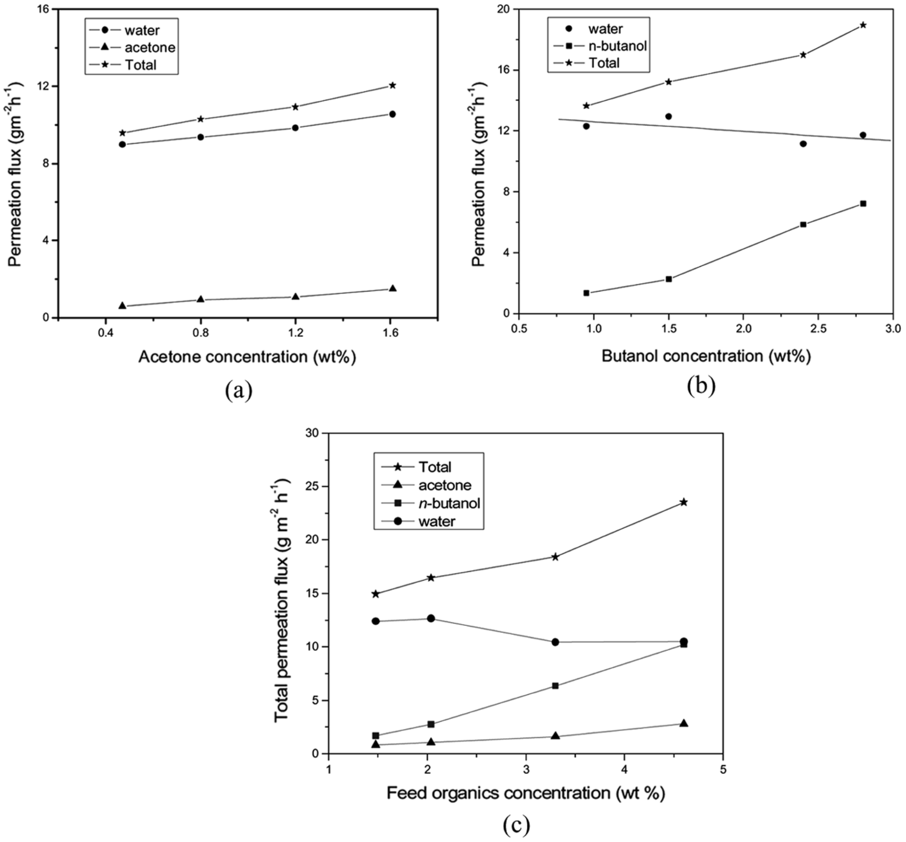

FIG. 5. Effect of feed organic concentration on permeation fluxes of organic and water for the binary acetone–water (a), *n*-butanol-water (b) and ternary *n*-butanol-acetone-water (c, $m_{n\text{-butanol}}$: $m_{acetone} = 2{:}1$) mixtures at 40°C.

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membrane was much more significant than the increase of the water flux (Fig. 5a). It had been found to be the similar case in the selective removal of propyl propionate from aqueous solutions using PEBA 2533 membranes (27), which showed that an increase of space available for diffusion and mobility of the polymer segments promoted in a swollen polymer led to the increase of the propyl propionate flux and water flux with the increase of propyl propionate concentration in the feed. And the increase in propyl propionate flux was much more significant than the increase in the water flux. Moreover, from Table 1, the solubility parameters (δ) of acetone was much closer to that of HTPB-PU than that of water, which indicated the strong affinity between the acetone and the polymer and more acetone molecules were sorbed into the membrane. Consequently, more acetone molecules were able to pass through the acetone swollen membrane and acetone permeation flux increases as the increase of acetone content in the feed solution.

However, the conclusion generated from the permeance versus feed butanol concentration plot (Fig. 5b) was not fully in agreement with the previous analysis. From Fig. 5b, the water flux almost kept constant with the increase of butanol concentration in the B/W mixture. This observation could be presumably associated with the water clustering developed in the membrane arising from repulsive interaction between water and butanol absorbed. Water itself exists in the form of hydrogen-bonded clusters, which implied that "free" water molecules might diffuse accompanied by clustered molecules and permeation of water through polymer membranes could be hindered by the formation of the water clusters (28). Furthermore, because butanol had a strong hydrophobic nature and low solubility in water, it enhanced the development of the water cluster. Therefore, the presence of butanol molecules shifted the water structure to a larger one which hinder the mass transfer of water through polymer membrane. Consequently, the water permeation almost kept constant with the increase of butanol concentration on the B/W mixture.

Figure 6 demonstrated that the tendency of the selectivities of acetone and butanol were reverse with increasing the feed concentration. The separation factor of acetone decreased with the increase of its concentration. A similar tendency had been reported by Liu et al. (6) about the recovery of acetone from the A/W solution using a homogenous PEBA 2533 membrane, which showed that a decrease in the separation factor of acetone was caused by the increase of the coupling effect on the permeation between acetone and water. Acetone could be dissolved arbitrarily in the water, and thus, had a strong interaction and cohesion effect to enhance the couple effect between acetone and water (29). Moreover, a better swelling of the hydrophobic membrane in contact with acetone resulted in a larger space between the polymer chains, which led to a decrease in the separation factor. This trend was consistent with the previous report (30). On the contrary, the separation factor of butanol ascended sharply with the increase of organic concentration. When the organic concentration of B/W increased, the swelling degree of the membrane ascended greatly (not overswelling), which could easily enhance the permeation of butanol. Because the development of water clusters depended on its circumstance, an increase of butanol molecules in the membrane tended to repel much more water molecules through the polymer membrane. Consequently, the separation factor of butanol increased with the increase of butanol concentration of the B/W mixture.

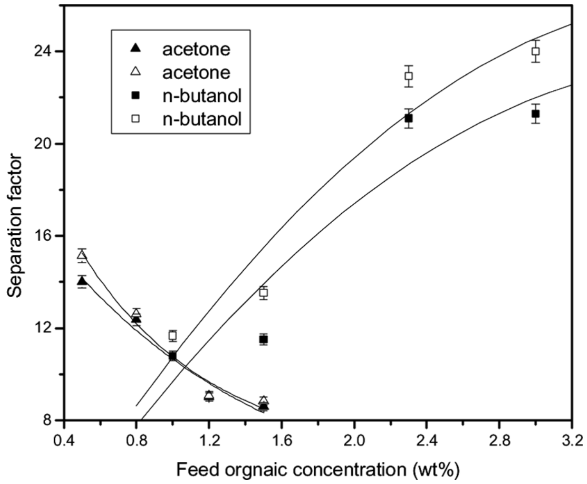

FIG. 6. Effect of organic concentration in the feedstock on selectivity for the pervaporation of binary acetone-water (▲), *n*-butanol-water (■) and ternary *n*-butanol-acetone-water (△□, $m_{n\text{-butanol}}$: $m_{\text{acetone}} = 2{:}1$) mixtures at 40°C.

From Fig. 5c. acetone and butanol were condensed from 1.5 to 11.9 wt% and 3.0 to 43.5 wt% at 40°C for the ternary mixtures, respectively. Comparing the experimental result of Figs. 5a–c, it could be seen that the total permeation flux for the ternary A/B/W was higher than that for the binary A/W or B/W under the same component concentration, which might be analyzed in terms of evaluating the swelling degree and the permeability coefficient (P_i). The permeability coefficient (P_i) was calculated by Eq. (5) in terms of experimentally measured flux, feed concentration, membrane thickness and activity coefficient (Fig. 7(a) and (b)), and the results were given in Table 2. The P_i of acetone and butanol for the ternary mixture were higher than that for the binary mixture in the same component concentration. Combined with the results of the swelling degree, both the permeant-permeant and permeant-membrane interactions led to the better flux and selectivity for the ternary mixture than the obtained data from that for the binary mixture.

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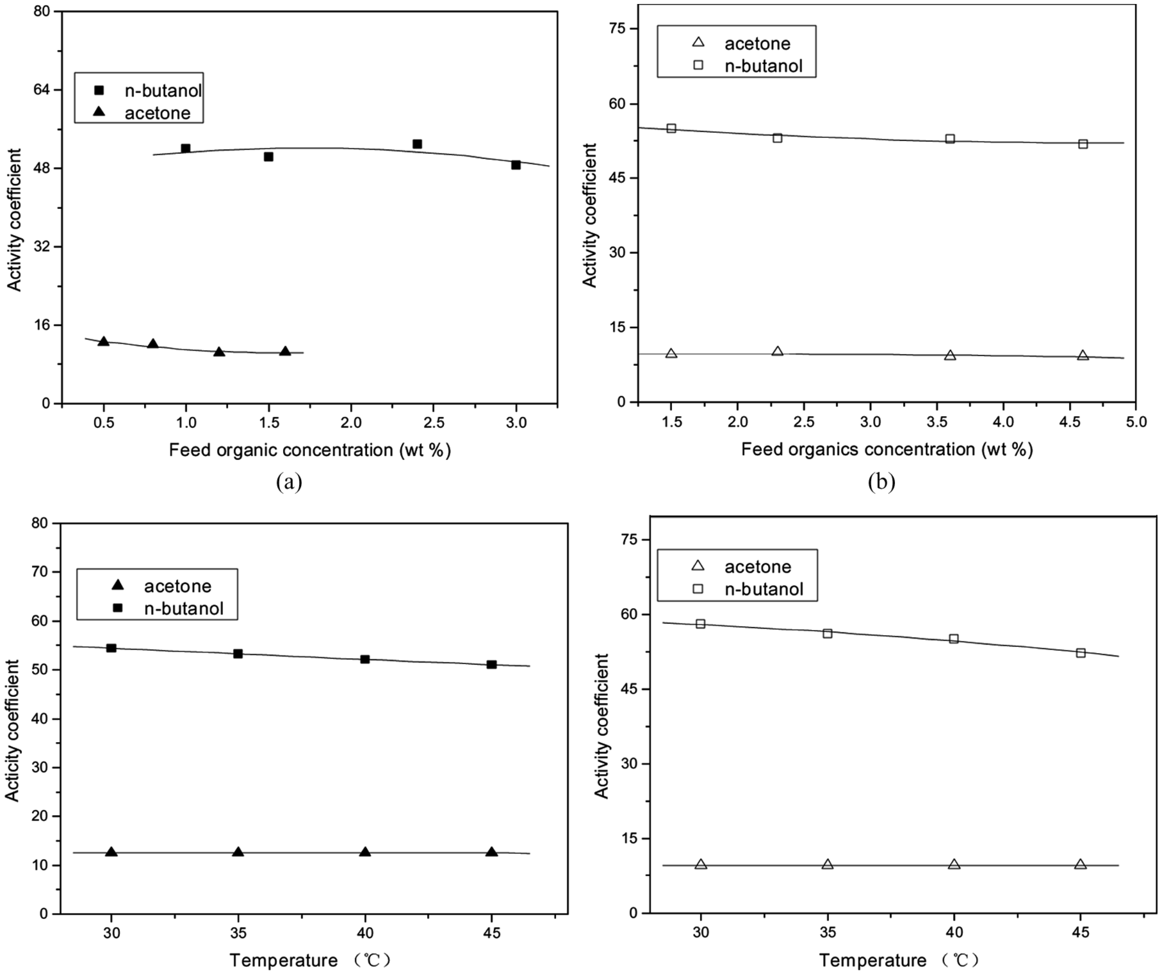

(a) (b) (c) (d)

FIG. 7. Effects of feedstock composition and operating temperature on the values of activity coefficient of acetone in water and of *n*-butanol in water. (a) acetone-water and *n*-butanol-water (at 40°C); (b) *n*-butanol-acetone-water (at 40°C, acetone: *n*-butanol = 1:2); (c) acetone-water (0.5 wt%) and *n*-butanol-water (1.0 wt%); (d) *n*-butanol-acetone-water (1.5 wt%, acetone: *n*-butanol = 1:2).

TABLE 2
Permeability coefficient (P_i) determined by Eq. (5) for organic/water mixtures at different organic concentrations

Initial organic concentration (wt%)	$P_{i,b} \times 10^{11}$ (m^2/s)		$P_{i,t} \times 10^{11}$ (m^2/s)	
	Acetone	*n*-Butanol	Acetone	*n*-Butanol
0.5	4.04	–	8.28	–
0.8	3.89	–	7.05	–
1	–	1.08	–	1.12
1.2	3.49	–	7.50	–
1.5	3.53	0.80	7.66	1.38
2.4	–	1.84	–	2.09
3	–	2.12	–	2.54

$P_{i,b}$ for the binary aqueous solution; $P_{i,t}$ for the ternary aqueous solution.

Effect of Operating Temperature

Since the diffusion and solubility of the penetrants in the membrane are dependent on the operation temperature, the permeation flux is also dependent on the temperature. The results in Figs. 8(a–c) and 9(a–c), illuminated that the temperature dependence of selectivity and permeation flux for the pervaporation of A/W, the B/W binary mixtures, and the A/B/W ternary mixture, respectively. The rising of feed temperature led to an increase in the total flux and the selectivity of acetone or butanol. This phenomenon was evidently different from some other reports using the PEBA membrane (6) or silicalite/silicone membrane (14), which showed that the selectivity of AB decreased with the increase of the feed temperature.

Based on the solution-diffusion model, the sorption of the penetrant into the membrane and the diffusion of the

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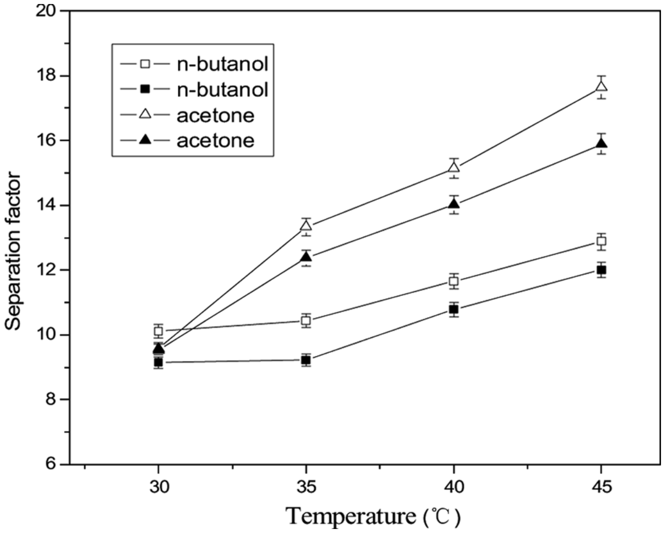


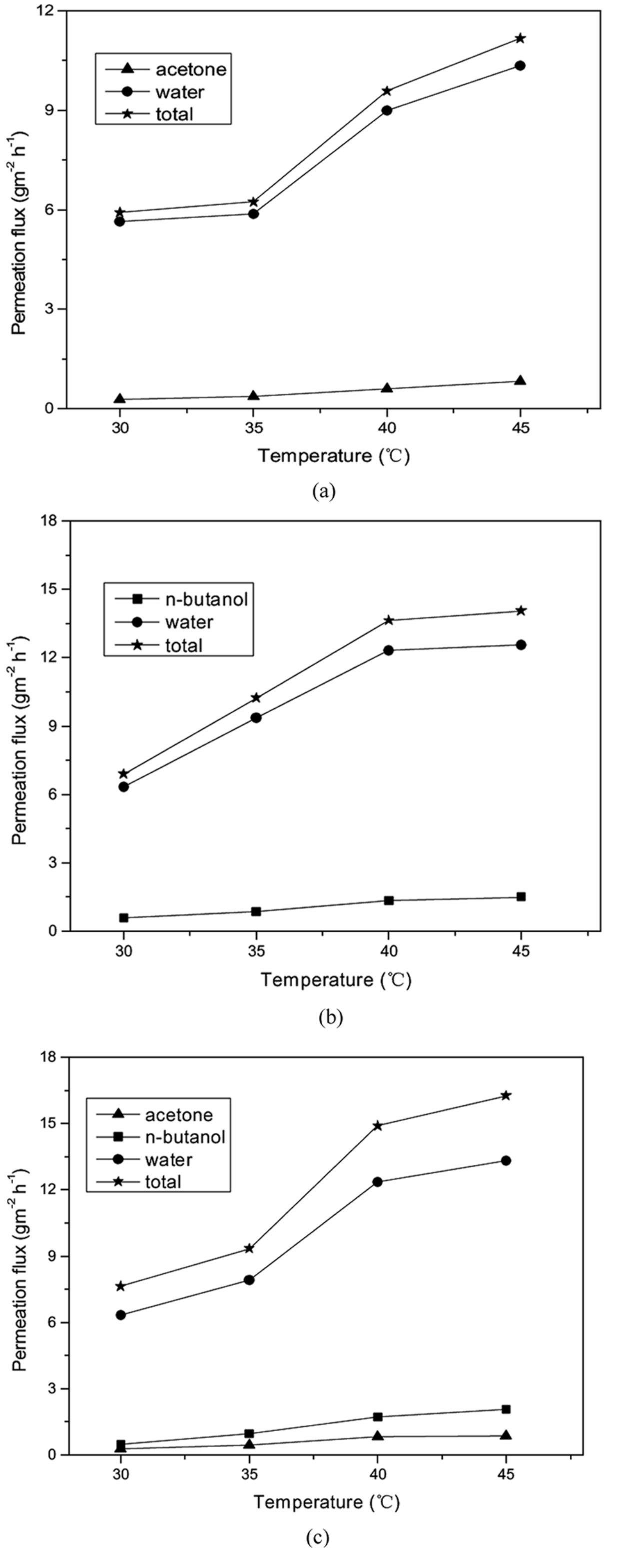
FIG. 8. Effect of operating temperature on selectivity for the pervaporation of binary acetone-water (▲), *n*-butanol-water (■) and ternary *n*-butanol-acetone-water (△□, $m_{n\text{-butanol}}$: $m_{acetone} = 2{:}1$) mixtures. (organic concentration: acetone–water, 0.5 wt%; *n*-butanol-water, 1 wt%; *n*-butanol-acetone-water, 1.5 wt%).

penetrant through the membrane were two major aspects in the pervaporation transport process. With the increase of the operating temperature, the movement of HTPB-PU molecular chain in the membrane was intensified and the permeating molecules became more energetic. On the other hand, an increase of temperature facilitated the thermal motion of the polymer chains of the membrane in terms of frequency and amplitude which got the permeant molecules to diffuse in the membrane more easily. Moreover, the adsorption-desorption rate of the permeation molecules was reinforced in the polymer chain and the overall diffusion rate had also increased. Thereby, the permeation flux increased with the increase of the operating temperature. The variation of the total flux with temperature was determined to follow an Arrhenius relationship:

$$J_i = J_0 e^{-E_a/RT} \tag{10}$$

where J_i ($\mathrm{kg\,m^{-2}\,h^{-1}}$) was the permeation flux of component *i*, J_0 ($\mathrm{kg\,m^{-2}\,h^{-1}}$) was the pre-exponential factor, E_a (kJ/mol) was the activation energy associated to the permeation process, R (kJ/mol K) was the gas constant, and T (K) was the absolute temperature.

The logarithmic plot of water and the organic compound fluxes versus the reciprocal of the absolute temperature for the A/W, B/W and A/B/W were displayed in Fig. 10(a–c) and the estimated values were listed in Table 3. The activation energy of permeation, characterizing the overall effect of temperature on the permeation flux, could be regarded as an important parameter. The apparent



(a)

(b)

(c)

FIG. 9. Effect of operating temperature on total permeation flux for the pervaporation of binary acetone-water (a), *n*-butanol-water (b) and ternary *n*-butanol-acetone-water (c, $m_{n\text{-butanol}}$: $m_{acetone} = 2{:}1$) mixtures. (organic concentration: acetone-water, 0.5 wt%; *n*-butanol-water, 1 wt%; *n*-butanol-acetone-water, 1.5 wt%).

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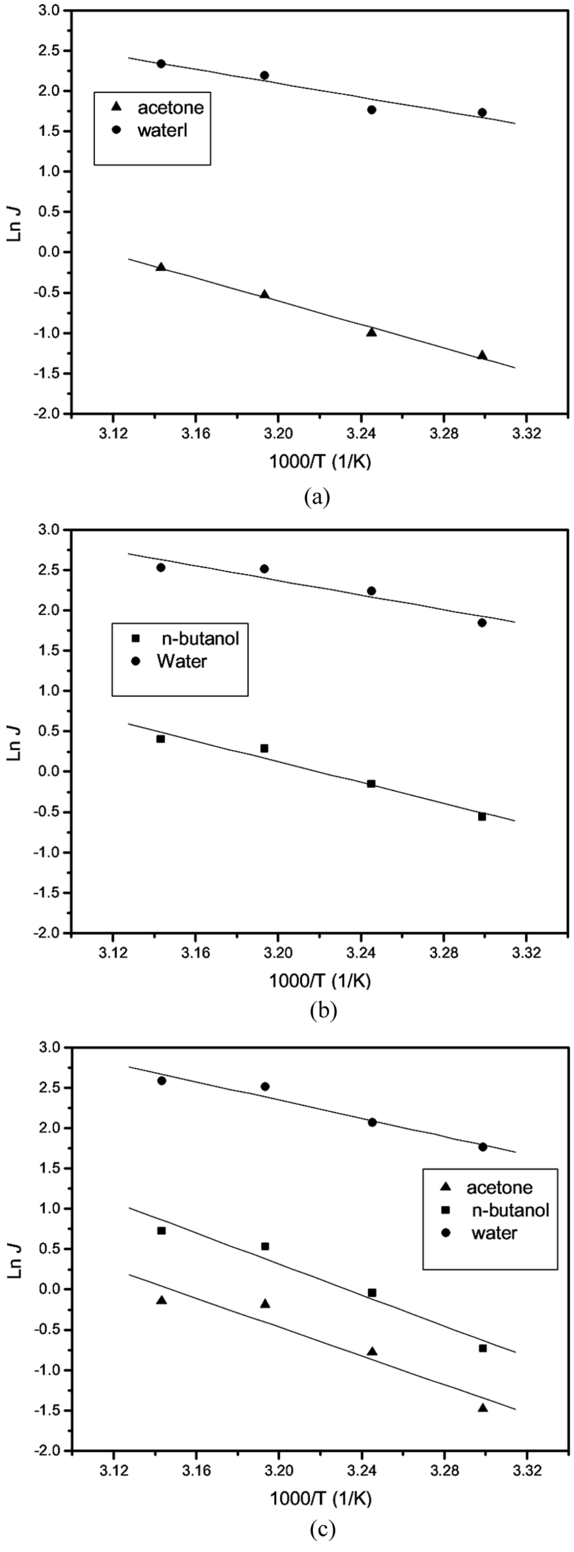

(a)

(b)

(c)

FIG. 10. Logarithmic plots of organic and water fluxes versus reciprocal of absolute temperature for acetone-water (a), *n*-butanol-water (b) and *n*-butanol-acetone-water (c) mixtures.

TABLE 3
Values of the activation energy (E_a) of organic and water fluxes for the acetone-water (0.5 wt%), *n*-butanol-water (1.0 wt%) and *n*-butanol-acetone-water (1.5 wt%, $m_{n\text{-butanol}}$: $m_{\text{acetone}} = 2{:}1$)

	E_a (kJ/mol)		
Feed solution	Acetone	*n*-Butanol	Water
Acetone-water	59.9	–	36.0
n-Butanol-water	–	66.6	52.5
Acetone-*n*-butanol-water	76.2	81.4	46.5

activation energy for the three compounds in the ternary mixtures had been calculated to be 76.2, 81.4, and 46.5 kJ/mol for acetone, butanol and water, respectively. In other words, the permeations of acetone and butanol through HTPB-PU membrane were considered to be more temperature-sensitive than that for water. Therefore, when the operation temperature increased, the permeation flux of butanol and acetone increased more than that of water. Consequently, the selectivity of acetone or butanol increased with the increase of the operating temperature.

The pervaporation performance for the ternary mixture was superior to that for the binary mixture of the corresponding component concentration, which also could be explained through evaluating the permeability coefficient (P_i) and the swelling degree of the membrane. The permeability coefficient (P_i) was calculated by Eq. (5) in terms of experimentally measured flux, feed concentration, membrane thickness, and activity coefficient (Fig. 7(c) and (d)), and the results were given in Table 4. It could be found that the permeability coefficient (P_i) was enhanced with the increase of the operating temperature and P_i of acetone

TABLE 4
Permeability coefficient (P_i) determined by Eq. (5) for organic/water mixtures at different feed temperatures

Feed operating temperature (°C)	$P_{i,b} \times 10^{11}$ (m^2/s)		$P_{i,t} \times 10^{11}$ (m^2/s)	
	Acetone	*n*-Butanol	Acetone	*n*-Butanol
30	1.78	0.41	2.37	0.43
35	2.35	0.63	4.78	0.66
40	4.04	1.08	8.28	1.12
45	5.30	1.14	9.05	1.54

$P_{i,b}$ for the binary aqueous solution; $P_{i,t}$ for the ternary aqueous solution.

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and *n*-butanol for the ternary mixture were higher than that for the binary mixture of the same component concentration. Therefore, it could be expected that a complex "coupling effect" occurred among the permeating components in the A/B/W solution because of the interactions of the permeant-permeant and permeant-membrane. Thus the membrane selectivity and flux of AB for the ternary mixture were larger than that for the binary mixture.

Membrane Separation Performances for AB Fermentation Broth

The above result verified that the HTPB-PU membrane could be applied for the recovery of AB from the *C. acetobutylicum* fermentation broth containing 11 g/l butanol, 5 g/l acetone, and 1 g/l ethanol. The influence of the operating temperature was displayed in Fig. 11. It indicated that the total flux, the acetone, and the butanol fluxes, the separation factors of acetone and butanol at 40°C, were 9.7 g/m^2 h, 0.5 g/m^{2}h, 1.1 g/m^{2}h, 15.3 and 13.7, respectively. Moreover, the selectivity of AB for the fermentation broth was higher than that for the ternary aqueous solution at similar AB concentration despite of the lower total permeation flux. It was in agreement with the results presented by O'Brien and Craig (31), who studied the in-situ product recovery for ethanol fermentation using the MPF-50 membranes by pervaporation. Due to the association of glucose and water molecules in the fermentation broth, water molecules were hindered though the HTPB-PU membrane. Moreover, because of more complex ingredients and deposition of other components in the fermentation broth such as higher viscosity and density, inorganic salts, glucose, polysaccharide, and other macromolecules, concentration polarization and the gel layer were formed in the membrane surface which led to the membrane flux decrease.

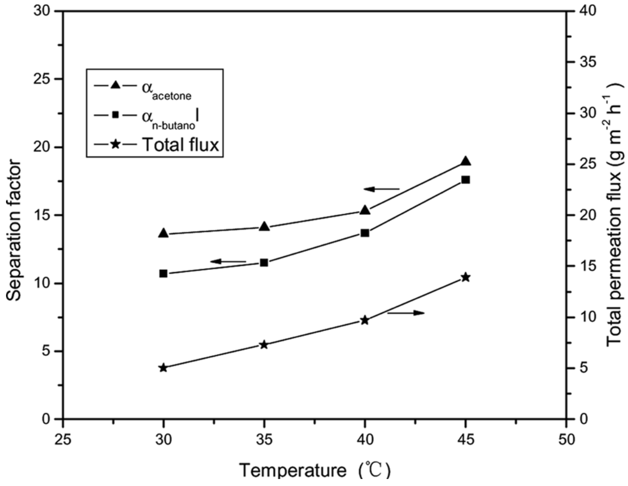

FIG. 11. Effect of operating temperature on selectivity and total permeation flux for the pervaporation experiments of fermentation broth.

CONCLUSIONS

The HTPB-PU membrane was prepared for the separation of AB from aqueous solutions as well as fermentation broth by pervaporation. The results showed that when the operation temperature ascended, both the total flux and the separation factor were increased. The permeation flux of acetone and butanol was increased with increasing feed organic concentration. The separation factor of butanol ascended with increasing the feed concentration, but the reverse tendency of acetone was obtained. The separation performance of the ternary mixture was superior to that of the binary mixture at the same component concentration, which was caused by the interactions of permeant-permeant and permeant-membrane through evaluating the swelling degree of the membrane, the permeability coefficient, and the activity coefficient.

The pervaporation performance for the fermentation broth was superior to that for the model solutions (ternary system) with similar composition. The separation factors of acetone and butanol for the fermentation broth at 45°C were up to 18.9 and 17.6, respectively. All the results above revealed that the recovery of AB from the fermentation broth using HTPB-PU membrane by pervaporation could be a promising application in the AB fermentation integrated with in-situ separation.

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