

Selective recovery of acetone-butanol-ethanol from aqueous mixture by pervaporation using immobilized ionic liquid polydimethylsiloxane membrane

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Abstract—An effective *in situ* recovery of acetone, butanol and ethanol (ABE) from fermentation broth is requisite to overcome the low productivity of ABE production. Pervaporation has proven to be one of the best methods for recovering ABE from fermentation broth. We fabricated an immobilized ionic liquid-polydimethylsiloxane (PDMS) membrane in which a $[\text{TF}_2\text{N}]^-$ based ionic liquid covalently bound to the PDMS backbone polymer and used it to recover ABE from aqueous solution by pervaporation. Permeate flux of immobilized IL-PDMS membrane was 7.8 times higher than that of conventional supported IL-PDMS membrane (where ILs are physically absorbed on the supported membrane). Butanol enrichment factor of immobilized IL-PDMS membrane was three-times higher than that of PDMS membrane. In addition, high enrichment factor both to acetone and ethanol as well as high operational stability of immobilized IL-PDMS membrane can enhance the efficacy of ABE recovery by employing this membrane.

Key words: Liquid Membrane, Ionic Liquid, Butanol, Pervaporation

INTRODUCTION

Due to concerns about climate change and dependence on fossil resources, many efforts have been made to develop alternative renewable fuels. Of particular interest are biofuels such as ethanol and butanol, which can be used both as liquid fuel and as feedstock chemicals [1,2]. Butanol can be produced by *Clostridium* species through acetone, butanol and ethanol (ABE) fermentation [3-5]. Moreover, butanol has some merits over ethanol as biofuel, such as high energy content, low vapor pressure, and the ability to mix with diesel fuel in any ratio [2,6]. Therefore, there is significant interest in establishing a methodology for efficient biological production of butanol [7,8]. However, the inhibition effect of butanol on the fermentation microorganisms which leads to low solvent productivity, and hence, high energy demand for butanol recovery from its diluted mixture, was a major drawback of butanol production through biological pathway [4,5,9]. Several *in situ* separation methods have been tried to overcome these limitations such as liquid-liquid extraction [9], membrane-based processes such as perstraction [10] and pervaporation (PV) [11,12]. Among these methods, PV using hydrophobic membrane has been recognized as promising. PV is considered as a mild and less energy consumption process, as well as having no harmful effects on the microorganisms; hence, it is a very effective method for the separation of diluted solute such as ABE from the fermentation stream [11]. Unlike distillation, PV is governed by solute-polymer interaction not by the vapor-liquid equilibrium [13]. The PV process is driven by a difference in chemical potential and can be explained by the solution-diffusion model, i.e., sorption of the feed components on the active surface layer of the membrane, diffusion of the components through the membrane,

and desorption at the permeate side [14]. According to the solution-diffusion theory, sorption and diffusion are the major steps controlling the transport of the permeative compounds through the membrane. Sorption into a membrane is a selective step based on the different solubility parameters of compounds and the membrane. It is important that the solutes should not swell the membrane too much because the selectivity of PV will be decreased. On the other hand, low sorption or swelling will result in a very low flux. In addition, the rate of compound transportation through the membrane is determined by diffusion, which is influenced by the molecular shape, molar volume of the permeates and structure of the membranes [15]. Thus, it is crucial to choose or develop membrane polymers that exhibit high selectivity and diffusivity for the target compounds under the operating conditions of separation process [16]. Several membranes such as styrene butadiene rubber (SBR), ethylene propylene diene rubber (EPDM), poly[-1-(trimethylsilyl)-1-propyne] (PTMSP), propylene (PP), polytetrafluoroethylene (PTFE), poly(methoxy siloxane) (PMS), polydimethylsiloxane (PDMS) and their modifications such as PDMS coated silicate membrane and PDMS/ceramic composite membranes have been used to recover butanol from aqueous solution by PV [4,7,11,12,17-19].

More recently, ionic liquids (ILs) have been recognized as a potential environmentally benign alternative to classical organic solvent mainly due to their thermal and chemical stability, and ability to solubilize a large range of organic, inorganic and polymer compounds [20-22]. ILs are molten salts which are liquid at room temperature (also called room temperature ILs-RTILs), and have extremely low vapor pressure. Their physiochemical properties could be finely tuned by combination of cation and anion. ILs have been used as promising solvents for recovery of butanol and other solutes from aqueous solution [6,16,23]. In addition, due to their non-volatility, ILs have been used as solvents in supported liquid membrane for separation process, which in turn enhances the membrane stability

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and eliminates the release of solvents into environment [24]. In recent studies, PDMS membranes in combination with ILs have shown a better recovery of organic solvents by PV than that of classical polymer membranes [8,25–28].

Homogeneous PDMS membrane itself is dense, nonporous and hydrophobic, which has proven to be effective for PV separation of butanol [8,26,29]. However, these properties result in a low flux and selectivity for the separation of many organic components including butanol. To improve the permeate flux, several porous materials such as silicate and ceramic have been used to prepare composite membrane. Furthermore, to improve the selectivity of PDMS membrane, liquid supports such as oleyl alcohol and ILs have been immobilized into PDMS as a supported liquid membrane by blending method [8,26]. However, in these studies, ILs were physically absorbed in the supported membrane, and therefore the long-term stability of these membranes in the recovery of organic solvents from aqueous solution or fermentation broth needs to be improved.

In the present study, however, an immobilized IL-PDMS membrane in which ILs covalently bound to the PDMS backbone polymer was prepared and examined for the PV separation of ABE from aqueous solution.

MATERIALS AND METHODS

1. Materials

Hydroxyl terminated PDMS (viscosity 18,000–22,000 cSt), tetraethyl orthosilicate (TEOS), (3-chloropropyl)triethoxysilane, 1-methylimidazole, bis(trifluoromethanesulfonimide) lithium salt (LiTf_2N) and dibutyltin laurate were obtained from Sigma-Aldrich and used without further purification. 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [Omim][Tf_2N], was provided by C-Tri (Suwon, Korea) and dried in vacuum oven for 24 hrs before use. All other reagents were of analytical grade.

2. Synthesis of Ionic Liquid Precursor

Fig. 1 is a schematic diagram for synthesis of $[\text{Tf}_2\text{N}]^-$ based IL precursor for preparation of immobilized IL-PDMS membrane. Generally, 1 : 1 molar ratio mixture of (3-chloropropyl)triethoxysilane and 1-methylimidazole were stirred under nitrogen pressure at 80 °C for 24 hrs. The unreacted substrates were thoroughly washed by diethyl ether. The yield of this reaction was about 87%. The chloride ion of the produced compound was exchanged with $[\text{Tf}_2\text{N}]^-$ by anion exchanger reaction with LiTf_2N (molar ratio of 1 : 1.2) in aqueous solution at room temperature. The produced water insoluble

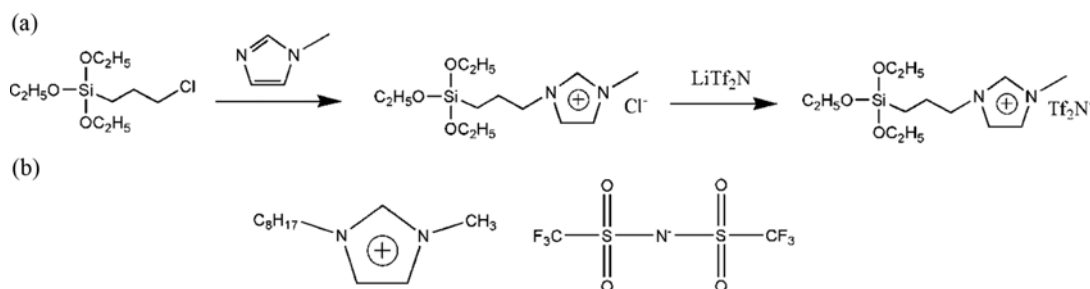


Fig. 1. Synthesis of ionic liquid precursor for preparation of (a) immobilized IL-PDMS membrane and (b) structure of [Omim][Tf_2N].

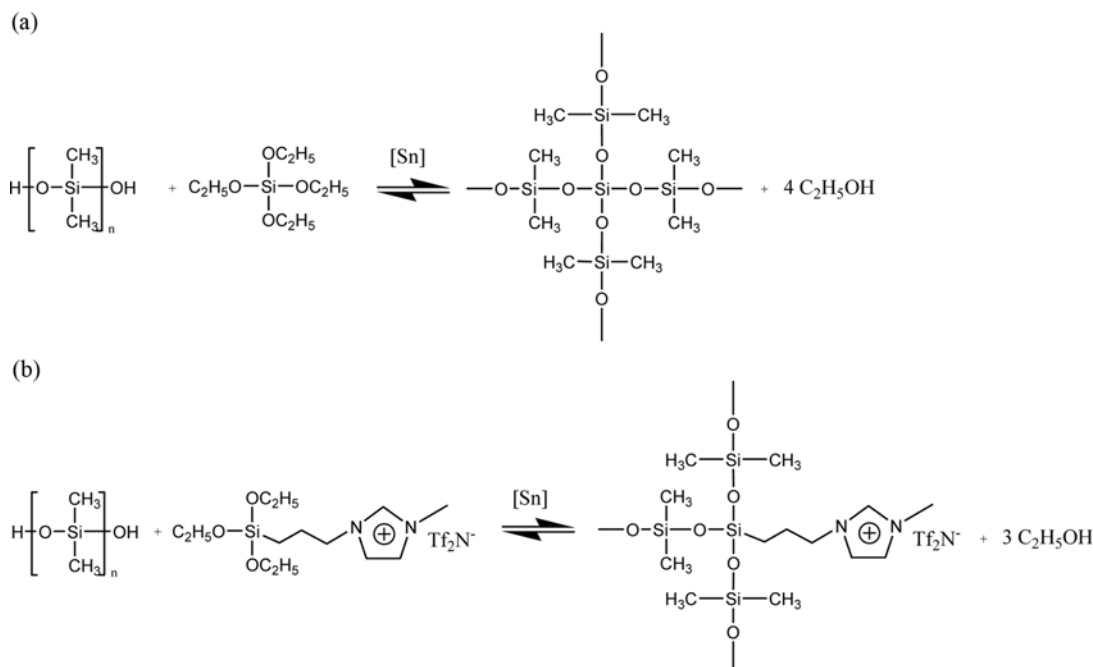


Fig. 2. Fabrication of (a) PDMS and (b) immobilized IL-PDMS membrane.

ble product was easily separated by decantation. The $[\text{Tf}_2\text{N}]^-$ based IL precursor was washed thoroughly by water and then dried under vacuum condition. The structure of $[\text{Tf}_2\text{N}]^-$ based IL precursor was confirmed by NMR analysis (Varian INOVA 400) with chloroform as solvent. ^{13}C NMR signals of $[\text{Tf}_2\text{N}]^-$ based IL precursor were as follows: 8.94, 9.53, 24.6, 29.34, 33.44, 36.70, 52.61, 122.52, 125.7, 137.87.

3. Membrane Preparation

The preparation of PDMS and immobilized IL-PDMS membrane is illustrated in Fig. 2. Typical protocol for preparation of PDMS and immobilized IL-PDMS membrane is as follows: 0.5 g hydroxyl terminated PDMS+2 g TEOS (or Tf_2N based IL precursor)+50 μL dibutyltin laurate+20 μL HCl 1 N in 10 mL solvent (chloroform: acetone volume ratio of 8 : 2) were stirred at 37 °C for 3 hrs. The homogeneous polymer solutions were cast on glass plates. The membranes were kept in vacuum desiccator to remove solvents. The membranes were then washed with 20% methanol solution and dried in vacuum desiccator. For preparing the supported IL-PDMS membranes, the PDMS membrane prepared as mentioned above was submerged in $[\text{Omim}][\text{Tf}_2\text{N}]$, and vacuum was applied to allow ILs fill the void volume of membrane for 24 hrs. The excess ILs on the surface of membrane were removed by paper tissue. According to our previous study, $[\text{Omim}][\text{Tf}_2\text{N}]$ showed as best ILs for butanol recovery from aqueous solution by liquid-liquid extraction; thus, it was selected as reference ILs in preparation of supported IL-PDMS membrane [6]. The concentration of $[\text{Omim}][\text{Tf}_2\text{N}]$ in supported IL-PDMS membrane was 5.2%.

4. Membrane Characterization

The thickness of membranes was measured by using a digital micrometer (ID-C112x, Mitutoyo, Kawasaki, Japan). The hydrophobic properties of membranes were examined by determining their water drop contact angle (Phoenix 300Touch, SEO, Korea).

The degree of swelling of membrane was measured by immersing the membrane in pure solvents at 25 °C for 72 hrs according to Eq. (1).

$$\text{Degree of swelling} = \frac{W_s - W_d}{W_d} \times 100 \quad (1)$$

where W_s and W_d denote weight of the swollen membrane and weight of the membrane before immersion, respectively. In addition, the

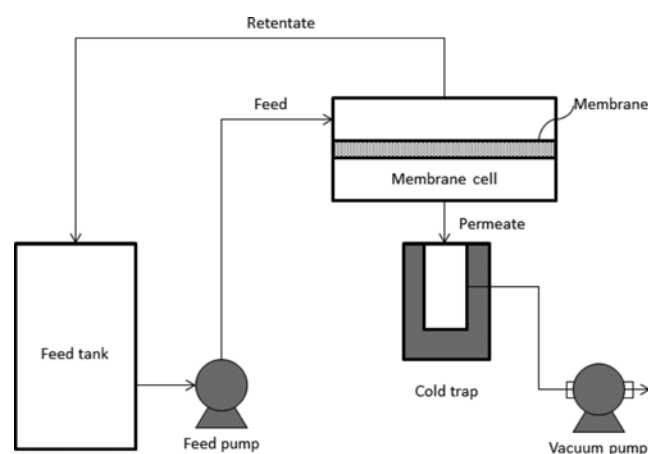


Fig. 3. Schematic diagram of the pervaporation apparatus.

ATR-FTIR spectra of membranes were recorded by Vertex 80V FT-IR spectrometer (Bruker, USA).

5. Pervaporation Experiments

Fig. 3 illustrates the apparatus used for PV experiments. Batch PV experiment was performed with a synthetic ABE aqueous mixture at concentration of 15 g/L (A : B : E weight ratio of 3 : 6 : 1) as feed solution. The PV was carried out at 25 °C with working volume of 50 mL, and effective membrane area was 3.14 cm². The feed stream was circulated by HPLC pump at flow rate of 2 mL/min. The permeate side of the membrane was maintained under vacuum pressure of 0.8 bar (the gauge pressure). The concentration of the ABE in feed and permeate solution was analyzed by CP 9001 gas chromatography (Chrompack, the Netherlands) using a DB-23 capillary column (30 m×0.25 mm I.D.; film thickness 0.25 μm , J&W Scientific, USA) and flame ionization detector (FID). All the experiments were duplicated and the mean value was presented. An enrichment factor, β , was defined as the ratio of the permeate concentration to the feed concentration of a compound, as was calculated in Eq. (2).

$$\beta = C_p / C_f \quad (2)$$

where C_f and C_p are the concentration (wt%) of a compound in the feed and permeate, respectively.

The permeation flux, J , was calculated as Eq. (3)

$$J = m / At \quad (3)$$

where m is the weight of the permeate (g), A is the effective area of the membrane (m²) and t is the operation time (hrs). To exclude the effect of membrane thickness on the calculated flux when comparing membranes, all the fluxes are normalized to a membrane thickness of 100 μm according to Eq. (4)

$$J_{100} = J \cdot d / 100 \quad (4)$$

where d is the thickness of membranes (μm).

RESULTS AND DISCUSSION

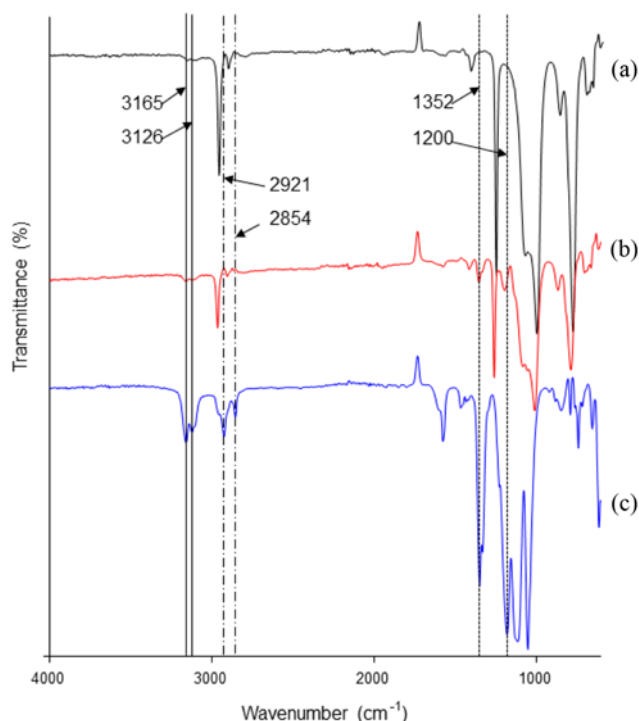
1. Preparation and Characterization of Membranes

Three different membranes (PDMS, supported IL-PDMS, and immobilized IL-PDMS membranes) were fabricated and their characteristics are summarized in Table 1. All three membranes showed high contact angle, which can be explained by the hydrophobic nature

Table 1. Properties of membrane

Membrane	PDMS	Supported IL-PDMS	Immobilized IL-PDMS
Contact angle (°)	107.64	114.66	101.45
Thickness (mm)	0.467	0.497	0.322
Degree of swelling			
Acetone	16.70	12.60	16.12
Butanol	15.62	16.12	23.51
Ethanol	1.83	3.37	8.00
ABE*	0.35	0.12	0.68

*Aqueous ABE solution at concentration of 15 g/L with the A : B : E mass ratio of 3 : 6 : 1



The dotted lines ($1,200$ and $1,352\text{ cm}^{-1}$) represent the C-F asymmetric and symmetric stretching in Tf_2N^- anion, respectively. The dashed lines ($2,854$ and $2,921\text{ cm}^{-1}$) represent the C-H symmetric and asymmetric stretching in $\text{Si}(\text{CH}_2)_3\text{N}$, respectively. The solid lines ($3,126$ and $3,165\text{ cm}^{-1}$) represent the NC(H)NCH stretching and HCCH asymmetric stretching in imidazolium ring, respectively.

Fig. 4. ATR-FTIR spectra of (a) PDMS, (b) supported IL-PDMS and (c) immobilized IL-PDMS membrane.

of PDMS polymer and $[\text{Tf}_2\text{N}]^-$ based ILs. The relatively higher contact angle of supported IL-PDMS membrane (114.66°) than that of PDMS membrane (107.64°) might be due to the hydrophobic nature of $[\text{Omim}][\text{Tf}_2\text{N}]$ (log P of 0.80 [6]). On the other hand, the relatively lower contact angle of immobilized IL-PDMS membrane (101.45°) compared to PDMS and supported IL-PDMS membrane might be speculated to be by the difference in the backbone polymer structure of their polymer and supported liquid (Fig. 2).

The integration of $[\text{Omim}][\text{Tf}_2\text{N}]$ and covalent binding of $[\text{Tf}_2\text{N}]^-$ based IL precursor into PDMS polymer in supported and immobilized IL-PDMS membrane, respectively, was confirmed by ATR-FTIR analysis (Fig. 4). The presence of $1,200$ and $1,352\text{ cm}^{-1}$ peaks corresponding to the C-F symmetric and asymmetric stretching, respectively, in both supported IL-PDMS and immobilized IL-PDMS membranes indicates the incorporation of $[\text{Tf}_2\text{N}]^-$ anion in PDMS polymer. In addition, the peaks at $2,854$ and $2,921\text{ cm}^{-1}$ corresponding to C-H symmetric and asymmetric stretching of $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}$ are observed only in immobilized IL-PDMS membrane. This indicates the presence of IL precursor cation in PDMS membrane, meaning the IL moiety was successfully bonded to the PDMS backbone polymer. However, the peaks at $3,126$ and $3,165\text{ cm}^{-1}$ corresponding to the NC(H)NCH stretching and HCCH asymmetric stretching in imidazolium ring, respectively, are observed clearly in immobilized IL-PDMS but less significantly in supported IL-PDMS membrane. This difference might be speculated to be due to the higher

Table 2. Pervaporation recovery of ABE from aqueous solution

Membrane	PDMS	Supported IL-PDMS	Immobilized IL-PDMS
Permeate flux* ($\text{g/m}^2\cdot\text{h}$)	142.21	20.50	160.25
Enrichment factor			
Acetone	0.84	1.70	1.61
Butanol	1.75	6.20	5.26
Ethanol	1.53	1.28	1.24

*The permeate flux was normalized to the membrane thickness of $100\text{ }\mu\text{m}$

ILs moiety content presented in immobilized IL-PDMS than that in supported IL-PDMS membrane.

2. Pervaporation Experiments on ABE Recovery

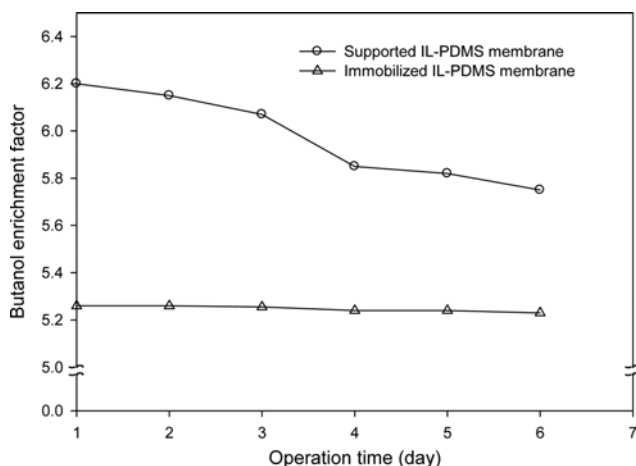
The permeate flux and enrichment factor for the recovery of ABE from aqueous solution by PV are presented in Table 2. PDMS and immobilized IL-PDMS membrane exhibit higher permeate flux compared to that of supported IL-PDMS membrane. The permeate flux of PDMS, supported IL-PDMS, and immobilized IL-PDMS membrane was 142.21 , 20.50 , and $160.25\text{ (g/m}^2\cdot\text{h)}$, respectively. The higher permeate flux of PDMS and immobilized IL-PDMS membrane compared to that of supported IL-PDMS membrane might be attributed to the fact that the void volume of PDMS membrane was decreased by filled ILs in supported IL-PDMS membrane. In addition, the hydrophobic nature of supported ILs respelled the permeation of water, resulting in the lower permeate flux. However, in immobilized IL-PDMS membrane, the incorporation of ILs moiety in PDMS backbone polymer might result in an asymmetric structure of PDMS polymer (Fig. 2). In addition, the substitution of one $-\text{Si-O}$ linkage in PDMS and supported IL-PDMS membrane by $-\text{Si-CH}_2-$ in immobilized IL-PDMS membrane might affect the mobility of the membrane and thereafter the permeability of the solutes in PV. This phenomenon has also been observed in the literature [15]. These increases in permeability are mainly due to the increase in permeate diffusivity, caused by a decreasing rigidity of the polymer backbone and an increasing in void volume available for the diffusion of the permeate molecules. These result in higher permeate flux of immobilized IL-PDMS compared to PDMS and supported ILs-PDMS membrane. However, the surface-view through SEM analysis hardly showed a difference in the morphology of these membranes (data not shown).

The swelling of these membranes in aqueous ABE solution further consolidated the experimental results on the enhanced permeate flux of immobilized IL-PDMS membrane (Table 1). The degree of swelling of immobilized IL-PDMS membrane in aqueous ABE mixture was about 2 and 5.6 times higher than that of PDMS and supported IL-PDMS membranes, respectively. It is well recognized that high solubility of solutes has a tendency to swell the membrane. In membrane separation, which is governed by solution-diffusion model, the high solubility of solutes in membrane is correspondent to the high permeability [30]. In addition, the relatively higher degree of swelling of immobilized IL-PDMS membrane toward pure butanol and ethanol solution compared to PDMS membrane might enhance the solute enrichment of this membrane.

Table 3. Properties of selected solvents, PDMS and ionic liquids [31,32]

Solvent	Molar volume (cm ³ /mol)	Solubility parameter, δ [(J/cm ³) ^{0.5}]
Water	18.02	47.4
Acetone	73.53	20.4
Ethanol	58.37	27.0
Butanol	91.26	23.8
[Omim][Tf ₂ N]	361.0	25.0
PDMS	-	14.9

All three membranes exhibit relatively high enrichment to butanol, which is the major component of ABE fermentation. This might be attributed to the smaller difference in solubility parameter between butanol and PDMS than that of water and PDMS (Table 3). The enrichment factor of butanol in PDMS, supported IL-PDMS and immobilized IL-PDMS membrane was 1.75, 6.20, and 5.26, respectively. The butanol enrichment factors of supported IL-PDMS and immobilized IL-PDMS membrane were 3.5 and 3.0 times higher than that of PDMS membrane, respectively. The higher butanol enrichment factor of two modified membranes might be explained by the interaction of [Tf₂N]⁻ based ILs toward butanol [6,16]. The permeate flux of immobilized IL-PDMS membrane, however, was 7.8-fold higher than that of supported IL-PDMS membrane. The higher permeate flux will provide higher productivity for butanol recovery by PV using immobilized IL-PDMS membrane. Interestingly, the supported IL-PDMS and immobilized IL-PDMS membranes also exhibit the enrichment to both acetone and ethanol, important products of ABE production, while PDMS membrane could enrich ethanol but not acetone. This might be attributed to the smaller difference in solubility parameter between the two solutes and [Tf₂N]⁻ based ILs compared to that of PDMS polymer (Table 3). Moreover, the interaction of these solutes with modified membranes might also contribute to the enrichment of acetone and ethanol (Table 1). The simultaneous removal of ABE would overcome the limitation of ABE production by biological route due to the inhibition effect of products, and hence, improve the efficiency of ABE recovery.

**Fig. 5. Operational stability of supported IL-PDMS and immobilized IL-PDMS membranes.**

3. Operational Stability of Membranes

The PV operational stability of supported and immobilized IL-PDMS membranes was examined and illustrated in Fig. 5. The butanol enrichment factor was maintained in immobilized IL-PDMS membrane while gradually decreased in supported IL-PDMS membrane. The long-term stability of immobilized IL-PDMS membrane might indicate the strong interaction of IL moiety and PDMS membrane due to the covalent binding. In contrast, the leaking of ILs which are physically adsorbed in PDMS membrane might cause a decrease in butanol enrichment factor of supported IL-PDMS membrane.

CONCLUSION

Immobilized IL-PDMS membrane, where IL with high selectivity to ABE covalently bound to PDMS backbone polymer, was fabricated. The recovery of ABE from aqueous solution using this membrane by PV showed great enhancement. The permeate flux of immobilized IL-PDMS membrane was 7.8-times higher than that of conventional supported IL-PDMS membrane and the butanol enrichment was three-times higher than that of PDMS membrane. In addition, immobilized IL-PDMS membrane also enhanced the recovery of accompanying products such as acetone and ethanol from ABE fermentation and exhibited higher operational stability compared to conventional supported IL-PDMS membrane.

Owing to high permeate flux and enrichment to three components of ABE fermentation, immobilized IL-PDMS would be promising membrane for the *in situ* separation of ABE by PV. Although their performance with a real, integrated ABE fermentation system and long-term operational stability, regeneration as well as reuse of the membrane and separation of ABE mixture need to be examined. These will be the objectives of further studies.

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