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Investigation of sorption characteristics of polymeric membranes containing ionic liquids for n-butanol recovery from aqueous streams

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ABSTRACT

Ionic liquid–polydimethylsiloxane (IL–PDMS) blending membranes were prepared to separate *n*-butanol from aqueous mixtures. The ionic liquids (ILs) used were [hmim][PF_6] (1-hexyl-3-methylimidazolium hexafluorophosphate), [bmim][PF_6] (1-butyl-3-methylimidazolium hexafluorophosphate), and [bmim][TF_2N] (1-Butyl-3-methylimidazolium bis-trifluoromethylsulfonylimide). Sorption experiments were carried out to define the sorption and separation capacity of the blending membranes using aqueous butanol solutions in the range of 1–5% (wt), and also sole solvents of butanol and water. The desorption experiments allowed to determine the selectivity of the membranes as the liquid composition inside the membrane could be obtained with the desorption step. The results obtained by IL–PDMS blends were compared with the results obtained by unblended PDMS membranes to show the effect of the IL in the PDMS matrix. [Hmim][PF_6]–PDMS-blended membranes showed lower selectivity. The addition of [bmim][PF_6] to PDMS enhanced the selectivity and sorption amounts mildly. [Bmim][TF_2N]–PDMS-blended membranes presented the best sorption and selectivity results showing a great affinity to butanol and a reasonable rejection to water.

Keywords: Ionic liquid; Sorption; Pervaporation membrane; PDMS

1. Introduction

As the fossil fuels are being depleted due to the limited reserves, potential energy recourses have attracted attention recently. Biobutanol, which can be produced by the biomass fermentation, is a potential energy resource that can be replaced with gasoline. The recovery of butanol from aqueous fermentation broth is an important concern of the industry. Since the fermentation bacteria cannot be grown at high butanol concentrations, the butanol production is limited by the toxicity of the butanol for the fermentation bacteria. The traditional processes for butanol removal from fermentation broth include distillation, extraction, gas stripping, and adsorption [1,2]. As the concentration of butanol is low in the final mixture, membrane separation processes give relatively feasible results in terms of economy for its recovery from the fermentation broth. Several studies have been reported on the recovery of butanol using membrane processes, especially focusing on the pervaporation (PV) technique. [3–8]. The crucial issue of the butanol separation by membrane processes is to develop the butanol-selective membrane that shows good selectivity and sorption properties for the butanol. Although the use of various materials in membrane systems have been investigated such as polytetrafluoroethylene [9], polyether block amide (PEBA) [4,5], and polysiloxanes, the studies for butanol recovery mostly tend on the use of polysiloxanes as they show good hydrophobicity and selectivity [3,6–8,10,11]. Recently the studies focus on the enhancement of the selective properties and performance of the membrane materials by doping the membranes by several additives or by blending them with various polymers. Ionic liquids (ILs) are promising candidates as additives in order to enhance the performance of the polymeric membranes.

ILs, which are organic salts with negligible vapor pressure, have been reported as a good separation medium for the butanol separation [12–16]. ILs are known as design solvents, as they are chemically and thermally stable, and have low vapor pressure and high ionic conductivity properties [17,18]. The use of ILs as a separation media by its stabilization into a support material has been gaining traction and these supported ionic liquid membranes give promising results for the separation of several solvents [19]. The immobilization of the ILs into the pores of a porous support material usually requires transforming the ionic liquid into a more stabile phase. To convert the ionic liquid into a quasi-solid form, gelation of the ionic liquid can be carried out using several gelation agents such as inorganic nanoparticles and low-molecular weight compounds [20,21]. The major limitation of the use of these gelled membranes is their mechanical strength. Although gelators allow IL contents higher than 90 wt.% in gels, low chemical and mechanical stability limit their use in PV [22]. Another solidification method of ILs is to dissolve the IL in a host polymer forming a IL-blended polymer. Investigation of IL-blended polymers which could overcome the limitations of the use of gelled ILs, is an attracting issue of the membrane science and needed to be focused more. The main advantage of polymer IL blends is that the IL–polymer-blended membranes do not require a support unlike the gelled ILs. IL-blended polymeric membranes involve doping the polymer solution with ILs. By this way, the polymeric–IL membrane has both the mechanical strength of the polymer and enhanced selectivity properties of the IL. Lu and co-workers reported a survey about applications of ILs in polymer science [23]. They have reported that preparation methods of IL-based polymers can be classified into three groups: doping of polymers with ILs, *in situ* polymerization of vinyl monomers in ILs, and polymerization of polymerizable ILs. In the literature, several polymers have been reported for the IL–polymer blended membranes such as poly(dimethyl siloxane) (PDMS) [12,13,24], polyvinyl chloride [25], polyvinyl alcohol [26], and PEBA [22]. PDMS is a very commonly used membrane material for several membrane separation processes with different purposes and, thus, PDMS–IL blends are one of the most focused polymer–IL system, especially, for the butanol recovery. Kohoutová et al. [13] studied [bmim][BF_4]–PDMS blending membranes containing IL in the range of 0–30 wt.% for butanol recovery. They have reported that the resulted membrane showed high stability as well as a reasonable selectivity during the experiments. Vopicka et al. [12] studied butanol sorption in blended poly(dimethylsiloxane)–benzyl-3-butylimidazolium tetrafluoroborate membranes. They have reported that as the content of ionic liquid increased in the polymer matrix, the selective sorption of butanol also increased. Izák et al. [24] compared PDMS with 1-ethenyl-3-ethyl-imidazolium hexafluorophosphate- and 1-ethenyl-3-ethyl-imidazolium bromide-blended PDMS impregnated into a ceramic ultrafiltration support membrane for butanol recovery from ABE mixtures. They have indicated that the presence of IL in the membranes increased the enrichment factor of butanol from 2.2 to 3.1 with 1-ethenyl-3-ethyl-imidazolium hexafluorophosphate and to 10.9 with 1-ethenyl-3-ethyl-imidazolium bromide. In this study, PDMS is blended with [hmim][PF_6], [bmim][PF_6], and [bmim][TF_2N]. The ILs composed of two different imidazolium-based cations ($[hmim]^+$ and $[bmim]^+$) with different alkyl groups and two different anions ($[PF_6]^-$ and $[TF_2N]^-$) were studied and compared to see the best anion–cation combination for the butanol uptake by means of sorption. In a PV process, the component that is sorbed by the membrane preferentially, will also be transported preferentially, hence the evaluation of the sorption characteristics of a membrane material is an important pre-step for PV. Thus, in this work the butanol sorption of the IL-blended membranes was evaluated in terms of butanol selectivity to determine the best IL–polymer configuration for a PV application to recover the butanol from aqueous mixtures. In particular, there is little information available on the $[TF_2N]^-$ based IL membranes for butanol separation, although this kind of IL membranes have a great potential for butanol recovery. In addition to investigating anion–cation effects on selectivity and determining the best anion–cation combination to develop the most selective polymer–IL membrane, this work also provides a discussion and evaluation of the use of $[TF_2N]^-$ based IL in the membranes for butanol recovery by comparing it with different ILs.

2. Experimental

2.1. Material

PDMS (RTV 615 A) and its cross-linking agent (RTV 615 B) were purchased from GE Silicone representative in Turkey. 1-Butanol was purchased from J.T. Baker. All the ionic liquids, [hmim][PF_6], [bmim][PF_6], and [bmim][TF_2N] were supplied from Merck.

2.2. Characteristics of the ILs

Some physical characteristics of the ILs are given in Table 1 [15]. Between the ILs, the less water solubility value and the higher distribution coefficient of BuOH belongs to [bmim][TF_2N], where these data may indicate that [bmim][TF_2N] is the most appropriate candidate for BuOH recovery from the aqueous mixtures between the given ILs. The chemical structures of the ILs used in this work are given in Fig. 1.

2.3. Membrane preparation

RTV 615 A + B was used as PDMS material. First, a mixture consisting of PDMS and 10% wt of its cross-linking agent was prepared. Then 10% wt acetone of the total solution was added to lower the viscosity of the mixture. The mixture was stirred for half hour at low speed and then degassed under the vacuum to avoid air bubbles. For the unblended PDMS membrane preparation, this mixture was cast onto the petri dishes and cross-linked for 1 h at 100˚C in an oven by heat treatment. In order to prepare Ionic liquid–polydimethylsiloxane (IL–PDMS) blended membranes, desired weight percentage of the IL was added to the mixture. The IL content to be added in the mixture was calculated considering the PDMS content without acetone in the mixture. After adding the IL, the mixture was stirred, degassed again, cast onto the petri dishes, and finally cross-linked in an oven at the same conditions. The IL contents in the PDMS were studied in the range of 10–30% of IL (wt).

2.4. Sorption and desorption experiments

Membranes with the known weights were immersed into closed vessels containing desired concentrations of mixtures and maintained at 30˚C in an oven. Every certain time intervals, the swollen membranes were wiped off and weighted until there was no change in the weights. Then, the sorption percentage of the membrane was calculated from the equation below:

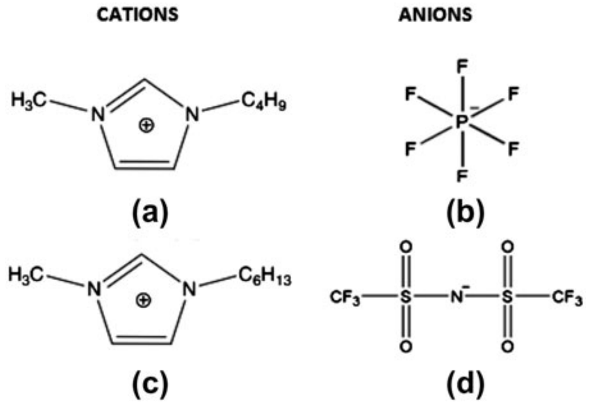

Fig. 1. Cation and anions of the IL used in this work (a) 1-butyl-3-methylimidazolium, [bmim]; (b) 1-hexyl-3-methylimidazolium, [hmim]; (c) Hexafluorophosphate, PF_6; and (d) bis(trifluoromethylsulfonyle)imide, TF_2N.

$$\text{Sorption\%} = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100 \qquad (1)$$

where m_{wet} and m_{dry} present the weight of the wet and dry membrane, respectively. Each sorption experiment was carried out using three vessels simultaneously and the reproducibility was ≤3%.

The liquid composition inside the membrane was determined from both a mass balance and the desorption experiments to ensure the accuracy of the results. After the sorption equilibrium was reached, the compositions of the mixtures in the vessels were determined using a Shimadzu GC 9A model gas chromatography. Afterward a mass balance could be performed, since the liquid amount inside the

Table 1
Some physical characteristics of ILs

Ionic liquid	Solubility in water (at 298.15 K, wt.%)	Water solubility in IL (at 298.15 K, wt.%)	Density (g ml^{-1})	Dielectric constant	Distribution coefficient between IL and water rich phases, D_{BuOH}*
[hmim][PF_6]	0.60	2.25	1.301	11.1	0.967
[bmim][PF_6]	1.70	2.69	1.369	14.0	0.742
[bmim][TF_2N]	0.51	1.75	1.436	9.7	1.025

*$D_{BuOH} = (C_{BuOH})IL/(C_{BuOH})water$.

membrane was already determined from the sorption experiments. Moreover, the experimental determination of composition of the liquid inside the membrane was achieved using the desorption experimental setup in Fig. 2.

First the swollen membrane was put into the sample tube 1. The tube 1 was heated to 100˚C with hot water while the receiver tube 2 was cooled with liquid nitrogen under the vacuum applied by a vacuum pump. The experiment ran approximately for 1 h, as all the liquid inside the membrane was collected in tube 2 after this procedure. Next, the composition of the liquid collected in tube 2 was analyzed using GC. Also, selectivities were calculated using the equation below where the feed and membrane in the equation indicate the compositions in the sorption solution and in the membrane, respectively:

$$\alpha_{\mathrm{BuOH/water}} = \frac{(C_{\mathrm{BuOH}}/C_{\mathrm{water}})_{\mathrm{membrane}}}{(C_{\mathrm{BuOH}}/C_{\mathrm{water}})_{\mathrm{feed}}} \tag{2}$$

3. Results and discussion

3.1. Characterization of the IL membranes

In this study, the IL membranes were [bmim][TF_2N]–PDMS, [hmim][PF_6]–PDMS, and [bmim][PF_6]–PDMS blended membranes. IL membranes were characterized by means of FTIR, differential thermal analysis (DTA), and thermogravimetric analysis (TGA) analysis.

3.1.1. FTIR analysis

Infrared (IR) spectra were recorded using a FTIR spectrophotometer (Perkin–Elmer Spectrum One) to identify the chemical bonds of the membrane materials. Fig. 3 presents the FTIR spectra of the membranes.

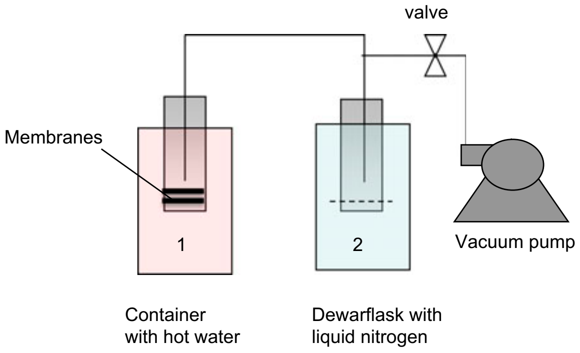

Fig. 2. Desorption setup.

PDMS used in this study is a two-component system, consisting of a vinyl terminate prepolymer and a cross-linker containing several hydride groups on shorter polydimethylsiloxane chains. The molecular weight of the PDMS 615 A + B from GE Silicone was reported by Stafie et al. [27]. They carried out a GPC analysis of the prepolymer and cross-linker as received from the supplier. Their data indicate that both have mainly a bimodal character of molecular weight (prepolymer: 4,000 and 67,000 g mol^{-1}, cross-linker: 1,500 and 60,000 g mol^{-1}). At 10:1 prepolymer/cross-linking ratio, they determined the average molecular weight of chains between cross-links for PDMS as 15,600 ± 800 g mol^{-1}.

All the membranes produced bands corresponded to the absorption of Si–O–Si groups as the blends are mainly composed of a silica network. The characteristic peaks of PDMS that can be observed in Fig. 3, are Si–O–Si stretching at 1,011 cm^{-1}, CH_3 bending in Si–CH_3 at 1,258 cm^{-1}, and CH_3 rocking in Si–CH_3 at 792 cm^{-1}. Peak at 2,965 cm^{-1} is attributed to CH_2 groups of the polymer backbone. [Bmim][TF_2N]–PDMS blending gave some characteristic peaks at 1,204 and 1,359 cm^{-1} that are related to C–F symmetric and asymmetric stretching, respectively. The infrared region between 1,400 and 1,000 cm^{-1} is mainly dominated by several peak assignments related to the anion [28]. The spectra of the bonds related to the imidazolium that are aromatic C–H stretching should be observed around 3,100–3,200 cm^{-1}, which are slightly observable for the [hmim][PF_6] and [bmim][TF_2N] blends.

3.1.2. TGA and DTA analyses

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the membranes were carried out using a SII Nanotechnology brand, SII6000 Exstar TG/DTA 6300 model equipment. The samples were heated from room temperature to 850˚C with a heating rate of 10˚C/min under flowing nitrogen. Fig. 4(a) shows the TGA curves of the membranes which were obtained by plotting the mass vs. temperature.

From the TGA curves, the initial decomposition temperature of the PDMS was determined as around 430˚C. The addition of the [bmim][TF_2N] to the membrane made the membrane slightly more thermally stable. Besides for this blending, two-step decomposition was observed. The presence of [bmim][TF_2N] in the polymer helped to absorb the thermal energy slightly. Although the anion presents a major influence on the thermal stability, this property is also

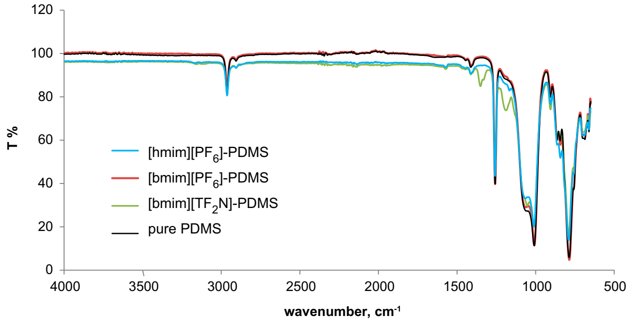

Fig. 3. FTIR spectrum of membrane materials in the 400–4,000 cm^{-1} spectral range.

affected by the cation; as the cation chain is shorter, thermal stability is higher [29]. Thus, it is expected that the thermal stability of the IL with [hmim]+ is slightly lower compared to a [bmim]$^+$ cation IL. On the other hand, as mentioned the anion of an IL has a major influence on the thermal stability. Studies indicate that [TF$_2$N]$^-$ anion provides a relatively higher thermal stability. Meine et al. studied thermal stability of imidazolium-based ionic liquids [30]. They compared four ILs; [bmim][TF$_2$N], [bmim][CH$_3$SO$_3$], [bmim]Cl, and [emim]Cl. They analyzed free imidazoles after aging the ILs with heat treatment to see the decomposition of the IL. They reported that [bmim][TF$_2$N] resists degradation consistently. The amount of the imidazoles remained practically constant over the next 9 d of aging at 250˚C. They concluded that their results clearly show [bmim][TF$_2$N] has a unique thermal stability compared with other ILs studied surprisingly. Therefore, when [bmim][TF$_2$N] is added to PDMS, this characteristic of the [bmim][TF$_2$N] also influences the blending membrane, which can be also observed from the TGA curves.

On the other hand, the addition of [bmim][PF$_6$] and [hmim][PF$_6$] to the PDMS membrane showed a similar pattern and made the membrane material less thermally stable. The amount of the total weight loss increased with the addition of these ILs during decomposition. The initial decomposition temperature decreased to 300 and 310˚C from 430˚C by the addition of [hmim][PF$_6$] and [bmim][PF$_6$], respectively. The DTG traces of these thermograms can be seen in Fig. 4(b). As can be seen from the DTG curves, addition of ILs in the PDMS resulted in different weight loss rates at different temperature ranges because of the presence of various physical attractions with the polymer.

DTA curves were obtained by plotting the heat flow difference between the sample and an inert reference against temperature. Fig. 4(c) presents DTA curves of the samples accompanied to the thermal gravity analysis in the temperature range of 25–850˚C. The DTA curves of the membranes show similar patterns with exothermic decomposition behaviors. The sharp peak observed for the [bmim][TF$_2$N]–PDMS blend at 472˚C may refer to the decomposition of the molecules related to the ionic liquid in the polymer matrix. In the literature the decomposition temperature of [bmim][TF$_2$N] is given as 461˚C [30] which also verifies the observed peak for the [bmim][TF$_2$N]–PDMS blend.

3.2. Evaluation of sorption and separation characteristics of the membranes

First, in order to define the sorption characteristics of pure PDMS and IL–PDMS blends, pure BuOH and water sorptions of each membrane material were obtained. To obtain the pure solvent sorptions, membranes with 20% of IL in the IL–PDMS blends were prepared with each IL. The resulting membranes showed different physical appearance and stability. The most stable and optically clear blend membrane was [bmim][PF$_6$]–PDMS blend showing almost a similar strength and appearance to the unblended PDMS. The blends with [hmim][PF$_6$] and [bmim][TF$_2$N] had a more gelly form with a unclear physical appearance. The gelly behavior of these two blends may indicate a lower mechanical strength compared to pure PDMS and [bmim][PF$_6$]–PDMS blend.

The sorption results of IL–PDMS blends were compared to pure PDMS membrane results to show the effect of IL in the membrane. The results are presented in Fig. 5. As can be seen from the figure, the water sorption of [hmim][PF$_6$] is higher than its butanol sorption. This result indicates that [hmim][PF$_6$]–PDMS blend membrane is not suitable for butanol recovery

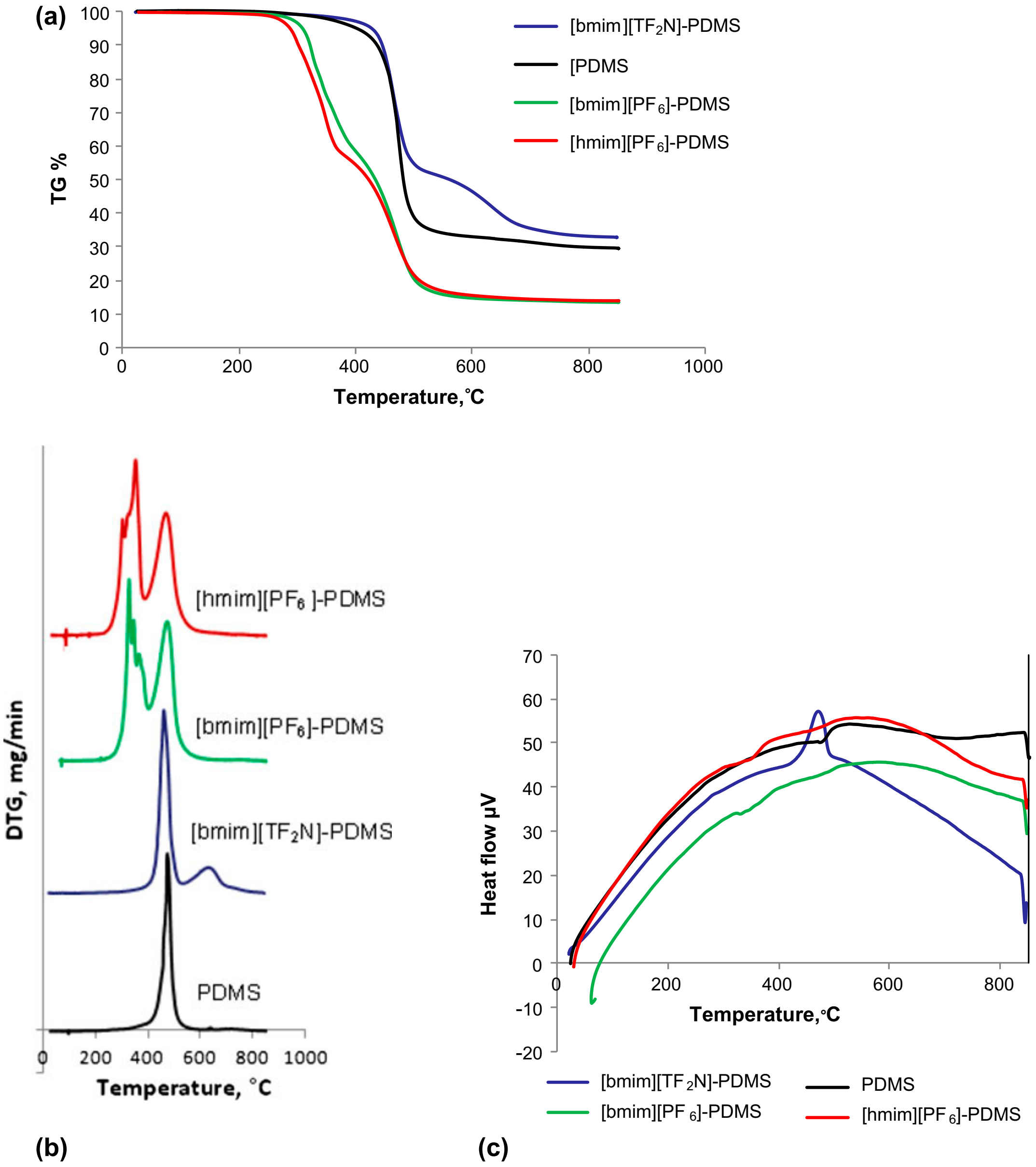

Fig. 4. Thermal analyze results of the IL membranes (a) TGA curves of the membranes; (b) DTG curves of the membranes; and (c) DTA curves of the membranes.

from aqueous mixtures in a PV system. The butanol sorptions of the rest of the membranes are higher than their water sorptions. The water sorption of pure PDMS is only 0.4% and its butanol sorption is 17%. The presence of IL in the PDMS enhanced the butanol sorption for all the blends. The highest BuOH sorption belongs to [bmim][TF_2N]–PDMS blend. Also, the water sorption of [bmim][TF_2N]–PDMS blend was lower than the other blendings. The [bmim][TF_2N]–PDMS showed a great affinity to BuOH at this IL content in the blend.

When [hmim][PF_6] and [bmim][PF_6] blendings are compared, it can be seen that the sorption results are very different from each other, although those two have the same anions and both have imidazolium-based cations. Here, the main difference is the length of the alkyl group linked on the cation, those are hexyl and butyl groups. The longer the alkyl chain, the more hydrophobic the structure, thus, [hmim][PF_6] can said to be more hydrophobic than [bmim][PF_6]. Although hydrophobicity is a preferred property for the membranes, the higher hydrophobicity resulted from the

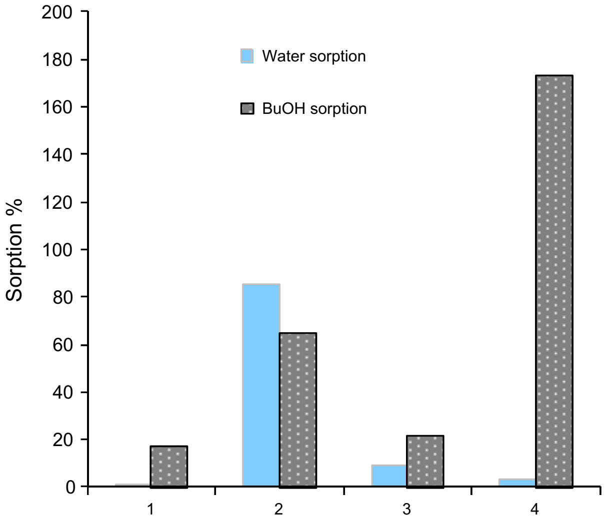

Fig. 5. BuOH and water sorption of pure PDMS and IL–PDMS blends containing 20% IL in the blend (1) PDMS; (2) [hmim][PF_6]–PDMS; (3) [bmim][PF_6]–PDMS; and (4) [bmim][TF_2N]–PDMS.

longer chains of the [hmim][PF_6] in the membrane caused shrinkage of the membrane in the presence of water. This deformation of the membrane evoked many rifts and gaps through the inner and outer sides of the membrane, which could be also observed physically. The presence of these gaps enhanced the water uptake and, thus, the water sorption results of [hmim][PF_6] were relatively higher. The water molecules penetrated into these openings because of the pressure effects. Therefore, this high water sorption of [hmim][PF_6]-based membrane can be interpreted as a mechanical penetration of the water molecules through the gaps, because of low breakthrough pressure of the hydrophobic membrane rather than a thermodynamic sorption. As a result, high water sorption results were obtained with this membrane. Thus, it can be concluded that the use of [bmim]$^+$ cation in the PDMS blending is more adequate for the BuOH uptake from an aqueous solution. When [bmim][PF_6] and [bmim][TF_2N] are compared, it can be seen that those two ILs have the same cations of [bmim]$^+$, while the anions are different. These different anions of [TF_2N]$^-$ and [PF_6]$^-$ provided different sorption results. [bmim][TF_2N]–PDMS blending has lower sorption values in the presence of water and higher sorption values in the presence of BuOH compared to [bmim][PF_6]–PDMS blending. This can be resulted from the higher hydrophobicity and lower polarity of the [TF_2N]$^-$ anion than the [PF_6]$^-$ anion. The solubility of BuOH and consequently BuOH sorption increases with decrease in polarity. Although both [hmim][PF_6] and [bmim][TF_2N] were more hydrophobic than [bmim][PF_6], the blending with [hmim][PF_6] formed gaps in the structure in the presence of the water, while the latter was still stable which makes its use more preferable.

The membranes were cut into squares with the same surface area and immersed in BuOH to exhibit and compare the swelling degree of each membrane. The membranes after reaching sorption equilibrium in BuOH are shown in Fig. 6. The degree of sorption of [bmim][TF_2N]–PDMS in BuOH was very high resulting in a major swelling compared to the other membranes. These results show that [bmim][TF_2N]–PDMS is the best candidate between the IL-blended membranes for BuOH recovery from aqueous solutions in terms of its potential in BuOH sorption and water rejection.

After obtaining sorption results of the IL–PDMS membranes in pure solvents, the sorption behavior of the membranes in a BuOH solution was investigated. A BuOH solution of 5% was prepared and membrane materials were immersed into this solution in the closed vessels until the sorption equilibrium. The membranes were weighted every certain time intervals to check whether the equilibrium had been reached. The sorption results of the membranes in the 5% (wt) BuOH solution is shown in Fig. 7.

The IL–polymer blends with [hmim][PF_6] and [bmim][PF_6] reached equilibrium after 9th day, while the [bmim][TF_2N]–PDMS blend and pure PDMS reached the equilibrium faster, on the first days. As can be seen from Fig. 7, the highest sorption results belongs to the [hmim][PF_6]–PDMS membrane. However, this higher sorption value results from the higher water content in the membrane, since the cracks were formed because of the shrinkage in the presence of the water. The cracks are filled mainly with the water molecules which are at higher concentration in the solution. The inclusion of the IL in the PDMS increased the sorption values for all the blends. After determining sorption values, the liquid compositions inside the membranes were obtained by means of desorption experiments described in Section 2.4. The desorption experiments provide information about the preferential sorption of the membrane. Preferential sorption is given by the difference in composition of a binary liquid mixture inside the polymeric membrane and outside in the liquid feed mixture, and affected by the molar volumes of the penetrants, the affinity of the penetrants toward the polymer, and the mutual interactions between the penetrants [31]. The desorption results are presented in Fig. 8.

From the desorption experiments, the BuOH content in the unblended PDMS membrane was obtained

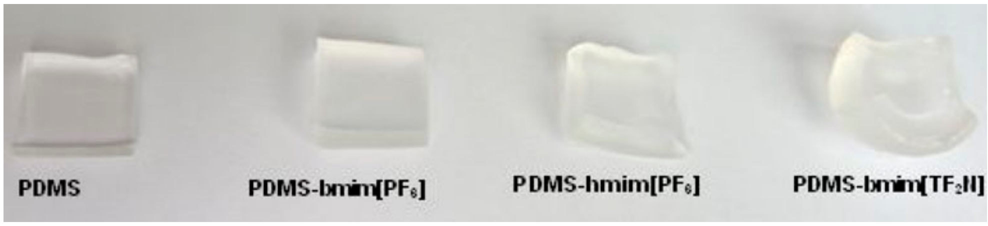

Fig. 6. The membranes after reaching sorption equilibrium in BuOH.

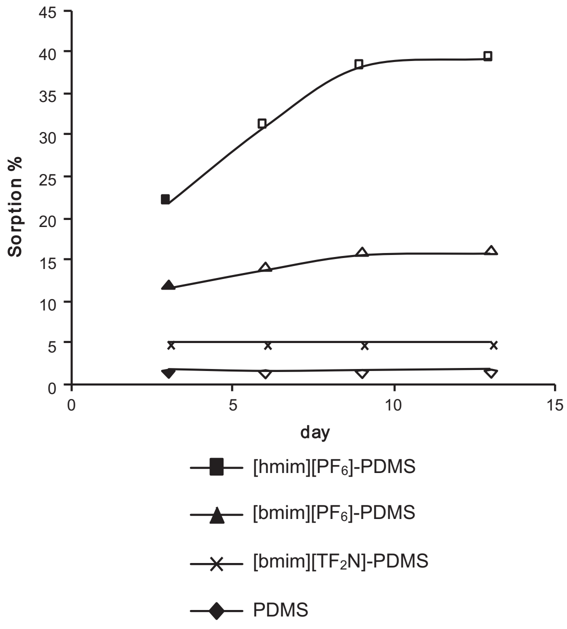

Fig. 7. Sorption results of pure PDMS and IL–PDMS blends (20% IL wt) in the 5% BuOH solution.

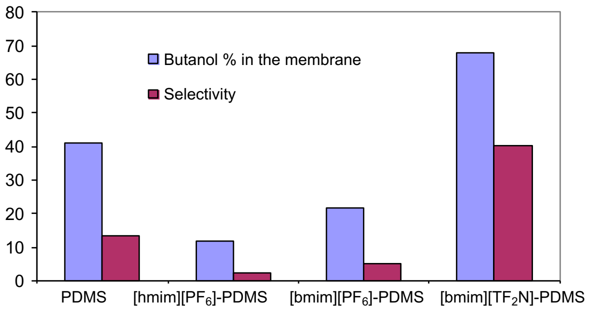

Fig. 8. Desorption results of the IL–PDMS blends (20% IL wt) and pure PDMS in the 5% feed solution: BuOH % in the membrane and the selectivities.

as 41.18%. Although the presence of the [hmim][PF_6] and [bmim] [PF_6] in the PDMS membrane enhanced the sorption results, the BuOH percent in the membrane decreased to 12% for [hmim][PF_6] and to 21.6% for [bmim][PF_6]. The highest BuOH concentration that is 68%, was obtained with [bmim][TF_2N] blend. This result is coherent with its pure solvent sorption results. Selectivities were obtained using Eq. (2). The selectivities were 13.30, 2.59, 5.23, and 40.38 for unblended PDMS, [hmim][PF_6]–PDMS blend, [bmim][PF_6]–PDMS blend, and [bmim][TF_2N]–PDMS blend, respectively. Again, the highest BuOH selectivity over water belongs to [bmim][TF_2N]–PDMS blends due to the highest BuOH content in the membrane. This can be explained by the higher hydrophobicity of $[TF_2N]^-$ anion than the $[PF_6]^-$ anion. The desorption results indicate that [bmim][TF_2N]–PDMS blend being the most potential candidate between the studied IL–PDMS blends, also shows a good selectivity compared to the polymer–IL blends encountered in the literature. Kohoutová et al. [13] obtained BuOH selectivity of $\alpha = 37$ using [bmim][BF_4]–PDMS membrane in PV of 5% wt BuOH solutions. It is worth to note that the selectivities reported in this study are sorption selectivities, thus may differ from PV selectivites since PV process is a function of sorption, diffusion, and desorption processes and PV selectivity is a product of sorption selectivity and desorption selectivity given by the below equations.

$$\alpha_{\text{pervaporation}} = \alpha_{\text{sorption}} \cdot \alpha_{\text{diffusion}} \tag{3}$$

$$\alpha_{\text{sorption}} = \frac{(c_i/c_J)_{\text{membrane}}}{(c_i/c_J)_{\text{feed}}} \tag{4}$$

$$\alpha_{\text{diffusion}} = \frac{(c_i/c_J)_{\text{permeate}}}{(c_i/c_J)_{\text{membrane}}} \tag{5}$$

Nevertheless, the sorption selectivities present a quantitative measure for PV selectivity. Thus, before performing PV tests evaluation of the sorption characteristics of the membranes could help to select the more appropriate material for the given solvent separation. Izák et al. [24] studied PV of ABE mixture using PDMS–tetrapropylammonium tetracyanoborate ionic liquid blend impregnated in a ceramic ultrafiltration module. They reported that the enrichment factor of butanol increased from 2.2 to 10.0 with the inclusion of IL in the membrane. Mai et al. [32] studied 1-octyl-3-methylimidazolium bistrifluoromethylsulfonylimide-based PDMS membrane for butanol recovery from ABE mixtures. They have bounded the IL to the PDMS backbone both covalent and physical, and reported that the PV enrichment factors were 6.20 for the physical bounded IL–PDMS and 5.26 for the covalent bounded IL–PDMS. Although the enrichment factor achieved by the covalent bounded one was slightly lower, they have concluded that the covalent bounded membrane performance is more stable than the physical bounded membrane. In this study, the sorption selectivity of [bmim][TF$_2$N]–PDMS corresponds to an enrichment factor of 13.6.

According to the desorption results, it was concluded that [hmim][PF$_6$]–PDMS blending is not suitable for the butanol recovery and thus, further investigations were considered for [bmim][TF$_2$N]–PDMS and [bmim][PF$_6$]–PDMS blendings.

3.3. Effect of the ionic liquid content in the membrane

10, 20, and 30% of IL content in the membrane were prepared for [bmim][TF$_2$N]–PDMS membranes to see the effect of the IL concentration in the membrane. On the other hand, for [bmim][PF$_6$]–PDMS, 20 and 25% of IL in the blends were prepared to see the effect of concentration in this membrane. Afterward, the sorption and desorption properties were investigated at each IL concentration. The sorption results in pure water, BuOH, and in 5% (wt) BuOH solution are given in Fig. 9(a) for [bmim][TF$_2$N]–PDMS at different IL concentrations.

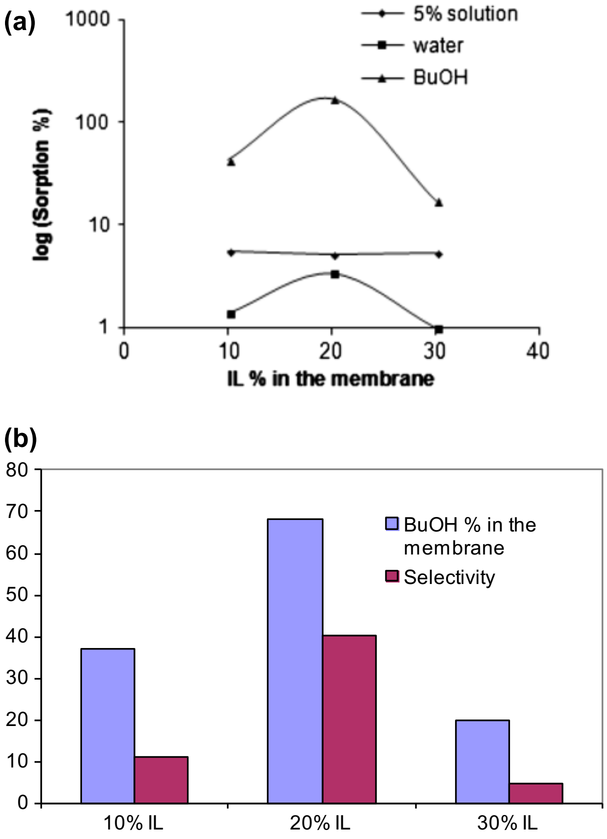

Fig. 9. Sorption and desorption results of [bmim][TF$_2$N]–PDMS membranes (a) The sorption percentages of [bmim][TF$_2$N]–PDMS membranes in pure BuOH, water, and BuOH solution (5%) at different IL concentrations in the membrane; and (b) Desorption results of the [bmim][TF$_2$N]–PDMS membranes at different IL concentrations in the 5% feed solution: BuOH % in the membrane and the selectivities.

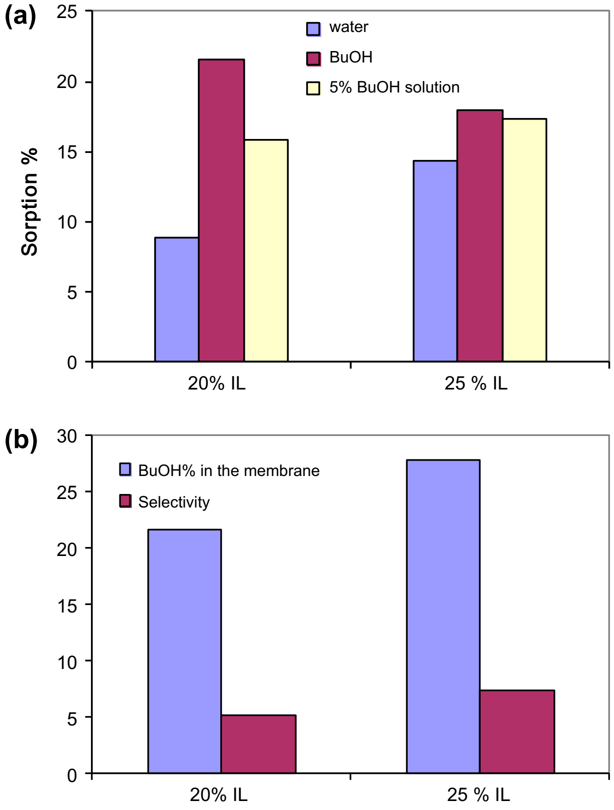

Fig. 10. Sorption and desorption results of [bmim][PF$_6$]–PDMS membranes (a) The sorption percentages of [bmim][PF$_6$]–PDMS membranes in pure BuOH, water, and BuOH solution (5%) at two different IL concentrations in the membrane; and (b) Desorption results of the [bmim][PF$_6$]–PDMS membranes at two different IL concentrations in the 5% feed solution: BuOH % in the membrane and the selectivities.

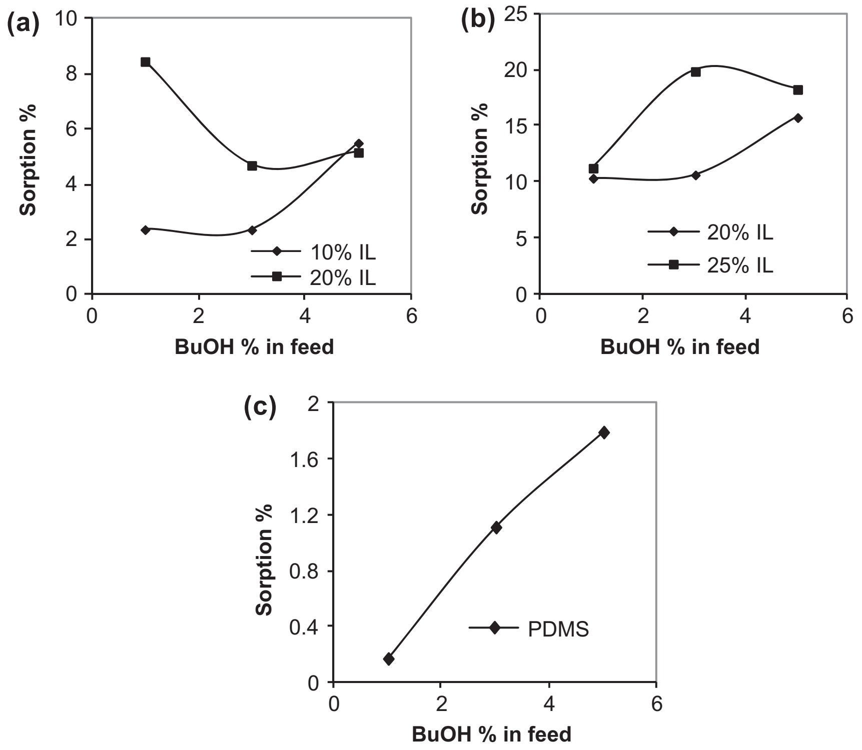

Fig. 11. Sorption results of the membranes at different feed concentrations: (a) [bmim][TF$_2$N]–PDMS; (b) [bmim][PF$_6$]–PDMS; and (c) PDMS.

The sorption results in 5% BuOH solution did not change very significantly with the IL concentration in the membrane. However, the sorption results in water and BuOH showed a maximum for the given range of IL content where the maximum sorption corresponds to 20% IL in the membrane. After this IL concentration, the sorption results began to decrease. This can be explained by low compatibility of [bmim][TF$_2$N] with PDMS at higher concentrations. Besides, when 30% of IL in the PDMS was used, a wetting phenomenon of the membrane surface was observed, which is resulted from a slight phase separation in the membrane. Desorption experiments were carried out for each of IL content to obtain the selectivity and BuOH % in the membrane. The results are presented in Fig. 9(b). As can be seen in Fig. 9(b), the selectivities as well as BuOH concentrations increase as the IL content increased from 10 to 20% IL, and after this point they decreased as the IL content increased to 30%. These results are coherent with sorption results showing a similar trend with the sorption curve given in Fig. 9(a). From the desorption and sorption results it can be concluded that the optimum IL content for [bmim][TF$_2$N]–PDMS membrane is 20% of IL.

For the [bmim][PF$_6$]–PDMS blends, the sorption and desorption of 20 and 25% IL are compared. The 25% IL membrane was also clear and stable like the 20% IL membrane, a phase separation was not observed. The sorption results were presented in Fig. 10(a).

Fig. 10(a) shows that as the IL content in the membrane increased, BuOH sorption decreased, while water sorption increased slightly. The solvation behavior of the solvents in a medium can be affected by their polarity. The [PF$_6$]$^-$ anion is more polar than [TF$_2$N] reflected by their dielectric constants (Table 1). On the other hand, less polar ILs are more beneficial for butanol recovery as there is an inverse relation between butanol solubility with polarity [15]. Thus, as the [bmim][PF$_6$] increases in the membrane, BuOH sorption decreases, while water sorption increases because of the polar effects. The sorptions increased very slightly in 5% BuOH solution when the IL content increased to 25% from 20%.

Fig. 10(b) shows the desorption results of the [bmim][PF$_6$]–PDMS membranes in 5% of BuOH solution. Although the BuOH sorption decreased and water sorption increased at the higher IL concentration, desorption results indicate that BuOH % in the membrane and thus, selectivity increased slightly with increasing IL content. Thus, the membrane shows different behavior for each component when it is in sole

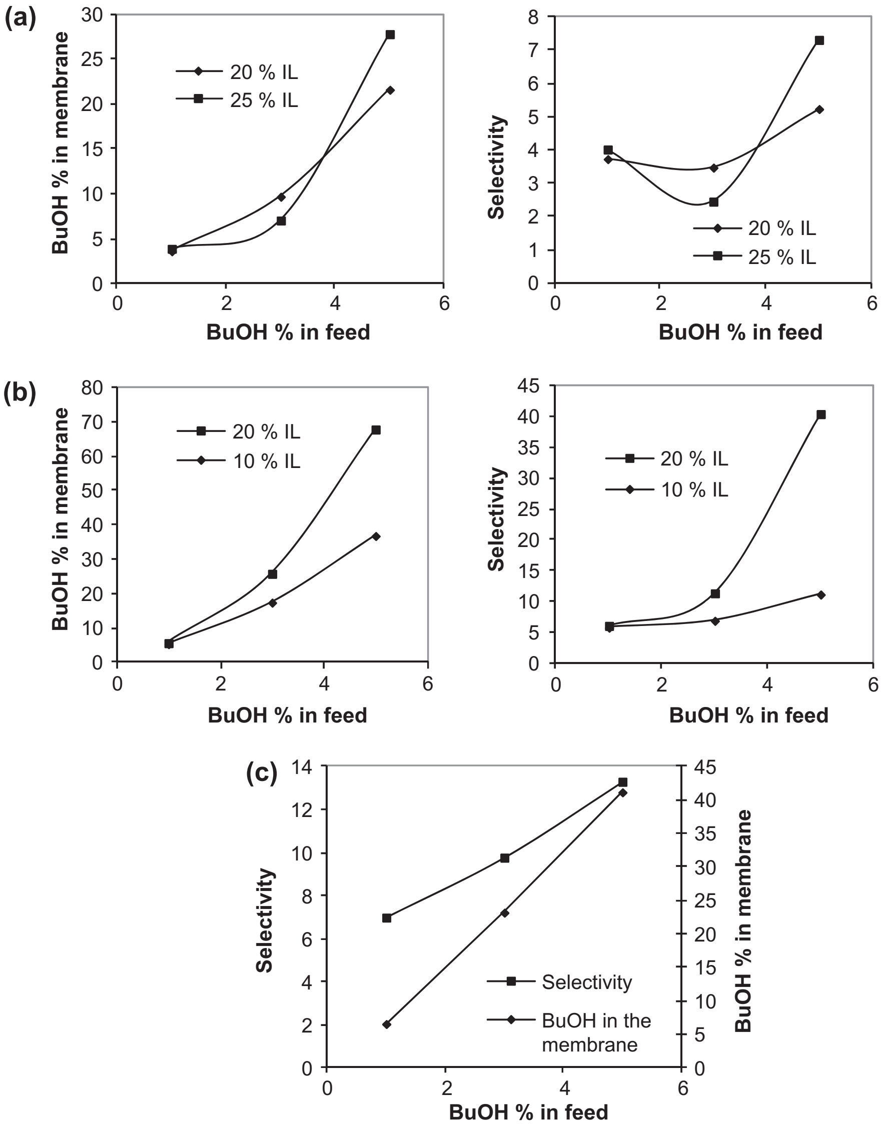

Fig. 12. Desorption results of the membranes at different feed concentrations (a) [bmim][PF_6]–PDMS; (b) [bmim] [TF_2N]–PDMS; and (c) PDMS.

solvents and binary mixtures of the solvents. This can be explained by the mutual effects of BuOH and water.

3.4. Effect of the feed concentration

The sorption and desorption results were evaluated for the membranes immersed into different sorption solutions at different concentrations to see the effect of feed concentration on the separation characteristics. The concentrations of the sorption solutions were 1, 3, and 5% BuOH (wt). As the BuOH concentration is low in ABE fermentation mixture (≤2%), the feed concentrations were selected relatively lower. PDMS, 20% [bmim][PF_6]–PDMS, 25% [bmim][PF_6]–PDMS, 10% [bmim][TF_2N]–PDMS, and 20% [bmim][TF_2N]–PDMS membranes were evaluated at these concentrations of feed solutions.

Fig. 11 shows the sorption results of the membranes at different feed concentrations.

As the BuOH concentration increases in feed, the degree of the swelling of the membrane tends to increase as a general trend. This relation is almost linear for the PDMS membrane. This is expected because the presence of the more selective component in the solution results in a swelling of the membrane, and the swelling increases as the more selective component increases in the solution. As can be seen in

Fig. 11, the presence of IL in the membrane increased the sorption results at all feed concentrations. For the [bmim][TF$_2$N]–PDMS membrane, the degree of sorption increased with increasing feed concentration at lower IL content in the membrane, however, for the higher IL content of 20% IL, the highest sorption was achieved at the lowest feed concentration. This result reflects a convenient separation potential for a possible PV application for BuOH recovery from a fermentation broth, since the BuOH concentration is very low in the fermentation mixture. [Bmim][PF$_6$]–PDMS membrane showed also similar trend to PDMS at the lower IL content yielding higher sorption results at higher feed concentrations. However, the degree of swelling began to decrease after 3% BuOH concentration in feed at the higher IL content. The presence of IL in the membrane enhanced the sorption of the membrane for both IL blends. Membranes with lower IL concentrations showed relatively similar trend to PDMS membrane that is increasing sorption degree with increasing BuOH concentration. As the IL concentration increases in the membrane, deviations of the sorption trends from the PDMS membrane behavior were observed. Fig. 12 shows the desorption results of the membranes. In general, as the BuOH concentration increased in feed, the BuOH concentration increased in the membrane as well, and these results were also reflected by the selectivity results. These results show that BuOH is sorbed preferentially over the studied composition range.

Desorption experiments show that BuOH concentration in the PDMS membrane was in the range of 6.6–41% when the feed concentration was in the range of 1–5%. The inclusion of [bmim][PF$_6$] in the membrane decreased the selectivities, but enhanced the degree of sorption. Thus, the use of this membrane should be considered with an optimization of fluxes and selectivities in a PV process. With the inclusion of [bmim][TF$_2$N] at 20% in the PDMS membrane, the BuOH concentration in the membrane increased giving the highest BuOH concentration of 68% for the 5% feed concentration. The increase in both sorption and selectivity using this IL in the membrane at 20% IL concentration indicates that this blending membrane has potential for a PV process in terms of flux and selectivity, being a promising membrane for the separation of butanol in ABE fermentation.

4. Conclusion

The sorption and desorption of PDMS and IL-blended PDMS membranes using [bmim][TF$_2$N], [bmim][PF$_6$], and [hmim][PF$_6$] were carried out to investigate the preferential sorption of BuOH in the membrane. [Hmim][PF$_6$]-blended membranes were not found to be appropriate for the BuOH separation. The effect of BuOH concentration in feed and IL concentration in the membrane on the separation characteristics were investigated. As the feed concentration increased, BuOH concentration in the membrane increased as well for the [bmim][TF$_2$N] and [bmim][PF$_6$]-blended membranes, indicating that the membranes uptake BuOH preferentially. The best results in terms of selectivity and sorption were achieved by using [bmim][TF$_2$N]-blended membranes. [bmim][TF$_2$N]–PDMS blending membrane was found to be a promising membrane for the BuOH separation in a PV process. High butanol enrichment factors achieved by [bmim][TF$_2$N]–PDMS blended membranes through sorption and desorption experiments lend credence to the further investigation of this membrane for its application in PV. This membrane could be enhanced using it as an active layer onto a porous polymeric support layer or by covalent bounding in order to improve the stability of the membrane when it is used in PV.

Nomenclature

α_{ij}	—	selectivity for component i over compound j
c_i	—	concentration of compound i (wt/wt)
m_{dry}	—	weight of the dry membrane (g)
m_{wet}	—	weight of the wet membrane (g)

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