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Improving performance of pervaporation membranes for biobutanol separation

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ABSTRACT

In view of the growing energy consumption, biofuels are becoming an important part of the fuel market. Biobutanol, thanks to its favorable properties, may replace gasoline in the future. However, appropriate purification and separation methods are required to improve the efficiency of biobutanol production. Membrane processes such as pervaporation (PV) offer a promising alternative to the traditional methods of biobutanol recovery from fermentation broths. The paper focuses on biobutanol separation by PV as well as evaluation of membrane performance and identification of the best production technology. PERVAP 4060 commercial membranes as well as novel ionic liquid membranes were used to concentrate butanol. The ionic liquid membranes were prepared by mixing ILs with polydimethylsiloxane (PDMS) and hardening by polycondensation. In general, PERVAP 4060 offers high butanol flux but low selectivity. On the other hand, the IL-PDMS membrane provides higher butanol selectivity, compared to the commercial membrane, but suffers from low flux caused by the additional layer resistance. The PV separation indices and the mass transfer coefficients for individual component were determined and discussed for the commercial and newly formed membranes.

Keywords: Pervaporation; Membranes; Ionic liquids; Biobutanol

1. Introduction

Biofuels, such as bioethanol, biobutanol, and biodiesel, pose an attractive alternative to conventional fuels due to the increasing demand for energy, limited supply of fossil fuels, and need to reduce global greenhouse gas emissions [1]. Biobutanol offers several significant advantages over bioethanol: higher energy content, lower vapor pressure, lower hygroscopicity, and much better miscibility with gasoline [2]. Its heat of vaporization is comparable to that of gasoline. Being suitable for combustion in spark-ignition engines, it is a perfect candidate to replace gasoline [3].

One of the possible methods of n-butanol production involves the acetone–butanol–ethanol (ABE) fermentation of biomass with *Clostridium* bacteria; however, this process requires further separation and

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purification of the product. *Clostridium* bacteria are able to utilize a wide variety of substrates such as sugar cane, corn, wheat, straw, and other materials containing cellulose as well as organic waste [4,5]. The quality and price of substrates determines the production cost [6]. There are several types of *Clostridium* bacteria giving different butanol concentrations in the fermentation broth: *Clostridium acetobutylicum* 10–16 g/dm^3, *Clostridium saccharoperbutylacetonicum* 7–11 g/dm^3, *Clostridium saccharobutylicum* 9–14 g/dm^3, and *Clostridium beijerinckii* 18–25 g/dm^3 [7–9]. The typical mass ratio of ABE in the broth attributed to *C. acetobutylicum* equals 3:6:1. The overall process efficiency may be considered low as the butanol concentration in the broth does not exceed 3 wt.%. Other limitations of conventional ABE fermentation include toxicity of butanol toward the bacteria, complexity of the process, and run under sterile conditions is high glucose concentration to *Clostridium* bacteria.

Separation of biobutanol from the fermentation broth is a complex technical problem. Distillation, gas stripping, vacuum flash, liquid–liquid extraction, extractive fermentation, perstraction, pervaporation (PV), membrane distillation, reverse osmosis, and adsorption are well-known methods for the separation of biobutanol reported in the literature. Each of these methods has advantages and disadvantages; however, all of them need further research to improve the economics of biobutanol production [10–12].

PV is a novel membrane technique for liquid/liquid separations that has been extensively studied in recent years. It is also proposed for butanol recovery from fermentation broths [13–16]. The mechanism of transport through the PV membranes involves dissolution and diffusion instead of vapor–liquid equilibrium considered the basis of distillation. PV membrane performance can be characterized by the following parameters: total and partial permeation fluxes (J_i), enrichment (β_i), separation factors (α_i) for individual components, and pervaporation separation indices (PSI) [17], which may be expressed by the equations shown below:

$$J_i = J_{tot} w_i \tag{1}$$

$$\alpha_i = \frac{w_{iP}}{w_{iF}} \cdot \frac{1 - w_{iF}}{1 - w_{iP}} \tag{2}$$

$$\beta_i = \frac{w_{iP}}{w_{iF}} \tag{3}$$

$$PSI = J_i(\alpha_i - 1) \tag{4}$$

where w_i is the mass fraction of component "i" in the permeate "P" and feed "F", respectively, and total flux (J_{tot}) is the ratio of the mass of the permeate (g) to the effective area of the membrane (m^2) and time of permeation (h).

Based on the solution–diffusion model, the PV transportation equation for an individual compound through the membrane can be expressed as follows:

$$J_i = K_i \rho_i \cdot \Delta a_i \tag{5}$$

where K_i is the overall mass transfer coefficient for individual component (m/s), ρ_i is the density of component "i" at operating temperature (kg/m^3), and Δa_i is an activity change of component "i". Activity change (Δa_i) is the driving force of permeation process. The change in the activity of mixture components on both sides of the membrane is expressed by the following equation:

$$\Delta a_i = \gamma_{iP} x_{iP} - \gamma_{iF} x_{iF} \tag{6}$$

where x_i is the mole fraction of component "i" in the permeate "P" and feed "F", respectively, and γ_i is the activity coefficient on both sides of the membrane.

Non-random two-liquid (NRTL) model is one of the methods of activity coefficient calculations. Here, the NRTL model was used to determine the activity coefficients of acetone, butanol, ethanol, and water in the liquid state at atmospheric pressure. All calculations were conducted with Matlab software [18].

1.1. Supported ionic liquid membranes for PV applications

There are three major types of PV hydrophobic membranes that may be applied to separate biobutanol, namely polymeric, inorganic, and composite membranes. Membranes made from polydimethylsiloxane (PDMS) are the most commonly used in n-butanol separation experiments [19,20]. Other types of polymeric membranes for butanol separation include polyether block amide [21], polytetrafluoroethylene [22], polypropylene, and PTMSP (poly(1-trimethylsilyl-1-propyne)) membranes [23].

Butanol selective fillers may be incorporated into PV membranes to improve their selectivity. Modern solvents—ionic liquids—can be used as fillers. After the ionic liquid is immobilized in the membrane, the size of the active layer with immobilized IL should be reduced. Ionic liquid membranes with specific ionic liquids (SILMs) can be designed and used for pervaporative separation of biobutanol [24].

Room-temperature ionic liquids, which are widely promoted as novel "green" solvents, are organic salts, which usually consist of a large and structurally complex cation and a small anion. They possess a number of favorable properties, which involve negligible vapor pressure, high thermal and electrochemical stability, and nonflammability. However, still ILs toxicity has not been examined. By choosing an appropriate cation–anion combination, ionic liquids may be "designed" to have high affinity for butanol [25].

As reported in the literature [26–28], ILs may be incorporated into PV membranes by several methods: immobilization in pores of the membrane, inclusion by additive coating, inclusion in the polymer matrix, gelation of ILs, covalent binding of ILs, or ion exchange (see Fig. 1). Each method has both advantages and disadvantages [29]. For example, immobilization in pores is easy to achieve. Inclusion by the additional coating ensures a lasting IL immobilization but is associated with excessive thickness of the membrane and additional mass transfer resistance. The next method—inclusion in the polymer matrix—allows incorporating various amounts of ILs and combining separation characteristics of the IL and polymer matrix. Gelation of IL increases its maximal content in the membrane, but leaching of the IL out of the polymer matrix and mechanical stability make this method questionable. For covalently bound method, stable and durable immobilization of ILs is possible, mixtures of poly-ILs and ILs can also be used, which may result in different properties compared to neat ILs. The last method of SILMs formation is based on ion exchange that ensures stable immobilization of ILs in the membrane but, as a result, different properties than those of neat ILs are obtained.

This paper evaluates the performance of different PV membranes and identifies the best production technology. Studies on butanol concentration by PV using commercial and novel ionic liquid-based membranes are described.

2. Materials and methods

2.1. Chemicals and reagents

Two-component liquid silicone rubber—PDMS (POLSIL Solar, Poland)—hardened at room temperature into transparent rubber with *Solar* catalyst (Silikony Polskie Chemical Plant, Poland) was used to prepare the PV membrane with the immobilized ionic liquid. Two ionic liquids 1-hexyl-3-methylimidazolium hexafluorophosphate [Hmim][PF6] and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [Bmim][Tf2N] acquired from IoLiTec (Germany) were used. The ILs are poorly soluble in water and have the affinity for butanol [30]. Chemical structures of ionic liquids used are shown in Fig. 2.

The aqueous feed for PV tests contained three organic components: acetone, n-butanol (here, also referred to as butanol), and ethanol (PoCh, Poland).

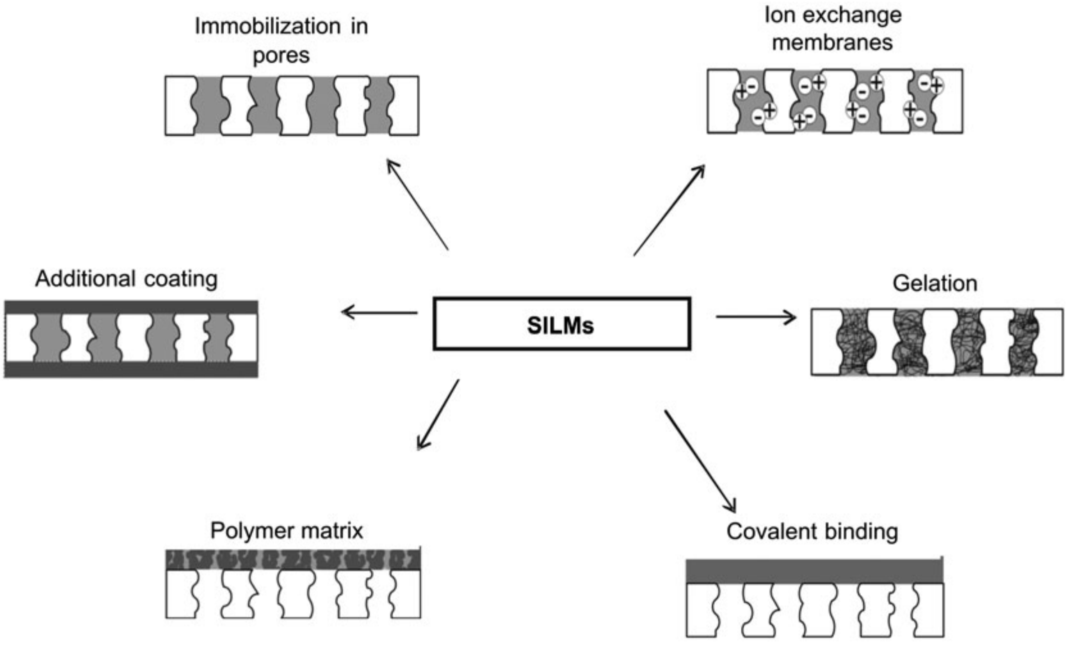

Fig. 1. Ionic liquid immobilization methods [29].

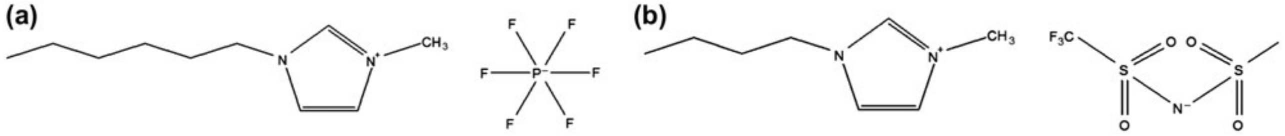

Fig. 2. Structural formulas of ionic liquids immobilized in the membranes: (a) 1-hexyl-3-methylimidazolium hexafluorophosphate [Hmim][PF6] and (b) 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [Bmim][Tf2N].

All chemicals were of analytical grade and were used without further purification.

2.2. Membranes

Commercial hydrophobic membrane PERVAP 4060 was purchased from Sulzer Chemtech (Germany). The active layer of the membrane was made of PDMS, 2 μm thick. The total thickness of the membrane was 160 μm.

Ionic liquid pervaporation membranes (SILMs) were prepared by mixing two-component liquid silicone rubber (POLSIL Solar) with the selected ionic liquid and hardening by polycondensation (with 8% wt. Solar catalyst). The mixture was then poured out on a level surface at room temperature and kept there for about 24 h until it was ready to use. The membranes were prepared with the maximal possible amount of selected ionic liquid: 36.5 wt.% for [Hmim][PF6] and 33 wt.% for [Bmim][Tf2N]. Hydrophobic ionic liquids used in the membrane formation are capable of selective butanol recovery, which was verified in liquid–liquid extraction process [31]. Due to the mechanical weakness of the formed polymer layer, 80-μm-thick nylon net was used as the membrane support. Therefore, the total thickness of the membrane was 160–200 μm. Membranes without ionic liquids were prepared in the same manner. Both pure PDMS and IL-PDMS membrane had the same thickness of about 160 μm. Fig. 3 presents microscopic images of the pure PDMS membrane with nylon net support and [Hmim][PF6]-PDMS membrane showing low transparency and visible agglomerations of ionic liquid.

2.3. PV experiments

The experiments on butanol concentration by PV were carried out using a Sulzer laboratory apparatus (Fig. 4), providing fixed pressure on the low-pressure side of the membrane (3 kPa), constant volumetric flow rate, and temperature for two types of membranes: PERVAP 4060 and the self-made membrane with and without IL. For PERVAP 4060 membrane, a total of 108 different experiments were performed. The flow rate (20, 40, and 60 dm^3/h) and temperature (50, 60, and 70°C) were varied. For ionic liquid membranes, the flow rate was 40 dm^3/h and the temperature was 50°C. The aqueous feed contained acetone (A), butanol (B), and ethanol (E) in the 3:6:1 ratio (w/w). Butanol concentration in the feed ranged from 0.25 to 3 wt.% for commercial PERVAP 4060 membrane and was constant (3 wt.%) for POLSIL membranes.

2.4. Analytical methods

The feed, permeate, and retentate compositions were analyzed by gas chromatography using an

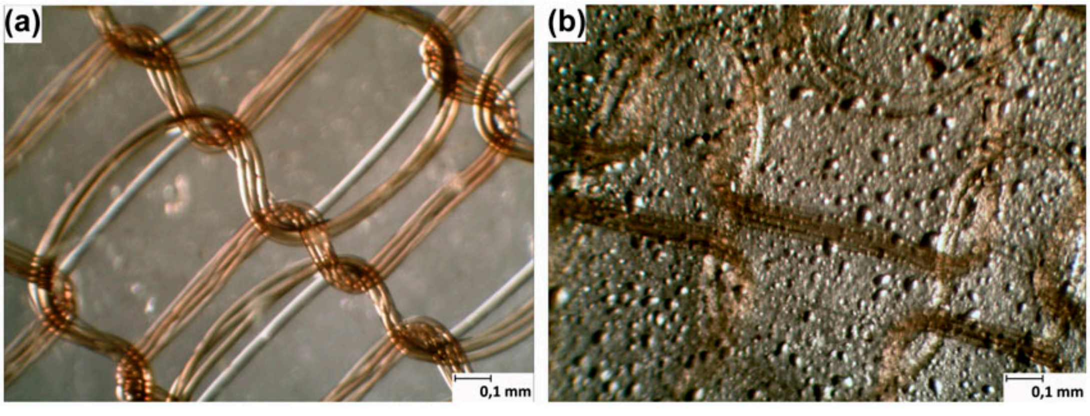

Fig. 3. Microscopic images of membranes (a) pure PDMS and (b) 36.5 wt.% [Hmim][PF6].

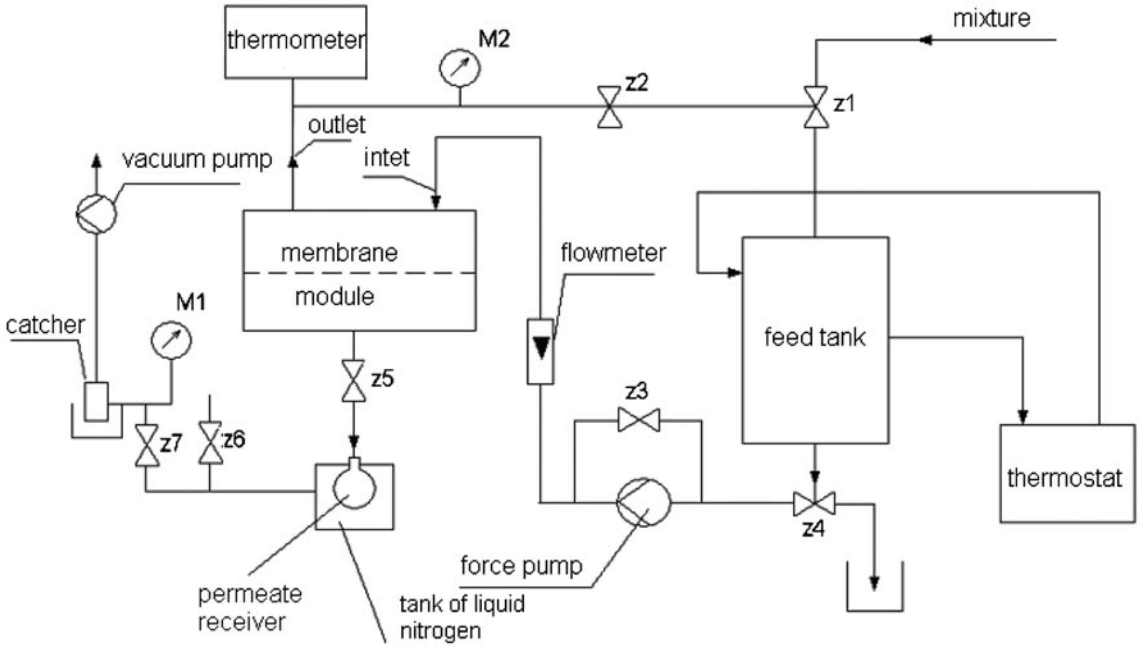

Fig. 4. Schematic diagram of PV equipment.

internal standard (methanol). Thermo-Finnigan chromatograph was equipped with FID and 30-m-long Quadrex Corporation column (BTR-CW-30V-1.0F, 0.53 mm), 1.0 μm thick.

3. Results and discussion

3.1. Results for pure PDMS membrane

The PV process was carried out on a self-made PDMS membrane (POLSIL) without IL. Table 1 lists selected performance data obtained for the pure PDMS membrane and for PERVAP 4060. The commercial membrane provides a high total flux rate (1–2.5 kg/m^2 h) but low butanol selectivity. The formed PDMS membrane is more selective (selectivity is 0.8–1.6 times higher) but operates at lower permeate flux rates.

The research on PERVAP 4060 membrane published earlier [32] showed the following relations: total mass flux of permeate increases along with

Table 1
Total permeate flux (J_{tot}) and enrichment factor (β) of feed components: A—acetone, B—butanol, E—ethanol, in PV process (3 wt.% B, 50˚C, 40 dm^3/h, and 3 kPa)

No.	Membrane	β_A (–)	β_B (–)	β_E (–)	J_{tot} (g/m^2 h)
1	POLSIL	17.6	12.8	3.4	44.92
2	PERVAP 4060	10.8	8.7	3.9	1,295.33

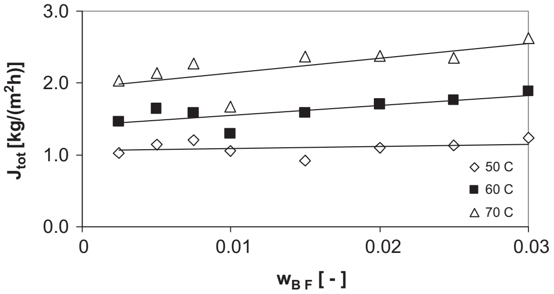

Fig. 5. Total mass flux of permeate (J_{tot}) at different temperatures and butanol concentrations (w/w) in the feed for 60 dm^3/h.

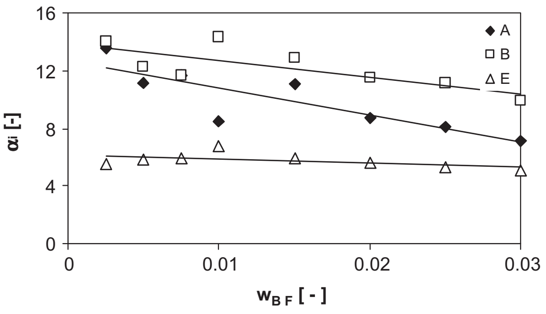

Fig. 6. Average separation factor of the organic phase (α_i) vs. butanol concentration in the feed (w/w).

Table 2
PV process (3 wt.% B, 50°C, 40 dm^3/h, and 3 kPa) parameters: total (J_{tot}) and partial (J_i) permeate fluxes, enrichment factors (β_i) of feed components: A—acetone, B—butanol, E—ethanol, at different concentrations of ionic liquid in the membrane (w_{IL})

No.	w_{IL} (wt.%)	β_A (–)	β_B (–)	β_E (–)	J_{tot} (g/m^2 h)	J_A (g/m^2 h)	J_B (g/m^2 h)	J_E (g/m^2 h)
1	0	17.6	12.8	3.4	44.92	11.88	17.23	0.76
2	25 [Hmim][PF6]	15.9	13.7	3.5	75.00	17.94	30.9	1.31
3	36.5 [Hmim][PF6]	12.9	12.6	7.7	82.34	15.96	31.09	3.15
4	33 [Bmim][Tf2N]	14.7	13.6	2.5	107.06	23.58	43.8	1.32

temperature and butanol content (Fig. 5). Separation factor is the highest for butanol, lower for acetone, and the lowest for ethanol, and decreases with increasing butanol concentration in the feed (Fig. 6). On the basis of experimental data, it can be concluded that the PERVAP 4060 membrane offers high flux rates but low butanol selectivity.

3.2. Results for SILMs

The PDMS membranes with and without ionic liquids, named SILMs, were tested in the PV system at 3% concentrations of butanol in the feed. Table 2 presents permeate fluxes and enrichment factors for the pure PDMS membrane (0 wt.% in Table 2) and membranes with specified contents of ILs.

Measured fluxes shown in Table 2 were relatively low, which was caused by additional resistance resulting from the membrane thickness. The active layer (IL layer) increased the overall thickness of the membrane, which amounted to about 160 μm. Therefore, further studies should focus on ionic liquid immobilization only in the active layer of the membrane and reduction in thickness of the active layer.

As can be seen from Table 2, higher total and partial fluxes for ionic liquid membranes were observed as compared with the pure PDMS membranes; however, the enrichment coefficient was similar. The introduction of ionic liquid into the PDMS membrane only slightly affects the selectivity toward butanol, but the partial permeate fluxes increase. Using the quaternary feed, the highest partial fluxes were recorded in the case of butanol. Fluxes of acetone and ethanol were two and twenty times lower, respectively. The membrane containing 33% [Bmim][Tf2N] provides higher partial fluxes of individual components than the membrane containing 36.5% [Hmim][PF6]. Studies reported in [33] show that [Bmim][Tf2N] is more hydrophobic than [Hmim][PF6], which results in the improved selectivity toward the organic components, including butanol. Butanol selectivity of [Bmim][Tf2N] is superior to that of [Hmim][PF6] (69 and 45, respectively).

The comparison of PV performance via PSI determined by Eq. (4) is shown in Fig. 7. Both separation factors and PSI values are decreasing in the following order: butanol > acetone > ethanol. The separation factors are in the ranges of 15–23, 19–24, 2.5–8 for acetone, butanol, and ethanol, respectively. The PSI values increase with increasing weight fraction of IL in the membrane excluding 36.5% [Hmim] [PF 6] membrane. The PSI values are very small compared with the performance of membranes without fillers reported in the literature [34]. As mentioned previously, this is due to the enhanced membrane thickness, resulting in low fluxes of components.

For the organic–water mixture, the overall mass transfer coefficient (K_i) for the individual component was calculated using Eq. (5). The results are given in Table 3. The values of the coefficients are two orders lower than those found in the literature for binary systems [16] and fermentation broth [35], and our results are similar to the results reported by Li et al. [36]. There are clear differences between K_i for the commercial and self-made membranes. PERVAP 4060 gives higher values of K_i for all the organic components of the mixture. The order of magnitude is greater than that of the results obtained with the pure PDMS membrane. The main reason is the different thicknesses of the analyzed membranes. It should be noted that the overall mass transfer coefficient for the individual component is higher for SILMs compared with the

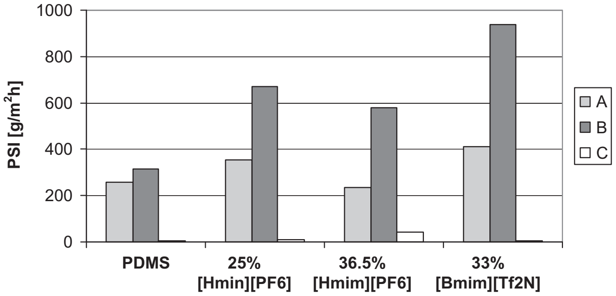

Fig. 7. PSI of membranes with different IL contents.

Table 3
The overall mass transfer coefficients (K_i) of feed components: A—acetone, B—butanol, E—ethanol, for different membrane studies in PV process (3 wt.% B, 50℃, 40 dm^3/h, and 3 kPa)

No.	Membrane	K_A 10^8 (m/s)	K_B 10^8 (m/s)	K_E 10^8 (m/s)
1	PERVAP 4060	16.63	7.52	22.14
2	PDMS	1.45	1.91	3.4
3	25% [Hmim][PF6]	2.42	3.21	5.69
4	36.5% [Hmim][PF6]	2.58	3.17	3.84
5	33% [Bmim]Tf2N]	3.41	4.28	14.58

pure PDMS membranes of the same thickness. Furthermore, the membrane containing [Bmim][Tf2N] has a higher K_i value than the membrane containing [Hmim][PF6]. From Table 3, it can be seen that for PERVAP 4060, the overall mass transfer coefficient of ethanol is the highest, followed by that of acetone and then butanol. In contrast, for the newly formed membranes, the sequence is as follows: ethanol > butanol > acetone.

Leaching of ionic liquids through the membrane pores is the additional fault of the polymer matrix method presented in this paper. Elution of ILs from the membrane structure during the PV process is described in the literature [37]. Although the leaching of ionic liquid out of the membrane was not measured in this study, certainly adding an additional layer enclosing the ionic liquid would be beneficial to the PV performance. At the same time, membrane thickness should be reduced.

4. Conclusions

n-Butanol recovery from aqueous solutions by PV using the PERVAP 4060 commercial membrane was performed for different temperature, feed flow rate, and feed composition. It has been observed that the PERVAP 4060 membrane operates at the high flux rate, but displays low selectivity for butanol. On the other hand, PV membranes produced from PDMS alone and PDMS combined with two different ionic liquids (PDMS-IL) operate at low fluxes caused by the membrane thickness, yet their selectivity is increased. The partial fluxes for membranes containing ionic liquids (SILMs), at 3% concentrations of butanol in the feed, were slightly higher compared with those of pure PDMS membranes, but the enrichment coefficient was similar. Perhaps, the trend will be different at different concentrations of butanol. SILM containing [Bmim][Tf2N] provides slightly higher partial fluxes of individual components than the membranes containing [Hmim][PF6]. This is because [Bmim][Tf2N] is more hydrophobic than [Hmim][PF6].

The PSI and the overall mass transfer coefficients for the individual component were determined and discussed for the commercial and newly formed membranes. The PSI values are decreasing in the following order: butanol > acetone > ethanol. At the same time, the overall mass transfer coefficients are higher for SILMs compared with those of pure PDMS membrane of the same thickness and lower than those of the PERVAP 4060.

The analysis of available papers suggests that the following challenges should be addressed when designing membranes using ionic liquids. The most important issue is to include ILs in the active membrane layer. Thickness of the active layer strongly influences the permeate flux. Elution of ILs through the pores is another obstacle. One should also take into consideration that properties of ILs may change after incorporation into the polymeric matrix.

Efficiency of the PV removal of biobutanol is dependent on factors related to the membrane properties and operating conditions. The former group of factors includes thickness of the active layer, membrane structure, adsorption capacity of fillers and modifications of membrane surface. Temperature and feed composition as well as pressure on the permeate side are the main factors influencing the energy demand of the PV process. Available comparison studies have shown that PV is highly competitive against other biobutanol separation processes, which encourages continuous improvement of the PV membrane design.

Acknowledgment

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List of symbols

a — activity, –

J — permeation flux, g/m^2 h

K — overall mass transfer coefficient, m/s

PSI — pervaporation separation indices, g/m^2 h

W — mass fraction of component, –

X — mole fraction, –

α — separation coefficient, –

β — enrichment coefficient, –

γ — activity coefficient, –

ρ — density, kg/m^3

Subscripts

i — individual component

F — feed

P — permeate

tot — total

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