



## Influence of ionic liquid content on properties of dense polymer membranes

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### ABSTRACT

Pervaporation was used for removal of butan-1-ol from its 5 wt.% of aqueous solution, at which the concentration of *Clostridium acetobutylicum* starts to decrease. The polydimethylsiloxane (PDMS) membrane containing 0, 10, 20 or 30 wt.% of benzyl-3-butylimidazolium tetrafluoroborate ([BBIM][BF<sub>4</sub>]) ionic liquid was used. Differential scanning calorimetry measurements showed that PDMS-[BBIM][BF<sub>4</sub>] membranes (though optically homogeneous) contained PDMS and [BBIM][BF<sub>4</sub>] phases. Pervaporation selectivity increased and total flux through membranes raised moderately with an increased content of [BBIM][BF<sub>4</sub>] in PDMS-[BBIM][BF<sub>4</sub>] membranes. Hence, immobilization of a proper ionic liquid in a membrane results in the creation of pervaporation membranes, effective in the removal of alcohol from fermentation broths.

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## 1. Introduction

Biofuels have recently gained industrial interest as a promising alternative to fossil energy sources. Biobutan-1-ol displays similar combustion properties as gasoline and could therefore offer the possibility of its direct replacement. Together with acetone and ethanol, butan-1-ol can be produced by the fermentation of biomass thanks to the well known bacterium *Clostridium acetobutylicum*. Under optimized conditions, glucose is fermented to the above mentioned products in a continuous mode [1–3]. A sustained efficient removal of the products by a membrane separation process, namely pervaporation, is therefore needed to maintain a stable growth. Pervaporation, which is considered a forward looking and modern membrane process for separation of various liquids or vapour mixtures, has proved

to be a suitable extraction method for a variety of organic solvents, including butan-1-ol [4,5].

Ionic liquids (ILs) have been recognized as a possible environmentally benign alternative to classical organic solvents, mainly due to their thermal stability and ability to solubilize a large range of organic molecules and transition metal complexes [6–9]. ILs are often called “designer solvents”, because of the facility to change their properties by variation of their components [10]. Polymer membranes containing ionic liquids (PM-ILs) offer a range of possible advantages. Molecular diffusion is much higher in ionic liquids than in polymers and it can be enhanced by a proper choice of IL components. Thus, PM-ILs allow high fluxes and faster separation. In addition, a low cost factor can be added, because only small amounts of ILs are necessary to form the membrane.

In our previous work we showed that PM-ILs have better separation properties than a classical polymer membrane [11]. The aim of this work is to carry out pervaporation using

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polymer matrices containing ILs, namely polydimethylsiloxane (PDMS) with benzyl-3-butylimidazolium tetrafluoroborate. Homogeneous PDMS membranes have been used in several separation processes, such as vapour permeation and pervaporation, where organic solutes are removed or recovered from vapours and diluted aqueous media [12].

## 2. Experimental

### 2.1. Materials

Benzyl-3-butylimidazolium tetrafluoroborate (Chemada Fine Chemicals, Israel) ([BBIM][BF<sub>4</sub>]), butan-1-ol, p.a. (Lach-Ner, s r.o., Czech Rep.) and nitrogen gas (Linde Gas a.s. UN1066, 99.99% purity, Czech Rep.) were used without further purification. PDMS Elastosil M4601 (component A) and a crosslinking catalyst (component B) were obtained from Wacker Silicones, Germany. The density of this virtually insoluble polymer is 1.13 g/cm<sup>3</sup> and its dynamic viscosity is approx. 25,000 mPa s at 20 °C.

### 2.2. PDMS-[BBIM][BF<sub>4</sub>] membrane preparation

PDMS component A was stirred thoroughly for 30 min with the crosslinking catalyst B and [BBIM][BF<sub>4</sub>]. While the weight ratio of the components A and B remained constant at 9:1, the concentration of [BBIM][BF<sub>4</sub>] in PDMS varied: 0, 10, 20 or 30 wt.% of the IL. The viscous mixture was spin-coated on a stainless steel plate and cured at 20 °C for 24 h. The average thickness of the resulting membrane was  $2.99 \pm 0.17 \times 10^{-1}$  mm.

### 2.3. Characterization of PDMS with IL by differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements were performed on the Perkin–Elmer Pyris 1 DSC calorimeter. Samples of about 5 mg were closed in Al sample pans and the system was flushed with dry helium during the DSC scan. The temperature scale was calibrated according to the melting points of cyclohexane and indium. The power output scale was calibrated with indium. The samples were scanned in the temperature range from –140 °C to 30 °C. Measurements in the standard DSC mode were performed at a constant heating rate of 10 °C/min and cooled at varying cooling rates of –10, –5 and –1 °C/min before the heating scan. The temperature modulated scans (DDSC) were performed in the same temperature interval as the standard DSC measurements. The isothermal-heating mode was used with period  $p = 60$  s, temperature amplitude  $A_T = 1$  °C and average heating or cooling rate of 1 °C/min. The glass transition temperature was calculated as “half  $c_p$  extrapolated” by Pyris software, melting and crystallization temperatures as an extreme of phase transitions peaks. Transition enthalpies were obtained by integration of the area of the peak. All calculated results are summarized in Table 1.

### 2.4. Pervaporation

A cell containing the membrane was immersed in a feed reservoir. The temperature of the feed was maintained at

37 °C, the optimum temperature for the butan-1-ol producing bacteria. The concentration of butan-1-ol in the aqueous feed was 5 wt.%, which is the highest possible concentration of butan-1-ol in the fermentation broth that will not inhibit the activity of the bacteria. The scheme of a gas-sweeping pervaporation set-up is shown in Fig. 1. One side of the membrane (membrane diameter 22 mm) was swept by nitrogen stream, while the opposite side of the membrane was in contact with the measured liquid mixture. The high flow rate of the sweeping gas guaranteed very low butan-1-ol concentration on the permeate side of the membrane.

Continuous sweeping gas (nitrogen) with the flow rate of 0.9 ml/s was located on the downstream side of the membrane. The permeate was carried away through a Teflon tube to a cold trap inserted in liquid nitrogen, where the permeate (butan-1-ol) condensed. The cold trap was protected from ambient humidity with silica gel. Typical experiments lasted for 48 h. The condensed (liquid) permeate was analyzed with a gas chromatograph (Thermo Electron Corporation, Finnigan GC ultra with polystyren-divinylbenzen stationary phase and TCD detector; column Agilent Technologies HP-PLOT 30 m  $\times$  0.530 mm; Temperature program: Initial 120 °C, hold for 5 min. Increase of 15 °C/min to 200 °C, hold for 10 min; Pressure program: Initial 20 kPa, hold for 5 min. Increase of 20 kPa/min to 70 kPa, hold for 13 min).

Separation factor and total flux were used to evaluate the performance of membranes. The total flux,  $J$ , was obtained from:

$$J = Q/At \quad (1)$$

where  $Q$  is the total amount of liquids permeated during time interval  $t$  and  $A$  is the effective surface area. The separation factor of a binary mixture of water-butan-1-ol,  $\alpha_{bw}$ , is defined as:

$$\alpha_{bw} = \frac{w_{bp}/w_{wp}}{w_{bf}/w_{wf}} \quad (2)$$

where  $w_{bp}$  is the weight fraction of butan-1-ol in the permeate,  $w_{bf}$  is the weight fraction of butan-1-ol in the feed,  $w_{wp}$  is the weight fraction of water in the permeate and  $w_{wf}$  is the weight fraction of water in the feed.

### 2.5. Sorption from liquid solution

Preferential and total sorption of liquid was measured as described by Izák et al. [13]. The preferential sorption  $\Omega_i$  (mol g<sup>-1</sup>) is evaluated from a change in the solution concentration caused by the sorption:

$$\Omega_i = \frac{n^s}{m_{p,0}} (x_i^s - x_i^b) = \frac{N^0}{m_{p,0}} \cdot (x_{i,0}^b - x_i^b) \quad (3)$$

where  $x_{i,0}^b$  and  $x_i^b$  are molar fractions of the component  $i$  in bulk of the original solution and the solution equilibrated with immersed membrane, respectively.  $n^s$  is the total amount of absorbed liquid and  $N^0$  is the initial mole number of binary solution brought into contact with  $m_{p,0}$  grams of a dry polymer.

**Table 1**

Glass transition temperature of PDMS ( $T_{g,PDMS}$ ), glass transition temperature of [BBIM][BF<sub>4</sub>] ( $T_{g,IL}$ ), melting temperature ( $T_m$ ), melting enthalpy ( $\Delta H_m$ ), crystallization temperature ( $T_c$ ), crystallization enthalpy ( $\Delta H_c$ ) and crystallinity ( $\chi$ ) of [BBIM][BF<sub>4</sub>], PDMS and their blends. Blend 10, Blend 20 and Blend 30 are PDMS blends containing 10, 20 and 30 wt.% of [BBIM][BF<sub>4</sub>], respectively. Measurements in the standard DSC mode were performed with constant heating rate 10 °C/min with the samples cooled with different cooling rates. DDSC: The temperature modulated scans.

Sample	Mode	CR <sup>a</sup> (°C/min)	$T_{g,PDMS}$ (°C)	$T_{g,IL}$ (°C)	$T_m$ (°C)	$\Delta H_m$ (J/g of sample)	$T_c$ (°C)	$\Delta H_c$ (J/g of sample)	$\chi$ (crystallinity %)
[BBIM][BF <sub>4</sub> ]	DSC	10		-60.4	-36.8	0.31	-49.3	-0.4	
	DSC	5		-54.5	-44.2	0.6			
	DSC	1		-54.4	-47.9	1.5			
	DDSC <sup>c</sup>			-57.7	-42.0				
PDMS	DSC	10	-124.9		-44.2	18.5	-73.1	-18.8	
	DSC	5	-125.3		-42.4	19.7	-38.7	-17.1	54
	DSC	1	-126.3		-44.5	14.5			
	DDSC <sup>c</sup>		-127.9						
Blend 10	DSC	10	-124.5		-44.6	16.6	-73.7	-16.3	
	DSC	5			-43.1	16.5	-70	-15	51
	DSC	1	-126.7		-45.3	11.7	-66.5	-14.5	
	DDSC <sup>c</sup>		-127.1						
Blend 20	DSC	10			-45.3	11.8	-71.3	-14	
	DSC	5			-43.2	15.2	-69.6	-13	53
	DSC	1	-128.5		-45.3	15.1	-66.4	-10.1	
	DDSC <sup>c</sup>		-127						
Blend 30	DSC	10	-124.2		-43.2	11.8	-70.8	-12.6	
	DSC	5			-42.9	13.8	-69.3	-11.5	50
	DSC	1	-127.7		-43.5	11.6	-64.1	-8.5	
	DSC	5/1 <sup>b</sup>	-130.2	-55.2					
	DDSC <sup>c</sup>		-126.7						
	DDSC <sup>d</sup>			-45.5					

<sup>a</sup> Cooling rate.

<sup>b</sup> CR = -1 °C/min and HR = 5 °C/min.

<sup>c</sup> DDSC measurement in the heating mode.

<sup>d</sup> DDSC measurement in the cooling mode.

We define preferential sorption as an excess amount of a substance absorbed by the membrane, in comparison with the bulk of the solution, which has the same total number of moles as the absorbed liquid. The positive values of  $\Omega_i$  mean preferential sorption of compound  $i$ , the negative values preferential sorption of other compounds.  $\Omega_i$  varies with the solution composition at constant temperature. The measurements in this work were done with aqueous solution of butan-1-ol with the concentration 5 wt.%. As changes of the concentration of butan-1-ol in the bulk after the immersion of the membrane were small and the values of equilibrium mole fractions  $x_i^b$  were nearly the same, the comparison of membranes with different amount of ionic liquid using preferential sorption was done directly.

The total sorption  $n^s$  is available from the experimental equilibrium swelling degree, i.e. the relative weight increase:

$$Q = \frac{m_p - m_{p,0}}{m_{p,0}} \quad (4)$$

where  $m_p$  is the mass of the swelled polymer membrane and  $m_{p,0}$  is the mass of the dry membrane. Then

$$n^s = \frac{Q}{M^s} = \frac{Q}{x_2^s M_2 + (1 - x_2^s) M_1} \quad (5)$$

where subscript 2 denotes butan-1-ol and  $M_i$  are molar masses of pure compounds. Then, the composition of the sorbed binary liquid is obtained by combining Eqs. (2) and (5):

$$x_2^s = \frac{Q x_2^b + \Omega_2 M_1}{\Omega_2 (M_1 - M_2) + Q} \quad (6)$$

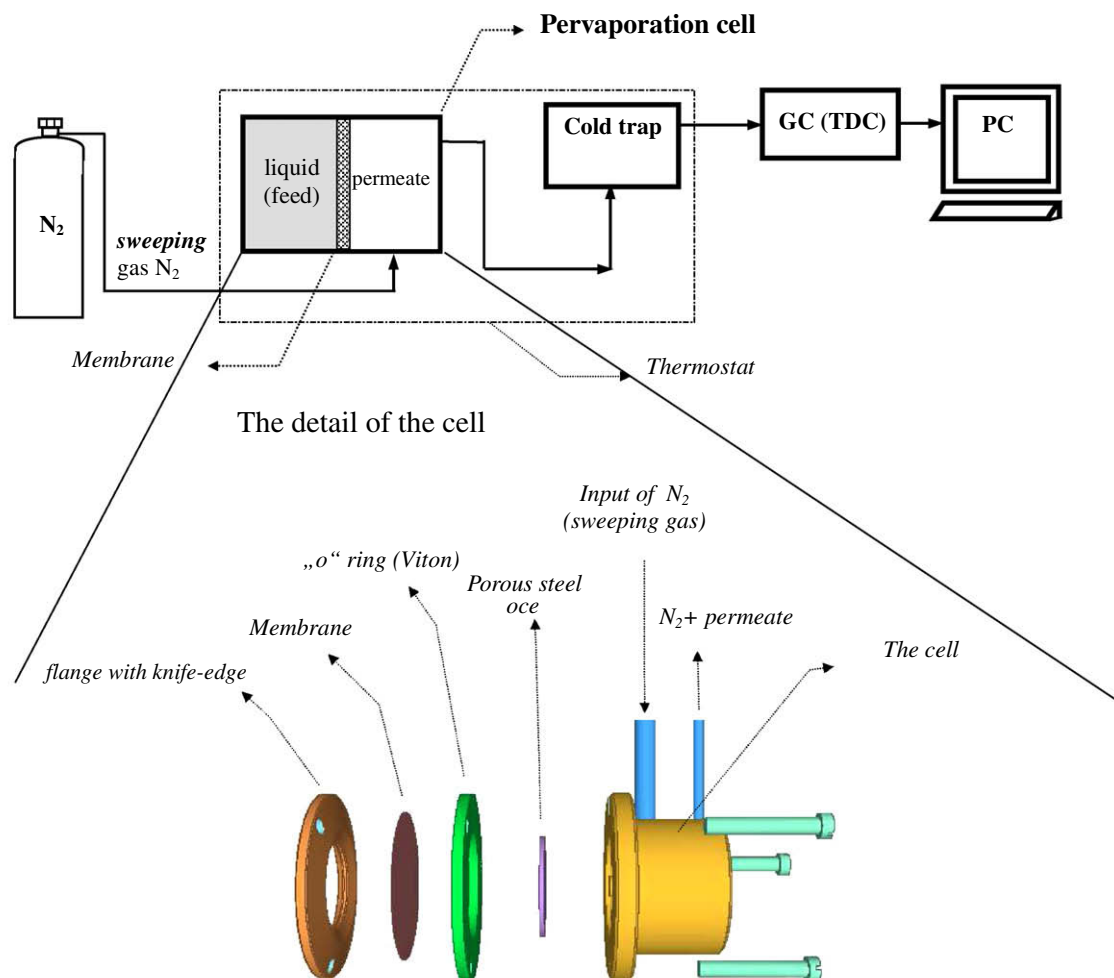
and separation factor using weight fractions in membrane and in bulk solution  $w_i^s, w_i^b$  (analogous to Eq. (2)):

$$\alpha_{bw}^s = \frac{w_2^s/w_1^s}{w_2^b/w_1^b} \quad (7)$$

can be evaluated.

The data on the preferential sorption from binary liquid solution of 5 wt.% butan-1-ol (1) + water (2) at the temperature of 37 °C were acquired by gas-liquid chromatography (GLC) measurement of the concentration change of the liquid mixture brought into contact with a large amount of polymer.

A polymer foil cut to small pieces was weighed into a small dry flask and then the solution of known concentration (molar fraction  $x_{2,0}^b$ ) was added (the flask had to be nearly full to keep the amount of the vapour phase as small as possible). The tightly closed flask was then kept at the constant temperature of 37 ± 1 °C in Binder dryer, the content of which was mixed by shaking. After three days, when the sorption equilibrium was established (the experiments performed in three and five days gave the same results), the equilibrium solution surrounding the foil together with the original solution were analyzed by Hewlett-Packard HP-5890II gas-liquid chromatograph. It was equipped with a 7673 AutoSampler, FID detector and a wide-bore 15 m long DB-WAX capillary column. Oven temperature was kept at constant value of 80 °C. The analysis of each sample was re-



**Fig. 1.** Scheme of pervaporation apparatus-type “gas-sweeping” and pervaporation cell construction adopted from Uchytíl P., Petříčková R., *J Membr Sci* 2002;209:67.

peated 10 times. The standard deviation estimated from replicated measurements was smaller than 1%. The equilibrium molar fraction  $x_2^b$  was then calculated from the initial mole fraction  $x_{2,0}^b$  and the ratio of peak areas for original and equilibrated solutions, respectively:

$$x_2^b = x_{2,0}^b \frac{A_2^b}{A_{2,0}^b} \quad (8)$$

This equation is valid at constant injection volume and on the assumption that total number of moles in both injections is the same. As the changes of concentration are small, the last assumption is fulfilled with sufficient precision.

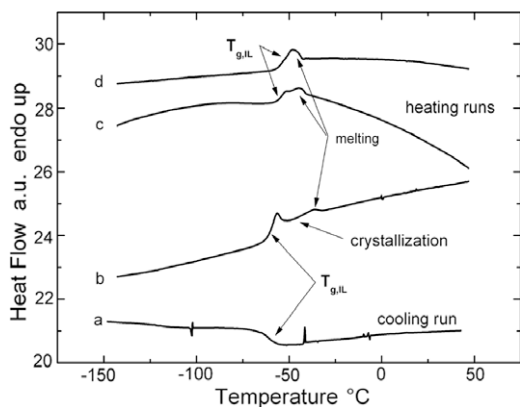
The total sorption was determined by gravimetric method. A piece of polymer foil ( $m_{p,0} \cong 0.13$  g) was immersed into a thermostatted Erlenmeyer flask containing about 40 g of binary liquid mixture. After three days the swollen foil was weighed. As the amount of sorbed liquid was very small, the usual method of weighing the swollen sample after drying between two sheets of filter paper produced unreliable results. A special procedure was imple-

mented. The foil was transferred from the solution into a tightly closed weighing bottle; its inner walls were covered by filter paper. The foil was put into a position, in which only its edges touched the paper (the dimensions of the weighing bottle must correspond to the dimensions of the foil sample). After the paper had drained off the excess liquid from the foil and equilibrium in the bottle had been established (about 2 h), the full bottle was weighed. The foil was then taken out quickly and the bottle with the wet paper was weighed again. The difference represented the weight of the swollen foil ( $m_p$ ). This procedure was found to be reproducible within  $\pm 2$  mg.

### 3. Results and discussion

#### 3.1. Compatibility of PDMS and [BBIM][BF<sub>4</sub>]

DSC curves of neat [BBIM][BF<sub>4</sub>] are presented in Fig. 2. The pronounced glass transition is observed on the cooling curve *a* (cooling rate, (CR) =  $-10$  °C/min) at about  $-60$  °C. Small peaks on the curve are random noise. No crystalliza-

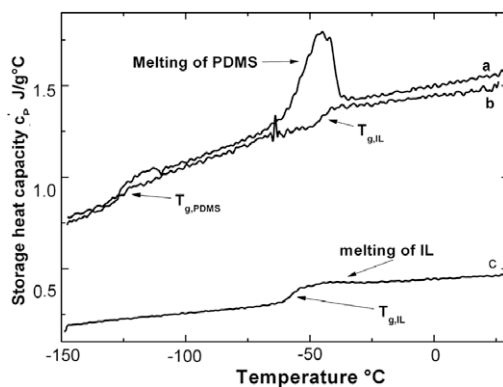


**Fig. 2.** Temperature dependences of DSC heat flow of neat [BBIM][BF<sub>4</sub>]; (a) cooling mode (−10 °C/min); (b–d) heating mode (10 °C/min) preceded by cooling at rates −10, −5 and −1 °C/min, respectively.

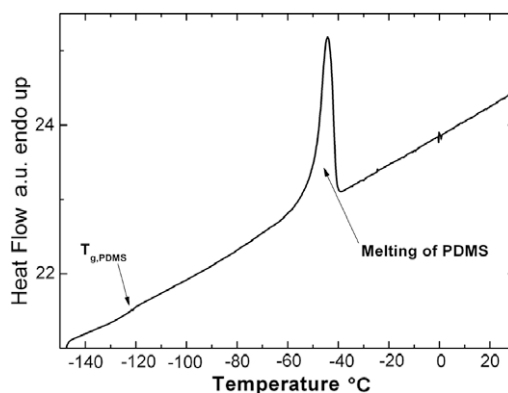
tion endotherm of [BBIM][BF<sub>4</sub>] is observed on the cooling curve. During cooling the melt is transformed directly into a glassy state. Nucleation and crystallization of [BBIM][BF<sub>4</sub>] is restrained by high melt viscosity near glass transition temperature. The crystallization and melting of [BBIM][BF<sub>4</sub>] are observed above the glass transition temperature in the heating run *b* (heating rate (HR) = 10 °C/min) following the cooling run *a*. The sum of the enthalpies of these transitions is practically zero. It confirms the crystallites of [BBIM][BF<sub>4</sub>] are formed, when the cooled glass is heated. The melting temperature, defined as the maximum of the melting endotherm, depends on the cooling rate of the melt. The decrease of CR shifts the crystallization and melting temperatures toward the glass transition temperature of [BBIM][BF<sub>4</sub>] (Table 1, Fig. 2, curves *a*, *b*, *c*). The confirmation of the endotherm observed is melting peak, which can be obtained by temperature modulated DSC (DDSC) [14,15]. The dependence of the storage heat capacity  $c_p'$  (a real part of the complex heat capacity  $c_p^*$ ) of neat [BBIM][BF<sub>4</sub>] is presented in Fig. 3, curve *c*. The pronounced glass transition is followed by a small broad melting endotherm with the maximum at −42 °C. Before the DDSC measurement, the sample was cooled by CR = −10 °C/min. This value is comparable with the values obtained by standard DSC measurements (see Table 1).

The neat PDMS has glass transition  $T_{g,PDMS}$  at about −125 °C and crystallization and melting transitions at about −43 °C and −70 °C, respectively (Table 1, Fig. 4). The agreement of the experimental glass transition temperature of PDMS and the literature one  $T_{g,PDMS} = -123$  °C [16] is very good.

The glass transition temperature of PDMS phase in PDMS-[BBIM][BF<sub>4</sub>] blends is practically independent on the blend composition and temperature history and it is equal to the one of the neat PDMS. The same holds for its melting temperature and for its crystallinity (Table 1, Fig. 4). PDMS crystallinity equals to the ratio of the melting enthalpy per gram of PDMS (the enthalpy is calculated from experimental melting enthalpy per gram of sample). The literature value of the enthalpy for fully crystalline neat PDMS is  $\Delta H_m = 35.09$  J/g [16].



**Fig. 3.** Temperature dependences of storage heat capacities  $c_p'$ ; (a and b) PDMS blend with 30 wt.% of [BBIM][BF<sub>4</sub>], DDSC heating mode and DDSC cooling mode, respectively; (c) neat [BBIM][BF<sub>4</sub>], DDSC heating mode.



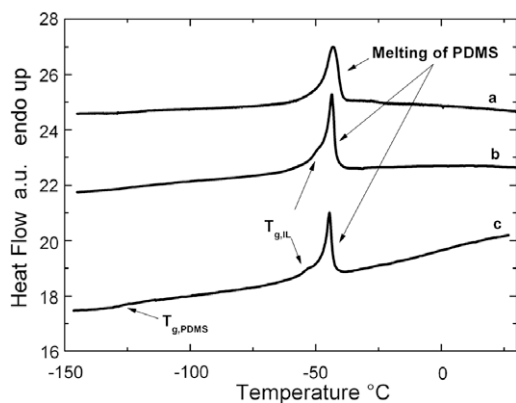
**Fig. 4.** Temperature dependences of DSC heat flow of neat PDMS. Heating mode (10 °C/min) preceded by cooling (−10 °C/min).

The [BBIM][BF<sub>4</sub>] glass transition temperature  $T_{g,IL}$  could not be found in the PDMS-[BBIM][BF<sub>4</sub>] blends containing 10 or 20 wt.% of [BBIM][BF<sub>4</sub>], plausibly because of the small concentration of [BBIM][BF<sub>4</sub>] in the samples. If the blend containing 30 wt.% of [BBIM][BF<sub>4</sub>] was cooled and heated slowly (CR = 1 °C/min, HR = 5 °C/min), the glass transition appeared. The presence of  $T_{g,IL}$  in this blend was confirmed by DDSC measurement (Fig. 5, curves *a* and *b*). The PDMS glass transition is visible on both curves *a* and *b*, but [BBIM][BF<sub>4</sub>] glass transition is observed only on the cooling curve *b*. This is due to the restraint of nucleation and crystallization of [BBIM][BF<sub>4</sub>] during cooling caused by high viscosity of the melt containing 30 wt.% of [BBIM][BF<sub>4</sub>]. The absence of glass transition of [BBIM][BF<sub>4</sub>] on the heating curve is apparent. The glass transition is hidden under the melting endotherm of PDMS.

These results unambiguously show that PDMS and [BBIM][BF<sub>4</sub>] are not miscible. Resulting blends contain amorphous and crystalline phases of PDMS and a dispersed phase of [BBIM][BF<sub>4</sub>].

### 3.2. Pervaporation of binary mixture water-butan-1-ol

The concentration of butan-1-ol in the aqueous feed was 5 wt.%, which is the highest concentration of butan-



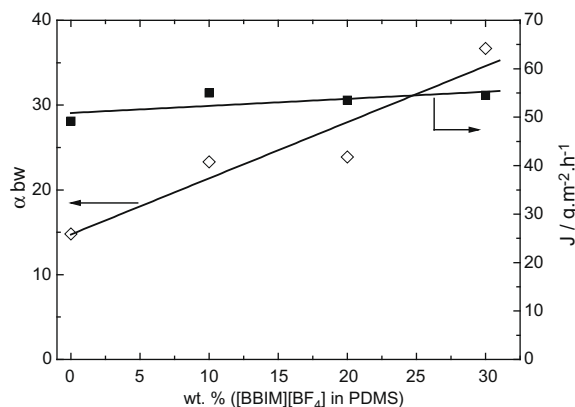
**Fig. 5.** Temperature dependences of DSC heat flow of the blend containing 30% of [BBIM][BF<sub>4</sub>]; (a) heating mode (10 °C/min) preceded by cooling (-10 °C/min); (b) heating mode (10 °C/min) preceded by cooling (-1 °C/min); (c) heating mode (5 °C/min) preceded by cooling (-1 °C/min).

1-ol in the fermentation broth non-inhibiting the activity of bacteria. The dependence of separation factor and total permeation flux on the [BBIM][BF<sub>4</sub>] concentration in the PDMS-[BBIM][BF<sub>4</sub>] membrane is shown in Fig. 6. While the total permeation flux depends only slightly on the [BBIM][BF<sub>4</sub>] concentration in the membrane, the separation factor increases considerably with the increased [BBIM][BF<sub>4</sub>] concentration. The highest separation factor,  $\alpha = 37$ , appeared, when 30 wt.% of ionic liquid was accommodated in PDMS.

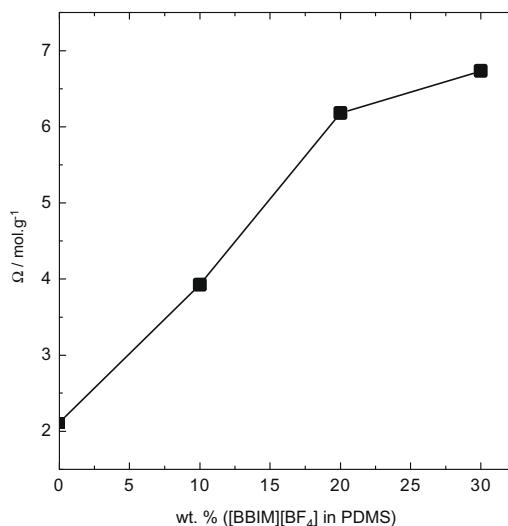
Hence, the immobilization of a proper ionic liquid in the membrane is an effective way to prepare pervaporation membranes for alcohol removal from fermentation broths.

### 3.3. Sorption of binary mixture water-butanol

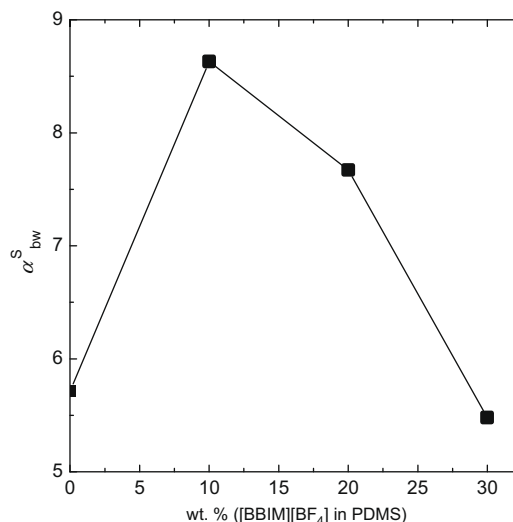
A dependence of the preferential sorption of butanol-1-ol from its aqueous solution on the amount of ionic liquid in the PDMS membrane is shown in the Fig. 7. Butanol-1-ol is sorbed preferentially and the preferential sorption is a linear function of ionic liquid amount reaching a plateau at 30 wt.%. Surprisingly, Fig. 8 shows that the value of separation fac-



**Fig. 6.** Dependence of separation factor  $\alpha_{bw}$  and total permeation flux  $J$  on [BBIM][BF<sub>4</sub>] content in PDMS membrane (pervaporation experiment).

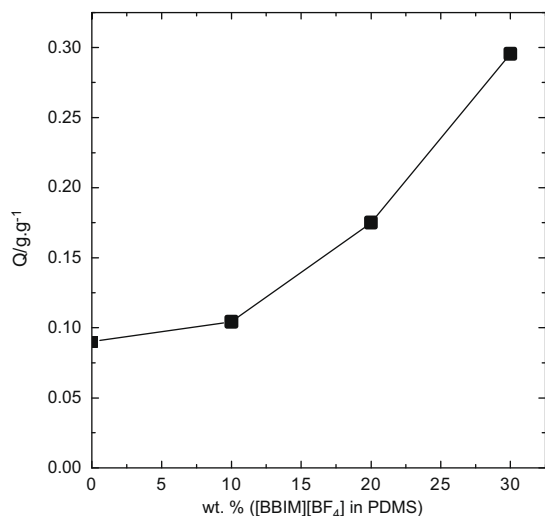


**Fig. 7.** Dependence of preferential sorption  $\Omega$ , of butanol-1-ol from 5 wt.% butanol-1-ol aqueous solution on [BBIM][BF<sub>4</sub>] content in PDMS membrane (sorption from liquid solution). The line is added due to better visualization.



**Fig. 8.** Dependence of equilibrium separation factor  $\alpha_{bw}^s$  of butanol-1-ol from 5 wt.% butanol-1-ol aqueous solution on [BBIM][BF<sub>4</sub>] content in PDMS membrane (sorption from liquid solution). The line is added due to better visualization.

tor is nearly independent on ionic liquid amount in PDMS, because total sorption increases with the amount of ionic liquid (Fig. 9). However, the fact that the separation factor is independent on ionic liquid amount in PDMS is not inconsistent with concentration dependence on pervaporation separation factor. Pervaporation process is composed of sorption, diffusion and desorption processes and the value of pervaporation separation factor is a result of all these particular processes. The differences between two separation factors and their trends lead to the conclusion that most probably the diffusion of butanol-1-ol in ionic



**Fig. 9.** Dependence of total sorption  $Q$  from 5 wt.% butan-1-ol aqueous solution on [BBIM][BF<sub>4</sub>] content in PDMS membrane (sorption from liquid solution). The line is added due to better visualization.

liquid is much faster than in PDMS during pervaporation and that diffusion of butan-1-ol is faster compared to water in PDMS membrane containing ionic liquid.

#### 4. Conclusion

The polydimethylsiloxane membranes containing 0, 10, 20 or 30 wt.% of ionic liquid (benzyl-3-butylimidazolium tetrafluoroborate) were used for separation of butan-1-ol from water. Differential scanning calorimetry measurements showed that PDMS and [BBIM][BF<sub>4</sub>] are not compatible and therefore PDMS-[BBIM][BF<sub>4</sub>] membranes (though optically homogeneous) contain amorphous and crystalline phases of PDMS and also a dispersed phase of [BBIM][BF<sub>4</sub>].

Pervaporation selectivity increased and the butan-1-ol flux through the membrane raised with the increased con-

tent of [BBIM][BF<sub>4</sub>] in the PDMS-[BBIM][BF<sub>4</sub>] membranes. Since equilibrium separation factor in liquid is nearly independent on ionic liquid amount in PDMS, diffusion is the major factor contributing to pervaporation selectivity from butan-1-ol + water mixture. The PDMS-[BBIM][BF<sub>4</sub>] membrane showed high stability as well as selectivity (the separation factor raised up to 37, if 30 wt.% of ionic liquid was accommodated in PDMS) during all experiments.

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#### References

- [1] Bahl H, Gottschalk G. *Biotechnol Bioeng Symp* 1984;14:215.
- [2] Bahl H, Andersch W, Gottschalk G. *Eur. J. Appl. Microbiol. Biotechnol.* 1982;15:201.
- [3] Bahl H, Dürre P. *Biotechnology and Medical Applications*. Weinheim: Wiley-VCH; 2001. p. 125.
- [4] Izák P, Schwarz K, Ruth W, Bahl H, Dyson PJ, Kragl U. *Appl. Microbiol. and Biotechnol.* 2008;78(4):597.
- [5] Izák P, Mateus NMM, Afonso CAM, Crespo JG. *J. Sep. and Purif. Technology* 2005;41:141.
- [6] Wasserscheid P, Keim W. *Angew. Chem. Int. Ed.* 2000;39(21):3772.
- [7] Scovazzo P, Visser A, Davis J, Rogers R, Koval C, DuBois D, Noble R. In: Rogers R, Seddon K, editors. *Industrial Applications of Ionic Liquids*. American Chemical Society Books; 2002 (Chapter 6).
- [8] Holbrey JD, Seddon KR. *J. Chem. Soc. Dalton Trans.* 1999:2133.
- [9] Dupont J, Souza RF, Suarez PAZ. *Chem. Rev.* 2002;102:3667.
- [10] Huang RYM, editor. *Pervaporation Membrane Separation Processes*. Amsterdam: Elsevier; 1991. p. 322.
- [11] Izák P, Ruth W, Fei Z, Dyson PJ, Kragl U. *Chem. Eng. J.* 2008;139/2:318.
- [12] Welton T. *Chem. Rev.* 1999;99:2071.
- [13] Izák P, Bartovská L, Friess K, Šípek M, Uchytíl P. *J. Membr. Sci.* 2003;214:293.
- [14] Schawe JEK. *Thermochim. Acta* 1995;260:1.
- [15] Schawe JEK. *Thermochim. Acta* 1995;261:183.
- [16] Van Krevelen DW. *Properties of Polymers*. Third completely revised ed. Elsevier; 1990.