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How ionic liquid changes properties of dense polydimethylsiloxane membrane?

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ABSTRACT

The polydimethylsiloxane (PDMS) 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. Pervaporation selectivity increased and the butan-1-ol flux through the membrane raised with the increased content of [BBIM][BF4] in the PDMS-[BBIM][BF_4] membranes (membrane from PDMS with immobilized ionic liquid).

The PDMS-[BBIM][BF_4] 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.

Keywords: Pervaporation; Ionic liquid; Fermentation; PDMS

1. Introduction

Butan-1-ol may be produced by fermentation of biomass [1]. The fermentation process is caused by *Clostridium acetobutylicum* bacteria, which is able to change glucose into mainly acetone, butan-1-ol, ethanol under convenient conditions [2]. The process is performed in a continuous mode so a sustained efficient removal of the products is needed to maintain a stable growth of bacteria [3]. Pervaporation is one of possibly applicable membrane separation processes because it has been proved to be a suitable extraction method for a variety of organic solvents [4].

Ionic liquids (IL) are considered to be environmentally benign solvents especially because of their low chemical reactivity and negligible vapor pressure. A large scale of possible combinations of cations and anions gives them a huge variety of chemical properties [5]. They are also called designer solvents. Molecular permeability is higher in IL's then in polymers. Hence by combination of polymer membrane with ionic liquid we obtain a membrane with mechanical properties of polymer but enhanced transport properties thank to the ionic liquid [6].

2. Experimental

Benzyl-3-butylimidazolium tetrafluoroborate (abbreviated [BBIM][BF_4]; Chemada Fine Chemicals, Israel) and nitrogen gas (Linde Gas a.s. UN1066, 99.99% purity, Czech Republic) were used without further purification. Polydimethylsiloxane (abbreviated PDMS)— Elastosil M4601 with crosslinking catalyst was obtained from Wacker Silicones, Germany.

PDMS was prepared according to instructions of the producer with addition of ionic liquid during

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Table 1
The glass transition temperature T_g of PDMS and [BBIM][BF_4] obtained by DSC

Sample	Mode	Cooling rate (°C/min)	T_g (°C)	T_m (°C)	ΔH_m (J/1g)	T_c (°C)	ΔH_c (J/1g)	Crystallinity (%)
[BBIM][BF4]	DSC	10	−60,4	−36,8	0,31	−49,3	−0,4	–
		5	−54,5	−44,2	0,6	–	–	–
		1	−54,4	−47,9	1,5	–	–	–
	DDSC	–	−57,7	−42,0	–	–	–	–
PDMS	DSC	10	−124,9	−44,2	18,5	−73,1	−18,8	–
		5	−125,3	−42,4	19,7	−38,7	−17,1	54
		1	−126,3	−44,5	14,5	–	–	–
	DDSC	–	−127,9	–	–	–	–	–

polymerization. The concentration of IL varied: 0, 10, 20, and 30 wt %.

The membrane was characterized by differential scanning calorimetry (DSC) to find the glass transition temperature. The samples were scanned in temperature range from −140°C to 30 C. The scan was performed in standard DCS mode and in temperature modulated mode. The glass transition temperatures, transition enthalpies were then calculated with Pyris software. Results of calculations are showed in Tables 1 and 2.

Blend 10, Blend 20 and Blend 30 are PDMS blends containing 10, 20 and 30 wt.% of [BBIM][BF_4], respectively. Measurements in the standard DSC mode were performed with constant heating rate 10°C/min with the samples cooled with different cooling rates.

Pervaporation experiments were performed in the apparatus described on Fig. 1 [7].

A cell with membrane was placed into a feed vessel. The temperature of the feed was hold optimal for the bacteria (37°C). The highest possible concentration of the feed is 5% wt, higher concentrations are lethal for the bacteria. One side of the membrane was in contact with liquid feed, the opposite was continually swept by flowing nitrogen to ensure concentration gradient through the membrane. The permeate was collected in a cold trap immersed in liquid nitrogen, protected from humidity with silica gel. Typical experiment

Table 2
The glass transition temperature T_g of PDMS and [BBIM][BF_4] blends containing 10, 20 and 30 wt % of ionic liquid obtained by DSC

Sample	Mode	Cooling rate (°C/min)	T_g PDMS (°C)	T_g IL (°C)	T_m (°C)	ΔH_m (J/1g)	T_c (°C)	ΔH_c (J/1g)	Crystallinity (%)
Blend 10	DSC	10	−124,5	–	−44,6	16,6	−73,3	−16,3	–
		5	–	–	−43,1	16,5	−70	−15	51
		1	−126,7	–	−45,3	11,7	−66,5	−14,5	–
	DDSC	–	−127,1	–	–	–	–	–	–
Blend 20	DSC	10	–	–	−45,3	11,8	−73,1	−14	–
		5	–	–	−43,2	15,2	−69,6	−13	53
		1	−128,5	–	−45,3	15,1	−66,4	−10,1	–
	DDSC	–	−127	–	–	–	–	–	–
Blend 30	DSC	10	−124,2	–	−43,2	11,8	−70,8	−12,6	–
		5	–	–	−42,9	13,8	−69,3	−11,5	50
		1	−127,7	–	−43,5	11,6	−64,1	−8,5	–
		5/1	−130,2	−55,2	–	–	–	–	–
	DDSC	heating mode	−126,7	–	–	–	–	–	–
		cooling mode	–	−45,5	–	–	–	–	–

T_g, PDMS—glass transition temperature of PDMS; T_g, IL—glass transition temperature of [BBIM][BF_4]; T_m melting temperature; H_m—melting enthalpy; T_c—crystallization temperature; H_c—crystallization enthalpy and crystallinity of [BBIM][BF_4], PDMS and their blends.

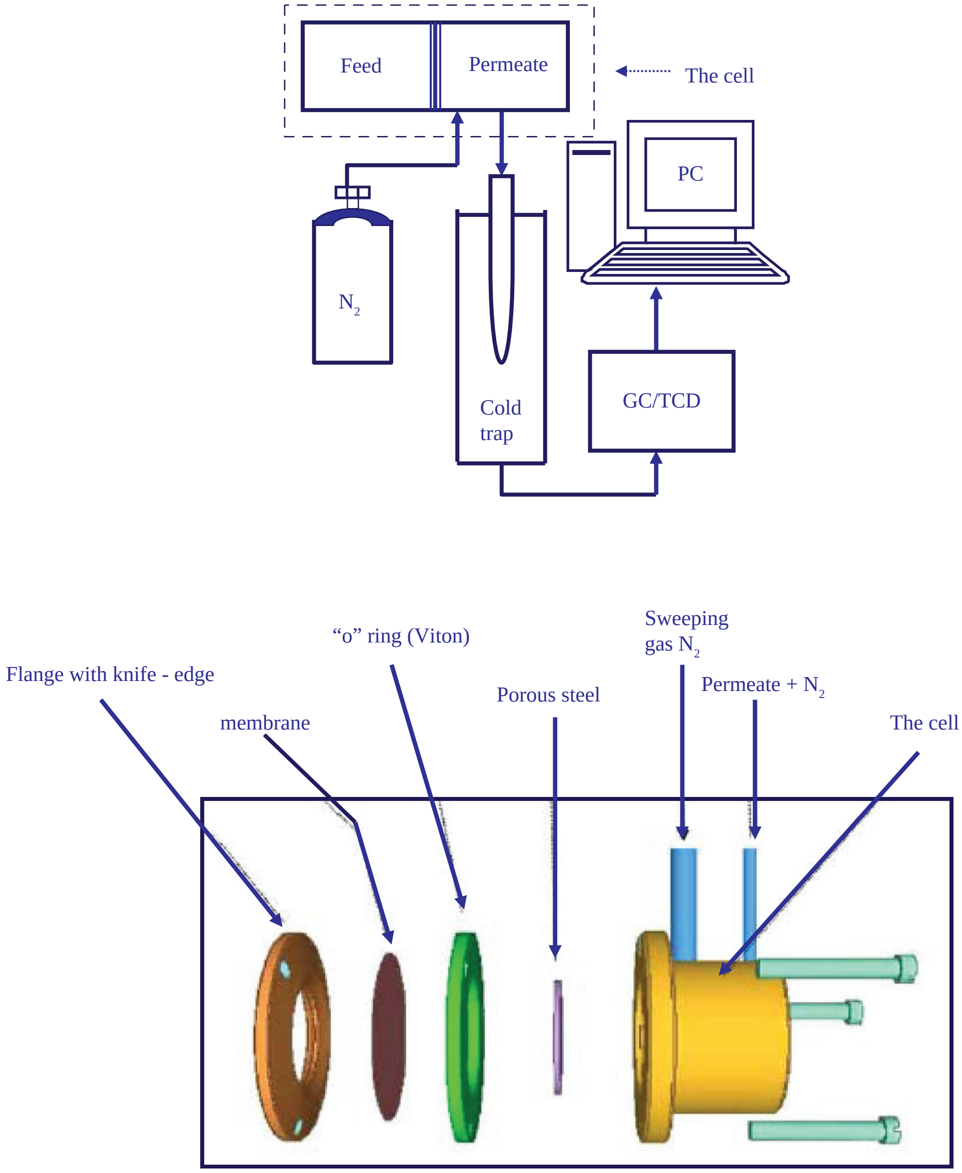

Fig. 1. Scheme of sweeping gas pervaporation apparatus, with the detail of the pervaporation cell.

lasted for 48 h. Liquid permeate was then put to gas chromatograph to determine its composition.

Membrane performance was evaluated by separation factor and total flux. The total flux is defined as follows:

$$J = Q/(At) \tag{1}$$

where Q is a total amount of permeate, A is membrane area and t is time interval.

The separation factor is usually calculated as:

$$\alpha_{bw} = \frac{w_{bP}/w_{wP}}{w_{bF}/w_{wF}} \tag{2}$$

Preferential and total sorption was also measured. The method is described in Izák et al. [8]. The preferential sorption is given by concentration change of the solution.

$$\Omega_i = \frac{n^s}{m_{\mathrm{P},0}}\left(x_i^s - x_i^b\right) = \frac{N^0}{m_{\mathrm{P},0}}\left(x_{i,0}^b - x_i^b\right), \tag{3}$$

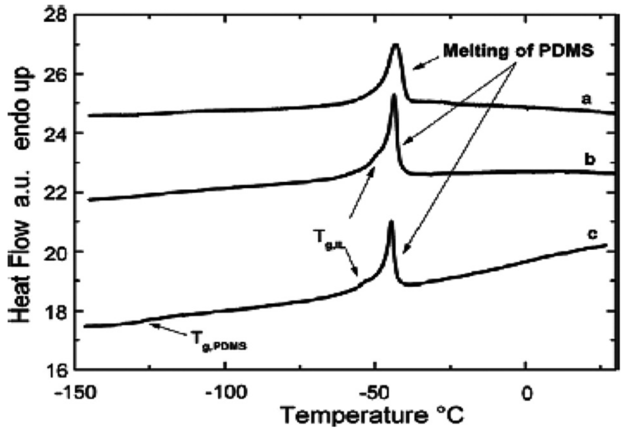

Fig. 2. Temperature dependences of DSC heat flow of the blend containing 30% wt. of [BBIM][BF$_4$]; a heating mode (10°C/min) preceded by cooling (10°C/min); b heating mode (10°C/min) preceded by cooling (−1°C/min); c heating mode (5°C/min) preceded by cooling (−1°C/min).

where $x^b_{i,0}$ and x^b_i 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.

If compound i is absorbed preferentially the value of Ω_i will be positive. Values of preferential sorption of other components will be negative then. The aqueous solution of butan-1-ol (5% wt) was used in this work. The total sorption can be calculated from the relative weight increase:

$$Q = \frac{m_P - m_{P,0}}{m_{P,0}} \tag{4}$$

Sorption data were obtained using gas liquid chromatography (GLC) to measure changes of concentration of liquid mixture being in contacted with polymer. Gravimetric method was used to measure total sorption.

3. Results and discussion

Compatibility of PDMS and ionic liquid was proved by DSC monitoring the glass transition temperature of neat polymer and polymer mixed with ionic liquid. On the cooling curve "c" (Fig. 2) we can see clearly the glass transition temperature of pure IL which is −60°C. It means that during the cooling is the melt transformed directly into a glassy state. Probably high melt viscosity near the glass transition restraint crystallization and nucleation of IL. On the heating run "b" we can see the crystallization and melting point of IL, which confirms forming of the crystallites when the cooled glass is heated. From the curve "a" results that the decrease of cooling run shifts the crystallization and melting temperature toward the glass transition temperature of IL.

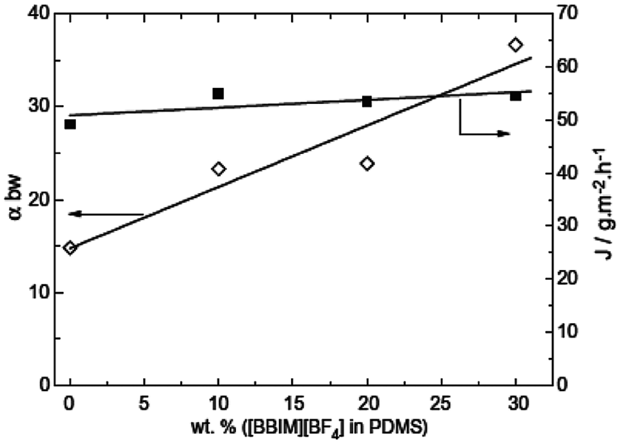

Fig. 3. Ionic liquid concentration dependence of separation factor and total permeation flux.

Pure PDMS was scanned by standard rates of 10°C/min cooling and heating. The glass transition temperature of neat PDMS is $T_g = -125$°C, its crystallization $T_c = -43$°C and melting temperature $T_m = -70$°C. The resulting membrane blend contains amorphous and crystalline phases of PDMS and dispersed phases of IL as can be seen on Fig. 2.

There are glass transition temperature of PDMS and glass transition temperature of ionic liquid visible of curve "c" of Fig. 2. The fact that PDMS 30% wt. of IL has two glass transition temperatures indicates that IL is dispersed in amorphous phase of PDMS.

Fig. 3 shows the dependence of separation factor and total permeation flux on the concentration of ionic liquid. As can be seen the separation factor increases with increasing concentration of ionic liquid and total permeation flux is nearly concentration independent. The highest separation factor occurs when PDMS contains 30% wt of ionic liquid.

4. Conclusion

To separate butan-1-ol from water by PDMS membranes with different ionic liquid content were used. IL (benzyl-3-butylimidazolium tetrafluoroborate) content in PDMS varied from 0, 10, 20 to 30% wt. According to results of differential scanning calorimetry, blend membranes contain dispersed phase of ionic liquid and crystalline and amorphous phases of PDMS.

Addition of ionic liquid to PDMS caused that pervaporation selectivity and permeability for butan-1-ol increased. Prepared membrane showed high stability as well. The immobilization of proper ionic liquid in the membranes is a good way for preparing pervaporation membranes which can be used for removal of products of fermentation.

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Symbols

A	membrane area
H	enthalpy
J	permeation flux
N	mole number of binary solution
T	temperature
Q	relative weight increase
M	mass
n^s	total amount of absorbed liquid
T	time
W	weight fraction
X	molar fraction
Ω	preferential sorption
α	separation factor

Subscripts

F	feed
P	permeate
P	polymer
b	butanol
c	crystallization
g	glass transition
i	component number
m	melting
w	water
0	initial state

Superscripts

s	sorption
b	bulk

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