

## **Effectiveness of toluene separation from gas phase using supported ammonium ionic liquid membrane**

IWONA CICHOWSKA-KOPCZYŃSKA\*, ROBERT ARANOWSKI

Department of Process Engineering and Chemical Technology

Gdansk University of Technology,

ul. Narutowicza 11/12, Gdansk, Poland

[iwona.kopczynska@pg.edu.pl](mailto:iwona.kopczynska@pg.edu.pl)

Phone: +48 58 347 18 69

Fax: +48 58 347 20 65

### **Abstract**

*Ammonium ionic liquids (ILs) are relatively cheap in synthesis and environmentally benign and despite that they have been very rarely used in gas separation. In this research we used several ammonium ILs as liquid membranes for removal of residual toluene from gas phase. Ionic liquids used in this study were composed of bis(trifluoromethylsulfonyl)imide anion [Tf<sub>2</sub>N] and trimethylbutylammonium [N<sub>1114</sub>], triethylbutylammonium [N<sub>2224</sub>], triethylhexylammonium [N<sub>2226</sub>], triethyloctylammonium [N<sub>2228</sub>] cations. Selected ILs formed stable membranes with limited swelling effect and good performance. The highest toluene permeability was recorded for [N<sub>2228</sub>][Tf<sub>2</sub>N] of 2666 barrers and for triethyl based ILs it was decreasing with carbon atoms number. The selectivity of toluene/N<sub>2</sub> separation was in a range of 29 to 120. For better process illustration, the factors influencing the permeation process, namely viscosity and partition coefficients were examined.*

Key words: ammonium ionic liquid, liquid membrane, toluene, separation, selectivity

## 1. Introduction

Ionic liquids are composed of a large asymmetric organic cation (ex. alkylimidazolium, alkylpyridinium, alkylammonium) and smaller organic or inorganic anion (ex. hexafluorophosphate, bis(trifluoromethylsulfonyl)imide) [1]. Those with a large number of fluoride atoms have low melting points [2]. The possibility of designing the anion and cation structure results in a formation of new ionic liquids [3]. Due to the huge number of possibilities, they are referred to as “tunable” fluids. Ionic liquids are a substitute for toxic and volatile organic compounds due to low volatility, which prevents from pollution of gas streams. Therefore they are gladly used in research on gas separation.

Unflagging interest is given to ammonium ionic liquids. The first one was obtained in 1914 by Walden. Among many fields, they have been used in extraction [4–6], catalysis [7] and gas separation, mainly CO<sub>2</sub> [8–13]. In organic separation they have been used rarely, mainly for extraction and separation from liquid phase, for example 1-butanol from diluted aqueous solutions [14,15].

Activity coefficients at infinite dilution for methyl(trioctyl)ammonium thiosalicylate ([N1888][TS]) and Ammoeng 100<sup>®</sup> reported by Reddy et al. suggest that ammonium-based ionic liquids are not well suited to aromatic-aliphatic extraction due to lower selectivity than for example imidazolium-based ionic liquids [16]. There are some additional literature data confirming this conclusion [17]. However, Matsumoto et al. obtained satisfying data for separation of cyclohexane and benzene through vapor permeation, they used N,N-diethyl-N-methyl-N-(2-methoxyethyl) ammonium tetrafluoroborate and got separation factor of 185 for 53 wt.% benzene and 950 for 11 wt.% benzene [18]. Also Domańska et al. performed separation of aromatic hydrocarbons from hexane and octane using ethyl(2-hydroxyethyl)dimethylammonium bis(trifluoromethylsulfonyl)imide and reported it as feasible [19]. They were also used to remove Bisfenol A from water [20].

Ammonium ionic liquids are cheaper in production than imidazolium ones, however still the cost is high,



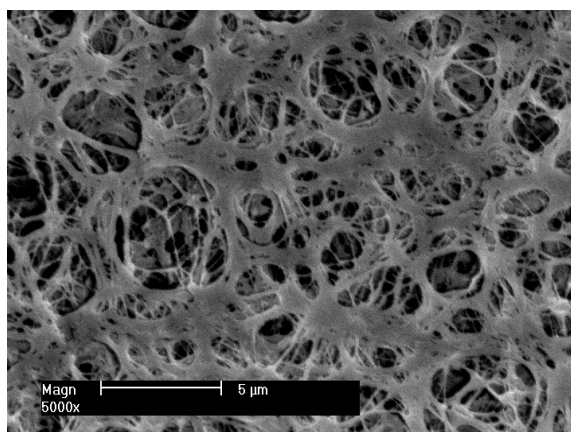
therefore using it in absorption system is hardly considered. In present study we used them in supported ionic liquid membrane system where ammonium ionic liquids were held in the membrane pores by capillary forces [21] to create membrane feasible for separation of toluene residues from gas phase. Using ionic liquids allowed to overcome common problems of the technology like: secondary stream pollution or loss of the membrane phase caused by vaporization [22–24]. Stability of polymer supports impregnated with ionic liquids has been widely studied and it has been proven that ILs can be easily embedded in polymer or ceramic supports and form a stable system suitable for gas separation [8,25–29].

Ammonium ionic liquids haven't been used in such systems before. In present paper we present the potential of utilization ammonium ionic liquids for toluene separation from toluene/N<sub>2</sub> model stream. Since all the ionic liquids used in this study are based on the same anion, the effect of alkyl chain length of cation substituent is discussed.

## **2. Experimental**

### *2.1. Materials*

Nitrogen was ultra-high purity and supplied by AirLiquid. Toluene was purchased from POCH S.A. GH Polypro (polypropylene) – PP supplied by Pall, Gelman Laboratory was used as a support with 80% porosity and average 0.2 μm pore size reported by the producer. Bulk density of the support sheet was 900 kg/m<sup>3</sup> and the initial thickness 92 μm. However, own analysis performed with digital image processing software have shown that the average pore size was about 4.7 μm, whereas 0.2 μm was the diameter of the smallest holes. SEM image is presented in Figure 1.



**Figure 1. Scanning electron micrograph of PP support [26]**

Nitrogen/toluene mixture was prepared according to the procedure described by Uyanik et al. [30]. The concentration of toluene was about 200 ppm (v/v), measured by GC method in all experiments. ILs used in this study were based on the bis(trifluoromethylsulfonyl)imide anion and cations with different alkyl chain lengths, all liquid at room temperature. Key properties of the ILs are presented in Table 1 and structures are presented in Figure 2.

Ionic liquids used in this study were: trimethylbutylammonium bis(trifluoromethylsulfonyl)imide [N<sub>1114</sub>][Tf<sub>2</sub>N], triethylbutylammonium bis(trifluoromethylsulfonyl)imide [N<sub>2224</sub>][Tf<sub>2</sub>N], triethylhexylammonium bis(trifluoromethylsulfonyl)imide [N<sub>2226</sub>][Tf<sub>2</sub>N], triethyloctylammonium bis(trifluoromethylsulfonyl)imide [N<sub>2228</sub>][Tf<sub>2</sub>N]. All chemicals were purchased from IOLITEC, Heillbron, Germany with purity higher than 99%.

**Table 1. Ionic liquids used in the experiments**

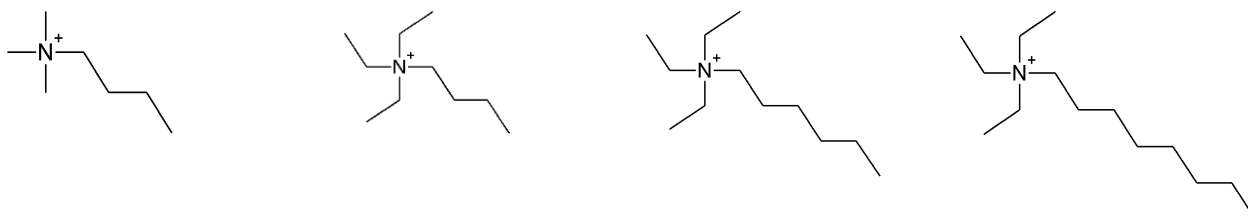
Abbreviation	Chemical Formula	Molar Mass [g/mol]	Purity [mass %]	Molecular volume [nm <sup>3</sup> ]*
[N <sub>1114</sub> ][Tf <sub>2</sub> N]	C <sub>9</sub> H <sub>18</sub> F <sub>6</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub>	396.37	>99	0.450



[N2224][Tf2N]	C <sub>12</sub> H <sub>24</sub> F <sub>6</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub>	438.45	>99	0.534
[N2226][Tf2N]	C <sub>14</sub> H <sub>28</sub> F <sub>6</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub>	466.51	>99	0.562
[N2228][Tf2N]	C <sub>16</sub> H <sub>32</sub> F <sub>6</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub>	494.56	>99	0.590

\*calculated on the basis of  $V_C = M / (\rho \cdot N_A)$ , where M- molar mass,  $\rho$  – density,  $N_A$  – Avogadro no.

a)



trimethylbutylammonium triethylbutylammonium triethylhexylammonium triethyloctylammonium

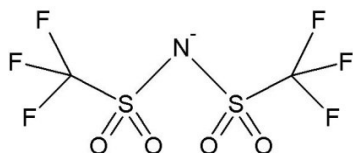
[N<sub>1114</sub>]<sup>+</sup>

[N<sub>2224</sub>]<sup>+</sup>

[N<sub>2226</sub>]<sup>+</sup>

[N<sub>2228</sub>]<sup>+</sup>

b)



bis(trifluoromethylsulfonyl)imide

[Tf<sub>2</sub>N]<sup>-</sup>

**Figure 2. Chemical structure of ionic liquids ions: a) cations; b) anion**

## 2.2. Physicochemical properties of ionic liquids

Prior to each experiment ionic liquids were kept in a vacuum dryer at 373 K for 24 h to remove traces



of water and volatile contaminants. After degassing, water content in ionic liquids was determined using Karl-Fischer coulometric titration method with Metrohm 831 KF Coulometer. Selected physicochemical properties that are important from the point of view of formation of liquid membrane and gas separation process were determined.

Surface tension for estimation of support wetting was determined by the pendant drop method using Tensiometer Krüss DSA 10 at room temperature. Measurements of dynamic viscosity coefficient were conducted in order to estimate diffusion resistance in liquid membrane using Brookfield Rheometer LV III. The temperature was kept constant within  $\pm 0.01$  K. The dependence of shear stress (Pa) vs. shear rate (1/s) was determined at several temperature points from 288 to 318 K.

Wetting properties of ionic liquids listed in Table 1 were estimated on the basis of advancing and receding contact angles that were determined with the dynamic sessile drop method using Tensiometer Krüss DSA 10. Despite the porosity of supporting material, the legitimacy of using that method was based on the size of the material pores which was much smaller than the size of the liquid drop. Advancing angle  $\theta_a$ , receding angle  $\theta_r$  and the hysteresis  $\theta_a - \theta_r$  were determined at 298 K. The relative humidity of the air was about 60%, therefore the time of drop stabilization was minimum to prevent water vapour from absorption and resulting changes in parameters to keep the error as low as possible. The shape of air/liquid interface of a drop was analysed using digital system and matched to a numeric model [31].

### 2.3. *Partition coefficients*

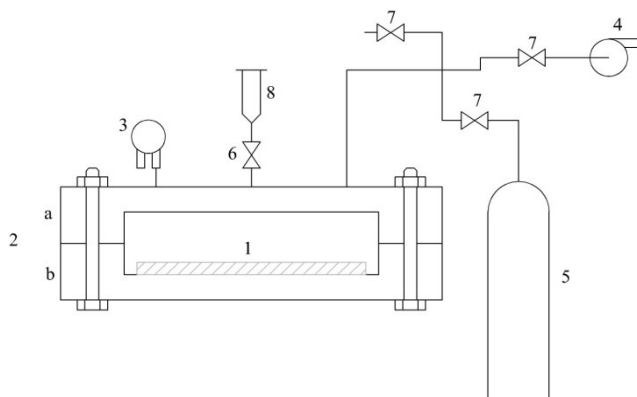
The partition coefficients,  $K$ , were calculated as a ratio of toluene mole fraction in gas phase ( $c_g$ ) and toluene mole fraction in liquid phase ( $c_l$ ). The concentration of toluene was analysed using headspace gas chromatography (Gas Chromatograph Clarus 500). Samples were prepared by adding previously degassed ionic liquid to a headspace vial. The vials were sealed and the samples were purged with a pure nitrogen. Then, toluene was added through septum. The samples were prepared using electronic balance



with a resolution of  $\pm 0.00001$  g. In order to provide that the vials are gas tight, control samples were prepared. Prepared mixtures were kept at the isothermal conditions at the desired temperature maintained with an accuracy of  $\pm 0.1$  K until equilibrium state was obtained, which was determined experimentally on the basis of phase composition. Detailed description of the procedure is given elsewhere by Cichowska-Kopczynska et al. [32].

#### 2.4. Preparation of supported ionic liquid membrane

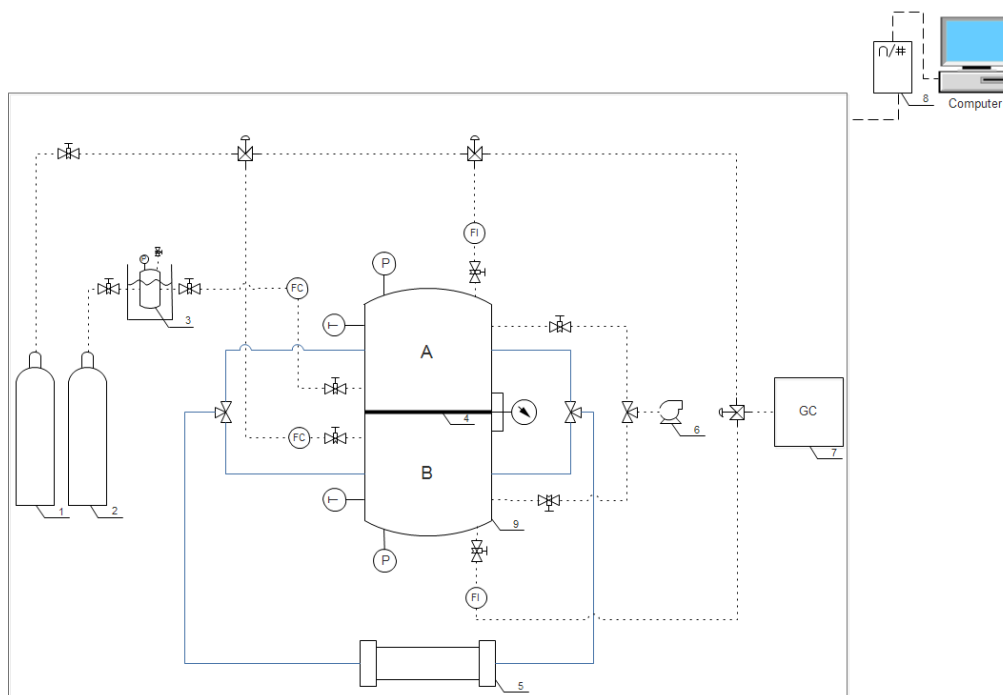
Supported ionic liquid membranes were prepared in a stainless steel vessel presented in Figure 3. Before each experiment, polymer supports and ionic liquids were again degassed in vacuum dryer Vacucell 55 according to the method described in the literature [33–35]. Degassed polymeric supports (1) was placed in a stainless steel pressure vessel (2). The vacuum was again applied using vacuum pump (4) to remove excess air from the pores of the polymer. The ionic liquid of amount of  $0.1 \text{ cm}^3$  per  $1.0 \text{ cm}^2$  of support surface was added to a glass syringe (8). The syringe was then mounted at the vessel top and the valve (6) was opened. After the liquid has been completely sucked to the vessel, nitrogen (5) was introduced through valve (7) to produce positive pressure of about 100 kPa, controlled with a pressure sensor (3). Overpressure was maintained for about an hour which, as investigated earlier, was enough to provide complete pores saturation. Subsequently, the pressure was released, membrane was carefully removed from the vessel and the excess ionic liquid was removed from membrane surface using blotting paper.



**Figure 3. Membrane preparation vessel (1 – membrane; 2 – pressure vessel (a,b – top and bottom part); 3 – pressure sensor; 4 – vacuum pump; 5 – gas container; 6,7 – valves; 8 – syringe)**

### 2.5. Measurement of permeation through supported ionic liquid membranes

The potential of ammonium ionic liquids in toluene removal from gas mixtures was estimated on the basis of separation selectivity. The experiments were performed in the experimental set-up shown in Figure 4 according to procedure described in previous paper [32]. Results obtained for  $N_2$  proved its low permeability and no difference in static and dynamic measurements was observed. Therefore  $N_2$  permeability was measured on the basis of the drop of pressure in the feed chamber and increase of pressure in permeate chamber. Toluene permeation experiments were conducted in dynamic system at transmembrane pressure of 15 kPa where the flow rates of feed and receiving phase were controlled by flowmeters.





**Figure 4 Experimental set-up for permeability and mechanical stability determination (1, 2 – gas containers, 3- gas sample container, 4 – SILM, 5 – thermostate, 6 – vacuum pump, 7- gas chromatograph, 8 - analog-digital converter, 9 – permeation chamber)**

## 2.6. *Membranes stability*

To estimate the stability of membranes based on ammonium ionic liquids several associated effects have been measured, i.e. wetting, swelling and mechanical resistance. Swelling of supports was determined on the basis of membrane thickness using microscope and digital camera that was recording the thickness increase in several time periods. Mechanical stability expressed as transmembrane pressure that results in membrane disruption was investigated in a laboratory test unit presented in Figure 4. Experiment consisted of evacuation of both parts (upper – permeate side and bottom – feed side) of the stainless steel chamber and introducing inert gas to the feed compartment at a rate of 50 Pa/s. Transmembrane pressure was measured using differential pressure sensor between feed and permeate side of the membrane. Additionally, separate absolute pressure sensors were used in both sides of the measuring chamber, so the difference in values indicated by the sensors was used for validation of differential pressure sensor indications. The pressure of inert gas at which the pressures in upper and bottom parts of the chamber levelled out was recognized as mechanical stability. Detailed description of the procedure is given by Cichowska-Kopczynska et al. [32].

## 3. Results and discussion

### 3.1. *Physicochemical properties of ionic liquids*

From the point of view of chemical technology, viscosity of ionic liquids used in gas separation processes is a key aspect due to related technical issues like pumping or mixing and also diffusion

resistance. Generally, ionic liquids have relatively high viscosity, however in supported ionic liquid technology it ensures that the liquid is held in the pores of the support. In this study dynamic viscosity coefficient was determined in a range of 288-318 K in 5 K intervals. Detailed results can be found in Supplementary information including comparison with data found in the literature. Viscosity values reported in this work are close to results obtained by Tokuda et al. and Gathee et al., but are significantly lower than those obtained by Dakkach et al. or Battaharje [36,37]. It is common for ionic liquid that large discrepancies of the values of physicochemical properties can be found. The most often reason is difference in water and organic impurities content in ionic liquids used in experiments. The purity of ILs used in this study given by producer was >99% and for example Machanova et al. used ILs with purity of 99.5% [38], Sun et al. used ILs with water content below 1000 ppm, but no exact values are reported [39]. Among examined ammonium ionic liquids, the lowest dynamic viscosity coefficient was recorded for  $[N_{1114}][Tf_2N]$  and was about 168 mPa·s at 288 K, decreasing with temperature to 98 mPa·s at 298 K and 43 mPa·s at 318 K. Elongation of three methyl chains to ethyl ones resulted in viscosity increase of 35% at 298 K. For triethyl ILs increase from butyl to hexyl chain gave 14% viscosity increase and from hexyl to octyl 24% increase. Therefore, diffusion resistance increases when using ionic liquids with higher carbon atoms number chains. In comparison to imidazolium ionic liquids it is several times higher, for example viscosity of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide is 49 mPa·s at 288 K [32].

As Okoturo et al. have summarized, the viscosity–temperature dependence can be approximated by the Arrhenius model if the ILs contained less symmetrical cations without functional groups in the alkyl chain. When the ILs contain small, symmetrical cations with low molar mass the viscosity – temperature dependence can be described by the VTF model. The ILs containing cations which were less symmetric, containing functional groups, or have higher molar mass cannot be accurately described by the Arrhenius neither VTF model. The temperature of ideal glass transition decrease with increasing size and molar



mass of the cation and anion [40]. Valderrama et al. have been investigating the generalized viscosity model based on Valderrama-Patel-Teja cubic equation of state and the geometric similitude concept to correlation and prediction the ionic liquids viscosity (particularly imidazolium cation based ionic liquids). They proposed generalized viscosity equation of state including a single adjustable parameter, which can be calculated using a single value of viscosity, and using such an estimated model enables predicting the viscosity at other temperatures and pressures with acceptable accuracy [41]. In this article, the viscosities of examined ionic liquids were approximated by the Vogel-Tamman-Fulcher (VTF) equation:

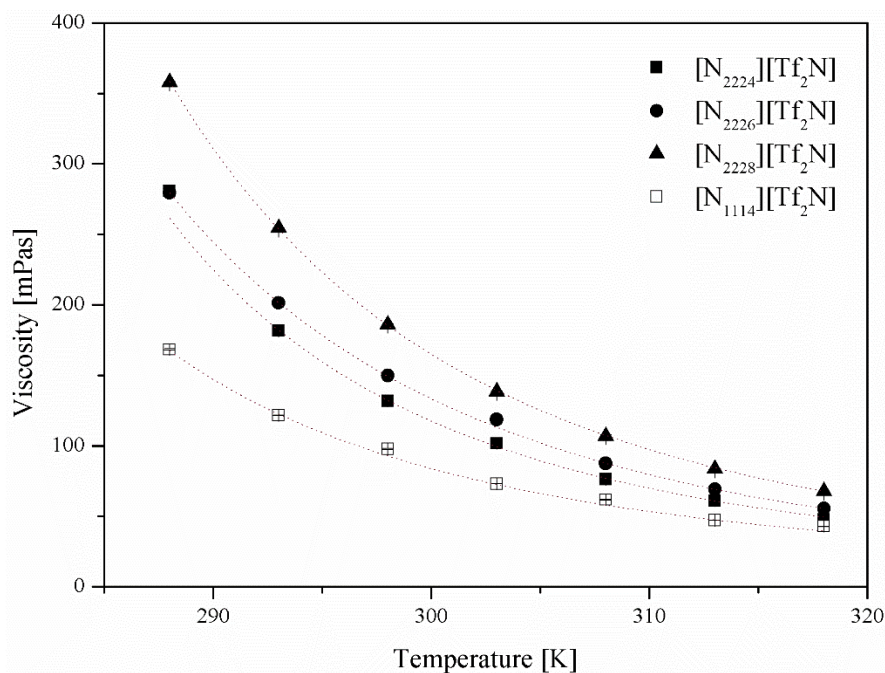
$$\eta = \eta_0 e^{\frac{B}{T-T_0}} \quad (1)$$

where  $\eta$  is viscosity (mPa·s),  $\eta_0$  is pre-exponential constant (mPa·s),  $T$  is temperature (K),  $B$  and  $T_0$  are equation constants. Regression of the experimental data was good with  $R^2$  in a range of 0.996 to 0.999 and is presented in Figure 5. Calculated values of  $\eta_0$ ,  $B$ ,  $T_0$  and  $R^2$  are listed in Table 2.

**Table 2** Calculated parameters of VTF equation (1)

Ionic liquid	$\eta_0$ [mPa·s]	$T_0$ [K]	$B$ [K]	$R^2$
[N2224][Tf <sub>2</sub> N]	0.6405	209.6800	470.7875	0.9985
[N2226][Tf <sub>2</sub> N]	0.1199	174.2641	882.1100	0.9997
[N2228][Tf <sub>2</sub> N]	0.3018	190.5808	689.7197	0.9999
[N1114][Tf <sub>2</sub> N]	0.8820	209.0656	414.1330	0.9963





**Figure 5 Viscosity vs temperature fitted with VTF equation**

The values of surface tension were examined in order to determine contact angles, and did not exceed  $32.5 \text{ mJ/m}^2$ , no relation with alkyl chain length was found (see Supplementary Information). The study on contact angles of ionic liquids at PP support indicated very good wetting properties. As described in detail elsewhere [8] slightly lower contact angles were recorded for ionic liquids with incorporated hexyl and octyl alkyl chains. Advancing contact angles for those were both  $21.3 \text{ deg}$  and based on this it was assumed that formation of supported liquid membrane with ammonium ionic liquids is possible.

### 3.2. Partition coefficients

Partition coefficients of toluene in  $\text{N}_2$ /ammonium ionic liquids system presented occurred to be low, which indicates good solubility (see Table 3). Triethyl based ILs had significantly lower coefficients than those reported for imidazolium ionic liquids [32]. For higher carbon atoms number in cation substituent, the partition coefficients were higher. Similar conclusion was given by Requejo et al. in research on  $[\text{N}_{1114}][\text{Tf}_2\text{N}]$  and  $[\text{N}_{4441}][\text{Tf}_2\text{N}]$  [42].

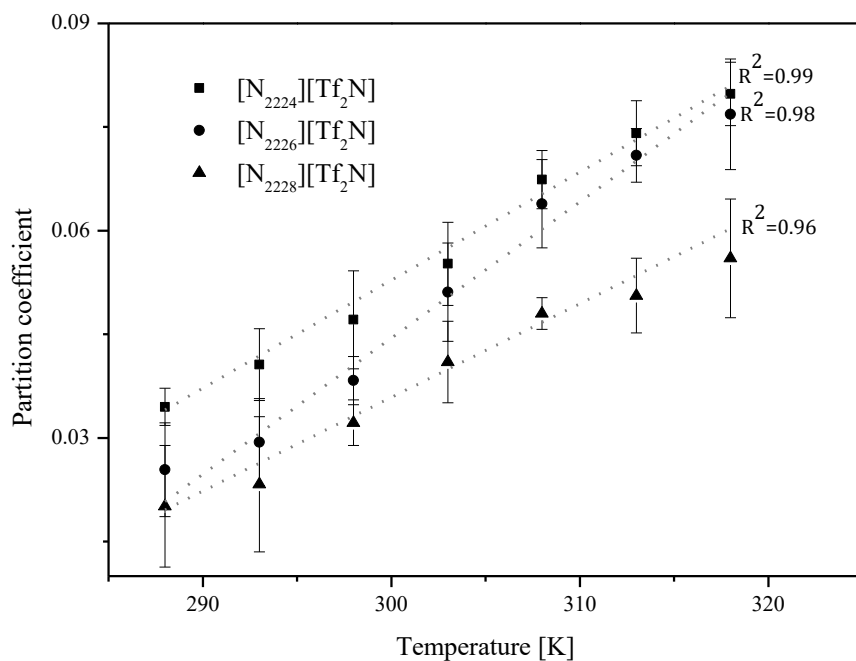


**Table 3 Partition coefficients of toluene**

Temperature [K]	[N <sub>2224</sub> ][Tf <sub>2</sub> N]	[N <sub>2226</sub> ][Tf <sub>2</sub> N]	[N <sub>2228</sub> ][Tf <sub>2</sub> N]	[N <sub>1114</sub> ][Tf <sub>2</sub> N]
288	0.0345±0.0027	0.0254±0.0068	0.0201±0.0088	0.0938±0.0093
293	0.0406±0.0052	0.0294±0.0063	0.0233±0.0098	0.0988±0.0044
298	0.0471±0.0071	0.0383±0.0035	0.0322±0.0033	0.1066±0.0044
303	0.0552±0.0060	0.0511±0.0071	0.0410±0.0059	0.1241±0.0015
308	0.0674±0.0042	0.0639±0.0064	0.0480±0.0023	0.1584±0.0061
313	0.0741±0.0047	0.0709±0.0039	0.0506±0.0054	0.1637±0.0048
318	0.0798±0.0046	0.0768±0.0080	0.0560±0.0086	0.1690±0.0063

In Figure 6 the impact of temperature on the partition coefficients is presented. Significant increase was observed with the increase of temperature, however for triethyl based ILs the values of partition coefficients at 318 K were still lower than the values obtained for imidazolium ILs containing [TfO] anion at 288 K [32]. This higher solubility should compensate noticeably higher viscosity of ammonium ILs. Moreover, ammonium ionic liquids present lower toxicity than imidazolium ones, therefore it would be favorable to use them instead [42]. Toluene affinity to ionic liquids used in this study is high and it increases with the increasing number of carbon atoms.





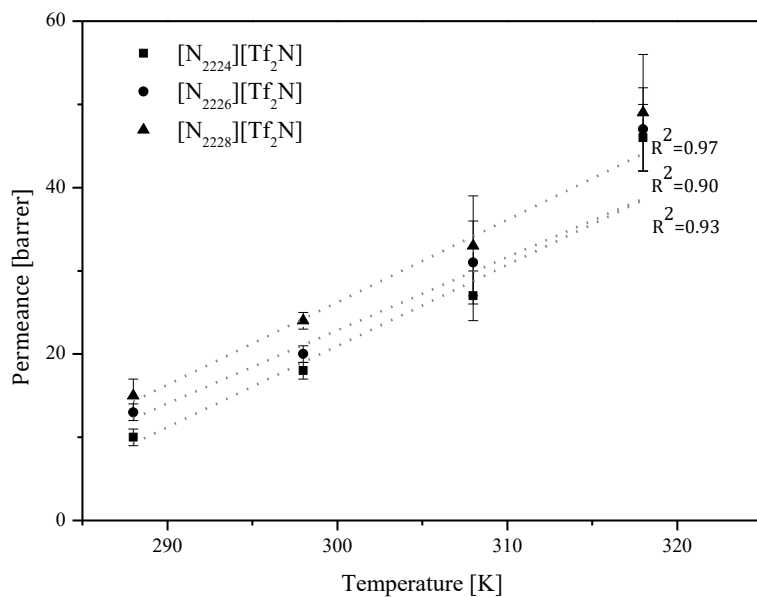
**Figure 6. Partition coefficients of toluene**

### 3.3. Single gas permeability

Permeability of pure nitrogen was measured in order to determine the selectivity of toluene/N<sub>2</sub> separation. Though some of the researchers report that the solubility of nitrogen in ionic liquids increases with temperature increase [43], several researchers report opposite effect [44,45], nevertheless nitrogen solubility in ionic liquids is very low as well as the observed permeability.

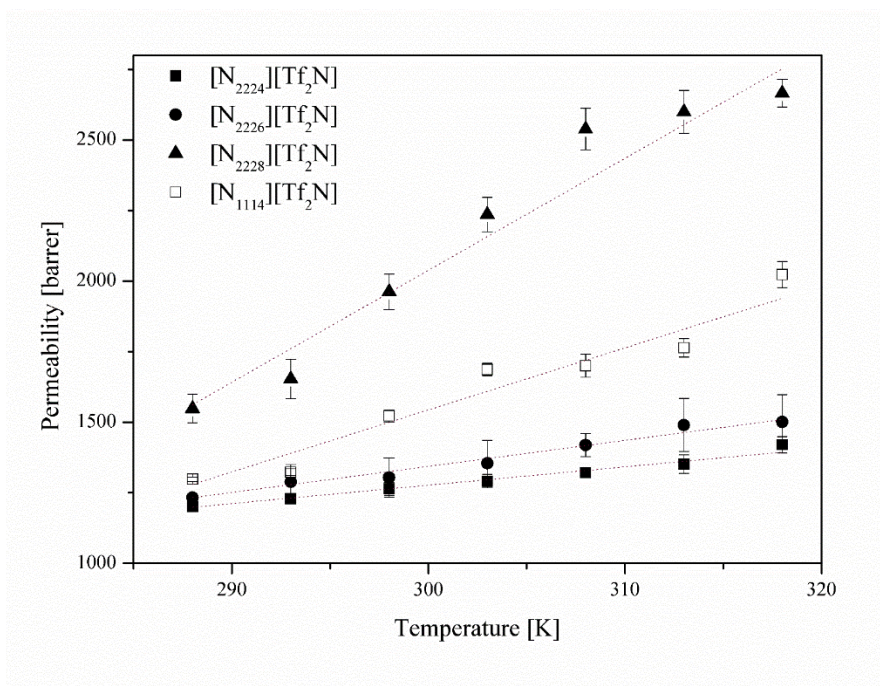
The calculated permeability increases with temperature (Figure 7) and elongation of the alkyl chain length of one substituent resulted in higher permeability. Nitrogen permeability occurred to be as low as 10 barrers for [N<sub>2224</sub>][Tf<sub>2</sub>N] which gives an optimistic perspective for selective separation of toluene. The highest values were reported for [N<sub>1114</sub>][Tf<sub>2</sub>N] due to the lowest viscosity of this specific ionic liquid among others used in this study.





**Figure 7 Nitrogen permeability through ammonium liquid membranes**

### 3.4. Toluene permeability through SILMs



## Figure 8 Permeability of toluene vs temperature

According to results presented in Figure 8, permeability increases with the temperature in regard to decreasing viscosity. Considering the alkyl chain length of ionic liquids despite viscosity increase, permeability increases with the carbon atoms number in ionic liquid structure. This is due to higher hydrophobicity. In case of  $[N_{1114}][Tf_2N]$ , as evidenced by permeability, higher partition coefficients and thus solubility were compensated by significantly lower viscosity resulting in transport properties that occurred to be better than for  $[N_{2226}][Tf_2N]$  and worse than for  $[N_{2228}][Tf_2N]$ . Also lower molecular volume of  $[N_{1114}][Tf_2N]$  of  $0.450 \text{ nm}^3$  that is 20% lower than that of  $[N_{2226}][Tf_2N]$  contributes to higher permeability. Kulkarni et al. studied the effect of ammonium cation structure on absorption potential. They used series of Aliquat and phenylated cations and observed that the aromatic ring in cation structure does not increase absorption capacity and the absorption properties are rather a result of a three-dimension network structure and the integration of the solute inside that structure [46]. They have also noticed that in comparison to imidazolium ionic liquids, the ammonium ones present higher absorption capacity [46]. In present study that was confirmed in case of  $[N_{2228}][Tf_2N]$  and  $[N_{1114}][Tf_2N]$  in regard to results presented in previous study where permeability for imidazolium ionic liquids was presented [32]. Though we have not examined imidazolium ionic liquids with 8 carbon atom chain, on the basis of the permeability increase with alkyl chain elongation, we can predict that permeability would not exceed the value obtained for  $[N_{2228}][Tf_2N]$  that is 2666 barrers at 318 K. The differences in permeability of toluene among the ILs were lower at reduced temperatures. The case was also observed for partition coefficients. Moreover for 4 and 6 carbon atoms the values of permeability were very close, whereas for 8 carbon atoms the values slightly stood out and increased with temperature faster than for  $[N_{2224}][Tf_2N]$  and  $[N_{2226}][Tf_2N]$ . This is a result of rapid viscosity decrease of  $[N_{2228}][Tf_2N]$  and intense increase of partition coefficients of  $[N_{2224}][Tf_2N]$  and  $[N_{2226}][Tf_2N]$ .



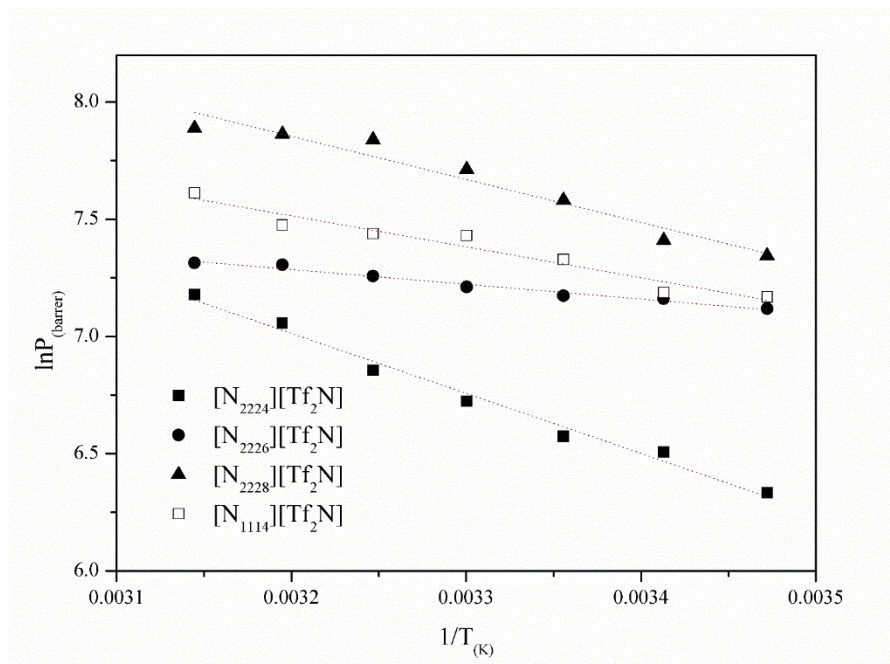


Temperature dependence of permeation flux is represented by Arrhenius equation:

$$J = J_0 e^{\frac{-E_J}{RT}} \quad (2)$$

Huang et al. pointed out that activation energy for permeation in Eq. (2) does include the enthalpy change resulting from solute phase change [47]. Taking into account permeation values in Eq. (3):

$$P = P_0 e^{\frac{-E_P}{RT}} \quad (3)$$



**Figure 9** Temperature dependence of toluene permeability

Since the activation energy of permeation includes the activation energy of diffusion and enthalpy of dissolution and the latter is generally negative for sorption processes, obtained positive  $E_p$  values (Table 4) display higher temperature impact on diffusion than on sorption of toluene in permeation process.

**Table 4** Infinite permeability, activation energy and  $R^2$  for permeation of toluene through SILMs

Ionic liquid	$P_0$ [barrer]	$E_p$ [kJ/mol]	$R^2$
[N <sub>2224</sub> ][Tf <sub>2</sub> N]	6312	3.99	0.9730



[N <sub>2226</sub> ][Tf <sub>2</sub> N]	10950	5.24	0.9716
[N <sub>2228</sub> ][Tf <sub>2</sub> N]	921723	15.28	0.9413
[N <sub>1114</sub> ][Tf <sub>2</sub> N]	125492	10.98	0.9380

The higher sensitivity to temperature changes of [N<sub>2228</sub>][Tf<sub>2</sub>N] and [N<sub>1114</sub>][Tf<sub>2</sub>N] is indicated by activation energy. Therefore the slope of permeability vs. temperature is higher for those ILs than for [N<sub>2224</sub>][Tf<sub>2</sub>N] and [N<sub>2226</sub>][Tf<sub>2</sub>N].

In Table 5 toluene and nitrogen permeability as well as ideal selectivity are presented. The overall selectivity was in a range of 29-120. The lowest values were observed for [N<sub>1114</sub>][Tf<sub>2</sub>N] and except one temperature point (288 K) for [N<sub>2224</sub>][Tf<sub>2</sub>N] due to lower viscosity and resulting lower diffusion resistance.

**Table 5 Permeation and selectivity**

Ionic liquid	Temperature [K]	Permeability		Selectivity
		[barrer]		
		toluene	N <sub>2</sub>	
[N <sub>1114</sub> ][Tf <sub>2</sub> N]	288	1298±8	18±2	<b>72</b>
	293	1323±12	20*	<b>66</b>
	298	1522±21	20±1	<b>76</b>
	303	1687±22	31*	<b>54</b>
	308	1700±41	28±2	<b>61</b>
	313	1764±33	42*	<b>42</b>
	318	2023±47	53±3	<b>38</b>
[N <sub>2224</sub> ][Tf <sub>2</sub> N]	288	1202±13	10±2	<b>120</b>
	293	1229±19	15*	<b>82</b>
	298	1264±23	18±2	<b>70</b>
	303	1291±24	22*	<b>59</b>
	308	1321±17	27±3	<b>49</b>
	313	1352±33	29*	<b>47</b>
	318	1420±29	49±6	<b>29</b>
	288	1234±13	13±4	<b>95</b>



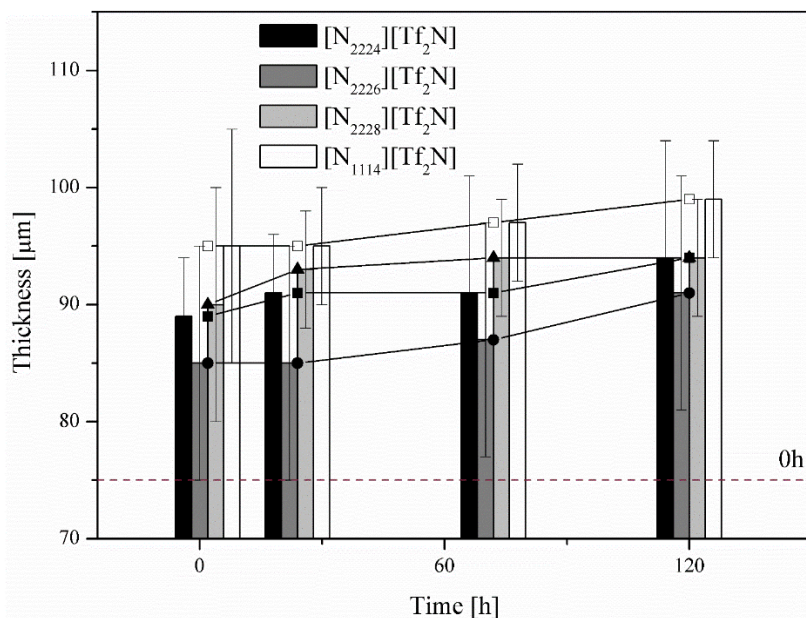
[N <sub>2226</sub> ][Tf <sub>2</sub> N]	293	1288±62	15*	<b>86</b>
	298	1304±70	20±2	<b>65</b>
	303	1354±82	24*	<b>56</b>
	308	1419±41	31±3	<b>46</b>
	313	1490±94	32*	<b>46</b>
	318	1501±96	53±6	<b>41</b>
[N <sub>2228</sub> ][Tf <sub>2</sub> N]	288	1548±51	15±2	<b>103</b>
	293	1653±70	18*	<b>92</b>
	298	1962±63	24±1	<b>82</b>
	303	2236±61	26*	<b>86</b>
	308	2539±74	33±4	<b>77</b>
	313	2600±76	33*	<b>79</b>
	318	2666±49	55±2	<b>48</b>

- - data calculated on the basis of nitrogen permeation vs temperature slope

### 3.5. Membranes stability

Membranes based on ammonium ionic liquids occurred to be stable for at least 30 days. During the experiment we have never reached the end of membranes life therefore we cannot estimate the overall life time. In fact, in comparison to our previous research with imidazolium ionic liquids [32] the average swelling effects were slightly lower for ammonium ILs. After 120 hours since preparation of the liquid membrane was complete, membranes reached the final thickness and no further swelling effect was noticed. The results are pictured in Figure 10. The maximum thickness increase of 32% was observed in case of [N<sub>1114</sub>][Tf<sub>2</sub>N], whereas other systems did not gain more than 25% of thickness. In case of imidazolium ionic liquids the 28-40% increase was observed [32]. As expected, [N<sub>1114</sub>][Tf<sub>2</sub>N] caused the biggest effect due to the lowest molecular volume of all ILs used in this study.

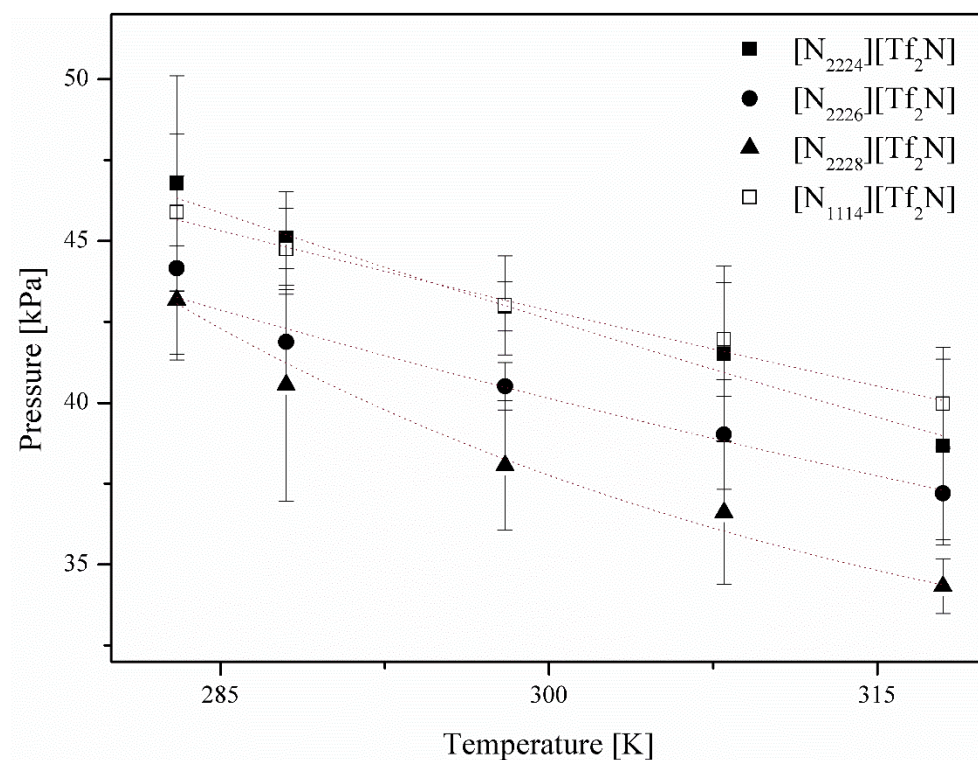




**Figure 10 Swelling effect**

No direct relation of thickness increase and carbon atoms number was found. However, as Izak et al. observed, swelling of polymers contacting with ionic liquids can be dependent on the water content in the membrane phase [48]. Though ionic liquids were dried before experiments they kept some water: 0.0542, 0.0248, 0.0624 mass%, respectively for 4, 6 and 8 carbon atoms in alkyl chain. As [N<sub>2228</sub>][Tf<sub>2</sub>N] caused higher swelling than [N<sub>2224</sub>][Tf<sub>2</sub>N] and [N<sub>2226</sub>][Tf<sub>2</sub>N] caused lower swelling than both of them and at the same time had more than two times lower water content it is likely that for pure ILs elongation of alkyl chain results in higher swelling, however water content plays an important role. Literature highlights the impact of water on ILs properties, in case of swelling location of water molecules in ILs structure impacts the penetration of ILs into the polymer changing the position of ions to gain minimum of interface free energy. In case of Nafion membranes it was found that polymer expansion occurs as a result of forming large clusters of ionic liquid cation solvated with water [48].

The stability of membranes in regard to pressure was estimated of the basis of maximum pressure possible to apply without mechanical damage of the system. As evidenced in Figure 11, it was observed that the pressure was declining with the elongation of alkyl chain length, so the lowest was recorded for  $[N_{2228}][Tf_2N]$ .



**Figure 11 Mechanical strength, expressed as trans-membrane pressure of ammonium ionic liquid based membranes**

In case of  $[N_{1114}][Tf_2N]$  it was slightly lower than for  $[N_{2224}][Tf_2N]$  at 283 and 288 K and higher at 298, 303 and 318 K. Though the swelling effect was the highest of all examined systems for  $[N_{1114}][Tf_2N]$  the mechanical stability was improved in comparison to other ILs. Those membranes seemed to be more elastic than others. However detailed research on interaction between ammonium ionic liquids and polypropylene would be beneficial in order to improve mechanical stability of SILMs, but reports on the influence of ILs on membrane structure are very limited.



#### 4. Conclusions

Ammonium ionic liquids though cheaper in production and more environmentally friendly than imidazolium ones, they are very briefly examined and rarely used in organics separation. In this research we proved that ammonium ILs can be successfully used in gas separation process with performance close to their imidazolium equivalents.

The selectivity of separation of toluene from nitrogen in a range of 29 up to 120 occurred to be promising for toluene removal, for example from industrial air. Properties of the ILs and resulting membrane systems can be easily adjusted to specific needs by changing the nitrogen substituents to tailor some of the most important technological factors like viscosity, permeability, selectivity or membrane stability. For example, despite the viscosity increase, elongation of one alkyl chain from 4 to 8 carbon atoms resulted in permeability increase from 1264 to 1962 barrers and selectivity increase from 70 to 82, respectively at 298 K. Considering stability of ammonium based ionic liquid membranes, mechanical properties were almost alike for  $[N_{2224}][Tf_2N]$  and  $[N_{1114}][Tf_2N]$  systems, above 45 kPa, and significantly better than for  $[N_{2226}][Tf_2N]$  and  $[N_{2228}][Tf_2N]$ . Moreover, in regard to permeability, performance of membranes based on  $[N_{1114}][Tf_2N]$  was better than of those based on  $[N_{2226}][Tf_2N]$  and  $[N_{2228}][Tf_2N]$ , though the solubility of toluene in  $[N_{1114}][Tf_2N]$  was lower. This was the result of the lowest viscosity of  $[N_{1114}][Tf_2N]$  among the tested ionic liquids. Low viscosity is also the reason of relatively high diffusion of nitrogen at low temperatures through the membrane based on  $[N_{1114}][Tf_2N]$  (18 barrers at 288 K and 20 barrers at 293 K). Therefore, the selectivity of  $[N_{1114}][Tf_2N]$  at low temperatures was lower than for other systems, however in moderate temperature range the selectivities of  $[N_{1114}][Tf_2N]$ ,  $[N_{2224}][Tf_2N]$  and  $[N_{2226}][Tf_2N]$  systems were very close, from 42 to 47 at 303K, and from 54 to 59 at 313 K. The selectivity of  $[N_{2228}][Tf_2N]$  system was significantly higher from 86 to 77, respectively.

Considering the obtained results, the most reasonable way during the design of a liquid membrane



system seems optimizing the permeation rate and selectivity for a given process conditions (temperature, pressure) and for a specific gas mixture. In this regard, the experimental work is needed to be performed to evaluate the overall liquid membrane performance and to make prediction of permeation parameters possible.

## Acknowledgements

This research was supported by the National Science Centre, grant no. 7563/B/T02/2011/40 in a title Removal of Volatile Organic Compounds from Gas Phase using Ionic Liquids.

## References

- [1] M.J. Earle, K.R. Seddon, Ionic liquids. Green solvents for the future, *Pure Appl. Chem.* 72 (2007) 1391–1398. doi:10.1351/pac200072071391.
- [2] J.G. Huddleston, H.D. Willauer, R.P. Swatloski, A.E. Visser, R.D. Rogers, Room temperature ionic liquids as novel media for ‘clean’ liquid–liquid extraction - *Chemical Communications* (RSC Publishing), *Chem. Commun.* (1998) 1765–1766. <http://pubs.rsc.org/en/content/articlelanding/1998/cc/a803999b#!divAbstract>.
- [3] C.P. Fredlacke, J.M. Crosthwaite, D.G. Hert, S. Aki, J.F. Brennecke, Thermophysical Properties of Imidazolium-Based ionic Liquids, *J. Chem. Eng. Data.* 49 (2004) 954–964.
- [4] U. Domańska, M. Wlazło, Z. Dąbrowski, A. Wiśniewska, Ammonium ionic liquids in separation of water/butan-1-ol using liquid-liquid equilibrium diagrams in ternary systems, *Fluid Phase Equilib.* 485 (2019) 23–31. doi:10.1016/J.FLUID.2018.12.009.
- [5] U. Domańska, M. Karpińska, A. Wiśniewska, Z. Dąbrowski, Ammonium ionic liquids in extraction of bio-butan-1-ol from water phase using activity coefficients at infinite dilution, *Fluid Phase Equilib.* 479 (2019) 9–16. doi:10.1016/J.FLUID.2018.09.024.





- [6] M. Królikowski, M. Królikowska, C. Wiśniewski, Separation of aliphatic from aromatic hydrocarbons and sulphur compounds from fuel based on measurements of activity coefficients at infinite dilution for organic solutes and water in the ionic liquid N,N-diethyl-N-methyl-N-(2-methoxy-ethyl)ammonium bis(trifluoromethylsulfonyl)imide, *J. Chem. Thermodyn.* 103 (2016) 115–124. doi:10.1016/J.JCT.2016.07.017.
- [7] E. Elhaj, H. Wang, Y. Gu, Functionalized quaternary ammonium salt ionic liquids (FQAILs) as an economic and efficient catalyst for synthesis of glycerol carbonate from glycerol and dimethyl carbonate, *Mol. Catal.* 468 (2019) 19–28. doi:10.1016/J.MCAT.2019.02.005.
- [8] I. Cichowska-Kopczynska, M. Joskowska, R. Aranowski, Wetting processes in supported ionic liquid membranes technology, *Physicochem. Probl. Miner. Process.* 50 (2014). doi:10.5277/ppmp140131.
- [9] M.E. Zakrzewska, A.A. Rosatella, S.P. Simeonov, C.A.M. Afonso, V. Najdanovic-Visak, M. Nunes da Ponte, Solubility of carbon dioxide in ammonium based CO<sub>2</sub>-induced ionic liquids, *Fluid Phase Equilib.* 354 (2013) 19–23. doi:10.1016/J.FLUID.2013.06.011.
- [10] X. Yuan, S. Zhang, J. Liu, X. Lu, Solubilities of CO<sub>2</sub> in hydroxyl ammonium ionic liquids at elevated pressures, *Fluid Phase Equilib.* 257 (2007) 195–200. doi:10.1016/J.FLUID.2007.01.031.
- [11] F. Nkinahamira, T. Su, Y. Xie, G. Ma, H. Wang, J. Li, High pressure adsorption of CO<sub>2</sub> on MCM-41 grafted with quaternary ammonium ionic liquids, *Chem. Eng. J.* 326 (2017) 831–838. doi:10.1016/J.CEJ.2017.05.173.
- [12] M.S. Manic, A.J. Queimada, E.A. Macedo, V. Najdanovic-Visak, High-pressure solubilities of carbon dioxide in ionic liquids based on bis(trifluoromethylsulfonyl)imide and chloride, *J. Supercrit. Fluids.* 65 (2012) 1–10. doi:10.1016/J.SUPFLU.2012.02.016.
- [13] J. Jacquemin, P. Husson, V. Majer, M.F. Costa Gomes, Influence of the cation on the solubility of CO<sub>2</sub> and H<sub>2</sub> in ionic liquids based on the bis(trifluoromethylsulfonyl)imide anion, *J. Solution Chem.* 36 (2007) 967–979. doi:10.1007/s10953-007-9159-9.





- [14] H.R. Cascon, S.K. Choudhari, 1-Butanol pervaporation performance and intrinsic stability of phosphonium and ammonium ionic liquid-based supported liquid membranes, *J. Memb. Sci.* 429 (2013) 214–224. doi:10.1016/J.MEMSCI.2012.11.028.
- [15] H.R. Cascon, S.K. Choudhari, G.M. Nisola, E.L. Vivas, D.-J. Lee, W.-J. Chung, Partitioning of butanol and other fermentation broth components in phosphonium and ammonium-based ionic liquids and their toxicity to solventogenic clostridia, *Sep. Purif. Technol.* 78 (2011) 164–174. doi:10.1016/J.SEPPUR.2011.01.041.
- [16] P. Reddy, K.J. Chiyen, N. Deenadayalu, D. Ramjugernath, Determination of activity coefficients at infinite dilution of water and organic solutes (polar and non-polar) in the Ammoeng 100 ionic liquid at  $T = (308.15, 313.5, 323.15, \text{ and } 333.15) \text{ K}$ , *J. Chem. Thermodyn.* 43 (2011) 1178–1184. doi:10.1016/J.JCT.2011.03.001.
- [17] R.L. Wolfrom, S. Chander, R. Hogg, Evaluation of capillary rise methods for determining wettability of powders, *Miner. Metall. Process.* 19 (2002) 198–202.
- [18] M. Matsumoto, K. Ueba, K. Kondo, Vapor permeation of hydrocarbons through supported liquid membranes based on ionic liquids, *Desalination.* 241 (2009) 365–371. doi:10.1016/J.DESAL.2007.11.090.
- [19] U. Domańska, A. Pobudkowska, M. Królikowski, Separation of aromatic hydrocarbons from alkanes using ammonium ionic liquid  $\text{C}_2\text{N}^+\text{Tf}_2^-$  at  $T = 298.15 \text{ K}$ , *Fluid Phase Equilib.* 259 (2007) 173–179. doi:10.1016/J.FLUID.2007.06.025.
- [20] A. Panigrahi, S.R. Pilli, K. Mohanty, Selective separation of Bisphenol A from aqueous solution using supported ionic liquid membrane, *Sep. Purif. Technol.* 107 (2013) 70–78. doi:10.1016/J.SEPPUR.2013.01.020.
- [21] H. Walczyk, Niskotemperaturowa kondensacja lotnych związków organicznych w obecności gazu inertnego w spiralnym wymienniku ciepła, *Pr. Nauk. Inst. Inżynierii Chem. PAN.* 6 (2006) 7–127.

- [22] P.R. Danesi, L. Reichley-Yinger, P.G. Rickert, Lifetime of supported liquid membranes: the influence of interfacial properties, chemical composition and water transport on the long-term stability of the membranes, *J. Memb. Sci.* 31 (1987) 117–145.
- [23] A.M. Neplenbroek, D. Bargeman, C.A. Smolders, Supported liquid membranes: stabilization by gelation, *J. Memb. Sci.* 67 (1992) 149–165. doi:10.1016/0376-7388(92)80022-C.
- [24] M. Teramoto, Y. Sakaida, S.S. Fu, N. Ohnishi, H. Matsuyama, T. Maki, T. Fukui, K. Arai, An attempt for the stabilization of supported liquid membrane, *Sep. Purif. Technol.* (2000). doi:10.1016/S1383-5866(00)00197-0.
- [25] M. Zubielewicz Kamińska-Tarnawska, E., Wpływ farb na czystość powietrza atmosferycznego. Lotne substancje organiczne (VOC). Legislacja i oznaczanie, *Przem. Chem.* 84 (2005) 151–155.
- [26] M. Joskowska, I. Kopczynska, B. Debski, D. Holownia-Kedzia, R. Aranowski, J. Hupka, Wetting of supports by ionic liquids used in gas separation processes, *Physicochem. Probl. Miner. Process.* 48 (2012) 129–140.
- [27] Q. Gan, D. Rooney, H. Xue, G. Thompson, Y. Zou, An experimental study of gas transport and separation properties of ionic liquids supported on nanofiltration membranes, *J. Memb. Sci.* 280 (2006) 948–956.
- [28] Q. Gan, D. Rooney, Y. Zou, Supported ionic liquid membranes in nanopore structure for gas separation and transport studies, *Desalination.* 199 (2006) 535–537.
- [29] B.C. Lee, S.L. Outcalt, Solubilities of gases in the Ionic liquid 1-n-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, *J. Chem. Eng. Data.* 51 (2006) 892–897.
- [30] A. Uyanik, N. Tinkiliç, Preparing Accurate Standard Gas Mixtures of Volatile Substances at Low Concentration Levels, *4171 (1999)* 141–142.
- [31] W.I. Sohn, D.H. Ryu, S.J. Oh, J.K. Koo, A study on the development of composite membranes for the separation of organic vapors, *J. Memb. Sci.* 175 (2000) 163–170.
- [32] I. Cichowska-Kopczyńska, M. Joskowska, B. Debski, R. Aranowski, J. Hupka, Separation of



toluene from gas phase using supported imidazolium ionic liquid membrane, *J. Memb. Sci.* 566 (2018) 367–373. doi:10.1016/J.MEMSCI.2018.08.058.

- [33] R. Fortunato, C.A.M. Afonso, A.M. Reis, J.G. Crespo, Supported liquid membranes using ionic liquids: study of stability and transport mechanisms, *J. Memb. Sci.* 242 (2004) 197–209.
- [34] R. Fortunato, C.A.M. Afonso, J. Benavente, E. Rodriguez-Castellón, J.G. Crespo, Stability of supported ionic liquid membranes as studied by X-ray photoelectron spectroscopy, *J. Memb. Sci.* 256 (2005) 216–233.
- [35] F. Hernandez-Fernandez, A. de los Rios, F. Tomas-Alonso, J. Palacios, G. Villora, Preparation of supported ionic liquid membrane: Influence of the ionic liquid immobilization method on their operational stability, *J. Memb. Sci.* 341 (2009) 172–177.
- [36] M. Dakkach, F.M. Gaciño, M.J.G. Guimarey, S.K. Mylona, X. Paredes, M.J.P. Comuñas, J. Fernández, M.J. Assael, Viscosity-pressure dependence for nanostructured ionic liquids. Experimental values for butyltrimethylammonium and 1-butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide, *J. Chem. Thermodyn.* 121 (2018) 27–38. doi:10.1016/J.JCT.2018.01.025.
- [37] A. Bhattacharjee, A. Luís, J.A. Lopes-da-silva, M.G. Freire, J. Pedro, Thermophysical properties of sulfonium- and ammonium-based ionic liquids, *Fluid Phase Equilib.* 958 (2014) 36–45. doi:10.1016/j.fluid.2014.08.005. Thermophysical.
- [38] K. MacHanová, A. Boisset, Z. Sedláková, M. Anouti, M. Bendová, J. Jacquemin, Thermophysical properties of ammonium-based bis{(trifluoromethyl)sulfonyl} imide ionic liquids: Volumetric and transport properties, *J. Chem. Eng. Data.* 57 (2012) 2227–2235. doi:10.1021/jc300108z.
- [39] J. Sun, M. Forsyth, D.R. MacFarlane, Room-temperature molten salts based on the quaternary ammonium ion, *J. Phys. Chem. B.* 102 (1998) 8858–8864. doi:10.1021/jp981159p.
- [40] V. V. Teplyakov, A.Y. Okunev, N.I. Laguntsov, Computer design of recycle membrane contactor systems for gas separation, *Sep. Purif. Technol.* 57 (2007) 450–454.

doi:10.1016/j.seppur.2006.06.002.

- [41] J.O. Valderrama, L.F. Cardona, R.E. Rojas, Correlation and prediction of ionic liquid viscosity using Valderrama-Patel-Teja cubic equation of state and the geometric similitude concept. Part I: Pure ionic liquids, *Fluid Phase Equilib.* 497 (2019) 164–177. doi:10.1016/J.FLUID.2019.04.031.
- [42] P.F. Requejo, I. Díaz, E.J. González, Á. Domínguez, Mutual solubility of aromatic hydrocarbons in pyrrolidinium and ammonium-based ionic liquids and its modeling using the Cubic-Plus-Association (CPA) Equation of State, *J. Chem. Eng. Data.* 62 (2017) 633–642. doi:10.1021/acs.jced.6b00655.
- [43] A. Finotello, J.E. Bara, D. Camper, R.D. Noble, Room-temperature ionic liquids: Temperature dependence of gas solubility selectivity, *Ind. Eng. Chem. Res.* 47 (2008) 3453–3459. doi:10.1021/ie0704142.
- [44] J. Jacquemin, P. Husson, V. Majer, M.F.C. Gomes, Low-pressure solubilities and thermodynamics of solvation of eight gases in 1-butyl-3-methylimidazolium hexafluorophosphate, *Fluid Phase Equilib.* 240 (2006) 87–95. doi:10.1016/j.fluid.2005.12.003.
- [45] J. Jacquemin, M.F. Costa Gomes, P. Husson, V. Majer, Solubility of carbon dioxide, ethane, methane, oxygen, nitrogen, hydrogen, argon, and carbon monoxide in 1-butyl-3-methylimidazolium tetrafluoroborate between temperatures 283 K and 343 K and at pressures close to atmospheric, *J. Chem. Thermodyn.* 38 (2006) 490–502. doi:10.1016/j.jct.2005.07.002.
- [46] P.S. Kulkarni, L.C. Branco, J.G. Crespo, C.A.M. Afonso, A comparative study on absorption and selectivity of organic vapors by using ionic liquids based on imidazolium, quaternary ammonium, and guanidinium cations, *Chem. - A Eur. J.* 13 (2007) 8470–8477. doi:10.1002/chem.200700160.
- [47] R.Y.M. Huang, X. Feng, Estimation of activation energy for permeation in pervaporation processes, *J. Memb. Sci.* 118 (1996) 127–131. doi:10.1016/0376-7388(96)00096-8.
- [48] P. Izak, S. Hovorka, T. Bartovsky, L. Bartovska, J. Crespo, Swelling of polymeric membranes in roomtemperature ionic liquids, *J. Memb. Sci.* 296 (2007) 131–138.

- [49] H. Tokuda, S. Tsuzuki, M.A.B.H. Susan, K. Hayamizu, M. Watanabe, How ionic are room-temperature ionic liquids? An indicator of the physicochemical properties, *J. Phys. Chem. B.* 110 (2006) 19593–19600. doi:10.1021/jp064159v.
- [50] M.H. Ghatee, M. Bahrami, N. Khanjari, Measurement and study of density, surface tension, and viscosity of quaternary ammonium-based ionic liquids ([N222(n)]Tf2N), *J. Chem. Thermodyn.* 65 (2013) 42–52. doi:10.1016/J.JCT.2013.05.031.

## SUPPORTING INFORMATION

Table S 1 Physicochemical parameters of ammonium ionic liquids (\* - this work)

Ionic liquid	Surface tension [mJ/m <sup>2</sup> ]	Temperature [K]	Viscosity [mPa·s]
[N <sub>1114</sub> ][ Tf <sub>2</sub> N]	30.35±0.05*	288	168.32±0.38*
			184.7[36]
		293	121.60±0.17*
			136.2[49], 137.7[37], 138.3[36]
		298	97.62±0.47*
			98.2[49], 102.17[36], 105.4[36]
[N <sub>2224</sub> ][ Tf <sub>2</sub> N]	31.01±0.14*	303	73.08±0.09*
			76.6[49], 82.19[36]
		308	61.79±0.44*
			65.2[37], 66.10[36], 65.33[36]
		313	47.19±0.03*
			49.3[49], 50.51 [36], 53.01 [36]
[N <sub>2224</sub> ][ Tf <sub>2</sub> N]	31.01±0.14*	318	42.83±0.14*
			43.22 [36]
		288	280.88±2.29*
		293	181.40±0.26*
		298	131.71±0.45*
		303	101.67±0.23*
[N <sub>2224</sub> ][ Tf <sub>2</sub> N]	31.01±0.14*	308	76.29±0.09*
		313	61.05±0.02*

	318	47.90±0.19*
<b>[N<sub>2226</sub>][ Tf<sub>2</sub>N]</b>	288	279.60±0.46*
	293	201.40±0.36*
32.46 ±0.99*, 34.1[50]	298	149.90±0.44* 167[39], 186.6[50]
33.7[50]	303	118.70±0.61* 137.9[50]
33.3[50]	308	87.55±0.07* 105.1[50]
32.9[50]	313	69.20±0.08* 81.64[50]
32.5[50]	318	55.48±0.12* 65.32[50]
<b>[N<sub>2228</sub>][ Tf<sub>2</sub>N]</b>	288	357.83±0.35*
	293	254.37±0.25*
21.75±0.28*, 33.1[50]	298	186.07±0.23* 202[39], 221.4[50], 238.7[38]
32.8[50]	303	138.47±0.31* 163.9[50], 178.9[38]
32.3[50]	308	106.85±0.92* 124.7[50], 134.7[38]
31.8[50]	313	83.57±0.12* 96.76[50]
31.4[50]	318	67.79±0.04*



