

# Use of pyridinium and pyrrolidinium ionic liquids for removal of toluene from gas streams

## Abstract

Separation of toluene from a toluene/N<sub>2</sub> gas mixture using supported liquid membranes based on a series of pyridinium (1-butylpyridinium-bis(trifluoromethylsulfonyl)imide - [C4Py][Tf<sub>2</sub>N], 1-hexylpyridinium trifluoromethanesulfone [C6Py][Tf<sub>2</sub>N]) and pyrrolidinium (1-butyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl)imide - [C4Pyr][Tf<sub>2</sub>N], 1-hexyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide - [C6Pyr][Tf<sub>2</sub>N], 1-butyl-1-methylpyrrolidinium trifluoromethanesulfone - [C4Pyr][TfO]) ionic liquids (ILs) was studied over a wide range of temperatures. The toluene permeability and selectivity of separation was investigated in terms of cation and anion type. It was found that both pyridinium and pyrrolidinium ILs show high toluene permeability, up to 2034 barrers, with satisfying separation selectivity. An analysis of two key factors that have an influence on this process, that is diffusion in a form of resistance resulting from the viscosity of membrane liquid and the solubility expressed by the partition coefficient, was made.

## 1. Introduction

Toluene is widely used as a substrate or solvent in the production of many chemicals. Toluene is also a common ingredient in many products, such as paints, solvents and varnishes. Due to its ubiquity, toluene poses a real threat to human health. Toluene is an irritant, a neurotoxin and is harmful to foetuses. In particular, during varnishing and painting, workers are exposed to toxic organic solvents; hence, there is a need to decrease the solvent vapour concentrations to acceptable levels by increasing the flow of air using a ventilation system. To prevent the release of toluene into the atmosphere, appropriate systems for cleaning exhaust streams should be used. Separation of toluene can be carried out with absorption, adsorption, oxidation, condensation and membrane methods. Many efforts have been made to develop absorption solvents that are effective, efficient, reusable and stable. All those requirements are fulfilled by ionic liquids (ILs), which are salts constituted by an asymmetric organic cation and organic or inorganic anion [1]. The main and the most valuable property of ionic liquids that makes them promising in separation technologies is their extremely low volatility and thermal stability. According to Bittner et al., 1-butylpyridinium bis(trifluoromethylsulfonyl)imide [C4Py][NTf<sub>2</sub>] and 1-hexylpyridinium bis(trifluoromethylsulfonyl)imide [C6Py][NTf<sub>2</sub>] are thermally stable up to 227 °C [2]. Nisopropylpyridinium hexafluorophosphate was found to be stable up to 400 °C [3]. Generally, pyridinium ionic liquids are considered to be slightly less stable than imidazolium ILs, for example for 1-methyl-3-butylimidazolium bis(trifluoromethylsulfonyl)imide ([Bmim][NTf<sub>2</sub>]), Wang et al. reported temperatures up to 327 °C [4]. Regardless, values reported in the literature usually cover a wide range of temperatures for the same ionic liquid, even from 235 to 540 °C for [5]. Usually, thermal stability is evaluated on the basis of TGA experiments, and onset values are reported; however, decomposition starts at temperatures lower than even 100 K [5–7]. Results reported in TGA measurements are dependent on the ionic liquid's structure, its purity and even on the TGA pan composition [8]. Nevertheless, the thermal stability of ionic liquids is high. Even in absorption processes, ionic liquids can be easily regenerated at relatively low temperatures; for example, removal of toluene can be performed at 75 °C with absorptivity values during the five reuse cycles between 92 and 97% for [Bmim][NTf<sub>2</sub>] [4]. Ma et al. also used imidazolium ionic liquids for toluene absorption and found that heating to 90 °C was highly efficient in toluene removal and even after several absorption-desorption cycles 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim][BF<sub>4</sub>]) retained its initial absorption capacity [9]. Another advantage of ionic liquids is the possibility of tuning their properties by substituting constituents to meet specific demands [10]. For example, the inclusion of a methyl group in the 1-alkyl-3-methylimidazolium cation reduces the amount of heptane dissolved in the IL, but the solubility of toluene remains the same [11]. For these reasons ionic liquids can be successfully used in organics extraction [12–16]. Recovery of volatile organic compounds using ionic liquids is focused mainly on liquid phase [17–20], whereas separation from gas phases is mainly based on imidazolium ionic liquids. Phase equilibria of binary mixtures of ionic liquids and hydrocarbons have been widely studied, and toluene is one of the most often used organics [21,22]. Yu et al. used imidazolium ILs with 2-, 4-, 8-, 10- and 12-carbon atom side chains and various anions to examine vapour-liquid equilibrium of toluene-ionic liquid systems [23]. The authors have also performed an examination of 1-methyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide in the capture of benzene, toluene and p-xylene and proved it to be efficient, effective and without any solvent loss [24]. Bedia et al. performed an analysis of toluene-ionic liquid interactions using the COSMO-RS method and confirmed that imidazolium, pyridinium and pyrrolidinium ionic liquids are suitable for separation of organics [25]. Though imidazolium ionic liquids have received much attention, pyridinium- and pyrrolidinium-based ionic liquids have begun to gain popularity [26–28] in many applications, including in the recovery of volatile organic compounds [29–32]. In comparison to imidazolium ionic liquids, N-butylpyridinium ionic liquids have a deeper aromatic character, and therefore, the interactions between these ionic

liquids and aromatic compounds are stronger [18]. Considering that the bis (trifluoromethylsulfonyl)imide anion gives ILs low viscosity, a pyridinium IL with a [Tf<sub>2</sub>N] anion is a suitable combination for separation of aromatics [18]. These ILs have been proven to display very good toluene selectivity in separation from toluene/heptane systems [33]. Pyridinium ionic liquids are slightly more expansive than imidazolium, but the utilization of ILs in supported liquid membrane technology reduces the amount of reagent to a minimum and since the ILs can be used for long-term periods, the positive effects related to the higher affinity towards aromatics overcome the disadvantageous cost.

Membrane technology has reduced energy consumption in comparison to other methods. Considering the different types of membranes utilized for gas separation, liquid membranes seem to be an excellent substitute of solid polymer membranes due to their lower diffusion resistance. A supported liquid membrane (SLM) is a two-phase system of liquid media held in the pores of a porous support by capillary forces [34]. The selection of membrane liquid is crucial for efficient separation. The most suitable are liquids that have low vapour pressure to prevent secondary pollution of the purified stream and degradation of the membrane caused by evaporation of the liquid. The liquid should have a proper viscosity that does not cause excessive diffusion resistance and at the same time prevents the liquid from being displaced from the pores of the support. The membrane liquid also must be compatible with the support, meaning it should not cause degradation due to chemical interactions or physical weakness due to swelling. Regarding the solution diffusion model of transport in supported liquid membranes, the compound that is separated has to be highly soluble in the membrane liquid. This work focuses on the use of membrane technology due to the ease of its utilization in existing ventilation ducts. Supported ionic liquid membranes (SILMs) has been extensively used in gas separation [35–37] with promising results, but to the best of our knowledge, pyridinium and pyrrolidinium ionic liquids have not been used in supported ionic liquid membranes for aromatic solvent removal. In this research, we characterized the potential of SLMs based on pyrrolidinium and pyridinium ILs for very low-concentration hydrocarbon separation from the gas phase utilizing low pressure difference

## 2. Experimental

### 2.1. Materials

The following ILs were purchased from IOLITEC, Heilbronn, Germany with purity higher than 99%: 1-butylpyridinium bis (trifluoromethylsulfonyl)imide ([C<sub>4</sub>Py][Tf<sub>2</sub>N] – CAS 187863-42- 9), 1-hexylpyridinium bis(trifluoromethylsulfonyl)imide ([C<sub>6</sub>Py][Tf<sub>2</sub>N] – CAS 460983-97-5), 1-butyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl)imide ([C<sub>4</sub>Pyrr][Tf<sub>2</sub>N] – CAS 223437-11- 4), 1-hexyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide ([C<sub>6</sub>Pyrr][Tf<sub>2</sub>N] – CAS 380497-19-8), and 1-butyl-1- methylpyrrolidinium trifluoromethanesulfonate ([C<sub>4</sub>Pyrr][TfO] – CAS 367522-96-1). The porous polypropylene GH Polypro (PP) used for membrane fabrication as the support was supplied by Pall, Gelman Laboratory. Ultrahigh purity hydrogen and nitrogen were obtained from Air Liquid S.A. Poland, toluene was obtained from P.P.H. Stanlab Sp. J. Poland. The gaseous mixture of toluene/N<sub>2</sub> with a toluene concentration of approximately 100 ppm (v/v) was prepared in a pressure tank according to the procedure given by Uyanik et al. [38]. The key properties of the ILs used in this study are presented in Table 1. ILs were based on the anions [TfO] and [Tf<sub>2</sub>N] in order to perform comparison of the impact of cation type on the permeability. All ionic liquids used in this study are liquid at room temperature.

### 2.2. Apparatus

A diagram of the laboratory setup for the permeance experiments is presented in Fig. 1. The apparatus consists of a stainless steel chamber divided into feed and permeate parts, a temperature stabilization system, an analyse system, a vacuum pump, a set of pressure sensors and flow controllers, signal converters and a data acquisition and archiving system. The main element of the apparatus is the permeation chamber (9) with a volume of: part A: 130.9 cm<sup>3</sup> ; part B: 127.7 cm<sup>3</sup> . The chamber is equipped with a water jacket connected to a circulation bath (5). Membranes with an active area of 11.3 cm<sup>2</sup> were placed between Teflon gaskets. The evacuation of chamber was conducted using the vacuum pump (6). The sweeping gas was fed to the chamber from gas container (1), the examined gas was fed from gas sample container (3), which was previously filled with gas from gas container (2). The pressure and temperature were monitored using sensors and the difference in pressure levels between parts A and B of the chamber was monitored with a differential pressure sensor. The gas flow was controlled and monitored using mass flow controllers and flow indicators. The feed, retentate and permeate flow lines were connected to a gas chromatograph (7). All the data from the controlling and monitoring equipment were transferred to the computer through an analogue-digital transducer.

Supported liquid membranes (4) were prepared using the preparation vessel presented in Fig. 2. The polymer support (1) was placed in a pressure vessel (2), and a vacuum was created using an oil pump (4) for 1 h to remove air from the pores. After degassing, a syringe with ionic liquid in the amount of 0.1 ml for every 1 cm<sup>2</sup> of the membrane (8) was mounted to the vessel. After the valve (6) was opened, the liquid was automatically sucked into the vessel as a result of the reduced pressure inside the apparatus. In the next step, the vacuum was reduced and an inert gas (nitrogen (5)) was introduced through valve (7) to produce a positive pressure of 70 kPa which was maintained for 1 h, as controlled by a pressure sensor (3). The prepared membrane was again degassed overnight. After this time, the excess liquid was removed from the surface of the membrane using a paper tissue before being placed into the apparatus.

### 2.3. Determination of the physicochemical properties of the ionic liquids

Prior to the experiments, the ionic liquids were kept in a vacuum dryer at 373 K for 24 h to remove any traces of water and volatile contaminants as they can strongly influence the ionic liquid physicochemical properties [39]. The water content in the ionic liquids was determined using the Karl-Fischer coulometric titration method with a Metrohm 831 KF Coulometer. Dynamic viscosity coefficients were measured using a Brookfield Rheometer LV III equipped with a temperature controller with an accuracy of  $\pm 0.01$  K. The surface tension of the selected ionic liquids was determined at room temperature using the pendant drop method with a Tensiometer Krüss DSA 10. The experiments were conducted immediately after reaching equilibrium and stabilization to minimize the absorption of water from the air.

### 2.4. Membrane stability

The stability of prepared membranes was evaluated in regard to the wetting of the support by the ionic liquids, the swelling effect and mechanical resistance. Characterization of the supports was performed on the basis of contact angles, membrane thickness and resistance to pressure according to procedures described in previous studies [40]. Prior to the experiments, the ionic liquids were kept in a vacuum dryer at 373 K for 24 h. Contact angles were measured using the dynamic sessile drop method with a Tensiometer Krüss DSA 10 at room temperature and the humidity of air was at a level of 60–70%. The advancing angle  $\theta_a$ , the receding angle  $\theta_r$  and the hysteresis  $\theta_a - \theta_r$  were determined by analysis of the drop shape and matching it to a numeric model [41]. Swelling of the liquid membranes was defined as the increase in membrane thickness at times of 2, 24, 72, and 120 h from the time the membrane was prepared. It was assumed that the membrane is a cylinder and the swelling was evaluated by measuring its height. The swelling effect was observed using an epi-fluorescence microscope L3001 with a digital camera attached. A series of pictures was taken and analysed using digital image processing software. The mechanical stability of the membrane was evaluated on the basis of the value of the pressure difference over the membrane that results in mechanical disruption. The experiments were performed in the apparatus presented in Fig. 1. Prior to the experiments, the supported ionic liquid membranes were equilibrated at room temperature for at least 120 h, and afterwards, the membranes were placed in the measurement chamber. The gas sampler was filled with inert gas (nitrogen). The desired temperature was set and both parts of the chamber were evacuated using the oil pump. The gas sampler and the membrane were equilibrated at a set temperature until the pressure in the gas sampler was stable. Data recording was set at high frequency and the gas from gas sampler was then released to the feed part of chamber (A) at a rate of 50 Pa/s. The experiment was finished when the pressure in both parts of the chamber became equal. The maximum pressure difference obtained was the result.

### 2.5. Solubility of toluene and partition coefficients

The solubility of toluene in the ionic liquids was measured in an equilibrium cell equipped with a working volume of 15 cm<sup>3</sup>. The cell was immersed in a water bath with a thermostat with an accuracy of  $\pm 0.01$  K. The system included a thermometer with accuracy of  $\pm 0.01$  K and a magnetic stirrer. The solubility was measured at 298 K with the cloud-point method and the amount of toluene in the ionic liquid was determined by the gravimetric method. A specific amount of ionic liquid was placed in a gas tight cell and continuously stirred as toluene was added dropwise until turbidity was observed. Partition coefficients were determined based on the toluene mole fraction ratio in the gas and liquid phases. Samples were prepared using an electronic balance with a resolution of  $\pm 0.00001$  g. 0.5 cm<sup>3</sup> of ionic liquid was placed in a headspace vial purged with nitrogen. Toluene was added to the samples in the amounts of 2, 4, 6, 8 and 10 · 10<sup>-3</sup> cm<sup>3</sup>. The mixtures were kept in a circulation bath at set temperatures (288, 298, 308, 318 K) until the equilibrium point (determined experimentally) was reached. Toluene content in the gas phase was determined using headspace gas chromatography (Gas Chromatograph Clarus 500). The partition coefficients,  $K$ , were calculated as the ratio of toluene mole fraction in gas ( $c_g$ ) and toluene mole fraction in liquid phase ( $c_l$ ). A detailed description of the procedure is given by Cichowska-Kopczynska et al. [40].

### 2.6. Permeability through supported ionic liquid membranes

To evaluate the selectivity of N<sub>2</sub>/toluene separation, single N<sub>2</sub> transport measurements were conducted. Pure gas permeability measurements were performed in the experimental apparatus shown in Fig. 1. Before placing a new membrane in the chamber after removal of used membranes, both parts were carefully cleaned, dried and blown with nitrogen. The thickness of the equilibrated membrane was measured and the membrane was then placed between Teflon gaskets. After the membrane was mounted in the system, the system was put under vacuum for 12 h to remove any possible traces of absorbed water and gases. This step allowed for determination of the gas tightness of the system. During this time, the gas sampler was filled with nitrogen and afterwards degassing at a set temperature was performed for the whole system. The feed chamber was then filled with nitrogen from the gas sampler at a rate of 25 Pa/s until a pressure difference of 15 kPa between the chamber parts was obtained. The pressure was measured continuously using pressure sensors. The permeance in barrer units was calculated using Eq. (1).

where:  $A$  – membrane area [m<sup>2</sup>],  $t$  – time [s],  $V_n$  – normal volume [cm<sup>3</sup>],  $l$  – membrane thickness, and  $p_i(f,p)$  – pressure of  $i$  in the feed and permeate. Toluene permeation experiments were conducted in a dynamic system using the experimental setup presented in Fig. 1 according to the procedure described in a previous paper [40]. A feed mixture of nitrogen and toluene was prepared in a 40 dm<sup>3</sup> gas container. The thickness of the equilibrated membrane was measured, and the membrane was then placed in the chamber and after setting up the system was put under vacuum for 12 h to remove any possible traces of absorbed water and gases. The flow rates of the feed and receiving phases were controlled by Bronkhorst EL-FLOW flowmeters. Nitrogen was used as the sweep gas according to the initial test of back permeance using helium, which

indicated no noticeable effect. This is a result of the very low solubility and permeability of nitrogen and higher nitrogen partial pressure on the feed side. The experiments were conducted at a transmembrane pressure of 15 kPa and the toluene concentration in input and output streams was analysed using an SRI Chromatograph with an FID detector until the toluene concentration levels were constant

### 3. Results and discussion

#### 3.1. Physicochemical properties of ionic liquids

The Newtonian character of ionic liquids used in this study was confirmed. The viscosity of pyridinium and pyrrolidinium ionic liquids is noticeably higher than their imidazolium equivalents. Moreover, for pyrrolidinium ILs, the viscosity is higher than for pyridinium, and for 6 carbon atoms chains it is N50% higher at the lowest temperature point. The viscosity of the examined ionic liquids increases with the elongation of the alkyl chain length and as was confirmed by Bittner et al. [2] and is in good agreement with literature data [2,42]. Regarding the impact of temperature, viscosity decreases exponentially. Therefore, the diffusion resistance is lower when using ionic liquids with lower carbon atoms number. Moreover, in agreement with literature data [43], a viscosity increase is observed when substituting [Tf2N] anion with [TfO], by as much as 75% at 288 K. All ionic liquids were examined after drying, however the ability of the ionic liquids to bind water depends mainly on the type of anion, and much less on the composition of the cation [44]. ILs based on the [Tf2N] anion kept less water, and [C4Pyr][TfO] contained approximately 0.23% which was approximately 5 and 6.7 times more than [C6Pyr][Tf2N] and [C4Pyr][Tf2N], respectively. The values of the surface tension were determined at room temperature, as the surface tension was only needed in order to evaluate the contact angles and no direct relation between surface tension and alkyl chain length can be assumed on the basis of the obtained data. Information found in the literature also suggests that there is no dependence [12]. Detailed results can be found in the Supporting information.

#### 3.2. Membrane stability

As the liquid is held in the pores of the porous support, in order to evaluate the stability of the membrane, it is necessary to check the compatibility of the materials. In general, the materials form a stable membrane if the liquid wets the solid, the liquid is held in the pores by capillary forces, chemical interactions do not cause the polymer material to decompose and the swelling of the polymer is limited. Therefore, several experiments were conducted to evaluate the membrane stability. Although, the producer of the polypropylene supports claims that the material has a pore size of 0.2  $\mu\text{m}$ , after examination, the diameter of the largest pores of membranes used in this study was found to be approximately 4.7  $\mu\text{m}$  with an average of 0.2  $\mu\text{m}$ . The good wettability of the polypropylene supports by pyridinium and pyrrolidinium ionic liquids was proven by means of advancing contact angles. Contact angles increased with the elongation of the alkyl chain length, however, the difference between pyridinium and pyrrolidinium ionic liquids was not noticeable, therefore the effect of the anion structure cannot be estimated. Cosines of the advancing contact angles were all in a range from 0.923–0.949 (Table 2), and the resulting contact angles were 18.4°–22.6°. The hysteresis values were in a range of 6.3°–14.4°. Thus, all ionic liquids used in this study wet the PP support very well and this contributes to the stability of prepared membranes. Good wetting abilities predispose the ionic liquids to cause swelling of the porous support. This effect was estimated based on the membrane thickness over several time periods. The thickness always increased after saturating the support with ionic liquid. The swelling of the polymer results from the diffusion of solvent molecules into the polymer structure. If the intermolecular interactions of the polymer monomers are strong, thanks to cross-linking and crystalline structures or strong hydrogen bonds, the swelling will reach a limit. However, if the interactions between the polymer and the solvent are stronger, “polymer dissolution” can occur [45]. The system strives to achieve a minimum of Gibbs mixing energy,  $G_{\text{mix}}$ , which is the driving force of the swelling process [46]. Swelling disturbs the diffusion of compounds removed during the membrane separation process by extension of the permeation path. Swelling may also result in structural changes in the polymer network and a reduction of the mechanical stability. The thickness of the pristine PP support was  $75 \pm 5 \mu\text{m}$ . After the completion of saturation with ionic liquid, the thickness was measured again after 2, 24, 72 and 120 h. It was observed that the thickness of membrane increased almost immediately after saturation and after 24 h the thickness increase had almost stopped. Elongation of the alkyl chain resulted in higher thicknesses only in the first 2-hour period after saturation. Subsequent measurements gave similar results, and after 120 h, all the membranes reached their final thickness, which was approximately the same in all cases. The average final thickness was  $96.6 \pm 6 \mu\text{m}$ , which was approximately 29% higher than that of the pure support. To evaluate the degree of polymer structure degradation, the resistance to transmembrane pressure was evaluated, and the results are presented in Table 3. The maximum pressure that did not cause mechanical damage of the membrane decreased with elongation of alkyl chains. This is probably due to increases in the hydrophobicity of ionic liquids resulting in stronger interactions with the polymer [47]. Substitution of the [Tf2N] anion with [TfO] resulted in a decrease in the mechanical stability of the membrane. The impact of temperature is highly important. Increasing of temperature causes decreases of the safe pressure. Interestingly, the decrease in mechanical stability was significantly greater for pyridinium ionic liquids, with an average of approximately 11.5 kPa, whereas the pyrrolidinium ionic liquid was in a range of 6.37–8.71. The reason is probably the greater molar volume expansivity of the pyridinium ionic liquids. However, we had trouble finding data for the volume expansivity of all the ionic liquids used in this study.

#### 3.3. Partition coefficients

The solubility of the toluene in ionic liquids was examined. The molar ratio of toluene in the IL was slightly lower for pyrrolidinium ILs, with values of 0.73 and 0.79, respectively, for [C4Pyr][Tf2N] and [C6Pyr][Tf2N]. The solubility in [C4Py][Tf2N] and [C6Py][Tf2N] was 0.75 and 0.81, respectively, and 0.68 in [C4Pyr][Tf2N]. These results are in

agreement with the ionic liquids structure, and the more aromatic pyridinium ILs were better solvents for toluene as was confirmed in further examination of partition coefficients. The partition coefficients of toluene in a gas/liquid system presented in Fig. 3 prove the high solubility of toluene in the ionic liquids used in this study. The partition coefficients for the pyridinium ILs were found to be close to that obtained for their imidazolium equivalents in previous studies [40]. This agrees with the findings of Arce et al., who studied the effect of the cation nature on the solvent properties for the extraction of aromatic hydrocarbons. They detected no significant differences in solute distribution ratios when comparing systems with 1-ethyl-3-methylimidazolium bis{(trifluoro-methyl)sulfonyl}imide [C2mim][Tf2N] and 1-ethylpyridinium bis{(trifluoro-methyl)sulfonyl}imide [C2Py][Tf2N], according to structural similarity of those ILs and the resulting analogous interactions with the hydrocarbons [48]. We noticed that replacement of [Tf2N] with the [TfO] anion results in a higher partition coefficient and thus lower solubility. This result is in agreement with the effect observed for imidazolium ionic liquids [40] in accordance to decreases in the anion hydrophobicity. It was also noted that elongation of the alkyl chain in the cation structure increases the solubility of toluene, which is consistent with literature [49]. However, when considering the impact of temperature, the intensity of the effect is different for pyridinium and pyrrolidinium ILs. For pyridinium ionic liquids, in lower temperatures, the partition coefficient decreased drastically with alkyl chain elongation, even by 102%; in higher temperatures, this effect decreased to approximately 39%. For pyrrolidinium ionic liquids the effect was the opposite: at lower temperatures the partition coefficients were approximately 40% lower, and the difference increased to 104% at 318 K.

### 3.4. Single gas permeability

To determine the selectivity during toluene/N<sub>2</sub> separation, experiments on pure nitrogen permeation were conducted. The solubility of nitrogen in ionic liquids has been found to be very poor [50] and the resulting permeability was also very low, which in case of separating of toluene from N<sub>2</sub> is highly desirable. In Figs. 4 and 5 the nitrogen permeability is presented for the pyridinium and pyrrolidinium SILMs, respectively. Elongation of the alkyl chain resulted in lower nitrogen permeability, as the solubility of nitrogen is low in all ionic liquids used in this study this is mainly the result of increasing viscosity resulting in higher diffusion resistance. The highest permeability of nitrogen was observed in [C4Py][Tf2N] which had the lowest viscosity. In the case of pyrrolidinium ILs, substitution of the anion to [TfO] caused a decrease in nitrogen permeability, which is in agreement with the higher viscosity and contrary to the imidazolium ionic liquids, where the [TfO] based ionic liquids had higher permeation for the more viscous [C4MIM][TfO] due to higher N<sub>2</sub> solubility [40]. A high selectivity of toluene separation from the stream is desirable, therefore nitrogen permeation should be as low as possible, and among the pyridinium and pyrrolidinium ILs, the latter are preferable in this regard.

### 3.5. Toluene permeability through SILMs

Toluene was chosen as it is often found in exhaust air and is representative of aromatic volatile organic compounds [18,51]. The permeation of toluene in liquid membranes based on ionic liquids was determined at several temperature points. Temperature increases resulted in linear toluene permeability increases (Figs. 6 and 7). Considering ionic liquids based on the same anion, the permeation increased with alkyl chain elongation, which is in agreement with the partition coefficients despite the increasing viscosity. On the basis of two key factors that have an influence on the process, that is the diffusion in the form of resistance resulting from the viscosity of the membrane liquid and the solubility expressed by the partition coefficient, it can be assumed that the pyridinium ionic liquids are more suitable for separation than the pyrrolidinium ionic liquids used in this study. On the other hand, regarding the selectivity of separation, pyrrolidinium ionic liquids are more appropriate according to their lower nitrogen permeability. Considering [Tf2N]-based ionic liquids, with 6 carbon atoms in their alkyl chain, the partition coefficients are very close, and the permeability was similar at lower temperatures. It can be concluded that at lower temperatures, toluene solubility factor predominates over diffusion; however, at some point (289.6 K), the situation changes and diffusion takes the lead over solubility. Therefore, the toluene permeability increase was higher in pyridinium based SILMs than in pyrrolidinium SILMs. In the case of 4 carbon atoms, this point was found at 314.69 K (see Fig. 8). In regard to the alkyl chain length, the permeation increases were observed due to the higher hydrophobicity and lower partition coefficients (Table 4). It was observed that nitrogen permeability was close to the values reported for imidazolium ionic liquid membranes [52] and was still very low according to the low solubility, which was confirmed by Anderson et al. [53] and Blath et al. who determined the N<sub>2</sub> Henry's constant of 1086 bars for n-hexylpyridinium bis(trifluoromethylsulfonyl) imide [54] and pointed out the difficulties with measuring the solubility of gases with low solubility and resulting in inconsistent data. There is a gap of data and information in the literature on the solubility and permeation of both nitrogen and toluene in pyridinium and pyrrolidinium ionic liquids. Anderson et al. studied gas solubilities in 1-hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide and found with high uncertainty that the Henry's constant of nitrogen is  $3390 \pm 2310$  bars [53]. Mahurin et al. studied the gas separation properties of pyridinium and pyrrolidinium based ionic liquids with benzyl substituents and [Tf2N] anions and found that the N<sub>2</sub> permeability was between 10 and 21.9 barrers at 298 K [55]. Nitrogen permeation was also studied using hollow fibre polydimethylsiloxane membranes. Leemann et al. used 100–160 fibres 250 mm in length, and the permeability was found to be from 250 to 850 barrers [56], however the vacuum at the permeate side was applied rising the driving force.

Yeom et al. studied N<sub>2</sub> permeation using polydimethylsiloxane membranes and obtained values of approximately 200 barrers, [57]. This confirms there is higher N<sub>2</sub> permeation in polymer membranes than in SILMs; therefore, the latter have higher potential in regard to selectivity. Yeom et al. also studied the permeation of chlorinated VOCs (methylene chloride, chloroform, 1,2-dichloroethane, and 1,1,2-trichloroethane), with results in the range of 200 to 1000 barrers at 318 K [57], which is noticeably lower than the results obtained in this study. They managed to remove up to 54% of the VOCs from the initial stream that contained from 0.3 to 1.5% vol. of toluene [58]. Permeation values of 1000 barrers and performance



obtained by Yeom et al. using PDMS membranes seem to be feasible [57], as opposed to authors whose results reached 200,000 barrers [56], such values put doubt in the quality of the membrane material. Toluene separation process using polymeric membranes was also studied by Feng et al., they used poly(ether imide) membrane with a feed vapour mole fraction of 0.02 the toluene permeation flux was approximately  $3.8 \cdot 10^{-8}$  mol/m<sup>2</sup> sPa at 296 K and permeate pressure 0.18–1.1 kPa [59]. The driving force of that process was much higher than that applied in this study. In this study, the vapour mole fraction was approximately  $1 \cdot 10^{-4}$ , and the pressure difference over the membrane was approximately 15 kPa, and still the removal rate reached 85% in spite of the very low concentration and pressure difference that was used. Lue et al. obtained toluene removal efficiencies from 50 to 78%, but the diffusion coefficients were upwards of  $8 \cdot 10^{-10}$  m<sup>2</sup>/s [60], whereas in this study the values were slightly higher, upwards of  $3 \cdot 10^{-9}$  m<sup>2</sup>/s. High toluene removal was also obtained by Heymes et al. who utilized an absorption – pervaporation system with di(2-ethylhexyl)adipate [61], but the concentrations were significantly higher, as well as the amount of absorbent needed for the process. The advantage of the liquid membrane over the technique proposed by Heymes et al. is the very low quantity of absorbent and low energy consumption. VOC permeation was mainly studied in solid polymer membranes; however, contradictory effects have been reported. Leemann et al. provided data on decreases in toluene permeability with increasing temperature [56], whereas Feng et al. reported the opposite effect [59]. The results found in the literature on the separation of toluene from the gas phase present mainly data on flat sheets or hollow fibre polymeric membranes; data on liquid membranes mostly include imidazolium ionic liquids or deal with separation from the liquid phase. Therefore, the data available in the literature enable a reliable comparison with the results included in this work. First, due to the different membranes and membrane systems. Second, due to significant differences in the process conditions, i.e., mainly the pressure and concentration of the component in the feed stream, which eventually lead to the questionable reliability of the results in some cases. The results of this study indicate that the permeability increases with temperature according to increases in the mobility of the solute in the membrane phase up to  $6.23 \cdot 10^{-13}$  mol·s/kg. The selectivity for toluene separation was always higher for ionic liquids with longer alkyl chains. Higher selectivity corresponds to lower operating costs and a smaller apparatus. Toluene separation was more efficient using [C6Py][Tf2N] and [C6Pyrr][Tf2N] than using their 4 carbon atom equivalents, which means that elongation of the alkyl chain results in an increase of the selectivity and researchers stated similar conclusions for liquid extraction processes [30]. However, considering that the 4- carbon atom ILs had higher selectivity for the pyrrolidinium ionic liquids. In cases of ILs with 6 carbon atoms, the selectivity was higher for pyrrolidinium up to 298 K, and at higher temperatures pyridinium performed better. This is the point at which the diffusion effect is more influential than the solubility effect, and the slope of permeation/ temperature for pyridinium is higher than for pyrrolidinium.

#### 4. Conclusions

Ionic liquids have applications in many chemical fields, especially in separation processes due their negligible volatility and high sorption capacities. Supported ionic liquid technologies are one of the most used systems due to the low volume of solvent needed. However, development of SILMs with good separation performance requires a proper support and membrane phase. Several issues must be taken into consideration when choosing a proper system, like the stability resulting from the compatibility of membrane components and the resulting swelling and the solubility and diffusivity of all the compounds present in the purified stream. Experiments revealed that the effectiveness of the separation process is highly dependent on the solvent properties of the ionic liquids used and the selection of the membrane phase needs to be done experimentally to optimize the impact of the diffusion factor and the solubility factor. Both pyridinium and pyrrolidinium have potential for separating toluene from gas streams, and permeation values were in a range of 637–2034 barrers and according to the low permeability of nitrogen, the selectivity towards separation from another gas like air is very promising

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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**Appendix A.** Supplementary data Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2019.112091>.

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