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Applications of Ionic Liquids in Gas Processing

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Abstract

Over the last decade ionic liquids have grown from relatively poorly understood materials to become integrated into industrial applications. These materials are, quite simply, comprised entirely of ions, and are liquid at room temperature. Given their nature, they have been described as “designer” solvents, with “tuneable” features that can be adjusted to suit the requirements of a particular process. A huge interest in using ionic liquids as an alternative medium for gas separation has become apparent because of such properties. For example, the high thermal stability of ionic liquids provide considerable potential to utilize them for CO₂ capture application. This paper investigates the potential of ionic liquids in gas processing applications. Initial screenings of the ability of ionic liquids for CO₂ separation up to 100 bar are presented.

Keywords: ionic liquid, CO₂ absorption, high pressure.

1. Introduction

During the last decade, ionic liquids have been transformed from poorly understood materials to the focus of many research activities, both in academic research and industrial applications¹. A huge interest in using ionic liquids as an alternative medium for CO₂ capture has become apparent because of its potential advantages compared to other conventional solvents, such as MEA². There are many ways in which an ionic liquid can be defined, and perhaps the most widely accepted definition is, “*A material that is composed solely of ions*”². Ionic liquids are a very versatile class of solvents, due to their unique characteristics, such as the ability to manipulate and tune their physicochemical properties through cation or anion selection³, non-volatility under ambient conditions, high thermal stability, as well as high CO₂ solubility, may overcome many of the problems associated with current CO₂-removal techniques⁴. It is also very important to note that ionic liquids are not solutions of ions in water, or other solvents.

Aqueous amine scrubbing (MEA, MDEA) is currently the most used technology for CO₂ capture. However, CO₂ capture using MEA, for example, would result in a 28 % energy loss, and therefore double the cost of electricity usage, due to the heat required to regenerate used aqueous MEA solutions⁵. Ionic liquids offer the possibility of reducing the energy demand for CO₂ stripping during solvent regeneration by as much as 16 % relative to aqueous MEA solutions⁶.

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The high thermal stability of ionic liquids provides considerable potential to utilize ionic liquids for CO₂ capture applications. Most ionic liquids are stable to over 300 °C and therefore less likely to degrade *via* oxidation, to react with impurities or to be corrosive⁷. And because ionic liquids have negligible vapor pressure, this creates a possibility of ionic liquids regeneration over a wide range of temperatures and pressures. Thus, this offers a new opportunity for process optimization that is not achievable using traditional aqueous liquid capture media.

One of the biggest drawbacks to the large scale use of ionic liquids in CO₂ capture is their higher cost compared to the conventional solvents they are proposed to replace⁸. However, “by reducing or eliminating process losses through thermal degradation, oxidative or chemical destruction and vapor loss, the amount of solvent needed for the process may be greatly reduced”¹. In addition, ionic liquids are synthesized at Qatar University from commercially available, cheap starting materials in order to reduce the cost of ionic liquids production. These will all help to counterbalance the apparent economic disadvantage of the ionic liquids, especially in industrial applications.

2. Methodology

2.1. Synthesis of Ionic Liquids

1-Bromoethane (55.0 cm³; 0.505 mol; b. pt. 38.4 °C) and toluene (20.0 cm³) were added drop wise to 1-methylimidazole (41.0 cm³; 0.499 mol) in a round-bottomed flask equipped with a stirring bar. The reaction mixture was stir-heated at 60 °C under a reflux condenser and maintained at this temperature for 3 h with stirring. A biphasic mixture was formed with a light yellow color in the upper layer and a slightly darker yellow in the lower layer. The mixture was transferred to a separating funnel where the bottom layer, which contained [C₂mim]Br and an excess of 1-bromoethane, was collected into another round-bottomed flask. The separated lower layer was then washed with hexane (3 x 50 cm³) in order to remove the excess of unreacted 1-bromoethane from the product before the hexane was removed under vacuum. The remaining viscous yellow liquid was then dried *in vacuo* at 80 °C for 15 h, at which point it solidified to yield a yellowish solid.

The bromide ionic liquid was dissolved in distilled water (200 cm³), and then transferred into a conical flask (500 cm³) equipped with a stirring bar. A slight excess of lithium bistriflamide was weighed (57.56 g; 0.201 mol) in a beaker, dissolved in distilled water (100 cm³), and then poured into the conical flask. The mixture was left to stir for 2 h at room temperature. A biphasic layer was formed, with a clear upper layer (aqueous layer) and yellow bottom layer (bistriflamide ionic liquid) respectively. The upper layer was decanted, and the bottom yellow layer was then transferred to a separating funnel. It was then washed with water (4 x 100 cm³). The bottom yellow layer was collected from the separating funnel and was left to dry for 15 h under high vacuum at 80 °C to remove any traces of water. The product was obtained as a yellow liquid.

These procedures were then repeated for the synthesis of [C₄mim][NTf₂] by replacing 1-bromoethane with 1-bromobutane, in the alkylation reaction with 1-methylimidazole.

2.2. CO₂ Solubility Measurements

Both ionic liquids synthesised with be tested for their ability for CO₂ absorption up to 100 bar, as described in details by Karadas *et al.*⁹. Measurements were performed using the high-pressure magnetic suspension balance (MSB) sorption device by Rubotherm

Präzisionsmesstechnik GmbH apparatus. This equipment is specially designed to measure sample mass change with high precision upon CO₂ absorption under high pressure and raised temperature. The CO₂ absorption in [C₂mim][NTf₂] and [C₄mim][NTf₂] were performed at both 46 °C and 66 °C, in order to mimicked the well-head temperature here in Qatar. The results are shown in Figure 4.

3. Results and Discussion

The large demand for ionic liquids has resulted in further development of their synthetic protocols, allowing large scale production of ionic liquids which are of consistently high purity while minimizing time and cost. With so many combinations of ionic liquids, it is very hard to generalize one synthetic protocol that is applicable for the synthesis of all ionic liquids. The synthetic routes used to prepare ionic liquids are varied. Here, the most popular and straight-forward way for the syntheses of [C₂mim][NTf₂] and [C₄mim][NTf₂] *via* alkylation were opted, as depicted in Figure 1. This synthetic protocol can be carried out using any alkylating agent (*i.e.* 1-bromoalkane) to yield bromide ionic liquids. These bromide ionic liquids then undergo an anion-exchange reaction with lithium bistriflamide, to yield the desired bistriflamide ionic liquids. This reaction is very well-known, clean and efficient reaction for the preparation of any bistriflamide ionic liquids ^{3,10}.

Figure 1: Two-step synthetic protocol for the preparation of bistriflamide ionic liquids.

Imidazolium ionic liquids are known to be a remarkable solvent for CO₂ solubility ref. It has been found that anion play the important role in determining the gas solubility in ionic liquids. It has been reported that the bistriflamide anion has the greatest affinity for CO₂ experimentally ¹¹, compared to other anions, such as the halides, triflate ([OTf]⁻), hexafluorophosphate ([PF₆]⁻), tetrafluoroborate ([BF₄]⁻), dicyanamide ([N(CN)₂]⁻) and ethanoate ([MeCO₂]⁻) ¹. Although fluorination effect are shown to have greatly enhanced the solubility of CO₂, these class of ionic liquids are very expensive and are not environmental friendly, due its high stability and low reactivity ¹².

Although the anion is the key factor in determining the physical dissolution of CO₂ in ionic liquids, the cation also plays a role. Despite a wide range of cations reported for CO₂ capture, many research groups have concentrated on imidazolium cation. This is because of the acidic C2 proton from the imidazolium ring can interact with anion

(especially carboxylate anion), to form an unstable carbene, which then coupled with CO_2 molecules, resulting the removal of CO_2 ¹³ (Figure 2).

Figure 2: Proposed mechanism for enhanced CO_2 solubility in imidazolium-based ionic liquids¹³.

Based on these literature reviews, we have decided to perform a simple screening of CO_2 solubility in imidazolium bistriflamide ionic liquids. Two different alkyl chain length on imidazolium were chosen; 1-ethyl-3-methylimidazolium bistriflamide, $[\text{C}_2\text{mim}][\text{NTf}_2]$ and 1-butyl-3-methylimidazolium bistriflamide, $[\text{C}_4\text{mim}][\text{NTf}_2]$. Their chemical structures were shown in Figure 3.

Figure 3: Chemical structure for $[\text{C}_2\text{mim}][\text{NTf}_2]$ and $[\text{C}_4\text{mim}][\text{NTf}_2]$.

The preliminary screening on the ability of these two ionic liquids to absorb CO_2 showed very promising results, at pressure up to 100 bar, as shown in Figure 4. It is also shown that CO_2 solubility are indeed better in $[\text{C}_4\text{mim}][\text{NTf}_2]$ than in $[\text{C}_2\text{mim}][\text{NTf}_2]$ at both 46 °C and 66 °C, as described in the literature. This might be associated with a “free volume” mechanism, where a gas molecule can arrange itself into the free volume of ionic liquids¹⁴.

However, more screening of different classes of ionic liquids, with different combinations of cations and anions are scheduled in order to identify the best system for CO_2 capture in Qatar. Besides, the effects of water content, as well as higher pressure CO_2 measurements (up to 200 bar) are also proposed to be studied. It is also very important to note that the CO_2 solubility measurement in ionic liquids at such high pressure has never been published. This will be the starting point and will be crucial for high pressure CO_2 absorption research in the near future.

Figure 4: CO₂ solubility measurements in both [C₂mim][NTf₂] and [C₄mim][NTf₂] at 46°C and 66 °C.

4. Summary

The use of ionic liquids for industrial application is proven to be possible, despite their reputation of being very expensive. Synthesis of ionic liquids using cheap materials can indeed lower the total operation cost for its application in CO₂ capture in Qatar's oil and gas industry. Preliminary results of CO₂ absorption using [C₂mim][NTf₂] and [C₄mim][NTf₂] showed that ionic liquid are very promising in replacing the conventional technology for CO₂ removal, at both 46 °C and 66 °C, at high pressure (100 bar) . However, more intensive studies have to be performed in order to introduce this future state-of-the-art technology using ionic liquid in the industry.

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