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Synthesis and usage of common and functionalized ionic liquids for biogas upgrading

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ABSTRACT

Halide imidazolium-based ionic liquids 1-butyl-3-methylimidazolium bromide [bmim][Br] and 1-propylamine-3-methylimidazolium bromide [pamim][Br] were synthesised and tested experimentally as absorbents for biogas upgrading. The former solvent is a conventional off-the-shelf room temperature ionic liquid (RTIL), which is soluble in water and expected to have a high CO_2 solubility. The second solvent is a new type of task-specific ionic liquid (TSIL) and has a straight amine-alkyl substitute incorporated to enhance CO_2 solubility. Experimental evidence suggests that the majority of known imidazolium-based ionic liquids are good CO_2 absorbents; adding these to a designed solvent that combines a long amino-alkyl lineal group is expected to improve the performance of CO_2 absorption over other alternatives under discussion.

CO_2 absorption experiments were conducted in an absorbing column packed with randomly placed Raschig rings. A biogas model consisting of CO_2 (43% v/v) diluted in N_2 was used to test CO_2 uptake with aqueous solutions of the above-mentioned ILs at 5%, 10% and 15% (w/w) concentrations. The gaseous and liquid streams were operated under concurrent flow with a gas–liquid volumetric ratio of 1:2. Additionally, absorption tests were conducted with aqueous solutions of monoethanolamine (MEA) mixed with the ILs under investigation to elucidate potential activations of these amino solutions. In this experiment, the ILs used for biogas upgrading do not present a higher absorption than amino solutions, and there were no significant synergy results from mixing them with MEA, which could have enhanced the CO_2 uptake.

1. Introduction

The capture of carbon dioxide (CO_2) through efficient and cost-competitive processes has become a major technological challenge for the reduction of atmospheric greenhouse gases. The development of low-emission technology and design of high-performance novel solvents to capture CO_2 by means of standard technology will be a main focus of chemical and process science in the near future [1]. In biogas upgrading, the processes of adjustment of calorimetric and chemical properties by removing CO_2 and undesirable compounds [2] are of interest due to the particularities of the generation and treatment of this biofuel, as well as its potential as a renewable source of energy. Prior experience in removing acid gases (obtained from the petroleum or natural gas industries) has contributed to the existing body of knowledge; however, in some cases, certain aspects have been rendered inapplicable.

Among the state-of-the-art technologies based on chemical absorption to upgrade biogas, the most widely used solvents are alkanolamines, such as monoethanolamine (MEA), diethanolamine (DEA) or methyldiethanolamine (MDEA). These solvents are generally dissolved in water to reduce corrosion problems and to enhance the CO_2 loading and rate of absorption [2,3]. These solutions for the upgrading of biogas, which is normally generated by anaerobic digestion at atmospheric pressure in the 40–60 °C temperature range, are characterised by a high capacity for removal of CO_2 from a crude biogas stream with a typical composition of 40–60% CH_4, 30–45% CO_2, water and other trace compounds [4]. Nonetheless, amino solvents mainly exhibit disadvantages as a result of chemical decomposition (with the consequent loss of CO_2-remotion performance), toxicological impacts for fugitive emissions, and equipment corrosion and high enthalpy of reaction, which makes the process highly energy-intensive for the amino regeneration. This disadvantage is a limiting factor for large-scale applications [5].

Several characteristics have drawn significant attention to ionic liquids (ILs) as an alternative absorption media to traditional

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Nomenclature

Notation of anions

$[Br]^-$	bromide anion
$[BF_4]^-$	tetrafluoroborate anion
$[DCA]^-$	dicynamide anion
$[Me]^-$	methide anion
$[NO_3]^-$	nitrate anion
$[PF_6]^-$	hexafluorophosphate anion
$[TfO]^-$	trifluoromethanesulfonate anion
$[Tf_2N]^-$	bis(trifluoromethylsulfonyl) amide anion

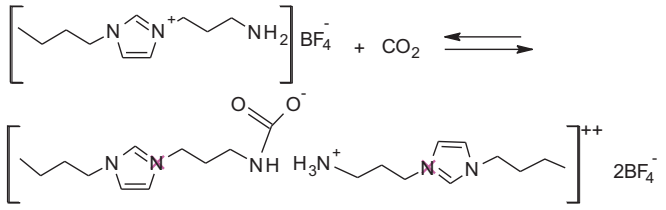
Mathematical abbreviations

C_o	initial carbon dioxide concentration (%)
$C(t)$	carbon dioxide concentration (%)
F_o	volumetric biogas flow ($L\,mim^{-1}$)
m_{CO_2}	mass of carbon dioxide absorbed (g)
m_s	mass of absorbent (kg)
t^{sat}	time of carbon dioxide saturation (min)

solvents [6]: thermal stability, potential high performance for CO_2 uptake and negligible vapour pressure. The low vapour pressure of the ILs prevents the emission of volatile organic compounds, offering a non-contaminated target gas. Additionally, an IL can be designed on a rational basis for a specific application because one can modify either the structure of the cation (using appropriate functional groups to obtain desired properties) or the selection of the anion. This versatility consequently opens a large group of potential alternative solvents.

The most frequently investigated room temperature ionic liquids (RTILs) are the alkyl-substituted methyl-imidazolium-based ILs, which are relatively easy to synthesise from commercial chemicals. A generally accepted acronym for this cation is [C_n-mim], where n represents the number of the carbons in the aliphatic chain [7].

Because the combinations of known cations and anions number is in the millions, the creation of a strategy is required for the rational design and selection of ILs for particular applications. Bates et al. [8] applied a task-specific concept to synthesise an IL specifically designed to capture CO_2. This task-specific ionic liquid (TSIL) was [pabim][BF_4], and an absorption reaction for CO_2 capture through an intermediate carbamate formation was proposed based on the ^{13}C NMR and FT-IR of gas-treated IL. The proposed reaction was an analogous mechanism for CO_2 uptake by amines [9].



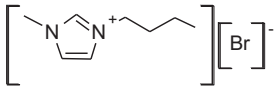
An alternative approach is discussed by Xie et al. [10], who utilised [bmim][Cl] to disrupt hydrogen bonds for the dissolution of the biopolymers chitin and chitosan under suitable conditions. These experiments explored the usage of [bmim][Cl] for CO_2 removal, and it was the first time that the solvent was studied for this application. Feng et al. [11] also applied the strategy of using an IL to improve CO_2 capture; that strategy was executed by blending four different kinds of amino acid ILs with aqueous solutions of MDEA (four in total). The conclusion was that these ILs enhance the absorption rate of CO_2, reinforcing the capacity for capture in the solvent and showing a method for the improvement of commercial solvents. Wang et al. [12] developed an integrated system with a mixture of an alcohol-functionalised ionic liquid and superbases to capture CO_2 under atmospheric pressure, and a favourable effect in increasing the CO_2 absorption ratio was demonstrated.

Although both the cation and the anion play an important role in the CO_2 solubility of imidazolium-based common ILs, experimental information suggests that the largest influence is related to the anion [13]. According to Muldonn et al. [14], CO_2 solubility increases with larger quantities of fluoroalkyl groups in the IL salt for a group of [bmim]-based ILs at 60 °C. The CO_2 uptake increases for the fluoroalkyl groups in the following order: nitrate ($[NO_3]^-$), tetrafluoroborate ($[BF_4]^-$), dicynamide ($[DCA]^-$), hexafluorophosphate ($[PF_6]^-$), trifluoromethanesulfonate ($[TfO]^-$), bis(trifluoromethylsulfonyl) amide ($[Tf_2N]^-$) and tris(trifluoromethylsulfonyl) methide ($[Me]^-$). This is represented by the following:

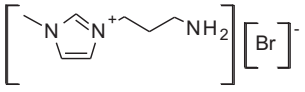
$$[NO_3]^- < [BF_4]^- < [DCA]^- < [PF_6]^- < [TfO]^- < [Tf_2N]^- < [Me]^-.$$

The cation plays a relatively less important role on CO_2 solubility [14], although it can be favoured by an alkyl group attached to the aromatic ring. For the homologous series of ILs [emim][PF_6], [bmim][PF_6] and [hmim][PF_6], higher CO_2 solubility is obtained for larger numbers of carbon atoms in the alkyl chain [15–18].

Considering the experimental evidence previously discussed, the IL with the largest number of carbon atoms n in its alkyl chain should have better CO_2 uptake capacity when two [C_n-mim]-based ILs with the same anion are compared. Furthermore, if a terminal amino group can be attached to this alkyl chain, CO_2 uptake might be improved compared to those ILs that have only an aliphatic chain because the amino group yields a zwitterion after absorption of CO_2 [19]. Assuming that an anion like bromide plays a relatively smaller role in CO_2 solubility and accounting for a comparable effect of anions (such as $[TfO]^-$, $[Tf_2N]^-$ or $[Me]^-$), a noticeable enhancement of CO_2 uptake capacity by [pamim][Br] in comparison with [bmim][Br] should be expected for biogas upgrading. Both ILs have an analogous chemical structure; they have the same number of atoms in the organic chain attached to the aromatic ring and almost identical molecular weights. The unique distinguishing difference between the two ILs is the amino group.



[bmim][Br]



[pamim][Br]

Imidazolium-based ILs exhibit a high viscosity (above 200 mPa) [11], which may increase the level of complexity of chemical operation processes in industrial-scale applications. Moreover, there is evidence that the viscosity of amine-based ILs is affected by CO_2 absorption [20–22]. The viscosity increases when CO_2 is absorbed. Although this drawback has been discussed in literature, there is little information on the use of ILs in packed systems for CO_2 absorption. In these systems, the viscosity of the absorption media becomes a limiting factor in the mass transfer and therefore in the separation. This is highly relevant, considering that packing columns offer well-known advantages in comparison with other contact systems and a high efficiency of separation [23].

The objective of this research is to determine the feasibility of using the ILs [bmim][Br] and [pamim][Br] as potential absorbents for biogas upgrading in packed systems. The theoretical superiority for CO_2 uptake of the task-specific IL was evaluated. A secondary objective is to evaluate a potential synergism for CO_2 absorption by mixing an MEA-aqueous solution and these ILs.