

SOLVENT PROPERTIES OF FUNCTIONALIZED IONIC LIQUIDS FOR CO₂ ABSORPTION

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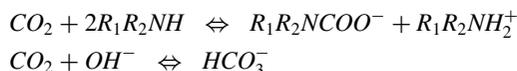
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Ionic liquids can be used as solvents for gas absorption operations in order to improve the process economy and general efficiency of gas separations. This work investigates solvent properties of ionic liquids and compares them to amine solutions used for absorption of carbon dioxide (CO₂). The CO₂ solubility into imidazolium-based Room Temperature Ionic Liquids (RTILs) was measured at temperatures between 298 and 363 K and pressures up to about 1 MPa. The study includes measured values of physical properties such as density and viscosity of the RTILs investigated. The results have shown a remarkable influence of the bulk physical properties of the solvent on the gas absorption rate. The absorption into amine solutions is faster than in ionic liquids at given temperatures due to the relatively high viscosity values of the RTILs. However, the very low vapour pressure and “design character” of the ionic liquids give considerable advantages as a solvent compared to amine solutions. It was possible to increase the ionic liquid volumetric gas load almost threefold by attaching functional groups to the ionic liquid, whereas for the traditional amine solutions the maximum gas load is stoichiometrically limited.

KEYWORDS: CO₂ absorption, Functionalized Ionic liquids, Solvent properties, ILs

INTRODUCTION

Chemical and physical absorption processes are extensively used in the natural gas, petroleum, and chemical industries for the separation of CO₂^[1]. Aqueous solutions of primary, secondary, tertiary, hindered amines and formulated amine mixtures are among the solvents for CO₂ chemical removal. Hindered amines are often used for selective H₂S removal from streams containing both H₂S and CO₂. The primary amines [scheme 1], especially monoethanolamine MEA, are the most common active agents of the solvents for acid gas scrubbing^[2]. About 75–90% of the CO₂ is capture using a MEA-based technology, producing a gas stream of high CO₂ content (>99%)^[3].



Scheme 1. Reaction mechanism for primary and secondary amines aqueous solution^[4].

The use of mixed amines as a solvent improves the performance of acid gas removal units since a given mixture is designed for the specific gas stream composition. This amine

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blend became a task specific gas treating solvent, applied in selective removal of H₂S in presence of CO₂, bulk separation CO₂ from oil recovery gases, and natural gas treatment^[5,6]. However, there is still a strong incentive for the development of low cost and efficient alternatives. The major drawbacks of the traditional gas absorption separation processes are mainly caused by the nature of the solvent, and the type of interactions given between the solute and the solvent. In an industrial gas absorption process it is desirable to achieve fast absorption rates and high solute capacity into a solvent that is easily regenerated and volume make-up is minimized.

Ionic liquids have been used as reaction media, in separation^[7,8,9] and extraction processes^[10] and furthermore, these seem suitable for being use as a solvent in gas absorption^[11,12].

Ionic liquids (ILs) are organic salts, which generally consist of a large organic, bulky asymmetric cations, such as: pyridinium, imidazolium, or phosphonium ions and either an inorganic anions such as Cl⁻, BF₄⁻, PF₆⁻, CF₃SO₃⁻, NTf₂⁻ or organic anions such as RCO₂⁻^[7], [Table 1]. The melting points of these organic salts are frequently found below 150 °C^[13], and occasionally as low as -96 °C.^[14] This implies the character of being liquid at room temperatures. Some ionic liquids are stable up to 500 K^[15].

The nature of the cation and the anion determines the physical and chemical properties of the ionic liquid. Therefore, it is possible to achieve specific properties by choosing the proper combination of a cation and an anion as effect of the existing dependence between the properties and the constituent ions of ionic liquids^[11].

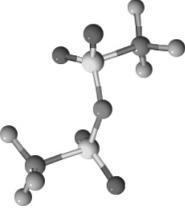
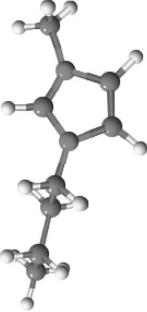
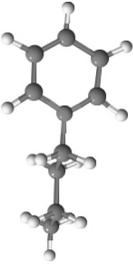
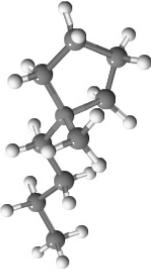
The potential of the room temperature ionic liquids for replacing the traditional solvents is attributed to their singular characteristics, among these are: Low vapor pressure^[17], wide range of polarities^[18,19], high thermal resistance^[7,16,17,18], and its special feature often referred as “designer character”. This is a special quality, considered as a property itself, which can be described as the ability of attaining a desired property by changing the ions structure, replacing either cation or anion, and also by attaching new functionalities to any part of the ionic liquid^[18].

In this work the solvent properties of ionic liquids are investigated and compared with the properties of the traditional aqueous amine solvents used for CO₂ absorption. Solubility measurements of carbon dioxide into various imidazolium-based ionic liquids were carried out and the results of this absorption were compared with the results given using aqueous amine solutions.

The ionic liquids used in this study were: 1-*n*-butyl-3-methylimidazolium tetrafluoroborate, [bmim]⁺[BF₄]⁻ and 1-*n*-butyl-3-methylimidazolium dicyanamide, [bmim]⁺[DCA]⁻; and the following four functionalized ionic liquids:

- Two amine appended imidazolium paired with tetrafluoroborate:
 - with a primary amine [Am-Im]⁺[BF₄]⁻
 - with a tertiary amine [3Am-Im]⁺[BF₄]⁻
- One hydroxyl functionalized cation paired with tetrafluoroborate [OH-Im]⁺[BF₄]⁻
- One primary amine functionalized cation paired with dicyanamide anion [Am-Im]⁺[DCA]⁻

Table 1. Anion and cation structures. Atoms coloured as: ●B, ●F, ●N, ●C, ●O, ●S, ●H

Anion			
	Tetrafluoroborate	Dicyanamide	Bis(trifluoromethylsulfoni)imide
Cation			
	1-Butyl-3-methylimidazolium	1-butyl-pyridinium	1-butyl-1-methyl-pyrrolidinium

EXPERIMENTAL

Samples of $[\text{bmim}]^+[\text{BF}_4]^-$, $[\text{bmim}]^+[\text{DCA}]^-$ were purchased from Merck and used as received. The functionalized ionic liquids were synthesized at Shell laboratories and used without further purification. Carbon dioxide was obtained from Praxair, with a purity of 99.996%, water content lower than 10 ppmv. Ethanolamine (99%) was purchased from Acros Organics and tetraethylenglycol ($\geq 97\%$) from Fluka.

Physical properties as density, viscosity and surface tension of the solvents were measured. The density and viscosity values were further used in the calculation of gas solubility and kinetic parameters. The density was measured with a density-meter Anton Paar DMA 5000, repeatability $1 \times 10^{-6} \text{ g}\cdot\text{cm}^{-3}$, and $0.001 \text{ }^\circ\text{C}$, at atmospheric pressure, and an standard deviation (STD) of $1.4 \times 10^{-6} \text{ g}\cdot\text{cm}^{-3}$. The determination of viscosity was carried out in an Ubbelohde viscosimeter placed in a heated water bath and argon gas was previously flushed trough the set up, STD 6 m Pa.s. The surface tension values were obtained using the ring method, with a tensiometer Kruss K11. The STD remained around $0.4 \text{ mN}\cdot\text{m}^{-2}$.

The CO_2 solubility measurements were performed in an Intelligent Gravimetric Analyzer (IGA 003 Hiden Analytical), at temperatures ranging from 298 to 363 K and pressures up to about 1.2 M Pa. The ionic liquid was loaded in the gravimetric microbalance, dried and degassed at 343 K and 10^{-2} Pa , using a vacuum pump (Baltzers TCP 121) for a period of minimum of 12 hours. The temperature of sample was kept constant with a regulated external thermostat bath (Julabo F25 MW) filled with oil, which was coupled to a jacket of both sample and counter side of the gravimetric balance; A more detailed description of the set up can be found in reference [20]. Once the sample was dried the experimental temperature and the sample mass were constant, CO_2 was introduced up to the desired pressure and the increment on weigh was monitored until the ionic liquid and the gas seemed to have reached equilibrium, when no further weight change was observed throughout time. The time required for reaching equilibrium at each pressure level strongly depended of the nature of the ionic liquid. Intervals between 8 and more than 48 hours were observed. In the solubility calculations the buoyancy effects were accounted for.

BULK PROPERTIES

The density of the ionic liquids used is higher than the water density and decreased linearly with an increase in temperature, as it is plotted in Figure 1. Additionally, it was observed that a rise in temperature caused a remarkable reduction in the ionic liquids viscosity. However, the viscosities of the RTILs are relatively high compared to traditional solvents and water. The large differences in viscosity can be seen in Figure 2, where the viscosity of one of the tested ionic liquids, $[\text{bmim}]^+[\text{BF}_4]^-$, is compared to the viscosity^[21,22] of an aqueous solution of 15% MEA, a common solvent in CO_2 absorption. The measured viscosity of $[\text{bmim}]^+[\text{BF}_4]^-$ at 303 K (79.5 m Pa.s) was almost 65 times higher than the viscosity of an aqueous solution of 15% MEA at the same temperature. Lines were plotted as a view aid in the figures.

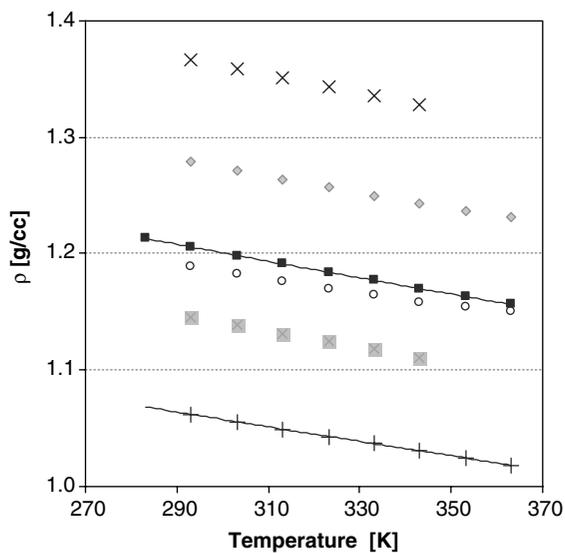


Figure 1. RTILs density as function of temperature ■ $[bmim]^+[BF_4]^-$, + $[bmim]^+[DCA]^-$, ◇ $[Am-Im]^+[BF_4]^-$, × $[3Am-Im]^+[BF_4]^-$, × $[OH-Im]^+[BF_4]^-$, ○ $[Am-Im]^+[DCA]^-$

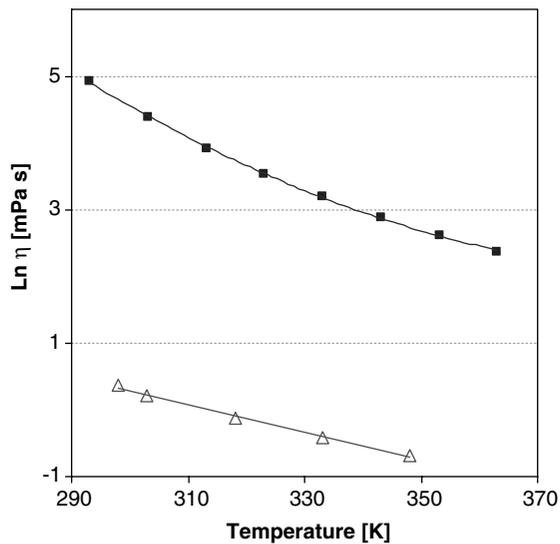


Figure 2. Viscosity of $[bmim]^+[BF_4]^-$ and MEA 15% Own data: ■ $[bmim]^+[BF_4]^-$ Data from [21] and [22]; △ MEA 15%

The surface tension of the screened Ionic liquids decreased slightly with an increment in temperature. The measured values for $[\text{bmim}]^+[\text{BF}_4]^-$ varied from 44.6 to 40.3 $\text{mN}\cdot\text{m}^{-1}$, when temperature was increased from 293 to about 360 K, while the surface tension of water decreases from 71.8 to 62.2 $\text{mN}\cdot\text{m}^{-1}$ for an identical range of temperatures.

CO₂ ABSORPTION

The absorption isotherms were obtained from the experiments conducted in the gravimetric balance. Considering the non-volatile character of the ionic liquids, it was assumed that the RTIL samples remained liquid during the whole experiment and, hence, the gas phase was assumed to be pure. Additionally, it was verified that the mass of the ionic liquid samples at the end of each experiment was the same as the mass initially loaded. The CO₂ solubility in terms of mole fraction was plotted as a function of the gas pressure with mole fraction defined as number of moles of CO₂ as a proportion of the total number of moles in the solution.

The obtained CO₂ solubility results were reproducible and comparable with reported values found in literature^{[12][23]}, as is shown in Figure 3. The CO₂ solubility into the tested non-functionalized ionic liquids at 303 K and 345 K is depicted in Figure 4. The deviations in mole fraction were smaller than 0.01 for the solubility data

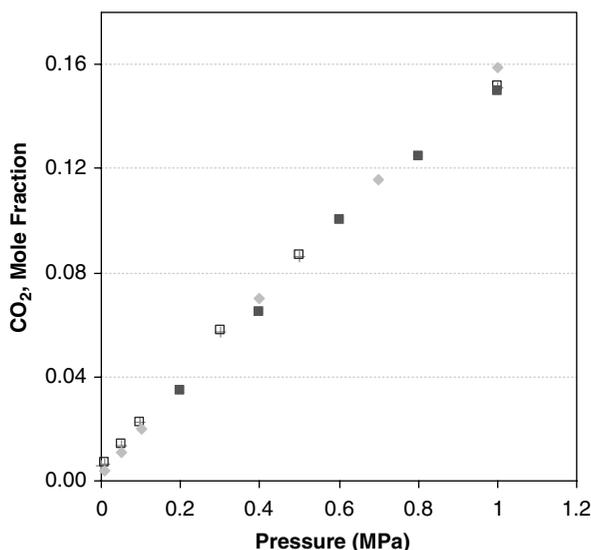


Figure 3. CO₂ solubility in $[\text{bmim}]^+[\text{BF}_4]^-$, at 298 K Own measurements: ■, + Data from: ■ Ref. [12], ◇ Ref. [23]

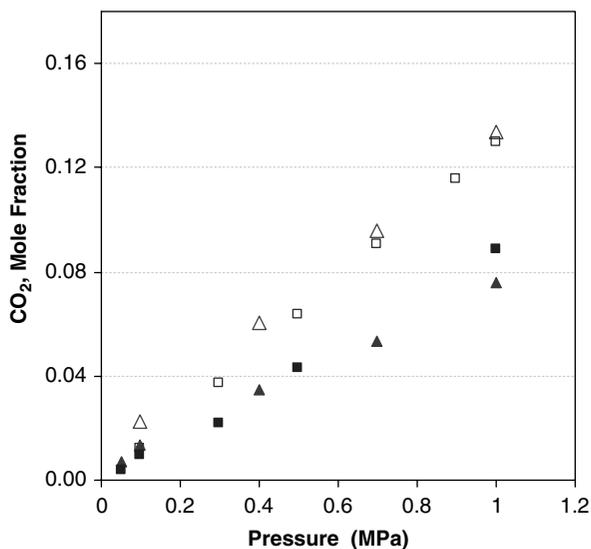


Figure 4. CO₂ solubility in non-functionalized RTILs [bmim]⁺[BF₄]⁻: □303 K, ■344 K [bmim]⁺[DCA]⁻: △ 303 K, ▲ 345 K

sets. CO₂ absorption increased with a rise in pressure and decreased when temperature was raised, for both [bmim]⁺[DCA]⁻ and [bmim]⁺[BF₄]⁻. CO₂ absorption at temperatures higher than 353 K was outside of the measurement limits of the equipment.

The ionic liquid samples were easily regenerated overnight by heating the CO₂ loaded RTILs up to around 353 K. The regeneration temperature was dependent on the ionic liquid type, on the vacuum pressure (10² Pa) and the regenerated liquid was used for carrying out further absorption experiments. It was observed that results obtained with a regenerated liquid did not differ from those obtained with a fresh sample.

The functionalized ionic liquids, which are often referred as task-specific ionic liquids, are targeted to improve the performance of a traditional ionic liquid in a given application by means of changes on the constitutive ion structure. In this study, in order to boost the CO₂ solubility in the ionic liquids and considering the reactive role of amine and hydroxyl groups in the chemical CO₂ absorption, functionalized RTILs were synthesized containing an amine or a hydroxyl functional group added to the IL cation structure. The gas absorption into the functionalized liquids improved in contrast with the non-functionalized RTILs, as was expected, although some changes were observed during the determination of the absorption isotherms. The CO₂ absorption into functionalized RTILs considerably needed more time reaching equilibrium at each pressure, especially for the amine containing ionic liquids, where for some samples more than 48 hours was required. Additionally, the viscosity was clearly increasing during the

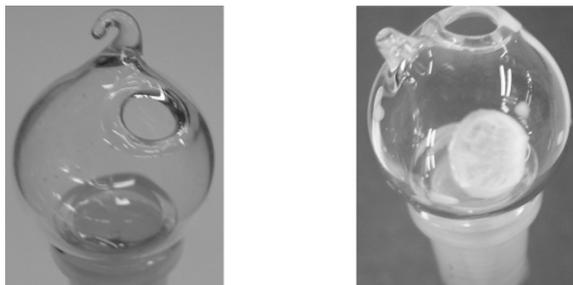


Figure 5. $[\text{Am-Im}]^+[\text{DCA}]^-$, fresh sample (left) and after CO_2 absorption (right)

absorption and it was manifested in changes on appearance and colour observed of the liquid once the measurement was completed, as is shown for $[\text{Am-Im}]^+[\text{DCA}]^-$ in Figure 5. It is likely that changes were a consequence of reactive interactions in the liquid phase resulting in the apparition of new species, possibly a carbamate formation and other bound-ion associations.

The four functionalized ionic liquids were regenerated at vacuum and at 350 K during at least one day. The following absorption experiments were performed with the regenerated samples and reduction in the CO_2 absorption capacity was not observed with exception of $[\text{Am-Im}]^+[\text{DCA}]^-$, where a 10% reduction after three measurements was observed. The CO_2 absorption behaviour of the functionalized ionic liquids remained similar to the non-functionalized ILs for the entire range of temperatures studied. The solubility increased with higher pressures and lower temperatures. The CO_2 absorption into non-functionalized and functionalized ionic liquids at 303 K is compared in Figures 6 and 7, showing the CO_2 absorption for the ionic liquids with dicyanamide and tetrafluoroborate as anion, respectively. The reported solubility results should be corrected for the liquid density changes during absorption, but as a consequence of the dramatic changes in the physical properties of the functionalized ionic liquids, the determination of an accurate value of the liquid phase density is difficult at the current experimental conditions. This fact adds an uncertainty to the measurements.

In general, the addition of an amine functional group improved the ionic liquid absorption capacity. The highest increment in CO_2 absorption was observed with primary amine groups appended to the cation structure for both type of anions, dicyanamide and tetrafluoroborate. In terms of mole fraction, the CO_2 solubility was doubled by the inclusion of a primary amine in the structure of imidazolium-base cations combined with dicyanamide and tetrafluoroborate. A small increment was observed when the tertiary amine was appended to the imidazolium cation paired with tetrafluoroborate and this smaller effect of the functionalization is possibly explained by the lower reactivity of the tertiary amine in comparison with the primary amines and CO_2 . The attached hydroxyl group did not cause any improvement of the CO_2 absorption behaviour in comparison to the ones exhibited by the non-substituted imidazolium tetrafluoroborate ionic liquid.

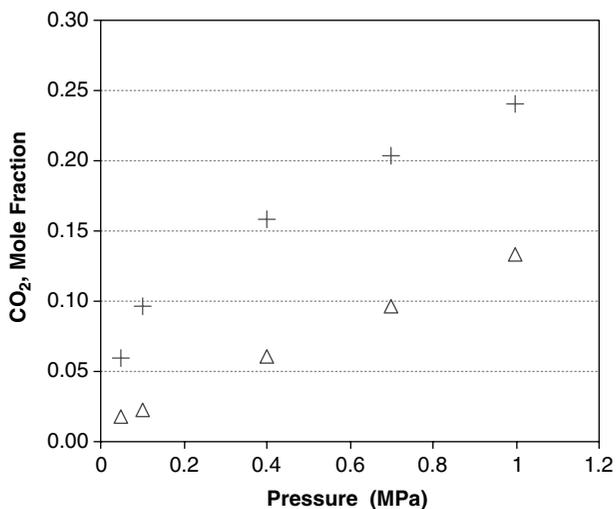


Figure 6. CO₂ solubility in [n-Im]⁺[DCA]⁻, at 303 K △[bmim]⁺[DCA]⁻, +[Am-Im]⁺[DCA]⁻

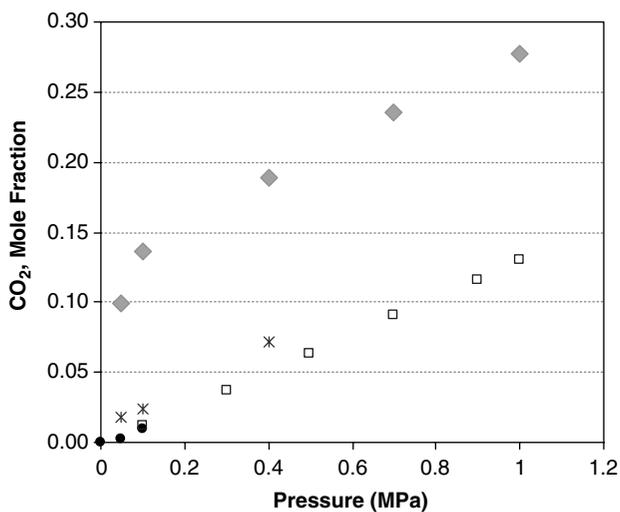


Figure 7. CO₂ solubility in [n-Im]⁺[BF₄]⁻, at 303 K □[bmim]⁺[BF₄]⁻, ◇[Am-im]⁺[BF₄]⁻, * [3Am-im]⁺[BF₄]⁻, ●[OH-im]⁺[BF₄]⁻

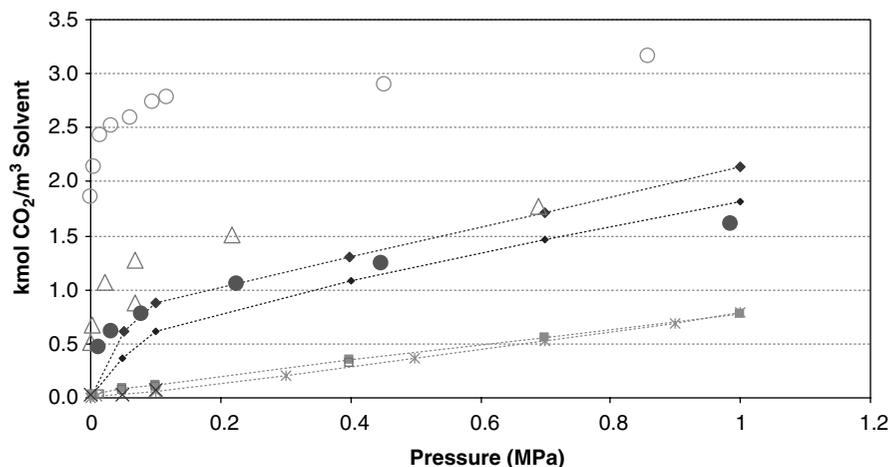


Figure 8. Volumetric solvent CO₂ loads. Dotted lines plotted for view aid purposes. **[bmim]⁺[BF₄]⁻*, ♦*[Am-im]⁺[BF₄]⁻*, □*[3Am-im]⁺[BF₄]⁻*, +*[OH-im]⁺[BF₄]⁻* ■*[bmim]⁺[DCA]⁻*, ▲*[Am-Im]⁺[DCA]⁻*, data for all RTILs at 303 K. ○ MEA 30% at 333 K from [24], △DEA 20% at 323 K from [25], ●MDEA 30 % at 333 K from [24]

In plants operated with MEA, DEA and MDEA the maximum recommended loads vary from 0.4 up to 0.5 moles of acid gas per mol amine, higher loads lead to faster corrosion rates^[26]. Estimated operational loads are at around 2 to 2.5 kmol CO₂·m⁻³ solvent for processes with solvents containing 30% MEA. A comparison of the solvent volumetric gas load between measured ionic liquids at 303 K and reported equilibrium CO₂ loads for primary, secondary and tertiary amines^[24,25] is found in Figure 8.

The CO₂ load for the primary amine substituted ionic liquids was the highest for the selected ionic liquids. However, at pressures higher than 0.5 MPa became interesting that the load of those two liquids still increases with pressure, while the amine solutions load remained at the same level at higher pressures.

CONCLUSIONS

Ionic liquids possess a feature that amine solvents do not have: namely “structural flexibility”. It was possible to change the ionic liquid structure in order to improve its performance as a gas solvent. The CO₂ load of ionic liquids increased almost threefold with primary amine groups incorporated to the ionic liquids structure. The non-functionalized ionic liquids exhibited lower CO₂ loads and the absorption behaviour was similar to physical solvents for CO₂ absorption.

Furthermore, it is a general agreement that a solvent should have a low volatility, be chemically and physically stable and easy to handle. The RTILs have shown very low

vapour pressures and were remarkably recyclable and reusable, contrary to amine solutions, which are volatile and demand a considerable amount of make-up solvent.

The viscosity and other physical properties may well be adjusted by choosing the right substitutions in cation and anions.

Finally, biodegradation and toxicological tests for ionic liquids structures are must still be carried out and the prices of ILs are still a disadvantage compared to the traditional organic solvents.

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