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## Dispelling some myths about the CO<sub>2</sub> solubility in ionic liquids

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Ionic liquids have been objects of extensive research for physical sorption of CO<sub>2</sub> and a number of myths have been perpetuated in the literature, for lack of a critical analysis, concerning their potential for CO<sub>2</sub> capture. This study carries a critical analysis of a number of widely accepted ideas and others not so well accepted that have been repeatedly expressed in the literature concerning the CO<sub>2</sub> physical sorption in ionic liquids. Using the CO<sub>2</sub> solubility in eicosane as benchmark, it will be shown that there is no evidence that ILs display a physical sorption of CO<sub>2</sub> larger than *n*-alkanes when analyzed in adequate concentration units; the fluorination of the ions has no impact on the CO<sub>2</sub> solubility and the oxygenation will marginally contribute to a decrease of the solubility. Ionic liquid-based deep eutectic systems are also shown to have a poor CO<sub>2</sub> solubility. Although these widely used approaches to physically enhance the CO<sub>2</sub> solubility in ILs do not seem to have any positive influence, this does not mean that other types of interaction cannot provide enhanced CO<sub>2</sub> solubility as in the case of the anion [B(CN)<sub>4</sub>] confirmed here by a critical analysis of the published data. The mechanism of CO<sub>2</sub> physical sorption in ionic liquids is discussed based on the results analyzed, supported by spectroscopic measurements and molecular simulations previously reported and further suggestions of possibilities for enhanced physical sorption based on fluorinated aromatic rings, other cyano based anions, mixtures with other ILs or solvents or the use of porous liquids are proposed.

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### 1. Introduction

Ionic liquids have been touted as promising novel solvents for a wide range of potential applications ranging from chemical synthesis and catalysis to engineering fluids and biotechnology.<sup>1</sup> However, few applications in process engineering seem to have attracted more attention than their application as solvents for CO<sub>2</sub> capture processes. A growing body of study has been reported covering attempts at understanding the basics behind the solvation of CO<sub>2</sub> in these fluids<sup>2–11</sup> to the design and economic evaluation of capture processes.<sup>12,13</sup> A number of interesting reviews have been published during the last few years<sup>14–31</sup> addressing various aspects of CO<sub>2</sub> capture processes. However, a number of ideas seem to be propagating between different articles without a proper critical analysis or when doubts have been cast upon some widely accepted ideas they have received little attention from the members of a growing community addressing these studies. This study intends to carry a critical analysis upon a number of widely accepted ideas, and on others not so well accepted, that have repeatedly been expressed

in the literature concerning CO<sub>2</sub> physical sorption in ionic liquids.

The most widespread idea is that ionic liquids are particularly good solvents for CO<sub>2</sub> presenting a very high solvation ability for this gas. A wide body of literature has been addressing the reasons behind this high solubility of CO<sub>2</sub> in ionic liquids.<sup>2–11</sup> Another is that fluorination of either the ionic liquid anion or cation can enhance the CO<sub>2</sub> solubility.<sup>8,18,19,22–24,27,32,33</sup> According to a number of authors, fluorination would, for different reasons adduced by various authors, increase either the interactions between the CO<sub>2</sub> and the ions or decrease the surface tension making the formation of cavities more favourable. Other chemical modifications of the IL have been investigated, such as the oxygenation of the cation chains<sup>34–37</sup> and the use of basic anions,<sup>2,12,38–42</sup> in particular acetate and more recently [B(CN)<sub>4</sub>].<sup>43–45</sup>

While the body of data available for CO<sub>2</sub> solubility in ionic liquids is quite large today, its quality is uneven. Although some critical review of the data is possible for systems for which a large body of data is available ([NTf<sub>2</sub>]-, [PF<sub>6</sub>]-, and [BF<sub>4</sub>]-based ionic liquids mostly) for many others it is quite difficult to evaluate the quality of data published when a very limited set of non-coherent data (or just a single set of data) is available. In this study, we will attempt to validate or dispel some ideas about CO<sub>2</sub> solubility in ionic liquids, making a critical review of the experimental

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data available and using CO<sub>2</sub> solubility in heavy alkanes as a benchmark for CO<sub>2</sub> solubility in ionic liquids. The alkanes were chosen because they are one of the families wherein CO<sub>2</sub> solubility has been most extensively studied and no special interaction between the gas and the solvent has ever been claimed to explain CO<sub>2</sub> solubility in alkanes and therefore it is widely accepted that only dispersion forces are present in these systems.

The approach followed here will start by developing a correlation for CO<sub>2</sub> solubility in alkanes that will serve as a benchmark for the rest of the study and will provide an estimate of the uncertainties in measurements of high pressure gas solubilities. Then, for the ionic liquids, for which a wide body of experimental data is available, a critical analysis of the data is carried out to try to ascertain the uncertainty of the data available in the literature using an approach similar to that reported by the IUPAC Project 202-005-1-100.<sup>17</sup> Finally, a number of widespread ideas about CO<sub>2</sub> solubility in ionic liquids will be evaluated against the benchmark established by CO<sub>2</sub> solubility in alkanes.

## 2. CO<sub>2</sub> solubility in heavy *n*-alkanes

The *n*-alkanes were adopted in this study as the benchmark because the solubility of CO<sub>2</sub> in these compounds is well studied in the literature,<sup>46–48</sup> with data available for a wide range of temperatures, pressures and CO<sub>2</sub> compositions.<sup>49–62</sup> The type of the phase diagrams are well established and, in spite of the CO<sub>2</sub> quadrupole, it is well established that essentially only dispersion forces are responsible for the solvation of the CO<sub>2</sub> molecule in these compounds. The heavier alkanes have a very low vapour

pressure and thus, to a large extent, the gas phase is also formed essentially by CO<sub>2</sub>, as observed in the ionic liquids, and the possibility of having a long homologous series of compounds with a moderately high molecular weight may also, to a fair extent, help us to understand the effect of the increase on the alkyl chain length and molecular weight variations on the gas solubility. Moreover the alkanes are thermally and chemically stable, biodegradable, and can be obtained from petroleum or by Fischer–Tropsch synthesis at a very low cost and so any solvent likely to hold a serious claim for CO<sub>2</sub> capture it is expected to have a performance superior to these compounds.

Most solubility data present in the literature is reported in mole fractions, which is quite useful for thermodynamic interpretations when chemical complexation is present, or for thermodynamic modelling because most models are developed on a molar fraction basis. Nevertheless, for practical process design purposes the important issue is not how much CO<sub>2</sub> can be dissolved in one mole of solvent but in a given amount, a defined volume or mass, of solvent. A comparison of the sorption performance of a solvent based on mole fractions is highly dependent on the solvent molecular weight, as depicted in Fig. 1. This is particularly relevant for ionic liquids because they have very large molecular weights that can vary widely with increasing alkyl chain lengths, fluorination or changes of the anions. Various authors recognized the relation between the molecular weight of the ionic liquids and the CO<sub>2</sub> solubility in them<sup>29,30,63</sup> and thus suggest the use of alternative units to analyze CO<sub>2</sub> solubility in heavy solvents. Because the correlation for the high pressure solubilities to be used in this study is based on that proposed by the IUPAC Project

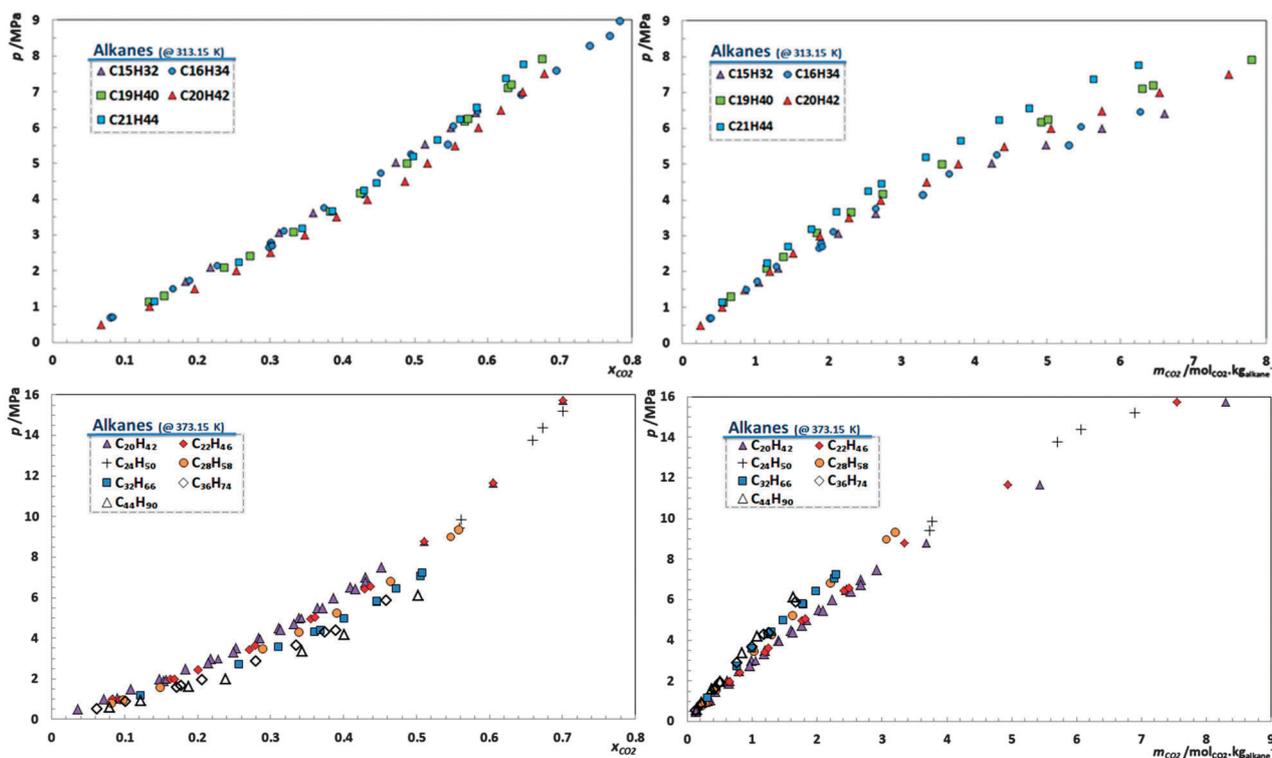


Fig. 1  $p$  vs.  $x_{\text{CO}_2}$  (left) and  $p$  vs.  $m_{\text{CO}_2}$  (right) phase diagrams for the systems alkanes + CO<sub>2</sub> at 313.15 K (top) and 373.15 K (bottom).

2002-005-1-100 (thermodynamics of ionic liquids, ionic liquid mixtures, and the development of standardized systems)<sup>17</sup> where the solubility is expressed in molality, this concentration unit will be used in this study. It has also been suggested by various authors<sup>17,63,64</sup> that expressing the amount of gas dissolved in moles per unit mass of solvent is a sound approach. The alternative adoption of a volumetric basis to express the solubility, suggested by other authors<sup>24</sup> is less effective, not because the all solvents do not possess the same density, but because the density is pressure and temperature dependent and the comparison would thus be less convenient requiring a reference state that depending on the melting point of the solvent would have to be hypothetical.

The pressure composition phase diagrams of CO<sub>2</sub> solubility in alkanes, perfluoroalkanes and ionic liquids have similar shapes: a region up to around the critical pressure of CO<sub>2</sub> (7.3 MPa) wherein the pressure increases almost linearly with the gas concentration, followed by a step increase of the pressure for higher concentrations, as shown in Fig. 2. Above this point, the two phase diagrams become very different. While for the alkanes and perfluorocarbons, the pressure levels up reach a critical point, for the ionic liquid the pressure keeps increasing and no critical point is observed. For perfluorocarbons, being a type I and not type III phase diagram, no further increase above the critical pressure of CO<sub>2</sub> is observed. For very high CO<sub>2</sub> concentrations, ILs do not present any advantage over conventional solvents and this study will not focus on the investigation of this region. This study will thus address only the CO<sub>2</sub> solubilities on the pressure region below 10 MPa.

The structure of the correlation for Henry's constants proposed by the IUPAC Project<sup>17</sup> was used here to correlate the solubility data of CO<sub>2</sub> in eicosane by Sato *et al.*,<sup>68</sup> Huie *et al.*,<sup>52</sup> Gasem *et al.*,<sup>61</sup> Huang *et al.*<sup>56</sup> and Nieuwoudt *et al.*<sup>50</sup>

$$p/\text{kPa} = K_{\text{H,CO}_2} m_{\text{CO}_2} e^{\sum_{i=1}^2 \sum_{j=0}^1 a_{ij} m_{\text{CO}_2}^j (T/\text{K})^i} \quad (1)$$

where  $K_{\text{H,CO}_2}$  is the Henry's law constant of CO<sub>2</sub> in eicosane on molality scale, expressed as

$$K_{\text{H,CO}_2} = e^{A - \frac{B}{(T/\text{K})} - C \ln(T/\text{K})} \quad (2)$$

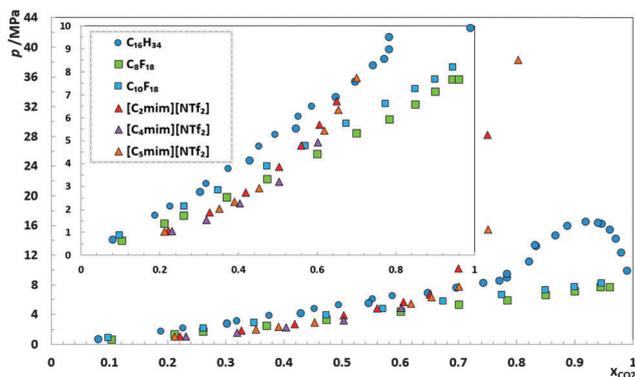


Fig. 2  $pTx$  phase diagram for the systems C<sub>16</sub>H<sub>34</sub>,<sup>50,65</sup> C<sub>8</sub>F<sub>18</sub>,<sup>64</sup> C<sub>10</sub>F<sub>18</sub>,<sup>64</sup> [C<sub>2</sub>mim][NTf<sub>2</sub>],<sup>66</sup> [C<sub>4</sub>mim][NTf<sub>2</sub>],<sup>67</sup> and [C<sub>5</sub>mim][NTf<sub>2</sub>].<sup>66</sup>

where  $m_{\text{CO}_2}$  is the CO<sub>2</sub> molality in the liquid phase. The elements of eqn (1), matrix  $a$ , and eqn (2) are listed in Table 1.

The correlation proposed by the IUPAC Project<sup>17</sup> used both carbon dioxide molalities and mole fractions. Furthermore, Almantariotis and coworkers,<sup>28</sup> contacting the original reference authors, argued that the correlation presented a typographical error in the equation and that it should be written only in terms of CO<sub>2</sub> mole fractions. As discussed above, because for practical applications, it is more interesting to compare the solubilities expressed in molality, the correlation used here was rewritten in carbon dioxide molalities.

As shown in Fig. 3a and b, the correlation provides an accurate description of the solubility data with an absolute average deviation of 3.5% for equilibrium pressures up to 10 MPa (0.9 MPa maximum pressure deviation) and 4.5% over all the pressure range evaluated.

Fig. 4 shows a comparison of the correlation with the CO<sub>2</sub> solubility data on the homologous series of  $n$ -alkanes. These results show that, overall, the correlation developed for eicosane provides a good description of the solubility of CO<sub>2</sub> in other  $n$ -alkanes, and that the solubilities of CO<sub>2</sub> in  $n$ -alkanes, when expressed in molality units in the pressure composition range of study, are quite similar as suggested by Carvalho and Coutinho.<sup>69</sup> Furthermore, for  $n$ -alkanes with a carbon number higher than 28 (octacosane), a behaviour shift towards lower solubilities (*i.e.* higher pressures) seems to be present. Nonetheless, this behaviour change is within the experimental data uncertainties, as depicted in Fig. 5.

The eicosane correlation will thus be used hereafter as the benchmark for the evaluation of the effects of the ionic liquids' molecular structures on the CO<sub>2</sub> solubilities here investigated.

### 3. Experimental uncertainty of high pressure solubility data

Nowadays, a very large database of experimental solubility of CO<sub>2</sub> in ionic liquids in a wide range of pressures and temperatures is available. Nonetheless, most of these data describe incomplete  $pTx$  phase diagrams, making a thermodynamic consistency analysis, to gauge the quality of these data, impossible. This limitation hampers the analysis of the quality of the experimental data, restricting it to a comparison between data from multiple sources in an attempt to define a most probable solubility from the agreement of the various sets of data. This analysis has been carried out for [C<sub>6</sub>C<sub>1</sub>m][NTf<sub>2</sub>] by Project 2002-005-1-100.<sup>17</sup> The proposed correlation for the recommended solubility values is claimed to describe the experimental data with a combined uncertainty of 10% at  $x = 0.1$  being higher than 0.1% for the low concentration limit and decreasing to 5% at  $x = 0.7$ . From the deviation plots reported in that study, it is possible to observe that a good deal of data present deviations from the recommended values as high as 20%.<sup>17</sup>

A similar approach can be performed for a few other compounds for which data from different authors is available. Results

Table 1 Eqn (1) parameters for eicosane and the ILs evaluated

	Eicosane	[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	[C <sub>8</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	[C <sub>4</sub> C <sub>1</sub> im][BF <sub>4</sub> ]	[C <sub>4</sub> C <sub>1</sub> im][PF <sub>6</sub> ]
A	39.60702	27.9082	39.4540	28.0577	23.98628
B	2382.3384	2362.952	2895.2156	2628.7415	2275.2518
C	4.24919	2.13201	4.02835	2.12699	1.62693
a <sub>10</sub>	-0.163919			1.00 × 10 <sup>-4</sup>	
a <sub>11</sub>	2.13182 × 10 <sup>-4</sup>			5.7005 × 10 <sup>-6</sup>	
a <sub>20</sub>	-6.61922 × 10 <sup>-6</sup>			8.04034 × 10 <sup>-4</sup>	
a <sub>21</sub>	3.67877 × 10 <sup>-3</sup>			4.45711 × 10 <sup>-6</sup>	

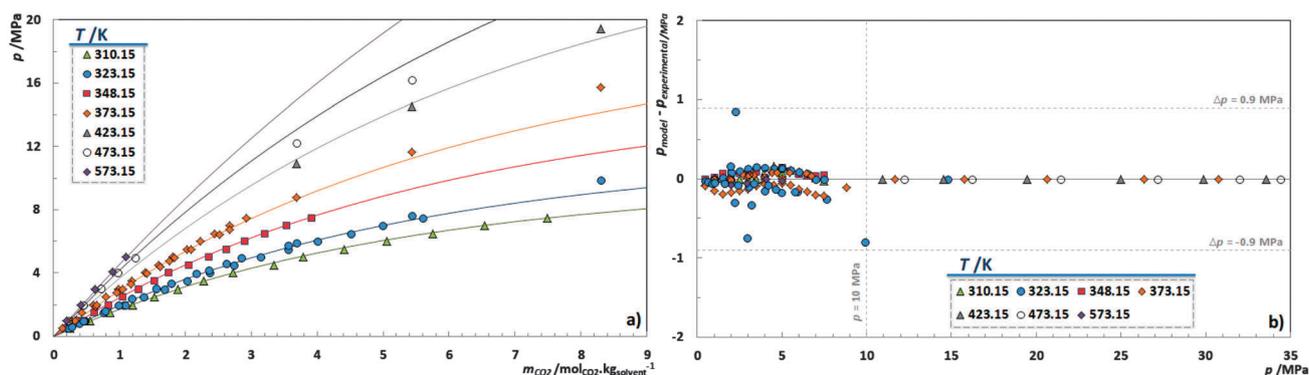


Fig. 3 (a)  $p_{m_{CO_2}}$  phase diagram for the system eicosane + CO<sub>2</sub> as function of temperature. The solid lines represent the eqn (1) for eicosane. (b) Pressure deviations for eicosane between eqn (1) and experimental data.<sup>50,52,56,61,68</sup>

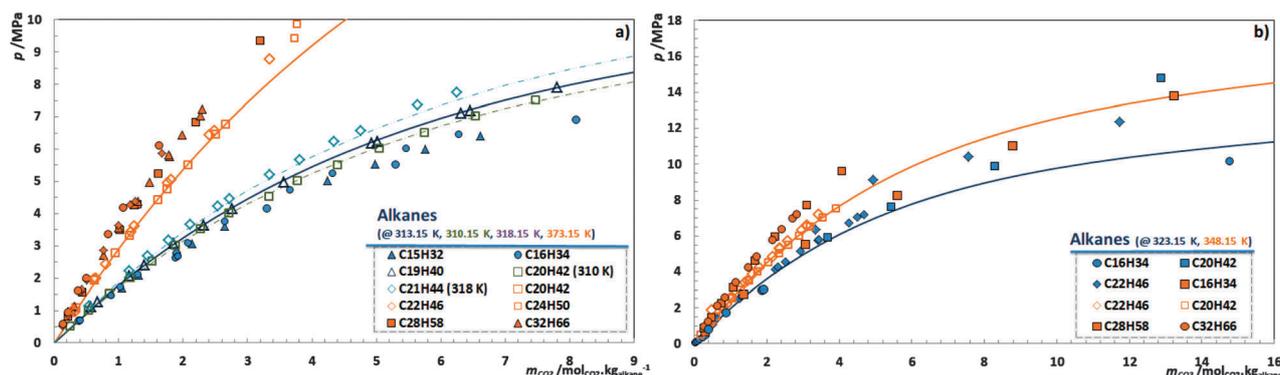


Fig. 4  $p_{m_{CO_2}}$  phase diagram for the systems *n*-alkanes + CO<sub>2</sub> as function of temperature: (a) 310.15 K, 313.15 K, 318.15 K and 373.15 K isotherms; (b) 323.15 K and 348.15 K isotherms.<sup>49,50,52,56,58,60,61,65,68,70–72</sup> The lines represent the eqn (1) for eicosane at the corresponding temperature.

for [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>], [C<sub>8</sub>C<sub>1</sub>im][NTf<sub>2</sub>], [C<sub>4</sub>C<sub>1</sub>im][BF<sub>4</sub>] and [C<sub>4</sub>C<sub>1</sub>im][PF<sub>6</sub>] are presented in Fig. 6.

Following the procedure described above, eqn (1) and (2) were fitted against experimental data for the systems CO<sub>2</sub> + [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>], [C<sub>8</sub>C<sub>1</sub>im][NTf<sub>2</sub>], [C<sub>4</sub>C<sub>1</sub>im][BF<sub>4</sub>] and [C<sub>4</sub>C<sub>1</sub>im][PF<sub>6</sub>] having as an objective function the minimization of the equilibrium pressure's %AAD. Moreover, to ensure that the pressure composition phase diagram follows the typical behavior described above, and depicted in Fig. 2, independently of the extension of the data available, the elements of the matrix *a* were fitted only against the CO<sub>2</sub> + [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>] experimental data and maintained constant for all the remaining systems, as reported in Table 1.

Similar to what was observed for the [C<sub>6</sub>C<sub>1</sub>im][NTf<sub>2</sub>] on the Project 2002-005-1-100<sup>17</sup> data for [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>], [C<sub>8</sub>C<sub>1</sub>im][NTf<sub>2</sub>], [C<sub>4</sub>C<sub>1</sub>im][BF<sub>4</sub>] and [C<sub>4</sub>C<sub>1</sub>im][PF<sub>6</sub>] present important discrepancies among the different literature sources, with deviations as high as 60% among authors.

Notoriously, a critical analysis of the data shows that for these widely studied archetypal fluorinated ionic liquids, no solubility enhancement is observed on the CO<sub>2</sub> solubility when compared to the *n*-alkanes, as distinct from the view widely accepted in the literature. In fact, for CO<sub>2</sub> molalities up to 3 mol kg<sup>-1</sup>, the *n*-alkanes perform better (*i.e.*, lower equilibrium pressures) than the ILs.

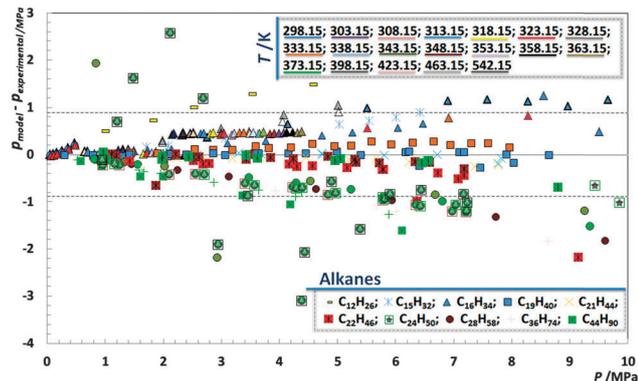


Fig. 5 Pressure deviations between experimental equilibrium pressures and those estimated by eqn (1). The dashed lines represent the average deviations obtained.

## 4. The effect of fluorination upon CO<sub>2</sub> solubility

One of the chemical modifications most widely investigated to enhance the solubility of CO<sub>2</sub> and other gases in ionic liquids is fluorination. Dias *et al.*<sup>64</sup> studied the solubility of CO<sub>2</sub> in aromatic and aliphatic perfluorocarbon compounds. The data at 313 K on the  $pTm$  scale adopted here is compared with the correlation developed for eicosane in Fig. 7.

The results are quite surprising as they seem to suggest that the aliphatic perfluorinated compounds have a CO<sub>2</sub> solubility

that is identical to that presented by eicosane, within their combined experimental uncertainties. However, it should be noticed that although not very significantly, the solubility of CO<sub>2</sub> in both perfluorobenzene and perfluorotoluene are indeed higher than those observed for the other compounds suggesting that the interactions disclosed by Besnard *et al.*<sup>84</sup> have some positive effect upon the solubility of CO<sub>2</sub> in these compounds. Similar results are observed for the various isotherms available in the 293–353 K range.

Brennecke and co-workers<sup>18,32,33</sup> were the first to attempt this approach to enhance the CO<sub>2</sub> solubility in ionic liquids. In their review on the solubility of gases in ionic liquids,<sup>18</sup> the authors show that on a  $pTx$  diagram the fluorination of the cation increases the CO<sub>2</sub> solubility but this effect seems to decrease with the increase of the fluorinated chain length. Muldoon *et al.*<sup>32</sup> state that ionic liquids containing increased fluoroalkyl chains on either the cation or anion do improve CO<sub>2</sub> solubility when compared to less fluorinated ones. Their statements are repeated on every major review on CO<sub>2</sub> solubility in ionic liquids published thereafter without question.<sup>19,22,23,27</sup> Other studies using predictive models reach the same conclusion.<sup>85</sup> Only Karadas *et al.*,<sup>24</sup> although still discussing the advantages of anion fluorination, because the interactions with the CO<sub>2</sub> are predominantly established by the anion, mention that Bara *et al.*<sup>85</sup> “found that the contribution of fluorination increases the CO<sub>2</sub> solubility (mol/volume) not more than 10% for the mentioned compounds”.

Based on predictions using the COSMO approach, Zhang *et al.*<sup>86</sup> suggested that ionic liquids based on the [pFAP]

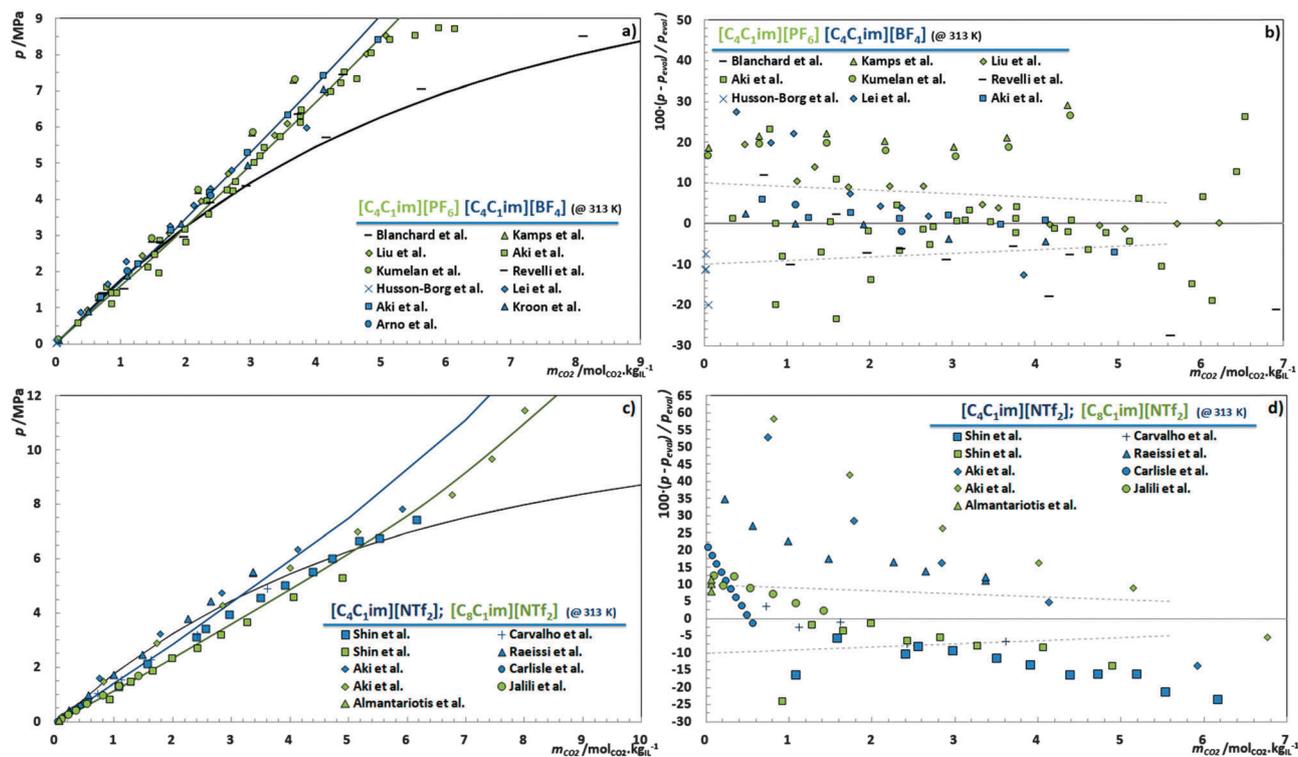


Fig. 6  $pTm_{CO_2}$  phase diagram of the experimental solubility pressures (a and c)<sup>8,33,41,67,73–83</sup> and the percentage deviation (b and d) between the experimental and the estimated equilibrium pressure values calculated by fitting eqn (1) to the experimental data (blue and green lines). The black line represents the values calculated with eqn (1) for eicosane.

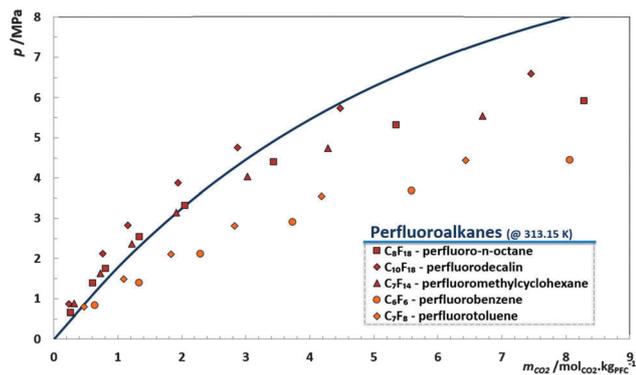


Fig. 7  $pm_{\text{CO}_2}$  phase diagram for the systems of perfluoroalkanes +  $\text{CO}_2$  at 313.15 K. The solid line represents the values calculated with eqn (1) for eicosane.

{tris(pentafluoroethyl)trifluorophosphate} anion were the best solvents for  $\text{CO}_2$ . To evaluate the effect of the fluorination of the ionic liquid cation and/or the anion we used the  $\text{CO}_2$  solubility in eicosane as a benchmark on the  $pTm$  scale adopted here. Solubility results for the fluorination of the cation alkyl chain were reported by Muldoon *et al.*,<sup>32</sup> Almontariotis *et al.*,<sup>8</sup> Yokozeki *et al.*,<sup>87</sup> Zhang *et al.*<sup>86</sup> and Althuluth *et al.*<sup>88</sup> A comparison of these data at 298 K, 313 K and 333 K is reported in Fig. 6 and 8. The behavior is similar for other isotherms available. The results clearly suggest that the solubilities are essentially identical, within the experimental uncertainty, and by no means superior to those observed for eicosane. The low and high pressure data of Muldoon *et al.*<sup>32</sup> are not fully coherent. This is particularly visible on the data on anion fluorination, presented in Fig. 8(a), wherein the low pressure data is in good agreement with the data by Yokozeki *et al.*<sup>87</sup> but the high pressure solubility data is clearly overestimated (orange and red squares). In spite of this data scatter, the low pressure data for the various ionic liquids, as observed with the cations, is in good agreement and is comparable with the  $\text{CO}_2$  solubility in eicosane and other ionic liquids. Furthermore, at temperatures below 333 K for ionic liquids, including fluorinated ILs, the  $\text{CO}_2$  solubility is in good agreement and is comparable with the  $\text{CO}_2$  solubility in eicosane, while above 313 K ILs present lower  $\text{CO}_2$  solubilities than eicosane.

This behavior denotes a non-ideal system with unfavorable solution enthalpy, compared to eicosane. A critical analysis of the available data for both perfluorocarbon compounds and heavily fluorinated ionic liquids shows that unlike the view widely accepted in the literature, no special effect of fluorination upon  $\text{CO}_2$  solubility is observed. The concept of the  $\text{CO}_2$ -philicity<sup>32</sup> proposed by some authors for the fluorinated molecules seems thus to be questionable, the only exception being the interactions disclosed by Besnard *et al.*<sup>84</sup> with fluorinated aromatic rings that have some positive effect upon the solubility of the  $\text{CO}_2$  in these compounds but which surprisingly have never been used in the design of task-specific ionic liquids for enhanced  $\text{CO}_2$  solubility.

## 5. The effect of oxygenation upon $\text{CO}_2$ solubility

Another effect discussed in most reviews is the effect of the oxygenation of the alkyl chain of the cation, either by introduction of ester, ether or carbonyl groups.<sup>19,21,24</sup> A number of studies in the literature highlight the favorable interactions of oxygen groups with  $\text{CO}_2$ . Besnard and co-workers<sup>90,91</sup> used spectroscopic studies to show the strong interactions of  $\text{CO}_2$  with hydroxyl groups<sup>90</sup> and complex formation with carbonyl-containing molecules.<sup>91</sup> In fact, studies of  $\text{CO}_2$  solubility in glymes also reveal large  $\text{CO}_2$  solubilities, as depicted in Fig. 9.<sup>41,92</sup>

As for the fluorination, Brennecke and co-workers<sup>32</sup> were pioneers in this field exploring the effect of the oxygenation of the ionic liquid on its ability to enhance the  $\text{CO}_2$  solubility. In their account of the results obtained for a broad range of oxygenated ionic liquids, the conclusion was that though having better environmental and toxicological properties than the fluorinated ionic liquids, no significant, if any, increase on the solubility was observed. These results are also supported by recent molecular simulation results by Pensado *et al.*<sup>6</sup> that led to the conclusion that “the presence of ester functions influences the relative size of the polar and nonpolar domains in the ionic liquids, but does not significantly affect the solvation of gases”. Deng *et al.*<sup>36</sup> also state, based on solubility measurements, that the “ $\text{CO}_2$  solubilities are not significantly

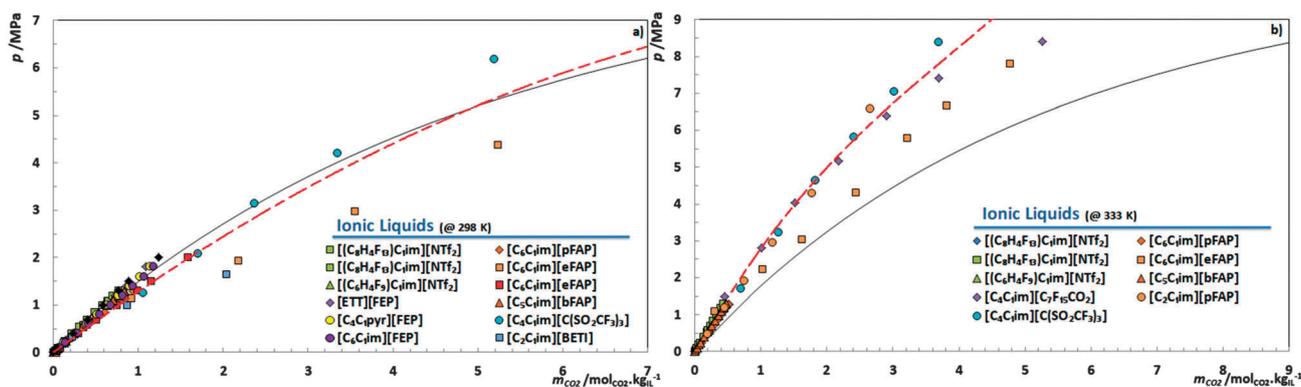


Fig. 8  $pm_{\text{CO}_2}$  phase diagram for the systems fluorinated ionic liquids +  $\text{CO}_2$  at (a) 298 K and (b) 333 K. The solid line represents the values calculated with eqn (1) for eicosane and the red dashed line the system  $\text{CO}_2$  +  $[\text{C}_6\text{C}_{1\text{im}}][\text{NTf}_2]$  equilibrium pressures.<sup>8,32,33,86–89</sup>

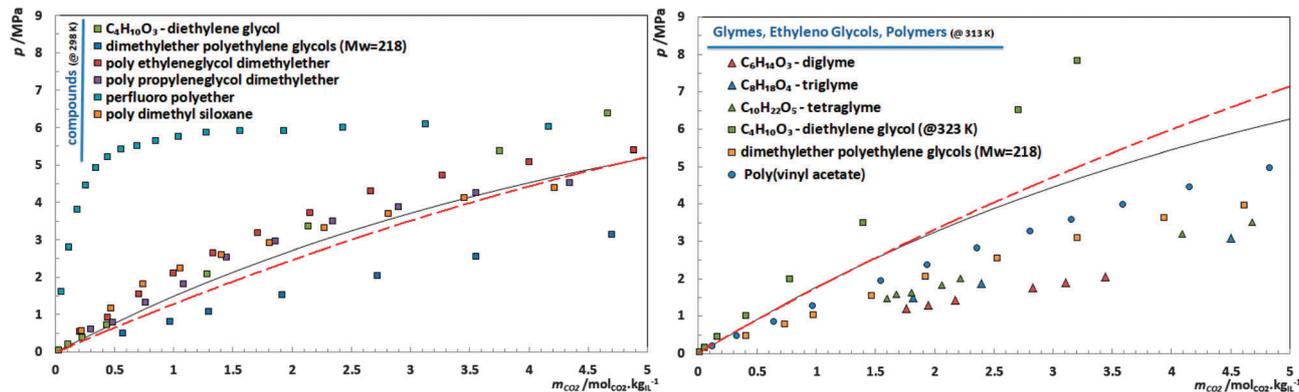


Fig. 9  $pTm_{CO_2}$  phase diagram of glymes, ethylene glycols and polymers at 298 K and 313 K.<sup>92–96</sup> The black line represents the values calculated with eqn (1) for the eicosane and the dashed red line the  $[C_6C_{1im}][NTf_2] + CO_2$  experimental equilibrium pressure values.<sup>32,33,97</sup>

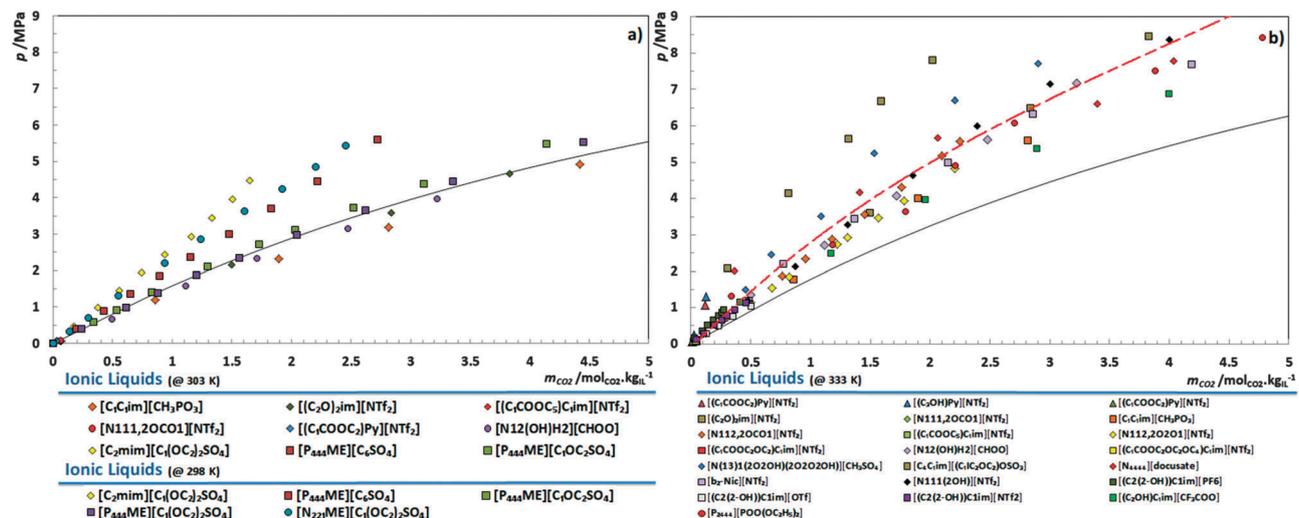


Fig. 10  $pTm_{CO_2}$  phase diagram of ILs with hydroxyl, ether and ester functionalization, at (a) 298 and 303 K and (b) 333 K.<sup>36,37,41,42,102,103</sup> The black line represents the values calculated with eqn (1) for eicosane and the dashed red line the  $[C_6C_{1im}][NTf_2] + CO_2$  experimental equilibrium pressure values.<sup>32,33,97</sup>

affected by the introduction of oxygen functional groups in the cations". However, recent results by Sharma *et al.*,<sup>34</sup> in striking contradiction to what was reported by Deng *et al.*,<sup>37</sup> suggest that "the absorption of  $CO_2$  in ether functionalized ILs is a chemical process. The  $CO_2$  absorption results indicate the predominance of 1:1 mechanism, where the  $CO_2$  reacts with one IL to form a carbamic acid".<sup>36</sup> The results of Jalili *et al.*<sup>35</sup> are also contradictory to those of Deng *et al.*<sup>36</sup> According to these authors, "The solubility of carbon dioxide in  $[hemim]^+ [NTf_2]^-$  ILs is greater than corresponding conventional  $[emim]^+ [NTf_2]^-$  containing the same anions, indicating that these solvents are more efficient for  $CO_2$  sequestration than the  $[emim]^+ [NTf_2]^-$ ".<sup>35</sup>

Recently, Seo *et al.*,<sup>98</sup> aiming at verifying Sharma *et al.*,<sup>34</sup> claim to have measured the carbon dioxide solubility in  $[hemim][NTf_2]$  and concluded that neither the physical properties nor the NMR spectra of the IL match those presented by Sharma *et al.*,<sup>34</sup>

†  $[hemim]^+ [af0\ 1-(2\text{-hydroxyethyl})\text{-3-methylimidazolium}]$ .

‡  $[emim]^+$ ,  $[C_2C_1im]^+$ ; 1-ethyl-3-methylimidazolium.

concluding thus, that the results presented by the authors are in error and that the ether-functionalized ILs do not pick up one mole of  $CO_2$  per mole of IL, as claimed.

The effect of the oxygenation of alkyl chains upon  $CO_2$  solubility is moreover a most interesting question because the two most successful industrial processes for natural gas sweetening, the Rectisol<sup>99</sup> and the Selexol<sup>100,101</sup> processes, are based on oxygenated compounds: methanol, in the first, and polyether compounds, in the second. A more detailed and critical analysis of this sort of compound seems thus to be in order.

The data for  $CO_2$  solubility in ionic liquids with oxygenated alkyl chains is presented in Fig. 10 and 11. It is difficult to independently evaluate the ether and ester modifications because often they are associated in the same compound. The only ionic liquids reported in the literature with just ether groups are  $[(CH_3CH_2O)_2im][NTf_2]$  by Revelli *et al.*,<sup>41</sup>  $[N_{112,2O2O1}][NTf_2]$  by Makino *et al.*<sup>102</sup> and  $[(CH_3OCH_2)C_1im]$ , with the anions  $[Cl]$ ,

§  $[(ETO)_2IM][NTf_2]$ ; 1,3-dioxyimidazolium bis(trifluoromethylsulfonyle)imide.

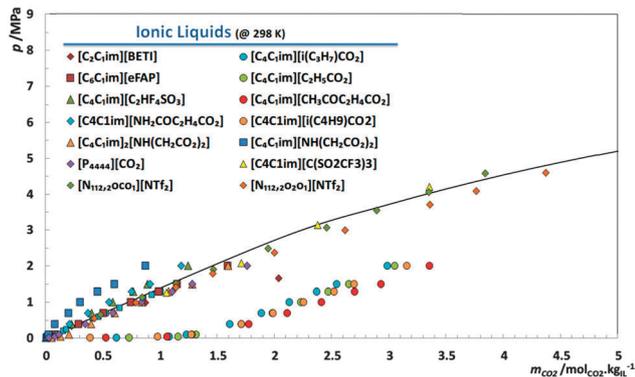


Fig. 11  $pTm_{\text{CO}_2}$  phase diagram of ILs with ether and ester functionalization, at 298 K.<sup>33,34,41,87,89,102,107</sup> The black line represents the values calculated with eqn (1) for eicosane.

$[\text{BF}_4]$ ,  $[\text{PF}_6]$ ,  $[\text{NTf}_2]$ ,  $[\text{CH}_3\text{PO}_3]$  and  $[\text{N}(\text{CN})_2]$ , by Sharma *et al.*<sup>34</sup> With the Sharma *et al.*<sup>34</sup> results shown to be wrong, those reported by Revelli *et al.*<sup>41</sup> and Makino *et al.*<sup>102</sup> present lower solubilities than the *n*-alkanes. Most other ionic liquids reported present simultaneously ester and ether groups.<sup>36,37,87,102,103</sup> For these compounds most solubility data is available only at atmospheric pressure<sup>36,37</sup> and thus an accurate evaluation is hard to produce. Nonetheless, those whose data is reported as function of pressure present equilibrium pressures similar or higher than those of the *n*-alkanes, as depicted in Fig. 10 and 11, indicating an adverse effect of oxygenation upon  $\text{CO}_2$  solubility for these compounds.

The anion's effect on IL-based solvation processes is more dominant than the cation's and therefore the oxygenation effect on the IL anion deserves an independent analysis. Anions containing the acetate functional group present chemisorption.<sup>2,40,104,105</sup> As this critical review deals with physisorption mechanisms, acetate will not be discussed in this study. The reader interested in the  $\text{CO}_2$  chemisorption in ionic liquids is invited to address the literature available on this subject.<sup>2,105,106</sup> The data for the hydroxyl-containing ionic liquids is far more complex. Most of the data available is for protic ionic liquids from a single source and is in poor agreement with the data by Mattedi *et al.*<sup>37</sup> The only high pressure solubility data available for  $[(\text{C}_2(2\text{-OH}))\text{C}_1\text{im}]$ -based ILs, with  $[\text{NTf}_2]$ ,  $[\text{OTf}]$  and  $[\text{PF}_6]$  anions, by Jalili *et al.*<sup>35</sup> is in good agreement with the eicosane correlation. The data for  $[(\text{C}_3\text{OH})\text{Py}][\text{NTf}_2]$  is available only at atmospheric pressure and if extrapolated would suggest, as the data for the protic ionic liquids does, that the hydroxylation of the cation would reduce the  $\text{CO}_2$  solubility.<sup>35</sup> Because the data available present serious conflicts, further data is required to strengthen these conclusions. In any case, no evidence for a favourable effect on  $\text{CO}_2$  solubility of hydroxyl-containing ionic liquids was found. In fact, all evidence points in the opposite direction. On the other hand, several glymes, glycols and polymers present enhanced  $\text{CO}_2$  solubilities, compared to ILs and *n*-alkanes as depicted in

¶  $[(\text{C}_2(2\text{-OH}))\text{C}_1\text{im}][\text{NTf}_2]$ , 1-(2-hydroxyethyl)-3-methylimidazolium bis(trifluoromethyl)sulfonylimide.

||  $[(\text{C}_3\text{OH})\text{Py}][\text{NTf}_2]$ , 1-(3-hydroxypropyl)pyridinium bis(trifluoromethyl)sulfonylimide.

Fig. 9, attracting attention to these compounds as feasible candidates for  $\text{CO}_2$  capture and separation.

Moreover, their enhanced solubility together with their inherent properties, such as negligible volatility, low viscosity and low toxicity, mark them as one of the most promising approaches for gas sweetening. A functionalization of ionic liquids with glyme-like chains could enhance  $\text{CO}_2$  sorption and should be attempted.

## 6. $\text{CO}_2$ solubility in mixtures of ILs

An approach that has been known to be growing in interest in the last few years is the use of mixtures of ILs to enhance the  $\text{CO}_2$  solubility and selectivity.

Through the use of mixtures of IL solvents, the authors expect to be able to not only control the molar volume and the solvent viscosity but also tune the Hildebrand solubility parameter, matching the solubility parameter of the ILs mixture with that of the gas of interest, thus enhancing both solubility and selectivity.<sup>108–110</sup> Nevertheless, the data available, although scarce, does not show evidence of an enhanced solubility, most of it being in good agreement with the theoretical predictions that could be estimated from pure IL solubility data, based on the mole fraction average of the pure components.<sup>104,110</sup>

In fact, despite the discrepancies observed among different authors discussed in section “3. Experimental uncertainty of high pressure solubility data” above and depicted in Fig. 12 (inner plots), if a comparison of data from the same source is carried out, only solubilities ranging between those of the binary mixtures ( $\text{CO}_2 + \text{IL}$ ) are observed, denoting no solubility enhancement, and never solubilities higher than those of *n*-alkanes.

On the other hand, the ability to tune the Hildebrand solubility parameter as a means of enhancing the solubility selectivity has been evaluated only by Finotello *et al.*<sup>108</sup> for  $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{CH}_4$ . Although the data reported by Finotello *et al.*<sup>108</sup> should be taken with care, because it presents an unusual behaviour, as depicted in Fig. 12d, the solubility selectivity determined using the reported Henry's constants seems to indicate that the ability to tune the solubility selectivity can be achievable, as depicted in Fig. 13. These selectivity results need to be confirmed by independent study.

## 7. Deep eutectic solvents for enhanced $\text{CO}_2$ solubility

Deep eutectic solvents (DES) are systems formed by a eutectic mixture of up to three compounds. Although DES have been characterized by some as a new class of ionic liquid analogue, mainly due to these systems sharing some properties with ILs, DES are, by definition, a mixture of a hydrogen bond donor and an acceptor, while ILs are a single ionic compound formed by an anion and a cation.<sup>114</sup>

Nonetheless, aiming to take advantage of the ILs large and asymmetric ions, low lattice energy and low melting points, DES systems containing ILs or salts have been receiving

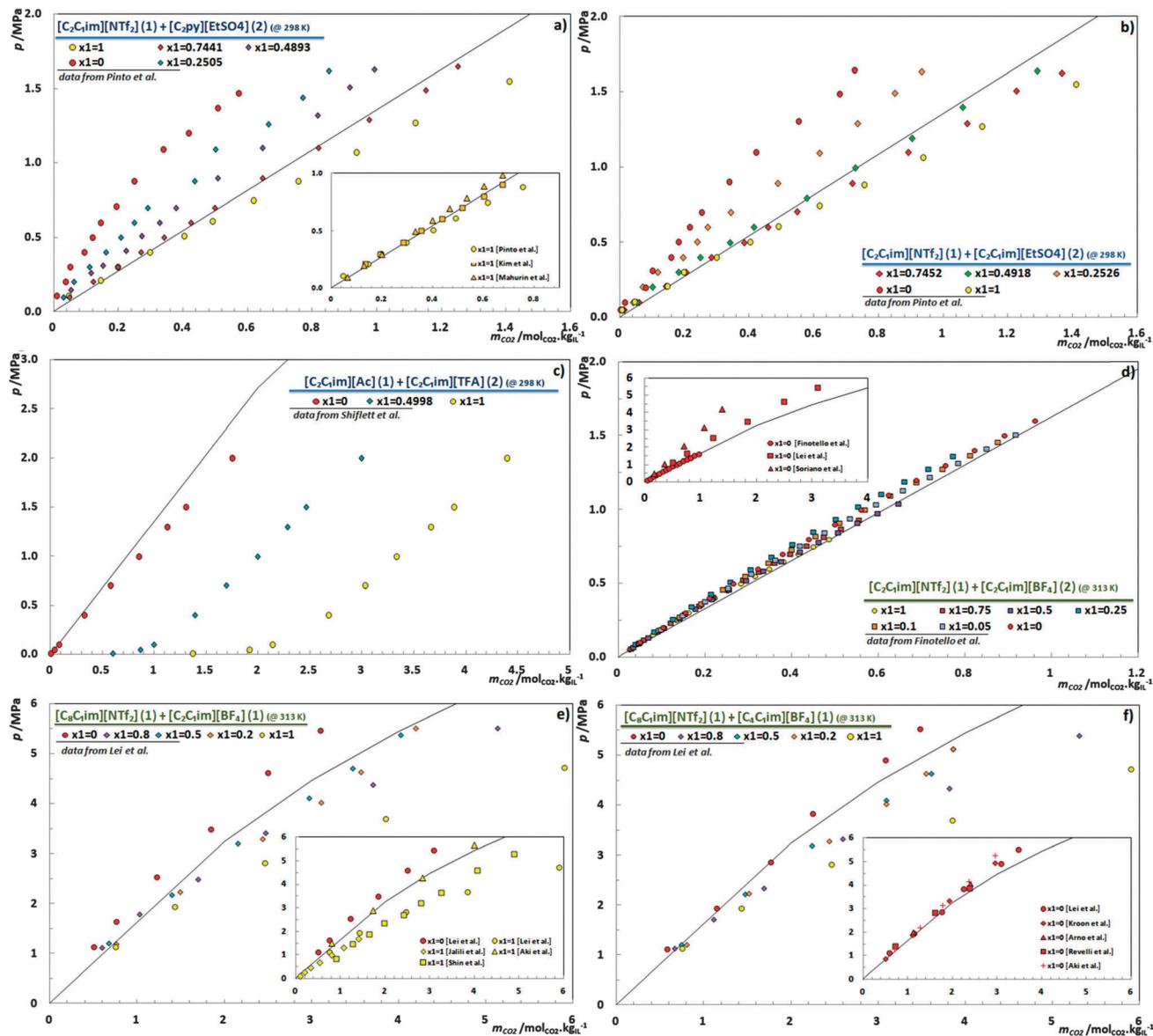


Fig. 12  $pT_{m_{CO_2}}$  phase diagram of mixtures of ILs +  $CO_2$ , at (a–c) 298 K and (d–f) 313 K.<sup>33,40,41,43,73,74,79,83,97,107,108,111–113</sup> The black line represents the values calculated with eqn (1) for eicosane.

increasing attention. The first IL-containing DES was reported for the system of choline chloride with urea<sup>115</sup> and subsequently extended to other quaternary ammonium or phosphonium salts with alcohols, carboxylic acids, amino acids, sugars and amides.<sup>116–119</sup> The use of ILs-containing DES for  $CO_2$  sorption arose naturally, with a number of studies focused on the use of choline chloride with carboxylic acids, alcohols and urea reported.<sup>119–125</sup> As depicted in Fig. 14, with the exception of choline chloride + glycerol (1:2), which presents solubilities similar to those of eicosane, the remaining DES systems present lower sorption capabilities. Only the system choline chloride + urea (1:2.5) reported by Li *et al.*<sup>124</sup> seems to present higher  $CO_2$  solubilities than those of eicosane, but this data should be taken with care because Mirza *et al.*<sup>120</sup> reported data for the same system, with a similar molar ratio (1:2), presenting lower  $CO_2$  solubilities than eicosane.

## 8. [B(CN)<sub>4</sub>]-based ionic liquids display an enhanced ability to dissolve $CO_2$

In a study dealing with gas separation using ionic liquid membranes Mahurin *et al.*<sup>36</sup> suggested that  $CO_2$  solubility in  $[C_2C_1im][B(CN)_4]$  was 30% higher than in  $[C_2C_1im][NTf_2]$  ionic liquid and consequently probably larger than almost all ionic liquids. This ionic liquid is particularly interesting due to its low viscosity that enhances mass transfer phenomena. Babarao *et al.*<sup>43</sup> carried out some molecular simulations attempting to explain this anomalous solubility based on weak cation–anion interaction of the ionic liquid. However, high pressure gas solubility data on these compounds has only recently been reported by Mota-Martinez *et al.*<sup>44</sup> for  $CO_2$  solubility in  $[C_6C_1im][B(CN)_4]$ , Mahurin *et al.*<sup>43,126</sup> and Makino *et al.*,<sup>45</sup> for  $CO_2$  solubility in

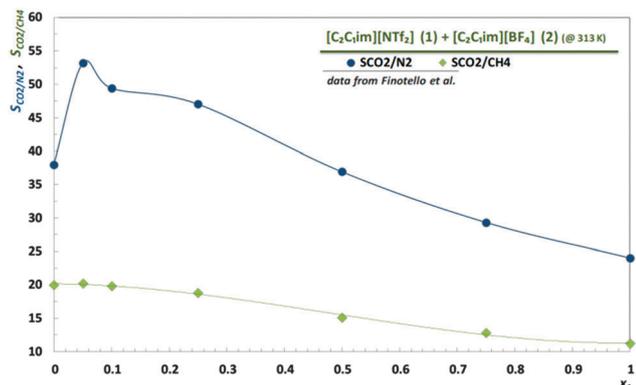


Fig. 13  $S_{\text{CO}_2/\text{N}_2}$  and  $S_{\text{CO}_2/\text{CH}_4}$  as function of  $[\text{C}_2\text{C}_1\text{im}][\text{NTf}_2]$  mole fraction at 313 K. The solid lines are guides for the eyes.

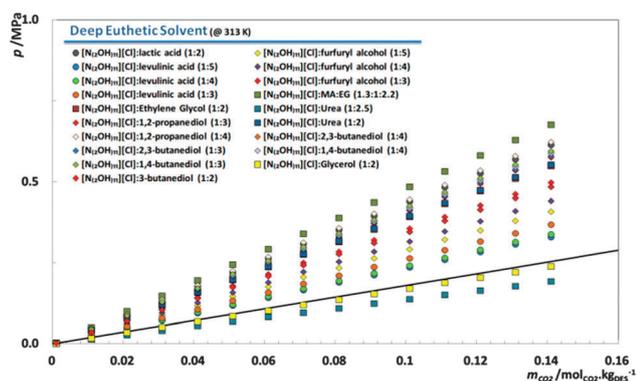


Fig. 14  $pTm_{\text{CO}_2}$  phase diagram of deep eutectic solvents at 313.15 K.<sup>119,120,122–125</sup> The black line represents the values calculated with eqn (1) for eicosane.

$[\text{C}_2\text{C}_1\text{im}][\text{B}(\text{CN})_4]$ , and Mahurin *et al.*,<sup>126</sup> for  $\text{CO}_2$  solubility in  $[\text{C}_4\text{C}_1\text{im}][\text{B}(\text{CN})_4]$ ,  $[\text{C}_2\text{C}_1\text{im}][\text{B}(\text{CN})_4]$ ,  $[\text{C}_4\text{C}_1\text{pyrr}][\text{B}(\text{CN})_4]$  and  $[\text{C}_4\text{C}_1\text{pip}][\text{B}(\text{CN})_4]$ . The authors suggest that the  $[\text{B}(\text{CN})_4]$  anion-based ILs would present a larger than usual  $\text{CO}_2$  solubility with an enhancement of about 70% over the predictions of the Carvalho and Coutinho correlation<sup>44</sup> that describes the solubility in a wide range of ionic liquids. Solubility data in other cyano-based anions is also very limited and to evaluate its effect on the  $\text{CO}_2$  solubility all high pressure solubility data collected from the literature are plotted in Fig. 15 wherein they are compared with the correlation for the  $\text{CO}_2$  solubility in *n*-alkanes and the Carvalho and Coutinho correlation.<sup>69</sup>

Unlike the data for  $[\text{N}(\text{CN})_2]$  available from different sources, that are in good agreement with each other and with Carvalho and Coutinho correlation<sup>44,127</sup> and in no case display solubilities larger than those predicted by the alkanes correlation, the data for  $[\text{B}(\text{CN})_4]$ -anion based ILs<sup>43–45,126</sup> suggests that the  $[\text{B}(\text{CN})_4]$ , denoting still a physical sorption mechanism, would indeed present a larger (up to 70%)<sup>44</sup> than usual  $\text{CO}_2$  solubility. This is the only instance studied on this study wherein a significant enhancement of the  $\text{CO}_2$  solubility was observed and a deeper understanding of the  $\text{CO}_2$  solvation in  $[\text{B}(\text{CN})_4]$ -based ionic liquids would be welcome as this could open the door to the development of

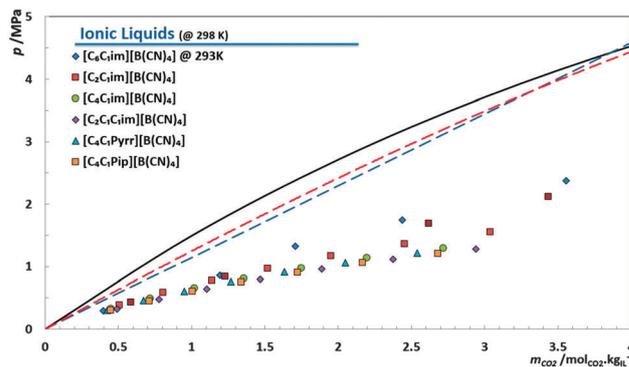


Fig. 15  $pTm_{\text{CO}_2}$  phase diagram of  $[\text{B}(\text{CN})_4]$  anion-based ionic liquids at 298 K.<sup>43–45,126</sup> The black line represents the values calculated with eqn (1) for eicosane, the red dashed the  $[\text{C}_6\text{C}_1\text{im}][\text{NTf}_2] + \text{CO}_2$  experimental equilibrium pressures<sup>32,33,97</sup> and the blue dashed line the values calculated using the Carvalho and Coutinho correlation.<sup>69</sup>

novel anions or functionalized ionic liquids with enhanced  $\text{CO}_2$  solubility. Recently, Gupta<sup>128</sup> in a study aimed at evaluating the cation impact on the  $\text{CO}_2$  solubility on  $[\text{B}(\text{CN})_4]$ -based ILs using *ab initio* calculations and molecular simulations, suggested that low cation–anion electrostatic interactions observed in these ILs are the key to their high  $\text{CO}_2$  solvation ability. This observation is further reinforced by the low aptness to  $\pi$ – $\pi$  stacking interactions and almost absent IL–IL hydrogen bonding capability reported by Weber and Kirchner<sup>129</sup> and Liu *et al.*<sup>130</sup> These results are important contributions for the understanding of the enhanced physical solubility of  $\text{CO}_2$  in ionic liquids and they could help design better ILs for enhanced  $\text{CO}_2$  solubility.

## 9. $\text{CO}_2$ chemisorption

Even though the solubility data herein evaluated makes clear that the physisorption of  $\text{CO}_2$  in most ionic liquids is controlled by their size, with  $\text{CO}_2$  essentially solvated in the voids of the ionic liquid,<sup>2,106,131,132</sup> and with interactions with the ionic liquids playing a secondary role in this process, which is, however, not true when some sort of chemisorption occurs. Probably, the most widely studied system, in which chemisorption rules the solvation process, is the  $\text{CO}_2 + 1\text{-butyl-3-methylimidazolium acetate}$ ,  $[\text{C}_4\text{C}_1\text{im}][\text{Ac}]$ . Many authors have investigated this system<sup>39,91,104,105</sup> providing evidence of reversible molecular complex formation between carbon dioxide and the ionic liquid, based on infrared spectroscopy, Raman, *ab initio* and single crystal X-ray studies. In fact, many have reported evidence of the formation of 1-butyl-3-methylimidazolium-2-carboxylate in the mixture of  $\text{CO}_2$  with  $[\text{C}_4\text{C}_1\text{im}][\text{Ac}]$ .<sup>91,105,106,131,132</sup> Nonetheless, the chemisorption mechanism is not always easily identified and consensual among the various authors, with the formation of a transient molecular complex or through a more complex process, involving a chemical reaction, typically under discussion. It has not been our goal in this study to discuss or propose a mechanism for the solubility of  $\text{CO}_2$  in ionic liquids, nor to discuss systems presenting sorption mechanisms other than physisorption. Thus, the reader is directed to the set of interesting studies

on the CO<sub>2</sub> chemisorption in ionic liquids available in the literature.<sup>91,105,106,132,133</sup>

## 10. Are ionic liquids good solvents for CO<sub>2</sub>?

For all the functionalized ionic liquids discussed in the previous sections, it has been shown that, with exception of ionic liquids based on the [B(CN)<sub>4</sub>]<sup>-</sup> anion, in no other case is the solubility reported, in molality units, higher than that observed for a generic *n*-alkane. The few cases wherein the data suggested that this could be the case can be attributed to poor experimental measurements. There could be, nevertheless, other ionic liquids displaying an enhanced solubility. To evaluate that possibility, all the systems available in the open literature for CO<sub>2</sub> solubility in ionic liquids and not discussed in any of the previous sections are compared here against the correlation proposed for the *n*-alkanes in Fig. 16.

Up to this point, we attempted to maintain the discussion as factual as possible letting the data speak for themselves. To avoid the trap of cherry picking, we strove to be as comprehensive as possible in the data used trying to collect all the high pressure experimental data previously reported, and in some cases resorting even to low pressure data to supplement the data used in the analysis. The conclusions previously stated are thus based on direct comparisons of data and not on questionable and subjective analysis. It has not been our goal on this study to discuss or propose a mechanism for the solubility of CO<sub>2</sub> in ionic liquids. Whether one believes that an enhanced solubility is present or not when compared with other common solvents, the point is that to a fair extent the CO<sub>2</sub> is soluble in these novel solvents and the solvation mechanism requires elucidation. This said, it is hard to neglect the fact that the results herein reported support a particular vision of CO<sub>2</sub> solvation in ionic liquids previously reported in the literature.

Two different points of view have been put forward concerning the CO<sub>2</sub> solvation in ionic liquids:

(i) On one side are those that claim that these compounds are CO<sub>2</sub>-philic and that the solvation occurs by specific interactions occurring between the anion and the positively charged carbon of the CO<sub>2</sub>, and support this vision with spectroscopic data and molecular simulations;<sup>4,18,80,135–138</sup>

(ii) On the other side are those that believe the interactions observed by spectroscopy do not explain the solubility of CO<sub>2</sub> by pointing out that spectroscopic data also show the most CO<sub>2</sub> in the ionic liquid to be present in a form akin to that observed in pure CO<sub>2</sub> and thus not bound to the ionic liquid;<sup>69,139,140</sup> furthermore, molecular simulations also suggest that the CO<sub>2</sub> is essentially solvated in the voids of the ionic liquid and that these compounds can easily reorganize themselves to accommodate large amounts of gas.<sup>136,141–143</sup>

The main goal herein is to factually compare the reported results of the experimental solubility data between various ILs and other compounds on a basis that removes the influence of the differences in molecular weight of the solvent from the analysis. The similarity between the solubilities displayed by many of the compounds analyzed on this study, with cations and anions of a widely different nature, and the similarity of the solubilities observed with non-polar solvents such as alkanes is nevertheless striking. A growing number of authors have been claiming that despite the favorable interactions between CO<sub>2</sub> and the IL observed by spectroscopy, these barely compensate for the CO<sub>2</sub>–CO<sub>2</sub> and IL–IL interactions which are broken, the CO<sub>2</sub> being essentially solvated in the voids of the ionic liquid, with the ILs reorganizing themselves to accommodate large amounts of gas. In fact, all the solubility data show a striking similarity of behaviour among different ionic liquids which can hardly be explained by specific interactions. It is actually difficult to imagine, based on the behaviours analyzed herein, that the explanation for those could be something other than mechanism (ii) above. This said, the striking results obtained with ionic liquids based on [B(CN)<sub>4</sub>]<sup>-</sup> anions cannot be ignored and would deserve further attention as their understanding could help to design ionic liquids with an enhanced CO<sub>2</sub>-philicity. It is not our contention in this study to discredit ionic liquids or their potential, but to warn the researchers interested in this field about some wrong ideas that have been propagating without appropriate analysis in the literature and led to an excessive body of fruitless study, spending resources that could be put to better use. A firm understanding of what works or does not work is the only way that a field can make progress and this is the true purpose of this study: to clarify what does improve the CO<sub>2</sub> solubility so that novel solvents for its capture can be successfully designed.

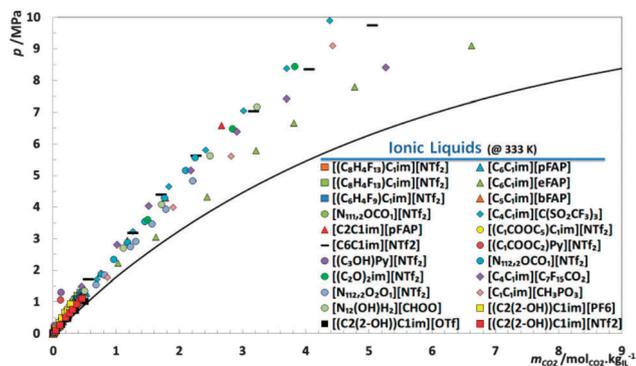


Fig. 16  $pTm_{\text{CO}_2}$  phase diagram of ionic liquids at 333 K. The solid line represents the values calculated with eqn (1) for eicosane.<sup>8,32,36,37,41,86–88,102,134</sup>

## 11. Perspectives

Ionic liquids are undeniably interesting compounds with a wide range of potential applications and with a unique ability to be designed to meet a specific set of requirements. This does not mean, however, that their application can be successful in all fields. These solvents have been the object of extensive research for physical sorption of CO<sub>2</sub> and a number of myths have been perpetuated in the literature, for want of a critical analysis, concerning their potential for CO<sub>2</sub> capture. In this study, we have critically revised a number of these ideas and tried to dispel some of them. The message is that as physical sorbents for CO<sub>2</sub>, the conventional ionic liquids are not particularly good and their

apparent high solubility results from their high molecular weight, when expressed in mole fractions and not from any special ability of these fluids to dissolve CO<sub>2</sub>. None of the widely accepted approaches to physically enhance CO<sub>2</sub> solubility in ionic liquids studied in this study, with the exception of [B(CN)<sub>4</sub>]<sup>-</sup> anions, seem to have any positive influence. This does not mean that these or other types of interactions not previously attempted cannot provide an enhanced CO<sub>2</sub> solubility. However, these results should constitute a cautious warning about attempting solutions that proved to be rather limited in their solubility enhancement and the pitfall that may arise when comparing results using an inadequate set of units. These conclusions do not, obviously, apply to the chemical sorption of CO<sub>2</sub> in ionic liquids that has been studied with success by different authors.

Four major potential new directions stem from this study concerning the enhancement of the CO<sub>2</sub> physical sorption in ionic liquids are as follows: (i) Understand and exploit the success of the [B(CN)<sub>4</sub>]<sup>-</sup> anion. If the reasons behind the high solubility of this compound are fully understood other anions may be designed to further enhance CO<sub>2</sub> solubility. In particular, there are a series of novel cyano-containing ions whose synthesis was recently the subject of a patent (WO 2014167034 A2) based on the study of Dillon and Platt;<sup>144</sup> (ii) Use the interactions disclosed by Besnard *et al.*<sup>84</sup> between CO<sub>2</sub> and fluorinated aromatic rings. Instead of the fluorination of the anion or the alkyl chains a better approach, never attempted, seems to be the use of fluorinated aromatic rings either in the cation or the anion to enhance CO<sub>2</sub> solubility in ionic liquids. (iii) Understand the enhanced solubility of CO<sub>2</sub> in glymes and develop either glyme-like functionalized ionic liquids or use the peculiar characteristics that mixtures of ethylene oxide-functionalized molecules with some ionic liquids present;<sup>145</sup> (iv) Use the notion that the solubility of CO<sub>2</sub> occurs in the 'pores' of the liquid and try to enhance it, either by using mixtures of ionic liquids, or ionic liquids with molecular solvents, with large positive excess molar volumes, or achieve these goals through the introduction into the ionic liquid of structures that may create an actual porosity in the liquid, developing porous ionic liquids with enhanced gas solubilities.<sup>146</sup> Ionic liquids should be particularly well suited as a basis for the development of porous liquids.

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