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# Theoretical screening of Ionic Liquid solvents for carbon capture

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Recently a number of Ionic Liquids have been experimentally shown to be efficient solvents of CO<sub>2</sub>. In order to screen for the best solvents, we develop here a theoretical prescription to accurately compute CO<sub>2</sub> solubility in a general solvent. The procedure involves computing chemical potentials using a first-principles density-functional-theory-based COSMO-RS approach, and computing the gas-fugacity of CO<sub>2</sub> with a cubic equation of state. The approach yields excellent agreement (within 10-15%) with recent solubility measurements over a range of temperatures and gas pressures of practical interest. Upon an expanded search over a wider class of cations and anions we discover Ionic Liquids with predicted molal solubility 80% higher than the highest experimental solubility of CO<sub>2</sub> observed so far. The study yields useful trends as a function of cation and anion, which can guide further exploration.

With global warming established as a critical problem to reckon with, it is extremely important to cut down CO<sub>2</sub> emission into the atmosphere. Prior to sequestration, it is necessary to separate the CO<sub>2</sub> from its emission source, e.g., flue gas in a coal-fired power plant. Of the limited few coal plants with commercial CO<sub>2</sub> capture capability, all use processes based on chemical absorption with a monoethanolamine (MEA) solvent. Unfortunately, MEA is a non-selective solvent, prone to degradation and equipment corrosion, and mandates large equipment sizes, thereby increasing cost.

Ionic Liquids (ILs) [1] constitute an alternative solvent system that offer distinct advantages over traditional solvents like MEA, some of which include: (1) high chemical stability; (2) low corrosion; (3) almost zero vapor pressure (*i.e.*, “green”); (4) supportable on membranes [2]; and (5) a huge library of anion and cation choices, which can be potentially optimized for CO<sub>2</sub> solubility and selectivity.

Over the last few years several ILs have been experimentally demonstrated [3-8] to be efficient solvents for CO<sub>2</sub>. A collection of this data does provide useful trends that can be used to optimize the choice of ILs for CO<sub>2</sub> capture. However, each new experiment costs time and money, and is often hindered by the fact that a specific IL may not be readily available. To this end, it is highly desirable to have a computational/theoretical tool that can quickly and accurately compute CO<sub>2</sub> solubility in any solvent (as a function of pressure and temperature). Atomic level simulations, either molecular dynamics, or binding-energy calculations can provide useful insights into the interactions of CO<sub>2</sub> with the cation and the anion [9-11]. However, accurate solubility computation in such complex fluids faces many challenges, including accurate force field development, clever Monte Carlo moves, and very long simulation times for good statistical averaging.

For fast exploration, design, and screening of effective solvents it is highly desirable to adopt a general-purpose thermodynamic approach that computes the chemical potential of a solute (CO<sub>2</sub> in this case) in any solvent at arbitrary dilution. A widely used method in this regard is COSMO-RS [12, 13], which uses the statistical distribution (histogram) of individual molecule’s surface charge density, called the  $\sigma$ -profile, to derive an expression for the ensemble-averaged Gibb’s free energy of an interacting system of molecules (solute + solvent at specified mole fractions) in the condensed (liquid) phase, from which one obtains the pseudo-chemical potential ( $\mu$ ) of each species (*i.e.*, the Gibb’s free energy per molecule without the mixing entropy contribution). If the pseudo-chemical potential of a solute molecule at a temperature  $T$  in a solution containing  $x$  mole-fraction of the solute is  $\mu_{\text{solution}}(x, T)$ , and that in the solute’s own liquid environment is  $\mu_{\text{self}}(T)$ , then assuming ideal mixing law we have under equilibrium ( $k_B =$  Boltzmann constant):

$$\mu_{\text{solution}}(x, T) + k_B T \ln x = \mu_{\text{self}}(T), \quad (1)$$

which leads to the following equation for solubility  $x$  at temperature  $T$  [13, 14]:

$$x = \exp\{[\mu_{\text{self}}(T) - \mu_{\text{solution}}(x, T)]/k_B T\}, \quad (2)$$

Eq. (2) has been successfully employed to compute solubility from a condensed phase, most recently of a hydrogen-bonded energetic solid in a number of Ionic Liquids [15].

Solubility of gases, on the other hand, is commonly expressed in terms of the partial pressure  $P(x, T)$  of the solute in the gas phase residing above the solution:

$$\phi(P, T)P(x, T) = x\phi(P^{\text{vap}}, T)P^{\text{vap}}(T)\gamma(x, T), \quad (3)$$

where  $P^{\text{vap}}(T)$  is the equilibrium vapor pressure of the solute (above its pure liquid phase) at temperature  $T$ ,  $\phi(P, T)$  is the fugacity coefficient, and  $\gamma(x, T)$ , the activity coefficient, is given by the reciprocal of the right-hand-side of eq. (2). By its very construction, eq. (3) is valid only for subcritical temperatures (*i.e.*  $T < T_c$ ). For  $T$  far below  $T_c$  the common recommendation [13] is to use eq. (3) along with experimentally measured or analytically-fitted vapor pressure. However, given that for CO<sub>2</sub>  $T_c \sim 31$  °C, most of the phase space of interest for solubility measurement, *i.e.*, 20-60 °C is in the near-subcritical to near-supercritical region. *In such a region, we find that eq. (3) (with analytically extrapolated vapor pressure in the near-supercritical region) leads to a consistent underestimation of  $P(x, T)$  as compared to experiment in all ILs, sometimes by 50% or more.* Such underestimation can also be seen in a recent COSMO-RS calculation of CO<sub>2</sub> solubility in organic carbonate solvents [16].

In this communication we attempt to overcome the above deficiency by expressing gas-solubility in terms of the chemical potential of the solute molecule in its gas phase  $\mu_{\text{ig}}(T)$ , defined at a given (low) reference pressure, say  $P^0 = 1$  bar. The chemical potential of the gas phase at a general pressure  $P$  can then be written as:

$$\mu_{\text{gas}}(P, T) = \mu_{\text{ig}}(T) + k_B T \ln\{\phi(P, T)P/P^0\} \quad (4)$$

Equating the left-hand-side of eq. (1) and the right-hand-side of eq. (4) yields the following (nonlinear) equation for  $P(x, T)$ :

$$P(x, T) = \frac{P^0}{\phi(P, T)} x \exp\{[\mu_{\text{solution}}(x, T) - \mu_{\text{ig}}(T)]/k_B T\} \quad (5)$$

where  $P^0 = 1$  bar, and the  $P$ ,  $T$ , and  $x$  dependence of all terms have been made explicit. Note that the right-hand-side of eq. (5) depends on the solvent only through the term  $\exp\{\mu_{\text{solution}}(x, T)/k_B T\}$ , *i.e.*, the gas-fugacity ( $= \phi P$ ) is proportional to the activity coefficient of CO<sub>2</sub> in the solution phase, and all other terms are intrinsic to CO<sub>2</sub> only. In order to best use eq. (5) we adopt the following strategy:

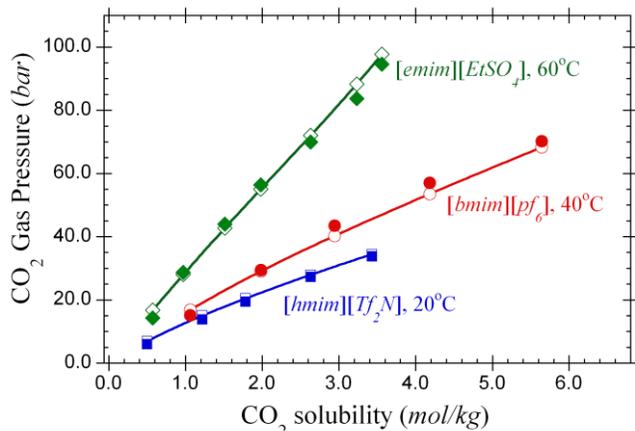
- The chemical potentials  $\mu_{\text{solution}}(x, T)$  are computed by COSMO-RS using the commercial version of the code COSMOtherm [13] with standard parameter settings as detailed in ref. [15].
- The fugacity coefficient  $\phi$  is computed using the Soave-

Redlich-Kwong (SRK) [17, 18] equation of state (EOS) for CO<sub>2</sub>. See supplementary material for more details. At  $T$  around  $T_c$ , the SRK EOS is known to become less accurate for  $P$  greater than  $P_c$  [18]. Thus, our analysis was confined to  $P$  not much higher than  $P_c = 73.7$  bar (for CO<sub>2</sub>).

• Finally,  $\mu_{ig}(T)$  is used a solvent-independent and  $P$ -independent fitting parameter. From a number of numerical experiments with CO<sub>2</sub> solubility in both conventional and IL solvents, we found that the following works well in the 20-60 °C temperature range:

$$\mu_{ig}(T) = \mu_{ig}(T_c) + \alpha(T - T_c), \quad (6)$$

where  $\mu_{ig}(T_c) = -4.43$  kcal/mol and  $\alpha = -0.02$  kcal/mol/K.

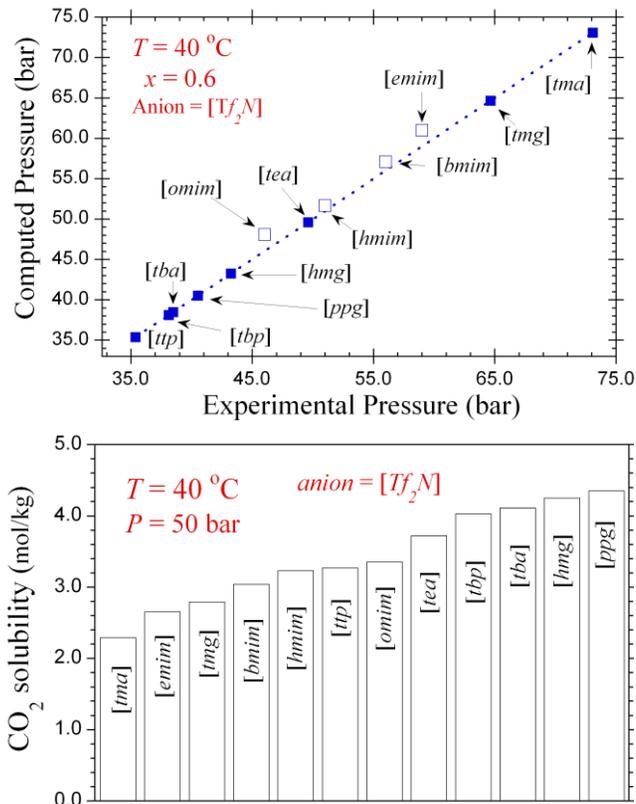


**Figure 1.** CO<sub>2</sub> gas pressure as a function of molality in three different ILs – comparison of computed (open symbols) vs. experimental (filled symbols) values. Abbreviations used: 1-ethyl-3-methyl imidazolium (*emim*), 1-butyl-3-methyl imidazolium (*bmim*), 1-hexyl-3-methyl-imidazolium (*hmim*), ethylsulfate (*EtSO<sub>4</sub>*), hexafluorophosphate (*PF<sub>6</sub>*), and bis(trifluoromethylsulfonyl)imide (*Tf<sub>2</sub>N*). Experimental data for [*hmim*][*Tf<sub>2</sub>N*] are from ref. [19], the rest are from ref. [4]. See supplementary material for structures.

With the above prescriptions we used eq. (5) to compute the CO<sub>2</sub> gas-pressure  $P$  for a number of Imidazolium-cation-based IL's that have been experimentally studied in some detail. Fig. 1 displays results for three such solvents, with different cations and anions, at different temperatures. We see excellent agreement between computed and experimental values for all three cases.

Following validation of the computational approach from results in Fig. 1 we were in position to screen a larger number of solvents for efficient dissolution of CO<sub>2</sub>. First, we explored the effect of varying cations for a fixed anion. The latter was chosen to be bis(trifluoromethylsulfonyl)imide (*Tf<sub>2</sub>N*), because of its high efficiency in dissolving CO<sub>2</sub> found in the experimental literature [2, 5, 19]. Fig 2(top) plots the computed pressure for a fixed CO<sub>2</sub> mole-fraction of  $x = 0.6$  at a constant  $T = 40$  °C, where experimental data was available for a number of solvents. These experimental points, available for solvents with cations [*emim*], [*bmim*], [*hmim*], and [*omim*] are indicated by open squares. The rest of the points (filled squares) are computed values. Several important points to note are: (1) for all (four) open squares the computed values are in excellent agreement with the experimental values (within 10% accuracy). In particular, our calculations correctly recover the experimental trend that  $P$  decreases with longer alkane-chain-length of the cation, thereby implying increasing CO<sub>2</sub> solubility (in terms of mole fraction, for a given  $P$ ) in the order [*emim*] < [*bmim*] < [*hmim*] < [*omim*]; (2) The filled squares, corresponding to computed-only points for non-imidazolium based cations, also appear to show the same trend. Thus, within the ammonium family we find increasing solubility (in mole fraction) in the order [*tma*] < [*tea*] < [*tba*]. The rate of solubility increase in this case is even more dramatic compared to

the imidazolium family because four functional groups are being altered simultaneously; and (3) the guanidinium and the phosphonium family display the lowest pressure, and therefore the highest solubility. However, for efficient solubility the guanidinium ion needs to be fully functionalized, as evidenced from relatively poor solubility in [*tmg*][*Tf<sub>2</sub>N*].



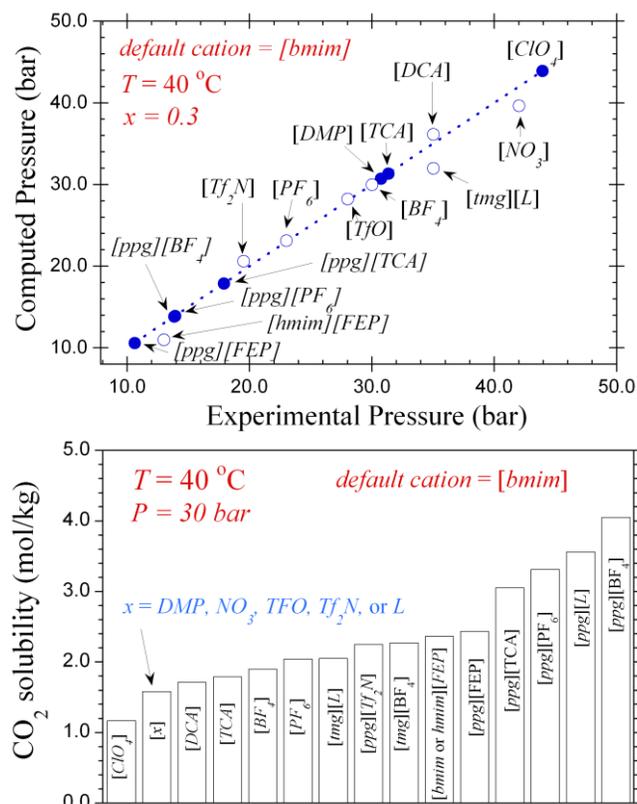
**Figure 2.** (top) Computed vs. Experimental CO<sub>2</sub> pressure for ILs with varying cations and a fixed anion [*Tf<sub>2</sub>N*]. Open symbols indicate available experimental data. All data are taken at  $T = 40$  °C for a fixed CO<sub>2</sub> mole-fraction  $x = 0.6$ ; (bottom) Computed solubility (in molality scale) at a fixed CO<sub>2</sub> gas-pressure of 50 bar. Abbreviations: tetramethylammonium [*tma*], tetramethylguanidinium [*tmg*], trihexyl(tetradecyl)phosphonium [*tpp*], 1-octyl-3-methyl-imidazolium [*omim*], tetrabutylphosphonium [*tbp*], tetraethylammonium [*tea*], tetrabutylammonium [*tba*], hexamethyl-guanidinium [*hmg*], pentamethylpropylguanidinium [*ppg*]. Experimental data for [*emim*][*Tf<sub>2</sub>N*] is from ref. [7], rest are from ref. [5]. For formal names and molecular structures see supplementary material.

For a more practically relevant comparison of the efficiencies of the various solvents in dissolving CO<sub>2</sub> we display in Fig. 2(bottom) the computed solubility in the molality scale [20] at a fixed pressure of 50 bar ( $T = 40$  °C). We find that the order of efficiency within a solvent class generally remains unchanged from Fig. 2(top), unless the cationic functional group becomes too large (e.g., [*tpp*] < [*tbp*]). However, there are a few shuffles in efficiency order among the different classes due to very different molecular weights of the cations. In particular, the all-functionalized guanidinium family [*ppg*] and [*hmg*] appear to be the most efficient, with a solubility of 25-30% more than the best imidazolium explored here. This is a result of both high molar CO<sub>2</sub>-solubility and low molecular weight of such solvents.

Next, we repeated the above study with varying anions and a fixed cation [*bmim*] for which several experimental data points were available for comparison. Fig. 3 summarizes these results, both in terms of molar (top) and molal (bottom) solubilities.

The open circles in Fig. 3(top) correspond to the cases where experimental data were available [5, 21, 22], which (for [*bmim*] cation) in the order of increasing mole-fraction solubility were:

$[NO_3] < [DCA] < [BF_4] < [TfO] < [PF_6] < [Tf_2N]$ . The agreement between computation and experiment was again excellent, within 15% accuracy, and the efficiency order is clearly reproduced. The filled circles (Fig. 3(top)) represent computed results for a few additional anions, including  $[ClO_4]$ ,  $[DMP]$ ,  $[FEP]$ , and  $[TCA]$ . Two additional experimental data points were also included, i.e.,  $[hmim][FEP]$  and  $[tmg][L]$ . In terms of both mole-fraction and molal solubility within the  $[bmim]$  class of cations, the  $[FEP]$  anion appears to be the best, in agreement with recent experiments [21]. Good agreement of computed solubility with experimental value for  $[tmg][L]$  is an important validation of our computational approach for the guanidinium class of cations.



**Figure 3.** (top) Computed vs. Experimental CO<sub>2</sub> pressure for ILs with varying anions and a fixed cation  $[bmim]$ . A few additional cation based ILs are also included. All data are taken at  $T = 40\text{ }^\circ\text{C}$  for a fixed CO<sub>2</sub> mole-fraction  $x = 0.3$ ; (bottom) Computed solubility (in molality scale) at a fixed CO<sub>2</sub> gas-pressure of 30 bar. Anion abbreviations used: perchlorate  $[ClO_4]$ , trifluoromethanesulfonate  $[TfO]$ , lactate  $[L]$ , dimethylphosphate  $[DMP]$ , nitrate  $[NO_3]$ , dicyanamide  $[DCA]$ , tricyanomethanide  $[TCA]$ , tetrafluoroborate  $[BF_4]$ , tris(pentafluoroethyl)trifluorophosphate  $[FEP]$ , hexafluoro-phosphate  $[PF_6]$ . Experimental data:  $[hmim][FEP]$  from ref. [21],  $[tmg][L]$  from ref. [22], and all remaining from ref. [5]. For formal names and molecular structures see supplementary material.

Finally, it was natural to combine the best cations from Fig. 2 with various anions from Fig. 3 to see if these ILs can have even higher molality-scale solubility of CO<sub>2</sub>. To this end, we have included in Fig. 3 results in ILs containing the  $[ppg]$  cation and the  $[L]$ ,  $[TCA]$ ,  $[BF_4]$ ,  $[FEP]$ , and  $[PF_6]$  anions. As Fig. 3(bottom) indicates, all five of these ILs possess higher molal CO<sub>2</sub>-solubility than the best imidazolium IL (i.e.  $[bmim]$  or  $[hmim][FEP]$ ). However, the molal solubility order as a function of anions drastically changes between the imidazolium and the guanidinium cation classes. In particular,  $[ppg][BF_4]$  appears to be ~80% more efficient than  $[ppg][FEP]$ , which, interestingly is not much more efficient than  $[bmim][FEP]$ . Results in  $[hmg]$ -

based IL's are similar to  $[ppg]$ , and not included here for clarity. Our search was by no means exhaustive, and leaves much room for higher efficiency.

In summary, we developed a computational approach that reproduces CO<sub>2</sub> solubility within 10-15% accuracy in a general (liquid) solvent over a range of temperatures and CO<sub>2</sub> pressures of practical interest. The accuracy of the method allows one to obtain useful trends and predict solvents that are expected to possess much higher solubility than the solvents explored so far in the experimental literature. In particular we predict that all-functionalized-guanidinium-cation and  $[BF_4]$  anion based ILs should possess ~80% higher (molality-scale) solubility than the best imidazolium-based ILs experimentally explored so far. We recognize that some of these predicted solvents could be unsuitable for practical reasons, e.g., high melting temperature, high viscosity, or possible chemical reactivity. Yet, we hope that the present approach could be used over larger classes of cations and anions to discover practically usable solvents with much higher CO<sub>2</sub> solubility.

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## References

1. T. Welton, *Chem. Rev.* **1999**, *99*, 2071; J. D. Holbrey, K. R. Seddon, *Clean Products and Processes* **1999**, *1*, 223; J. Dupont, R. F. de Souza, P. A. Suarez, *Z. Chem. Rev.* **2002**, *102*, 3667.
2. J. Ilconich, C. Myers, H. Pennline, D. Luebke, *J. Membrane Sci.* **2007**, *298*, 41.
3. L. A. Blanchard, D. Hancu, D.; E. J. Beckman, J. F. Brennecke, *Nature* **1999**, *399*, 28; L. A. Blanchard, J. F. Brennecke, *Ind. Eng. Chem. Res.* **2001**, *40*, 2550.
4. L. A. Blanchard, Z. Y. Gu, J. F. Brennecke, *J. Phys. Chem. B* **2001**, *105*, 2437.
5. S. N. V. K. Aki, B. R. Mellein, E. M. Saurer, J. F. Brennecke, *J. Phys. Chem. B* **2004**, *108*, 20355.
6. M. J. Muldoon, S. N. V. K. Aki, J. L. Anderson, J. K. Dixon, J. F. Brennecke, *J. Phys. Chem. B* **2007**, *111*, 9001.
7. A. M. Schilderman, S. Raeissi, C. J. Peters, *Fluid Phase Equilibria* **2007**, *260*, 19.
8. J. Kumelan, A. P-S. Kamps, D. Tuma, G. Maurer, *J. Chem. Eng. Data* **2006**, *51*, 1802.
9. C. Cadena, J. L. Anthony, J. K. Shah, T. I. Morrow, J. F. Brennecke, E. J. Maginn, *J. Am. Chem. Soc.* **2004**, *126*, 5300.
10. J. Deschamps, M. F. C. Gomes, A. A. H. Padua, *ChemPhysChem* **2004**, *5*, 1049.
11. B. L. Bhargava, S. Balasubramanian, *Chem. Phys. Lett.* **2007**, *444*, 242.
12. A. Klamt, G. Schüürmann, *J. Chem. Soc. Perkin. Trans.* **1993**, *2*, 799.
13. A. Klamt, *COSMO-RS: From Quantum Chemistry to Fluid Phase Thermodynamics and Drug Design*, Elsevier, 2005. The commercial implementation, COSMOtherm, C2.1 R 01.06 was used in this work.
14. For dissolution from the solid phase, an additional Gibb's free energy of fusion needs to be included in eq. (2).
15. A. Maiti et al., *Phys. Chem. Chem. Phys.* **10**, 5050 (2008).
16. P. Kolář et al., *Fluid Phase Equilibria* **2005**, *228*, 59.
17. G. Soave, *Chem. Eng. Sci.* **1972**, *27*, 1197.
18. D. P. Tassios, *Applied Chemical Engineering Thermodynamics*, Springer-Verlag, Berlin, Germany (1993).
19. J. Kumelan, A. P-S. Kamps, D. Tuma, G. Maurer, *J. Chem. Thermodynamics* **2006**, *38*, 1396.
20. Solubility in the molality scale is defined as  $m = x / ((1-x)M_w)$ , where  $x$  is molar solubility and  $M_w$  the solvent molecular weight.
21. X. Zhang, Z. Liu, W. Wang, *AIChE J.* **2008**, *54*, 2717.
22. S. J. Zhang, X. L. Yuan, Y. H. Chen, X. P. Zhang, *J. Chem. Eng. Data* **2005**, *50*, 230.