# Understanding The Solubility Of Gases In Alkyl-Imidazolium Based Ionic Liquids By A Molecular Modelling Approach.

Jordi S. Andreu[1,2], Lourdes F. Vega[1,2]*,
[1]Institut de Ciencia de Materials de Barcelona, Consejo Superior de Investigaciones Científicas,
Campus de la UAB, 08193 Bellaterra, Barcelona, Spain
[2]MATGAS Research Center and Air Products and Chemicals,
Campus de la UAB, 08193 Bellaterra, Barcelona, Spain
E-mail: vegal@matgas.com; fax: +34-935929951

Room temperature ionic liquids (ILs) are currently receiving much attention due to their interesting physico-chemical properties: negligible vapor pressure, extremely wide range of compositions (which allows the tuning of physical properties through design), etc. For these reasons, ILs are being postulated as promising alternative solvents for a number of technological applications in the context of green processes.

A careful characterization of them is needed prior they are put into final use for a specific application; this includes knowledge of the relationship between the structure and the properties. This knowledge can be obtained by experimental techniques, simulations and/or theoretical approaches. A main advantage of a theory or equation of state versus the other techniques is the speed in which these calculations are performed, provided they are accurate enough to reproduce the experimental data. This work deals with developing accurate molecular models for ILs and gases in the context of a molecular-based equation of state, the soft-SAFT equation, searching for predictive tools for these systems.

## Introduction

ILs are usually defined as organic salts that are liquid below 100ºC with a set of physico-chemical properties which make them suitable for several applications. These salts are typically composed by an asymmetric organic cation like imidazolium, ammonium, pyrrolidinium, pyridinium, etc, and an organic or inorganic anion such as chloride, bromide, hexafluorophosphate, tetrafluoroborate, bis(trifluoromethylsulfonyl)imide and others. Since they are salts, they tend to have extremely low vapor pressure (limiting their volatility), good thermal stability, low melting point, high ionic conductivity and large electrochemical window. The main feature of ILs is that their properties can be easily tailored by the selection of the anion and the cation. The number of potential ILs that can be synthesized is huge and their properties can be tuned according to the desired applications. For this reason, a good understanding about the dependence of their physico-chemical properties on their microscopic structure and theoretical predictive tools is desired in order to enhance the design of new ILs for selected applications.

Their tunable and unique properties make them a good alternative to traditional solvents used in synthesis and extraction, offering the possibility to develop new processes. Specifically, understanding $CO_2$ solubility in ionic liquids has become an important issue for several applications, like supercritical fluid extraction and gas separations [1], [2].

As a first step for the modeling work we have focused on three of the most studied families of ILs found in literature. These ILs are the [$C_n$-mim][$BF_4$] , the [$C_n$-mim][$PF_6$] and the [C$_n$-mim][Tf$_2$N] families. The approach we followed in this work is the following: first of all, a molecular model for the ILs was developed and parameters fitted to available experimental data (density versus temperature), providing a correlation of the molecular parameters with the molecular weight of the ILs. Before fitting any binary data, molecular parameters from the pure compounds were used to check if the model was able to capture the behavior of the mixture. Then, a unique energy binary is used as a temperature independent fitting parameter in order to obtain quantitative agreement with experimental data of mixtures.

## The *soft*-SAFT EoS

SAFT equations are usually written in terms of the residual Helmholtz free energy. Each term in the equation represents different microscopic contributions to the total free energy of the fluid. The equation is written as:

$$a^{res} = a^{ref} + a^{chain} + a^{assoc} + a^{polar} \tag{1}$$

where $a^{res}$ is the residual Helmholtz free energy density of the system. The superscripts *ref*, *chain*, *assoc* and *polar* refer to the contributions from the reference term, the formation of the chain, the association, and the polar interactions, respectively, depending on the system under study.

In the soft-SAFT EoS, [3], [4], [5] the reference term is a Lennard-Jones (LJ) spherical fluid, which accounts both for the repulsive and attractive interactions of the monomers forming the chain. As in previous works the accurate EoS of Johnson et al. [6] is used here. For the case of mixtures the same equation is used by applying the van der Waals one-fluid theory, with generalized Lorentz-Berthelot mixing rules:

$$\sigma_{ij} = \eta_{ij}\left(\frac{\sigma_{ii}+\sigma_{jj}}{2}\right) \tag{2}$$

$$\varepsilon_{ij} = \xi_{ij}\left(\varepsilon_{ii}\varepsilon_{jj}\right)^{1/2} \tag{3}$$

here $\eta$ and $\xi$ are the size and energy binary adjustable parameters, respectively. The equation is used in a purely predictive manner from the pure component parameters when $\eta$ and $\xi$ are equal to unity, while values different from unity mean the use of one or two binary parameters, taking into account the differences in size and/or energy of the segments forming the two compounds in the mixture.

The chain and association terms come from Wertheim's theory [7]:

$$a^{chain} = \rho k_B T \sum_i x_i (1-m_i) \ln g_{LJ} \tag{4}$$

$$a^{assoc} = \rho k_B T \sum_i x_i \sum_\alpha \left(\ln X_i^\alpha - \frac{X_i^\alpha}{2}\right) + \frac{M_i}{2} \tag{5}$$

here $\rho$ is the molecular density, T is the temperature, $m$ is the chain length, $x_i$ is the molar fraction of component $i$, $k_B$ the Boltzmann constant and $g_{LJ}$ is the radial distribution function of a fluid of LJ spheres at density $\rho_m = m\rho$, evaluated at the bond length σ. $M_i$ the number of associating sites of component *i*, and $X_i^\alpha$ the mole fraction of molecules of component *i* non bonded at site α, which accounts for the contributions of all the associating sites in each specie.

The leading multipolar term for fluids of linear symmetrical molecules, like carbon dioxide, nitrogen, acetylene, etc., is the quadrupole-quadrupole potential. An expansion of the Helmholtz free energy density in terms of the perturbed quadrupole-quadrupole potential with the Padé approximation was proposed by Stell et al. [8]:

$$a^{qq} = a_2{}^{qq}\left(\frac{1}{1-\dfrac{a_3{}^{qq}}{a_2{}^{qq}}}\right) \tag{6}$$

Expressions for $a_2$ and $a_3$, the second and third-order perturbation terms, were derived for an arbitrary intermolecular reference potential [9], [10] and involve the state variables, molecular parameters, and the integral for the reference fluid. A detailed derivation of these expressions is given elsewhere [11]. This new term in the soft-SAFT EoS involves an additional molecular parameter, *Q*, the quadrupolar moment.

## The molecular model

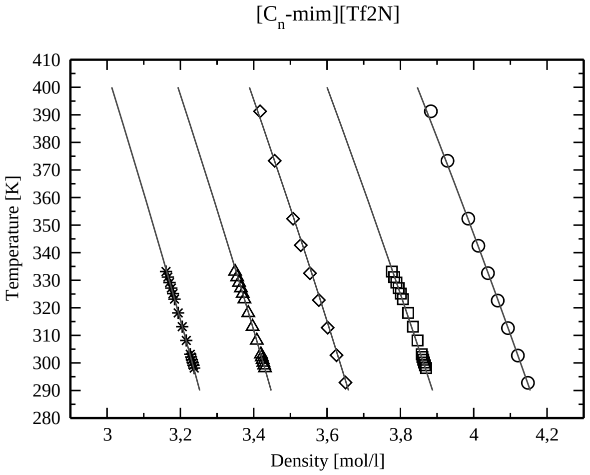
In order to use soft-SAFT for a particular system, a molecular model of each compound should be chosen. The carbon dioxide molecule was modeled as a LJ chain in which explicit quadrupolar interactions were taken into account. In this case, the molecule was represented by five molecular parameters: *m*, the chain length, σ, the segment size, ε, the energy parameter of the segments making the chain and those related to the quadrupolar interactions: the quadrupolar moment *Q* and $x_p$, defined as the fraction of segments in the chain that contain the quadrupole. The value for the quadrupole moment *Q* for this molecule obtained from the fitting is in agreement with the ones present in literature [12], [13]. Regarding the molecular parameter $x_p$, it was fixed to 1/3 for carbon dioxide, thus mimicking the molecule as three segments with a quadrupole in one of them. Therefore, with $x_p$ and *Q* fixed, only the usual *m*, *σ* and *ε* parameters need to be adjusted.

Based on results obtained from molecular dynamics simulations [14], [15], [16] showing the ion pairing of these systems, we have modeled these ILs as LJ chains with one associating site in each molecule [17]. This model mimics the neutral pairs (anion plus cation) as a single chain molecule with this association site describing the specific interactions because of the charges and the asymmetry.

Following a similar approach, a model for the [$C_n$-mim][$Tf_2N$] family of ILs have been developed leading also a good agreement with the experimental results present in literature.

## Results

A needed step before applying the equation to mixtures is to obtain the molecular parameters of the pure compounds. We have used the molecular parameters for $CO_2$ obtained in a previous work [18]. Regarding the ILs, the chain length, size and energy parameters were obtained by fitting to available density-temperature data. In order to keep the minimum number of fitted parameters, we have decided, as a first approximation, to use the association parameters previously used for the alkanols, thus avoiding further fitting.



**ure 1.** Density versus temperature diagram the [$C_n$-mim][$Tf_2N$] ILs family: symbols experimental data from different authors m n=2 circles to n=6 asterisks) and solid s are soft-SAFT calculations :esponding to the pure compounds ımeters in the fitting procedure.

Following previous works [19], we were able to correlate the molecular parameters of the ILs with their molecular weight. These correlations enable the equation with predictive power, as they provide the possibility to predict the behavior of heavier members of the series, not included in the fitting procedure. This is particularly useful for the case of ILs, as it has been demonstrated than the toxicity of the ILs increases as the alkyl chain length increases, making experimental measurements more dangerous [20].

## Mixtures: solubility of $CO_2$ in ionic liquids

We present and discuss here calculations performed with the aforementioned models within the soft-SAFT approach as applied to those families of ILs with $CO_2$, compared with available experimental data.

We first studied the mixture [$C_4$-mim][$BF_4$] + $CO_2$ at low pressures at four different temperatures, between T=283K and T=348K. Figure 2a depicts the solubility isotherms obtained for these mixtures as compared to available experimental data [21]. Soft-SAFT calculations presented here were done with pure component parameters, and hence they are pure predictions. It is striking to see the accuracy of these calculations as compared to the experimental data, indicating that the simple model presented in the previous section is able to capture the solubility of these mixtures in quantitative agreement with experimental data.

Within the same family, predictive results for [$C_2$-mim][$BF_4$] + $CO_2$, [$C_4$-mim][$BF_4$] + $CO_2$ and [$C_6$-mim][$BF_4$] + $CO_2$ mixtures at high pressures are obtained within that model. The model is able to capture the sharp increase in pressure at a given $CO_2$ composition, without any fitting. However, quantitative predictions with experimental data are not obtained in this case. Soft-SAFT is able to quantitatively reproduce the behavior of these mixtures at high pressures with a single temperature independent binary parameter $\xi$=0.985 (very close to unity) for all members of the family.

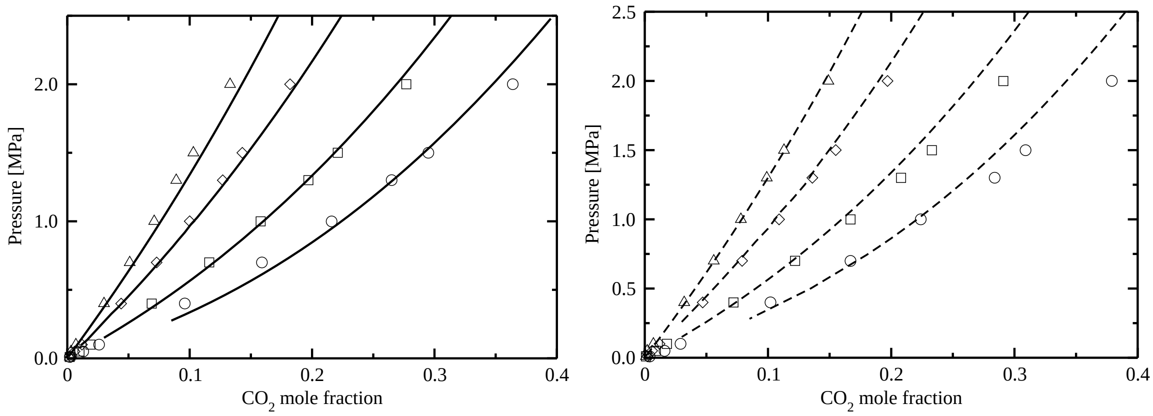
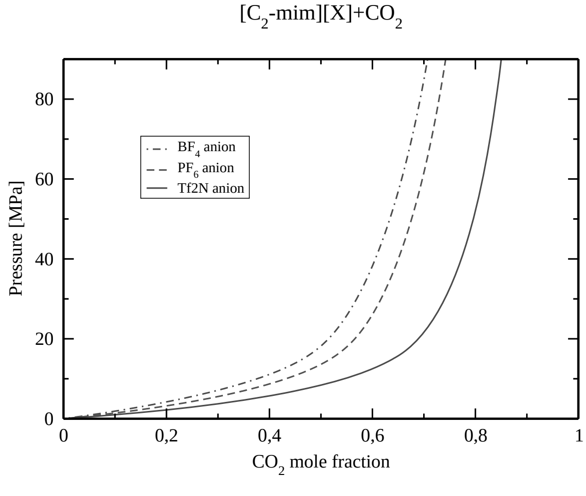


**Figure 2. a)** Solubility of $CO_2$ in the [$C_4$-mim][$BF_4$] at four different temperatures: T=283K (circles), T=298K (squares), T=323K (diamonds) and T=348K (triangles). Solid lines are predictions with soft-SAFT model without fitting. **b)** Solubility of $CO_2$ in the [$C_n$-mim][$PF_6$] at low pressures. Symbols as in figure 1a. In that case, the use of a binary parameter independent of temperature is needed to fit the experimental data ($\xi$=0.970).

As in the previous case, the same methodology was applied to the systems [$C_n$-mim][$PF_6$] + $CO_2$ and [$C_n$-mim][$Tf_2N$]. Soft-SAFT results concerning $CO_2$ solubility isotherms in [$C_4$-mim][$PF_6$] up to 2MPa and at four different temperatures are shown in Figure 2b. Contrary to what happens to the [$C_4$-mim][$BF_4$] family, the solubility of $CO_2$ estimated from the pure compounds parameters at low pressures is overestimated, as well as the solubility isotherms at high pressures. Again, these deviations respect to the experimental data [22], [23], [24] were corrected by using a single binary parameter ($\xi$=0.970 in this case) for all isotherms and for all compounds of the family, showing excellent agreement with experimental data.

Finally, taken advantage of the fact that the parameters of the equation are independent of the thermodynamic conditions we present a comparison of the solubility of $CO_2$ in the three families at the same conditions, for the same cation. As shown in Figure 3 the solubility increase is [$BF_4$]<[$PF_6$]<[$Tf_2N$].



**ure 3.** Predicted solubility of $CO_2$ in -mim][$BF_4$], [$C_2$-mim][$PF_6$] a [$C_2$-n][$Tf_2N$] using the soft-SAFT model at 363.15 K.

## nclusions

We have shown the capability of soft-SAFT to reproduce the solubility of $CO_2$ in different families of ILs in a wide range of temperatures and pressures with a simple model for the IL. The key of the model is to mimic the strong pair interaction between the anion and the cation as a specific associating site in an end of the LJ chain which represents the IL. Only five parameters were needed to model the ILs. The model was able to capture the sharp rise in pressure as the solubility of $CO_2$ increases from pure component parameters, without the need of any specific assumption regarding the interaction of the ILs with $CO_2$. Further more, the equation can be used for comparative purposes of different compounds, searching for trends within different families.

*Acknowledgments*. Several helpful discussions with C. Rey-Castro and F. Llovell are gratefully acknowledged. Financial support has been provided by the Spanish Government, (project CTQ2005-00296/PPQ), the Catalan Government (2005SGR-00288), and Air Products and Chemicals. J.S.A. acknowledges a grant from MATGAS 2000 AIE.

**References:**

[1] Blanchard, L.A., Brennecke, J.F., *Ind. Eng. Chem. Res.*, 40, **2001**, p. 287.
[2] Baltus, R.E., Counce, R.M., Culbertson, B.H., Luo, H., DePaoli, D.W., Dai, S., Duckworth, D.C., *Sep. Sci. Technol.*, 40, **2005**, p. 524.
[3] Blas, F.J., Vega, L.F., *Mol. Phys.*, 92, **1997**, p. 135.
[4] Pàmies, J.C., Vega, L.F., *Ind. Eng. Chem. Res.*, 40, **2001**, p. 2532.
[5] Blas, F.J., Vega, L.F., *Ind. Eng. Chem. Res.*, 37, **1998**, p. 660.
[6] Johnson, J., Zollweg, J., Gubbins, K.E., *Mol. Phys.*, 78, **1993**, p. 591.
[7] Wertheim, M.S., *J. Stat. Phys.*, 35, 19, Ibid., 42, **1984-1986**, p. 459, 477.
[8] Stell, G., Rasaiah, J.C., Narang, H., *Mol. Phys.*, 27, **1974**, p. 1393.
[9] Two, C.H., Gubbins, K.E., Gray C.G., *Mol. Phys*, 29, **1975**, p. 713.
[10] Two, C.H., *PhD Dissertation, University of Florida,* **1976**.
[11] Gubbins, K.E., Two, C.H., *Chem. Eng, Sci.*, 33, **1978**, p. 863.
[12] Vrabec, J., Stoll, J., Hasse, H., *J. Phys. Chem. B*, 105, **2001**, p. 12126.
[13] Vrbancich, J., Ritchie, G.L.D., *J. Chem. Soc. Faraday II*, 76, **1980**, p. 648.
[14] Urahata, S.R., Ribeiro, M.C.C., *J. Chem. Phys*, 120 (4), **2004**, p. 1855.
[15] Morrow, T.I., Maginn, E.J., *J. Chem. Phys. B.*, 106, **2002**, p. 12807.
[16] Del Pópolo, M.G., Voth, G.A., *J. Phys. Chem. B.*, 108, **2004**, p. 1744.
[17] Andreu, J.S., Vega, L.F., *J. Phys. Chem C.*, 111, **2007**, p. 16028,
[18] Dias, A.M.A., Carrier, H., Daridon, J.L., Pàmies, J.C., Vega, L.F., Coutinho, J.A.P., Marrucho, I.M., *Ind. Eng. Chem. Res.*, 45, **2006**, p. 2341.
[19] Pàmies, J.C., Vega, L.F., *Ind. Eng. Chem. Res.*, 40, **2001**, p. 2532.
[20] Ranke, J., Mölter, K., Stock, F., Bottin-Weber, U., Poczobutt, J., Hoffmann, J., Ondruschka, B., Filser, J., Jastorff, B., *Ecotoxicol. Environ. Saf*, 58, **2004**, p. 396.
[21] Shiflett, M.B., Yokozeki, A., *Ind. Eng. Chem. Res.*, 44, **2005**, p. 4453.
[22] NIST Chemistry Webbook, http://webbook.nist.gov/chemistry
[23] Shariati, A., Peters, C.J., *J. Supercrit. Fluids,* 30, **2004,** p. 139.
[24] Shariati, A., Gutkowski, K., Peters, C.J., *AIChE*, 51, **2005**, p. 1532.