SYSTEMATIC STUDY ON THE SOLUBILITY OF GASES IN ALKYL-IMIDAZOLIUM BASED IONIC LIQUIDS FROM A MOLECULAR MODELING APPROACH

Jordi S. Andreu, Institut de Ciència de Materials de Barcelona, Consejo Superior de Investigaciones Científicas (ICMAB-CSIC) and MatGas Research Center, Bellaterra. Barcelona, Spain.
Lourdes F. Vega, Institut de Ciència de Materials de Barcelona, Consejo Superior de Investigaciones Científicas (ICMAB-CSIC), MatGas Research Center and Air Products and Chemicals Inc, Bellaterra. Barcelona, Spain.

Introduction

Much scientific and technological interest is currently focused on room temperature ionic liquids (ILs). This is due the “designer” properties of some ILs, particularly those based on the imidazolium cation where the physical properties of the liquid may be controlled by incorporation of appropriate functional groups, along with the environmentally friendly properties of ILs, most notably negligible vapor pressure, high thermal stability, good solvent ability toward a wide range of solutes, etc., making ILs attractive candidates as replacements for volatile organic solvents. 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. Theoretical approaches offer the advantage of the speed in which these calculations are performed, provided they are accurate enough to reproduce the experimental data.

The soft-SAFT Equation of State

Within the framework of SAFT, the EoS of a fluid is a perturbation expansion given in terms of the residual molar Helmholtz energy. The Helmholtz energy is defined as the difference between the total Helmholtz energy and that of an ideal gas at the same temperature T and molar density ρ. SAFT implicitly assumes that there are three major contributions to the total intermolecular potential of a given molecule: *a)* the repulsion-dispersion contribution typical of individual segments *b)* the contribution due the fact that these segments can form long lived chains and *c)* the contribution due to the possibility that some segments form association complexes with other molecules. Furthermore, we added a new term a^{polar} which takes into account the quadrupolar interactions between molecules, in case they exist. According to this scheme, the residual Helmholtz energy can be written as:

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

Here, 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, [1], [2], [3] the reference term is a Lennard-Jones (LJ) spherical fluid, which accounts for both the repulsive and attractive interactions of the monomers forming the chain. As in previous works the accurate EoS of Johnson et al. [4] 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 η and ξ are the size and energy binary adjustable parameters, respectively. The equation is used in a purely predictive manner from the pure component parameters when η and ξ 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 [5], and they are formally identical in the different versions of SAFT:

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

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

here ρ 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^α 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. [6]:

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

Expressions for a_2 and a_3, the second and third-order perturbation terms, were derived for an arbitrary intermolecular reference potential [7], [8] and involve the state variables, molecular parameters, and the integral for the reference fluid. A detailed derivation of these expressions is given elsewhere [9]. This new term in the soft-SAFT EoS involves an additional molecular parameter, *Q*, the quadrupolar moment, which is usually taken from experimental data.

The molecular model for gases and the ionic liquids

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, H_2 and Xe obtained in previous works [10], [11], without any further fitting. In this way, the transferability of these models as well as the performance of the equation is enhanced. We refer to those previous works for a detailed explanation on those models.

Two different models for the ILs have been used in this work. The first model is applied for the alkyl-imidazolium ILs with the $[BF_4]^-$ and $[PF_6]^-$ anions [12]. Based on results obtained from molecular dynamics simulations and experimental evidences [13], [14], [15], we have modeled these ILs as LJ chains enclosing anion plus cation together and using one associating site in each molecule, which accounts for the competition between counter ions from different molecules. The chain length, size and energy parameters were obtained by fitting the equation to experimental density data available in literature; the specific data was selected according to its robustness and wide thermodynamic range. In order to keep the minimum number of fitted parameters, at first approximation, the association parameters previously used for the alkanols family were used, thus avoiding further fitting.

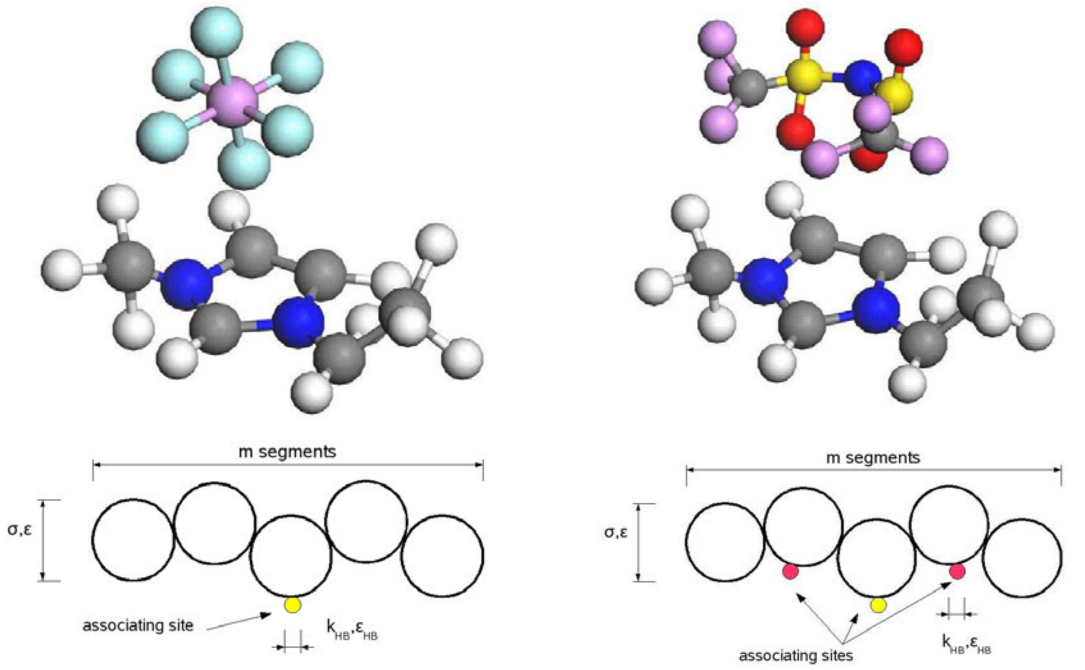

Figure 1. Sketch of the models used to describe the alkyl-imidazolium families of ILs studied in this work. The associating sites account for the competitive attraction between counterions. Left: alkyl-imidazolium [PF6] ILs, right alkyl-imidazolium [Tf2N] ILs.

The members of the alkyl-imidazolium $[Tf_2N]$ family have been modeled with a different approach [16]. Since in the soft-SAFT EoS an associating site is used to represent short range and highly directional attractive forces between molecules, we used this feature to mimic the main interactions between counter ions. The main interaction between counterions is due the coulombic forces as a consequence of their opposite charge. Moreover, the delocalization of the anion electric charge due the oxygen atoms attached to the nitrogen enhance the possibility of interaction with the surrounding cations through them. According to these interactions we used a site *A* representing the nitrogen atom and 2 *B* sites representing the delocalized charge due to oxygen atoms on the anion. Each type of associating site is identically defined, but only *AB* interactions were allowed between different IL molecules. As well as for the model used for the other two ILs presented in this work, the chain length, size and energy parameters were fitted to experimental density data while the the same associating parameters values were also used for this family. This was done for two different reasons: to avoid further fitting of parameters and to check the transferability of the new model. A sketch of these two models is provided in figure 1.

Results I: Pure compounds

Following previous works, we were able to correlate the molecular parameters of the ILs with their molecular weight. Three of the molecular parameters for the alkyl-imidazolium family correlate with the molecular weight, while the other two parameters (those corresponding to the association) were kept constant for the whole family of ILs. None of these parameters are temperature dependent and this implies that those models are independent of the thermodynamic conditions. The correlation for the molecular parameters of the [C_n-mim][PF_6] is as follows:

$$m = 0.0188M_w - 0.7590 \tag{7}$$
$$m\sigma^3\ (\AA^3) = 1.926M_w - 221.350 \tag{8}$$
$$m\varepsilon/k_B\ (K) = 8.540M_w - 514.820 \tag{9}$$

The correlation for the molecular parameters of the [C_n-mim][BF_4] is:

$$m = 0.0188M_w + 0.2440 \tag{10}$$
$$m\sigma^3\ (\AA^3) = 1.847\ M_w - 119.760 \tag{11}$$
$$m\varepsilon/k_B\ (K) = 8.530\ M_w - 40.123 \tag{12}$$

and the correlation for the molecular parameters of the [C_n-mim][Tf_2N] reads as:

$$m = 0.0059M_w + 3.4919 \tag{13}$$
$$m\sigma^3\ (\AA^3) = 1.877\ M_w - 313.670 \tag{14}$$
$$m\varepsilon/k_B\ (K) = 2.898\ M_w - 1000.700 \tag{15}$$

These correlations enable the equation with predictive power, as they provide the possibility to predict the behavior of heavier members of these series, not included in the fitting procedure, providing then the possibility of studying compounds for which few solubility data have been reported. Moreover, 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 [15].

Once the models for the pure compounds were developed and parameters obtained, they are used to predict the solubility behavior of hydrogen, carbon dioxide and xenon in the selected imidazolium families of ILs. Results concerning the application of these models to available data are presented and discussed in the next section.

Results II: Solubility of gases in alkyl-imidazolium ionic liquids

We present and discuss here calculations performed with the aforementioned models with the soft-SAFT EoS as applied to three families of ILs with H_2, CO_2 and Xe, compared with available experimental data.

We first studied the mixtures [C_4-mim][BF_4] + CO_2 and [C_4-mim][PF_6] + CO_2 at low pressures in a wide range of temperature (T=283K-348K). The soft-SAFT calculations obtained were done with pure component parameters, and hence they are pure predictions. The accuracy of these calculations as compared to the experimental data is good, 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. However, small deviations in the [PF_6] family were found and the use of one independent temperature parameter (ξ=0

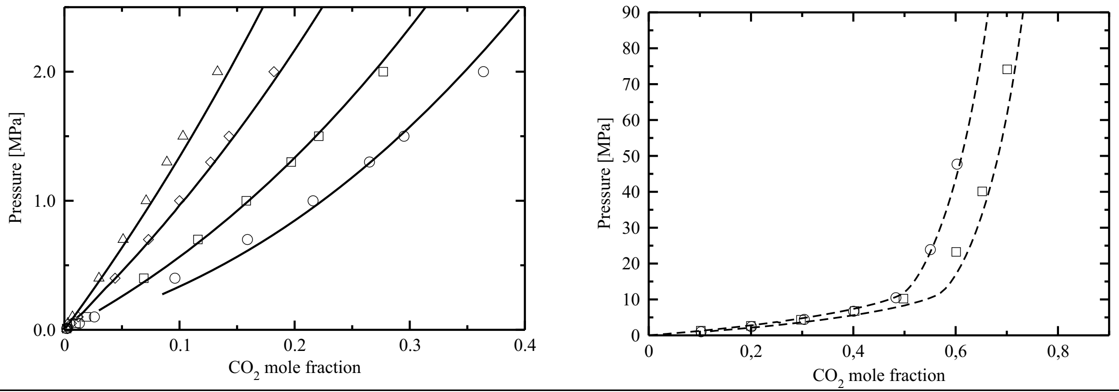

Figure 2. a) Solubility of CO_2 in the [C_4-mim][BF_4] at four different temperatures: T=283K (circles), T=298K (squares), T=323K (diamonds) and T=348K (triangles). Solid lines are predictions with soft-SAFT model without fitting. **b)** Solubility of CO2 in the [C_n-mim][BF_4] at 330K. Symbols represent experimental data for n=4 (circles) and n=6 (squares). Dashed lines corresponds to the soft-SAFT model with ξ=0.985 at n = 2, 4.

Predictions at high pressures and for other members of these families of ILs were performed next (figure 3). 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 were not obtained in this case. Soft-SAFT is able to quantitatively reproduce the behavior of these mixtures at high pressures with a single binary temperature independent parameter ξ=0.985 (very close to unity) for all members of the [PF_6] family.

This transferable parameter allows the model to capture the experimental trend exhibited by these systems even at high concentrations of CO_2, reproducing the sharp rise in the pressure with the correct slope in almost quantitative agreement with experimental data, as in the previous case. Note that the ξ parameter (equation 3) takes into account the differences in energy of the segments forming the chains (van der Waals type interactions), no s

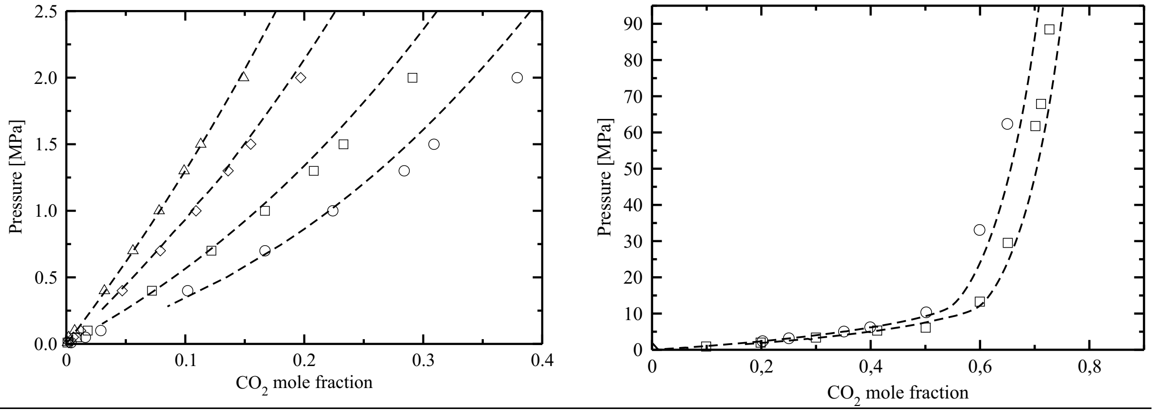

Figure 3. a) Solubility of CO_2 in the [C_n-mim][PF_6] at low pressures. Symbols as in figure 2a. In that case, the use of a binary parameter independent of temperature is needed to fit the experimental data ($\xi=0.970$). **b)** Solubility of CO_2 in [C_4-mim][PF_6] and [C_6-mim][PF_6] at high pressures. Symbols are experimental data for n=4 (circles) and n=6 (squares). In this case, the same binary parameter value is used at low and high pressures.

Next, results concerning the applicability of the soft-SAFT model developed for the Tf_2N family are presented. Pure predictions for the systems [C_n-mim][Tf_2N] + CO_2 were used to test the model of the pure compounds. As in the previous cases with simpler ILs, the main trends of these systems were well described without any fitting of the binary parameters. However, a temperature independent mixture parameter was needed to describe the experimental data available for these systems, obtaining excellent results. In that case, a different value of this parameter is needed for each member of the ionic liquid family ($\xi=0.985$ for n=2; $\xi=0.972$ for =4; $\xi=0.948$ for n=6), contrary to the previous case in which one parameter sufficed for the whole family. This situation can be understood through the more complex nature of the anion, which has a more complex atomic structure and conformation.

According to the good performance of these models describing the solubility behavior of H_2 and Xe in these ILs, and also to the small values obtained for energy binary parameter, the equation was used as a predictive tool to compare the different solubility behavior of these three gases in these families of alkyl-imidazolium based ILs, at similar thermodynamic conditions.

Two comparative predictions of the solubility of gases in alkyl-imidazolium ILs using the aforementioned models are presented next. First, we compare the solubility of CO_2 and H_2 in different members of the [C_n-mim][Tf_2N] family at T=333K and in [C_n-mim][PF_6] family at T=330K (figure 4). We observe that the highest absorption capability of these gases is found for the ILs with the longest alkyl chain length. The same behavior was found for mixture with xenon.

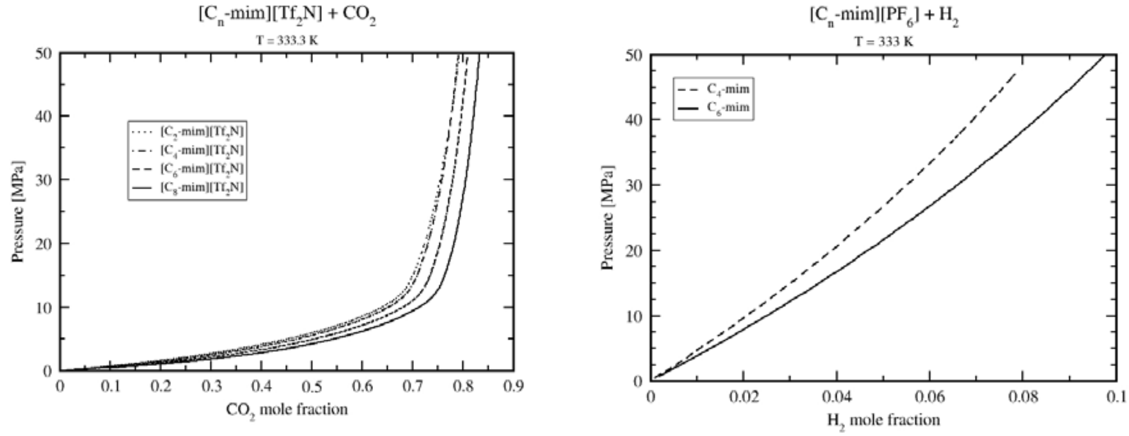

Figure 4. Solubility of carbon dioxide in [C_n-mim][Tf_2N] for n=2 (dotted line), n=4 (dashed-dotted line), n=6 (dashed line) and n=8 (solid line) at T=333.3K using the optimized parameters. We see that CO_2 solubility increases as the chain length of the imidazolium ring increases (left). The same behavior is observed for mixtures with hydrogen and the alkyl imidazolium hexafluorophosphate IL (right).

Secondly, we compare the strong anion dependence on the absorption of H_2, CO_2 and Xe (figure 5), showing that the [Tf_2N]$^-$ anion enhances the absorption within the imidazolium family.

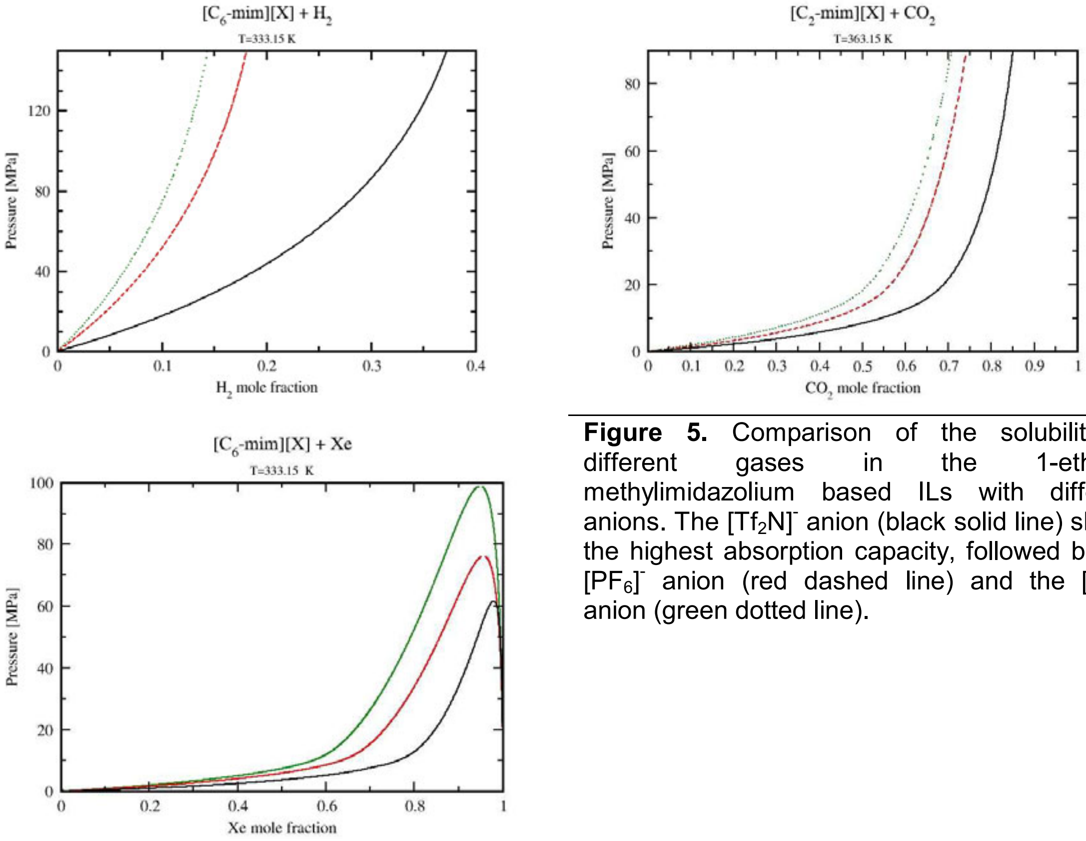

Figure 5. Comparison of the solubility of different gases in the 1-ethyl-3-methylimidazolium based ILs with different anions. The [Tf_2N]$^-$ anion (black solid line) shows the highest absorption capacity, followed by the [PF_6]$^-$ anion (red dashed line) and the [BF_4]$^-$ anion (green dotted line).

Conclusions

We have shown the capability of soft-SAFT to reproduce the solubility of H_2, CO_2 and Xe in three 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 the IL molecule. Only five parameters were needed to model the ILs while the association parameters were kept constant throughout the three families. The models were able to capture the sharp rise in pressure as the solubility of the gases increases from pure component parameters, without the need of any specific assumption regarding the interaction of the ILs with the gases. Moreover, the robustness of the soft-SAFT equation as well as the models developed provides a fast tool which can be used to evaluate the absorption capacity of this alkyl-imidazolium ILs for others gases of interest.

Acknowledgements

Discussions with Drs. Brian K. Peterson and Carlos Rey-Castro are gratefully acknowledged. Financial support has been provided by the Spanish Government, Ministerios de Educación y Ciencia y Ciencia e Innovación, (projects CTQ2005-00296/PPQ and CTQ2008-05370/PPQ) and the Catalan Government (2005SGR-00288). J.S.A. acknowledges a grant from MATGAS 2000 AIE.

References

1. F.J. Blas, L.F. Vega (1997), *Mol. Phys.*, 92, pp. 135.
2. J.C. Pàmies, L.F. Vega (2001), *Ind. Eng. Chem. Res.*, 40, pp. 2532.
3. F.J. Blas, L.F. Vega (1998), *Ind. Eng. Chem. Res.*, 37, pp. 660.
4. J.K. Johnson, J. Zollweg, K.E. Gubbins (1993), *Mol. Phys.*, 78, pp. 591.
5. M.S. Wertheim (1984-1986), *J. Stat. Phys.*, 35, 19, Ibid., 42, pp. 459, 477.
6. G. Stell, J.C. Rasaiah, H. Narang (1974), *Mol. Phys.*, 27, pp. 1393.
7. C.H. Two, K.E. Gubbins, C.G. Gray (1975), *Mol. Phys*, 29, pp. 713.
8. C.H. Two, (1976), *PhD Dissertation, University of Florida*.
9. K.E. Gubbins, C.H. Two (1978), *Chem. Eng, Sci.*, 33, pp. 863.
10. A.M.A. Dias, H. Carrier, J.L. Daridon, J.C. Pàmies, L.F. Vega, J.A.P. Coutinho, I.M. Marrucho (2006), *Ind. Eng. Chem. Res.*, 45, pp. 2341.
11. J.C. Pàmies, L.F. Vega (2001), *Ind. Eng. Chem. Res.*, 40, pp. 2532.
12. J.S. Andreu, L.F. Vega (2007), *J. Phys. Chem. C*, 111, pp. 16028.
13. S.R. Urahata, M.C.C. Ribeiro (2004), *J. Chem. Phys*, 120 (4), pp. 1855.
14. T.I. Morrow, E.J. Maginn (2002), *J. Chem. Phys. B.*, 106, pp. 12807.
15. M.G. Del Pópolo, G.A. Voth (2004), *J. Phys. Chem. B.*, 108, pp. 1744.
16. J.S. Andreu, L.F. Vega (2008), *J. Phys. Chem.* (in press).
17. J. Ranke, K. Mölter, F. Stock, U. Bottin-Weber, J. Poczobutt, J. Hoffmann, B. Ondruschka, J. Filser, B. Jastorff (2004), *Ecotoxicol. Environ. Saf*, 58, pp. 396.