Modelling the Solubility of Gases in Saturated and Substituted Perfluoroalkanes[*]

by A.M.A. Dias[1], J.C. Pamies[2], L.F. Vega[2], J.A.P. Coutinho[1] and I.M. Marrucho[1]**

[1]*CICECO, Department of Chemistry, University of Aveiro, 3810-193, Aveiro, Portugal*
[2]*Institute of Materials Sciences of Barcelone, (ICMAB-CSIC), 08193 Bellaterra, Barcelona, Spain*

The importance of the study of fluorinated molecules is justified by the innumerous applications that these compounds are founding in many diverse and interesting areas as a consequence of their unusual properties. They are being used as substitutes for chlorinated solvents, surfactants in supercritical solvents, environmental probes, and in numerous biomedical applications. The choice of the best fluoroalkane to be used for a given application depends on its properties and in some cases, such as in biomedical applications, that choice has to be precise. Thus, the knowledge of the thermodynamic properties of these compounds is of extreme importance as well as the ability to describe and predict them at different conditions using thermodynamic models. In this work, the soft-SAFT EoS is used to describe the solubility of gases as oxygen, xenon and radon in saturated and substituted perfluoroalkanes. The conclusions reached in this work corroborate the experimental evidences reported in the literature indicating that the interaction between the oxygen and the CF_3 terminal group is stronger than the interaction between the oxygen and other fluorinated groups in the molecule.

Key words: solubility, modelling, perfluoroalkanes, oxygen, xenon, radon, soft-SAFT EoS

The first fluorinated compounds were synthesised during the II World War, as part of the Manhattan project, when scientists were looking for a material that was able to resist to chemical attack and long-term thermal stability at high temperatures to serve as coating for volatile elements in radioactive isotope production. The importance of the inclusion of fluorine atoms in organic molecules is well documented from the number of publications/year regarding fluorinated compounds, which increased from 35 in 1960 to about 910 in 2004. The recent increase in the number of publications is related with the applications that highly fluorinated compounds find in different areas including biomedical [1,2], industrial [3,4,5] and environmental [6].

Despite the current interest in these fluorinated compounds, there are questions related to their behaviour that are still unanswered, most often due to lack of experimental data. Previous measurements of the solubility of oxygen in linear perfluoroalkanes from C_6 to C_9 and perfluorodecalin showed that the temperature dependence of solubility, thus the enthalpy of solution, is important for linear perfluorocarbons but negligible for perfluorodecalin [7]. The differences in enthalpies of solution of oxygen between linear and cyclic and aromatic perfluorocarbon compounds, available in the literature, lead to the study of the effect of the CF_3 end group on the enthalpy of solution of oxygen in these compounds. Experimental data showed the enthalpies of solution and solvation to be strongly influenced by the presence of CF_3 end-groups on the perfluorocarbon molecule [8]. The inability of cubic equations of state to describe this effect [7,9] lead to the use of an association model such as soft-SAFT, to model the solubility of oxygen in perfluorocarbon compounds.

MODELLING

The soft-SAFT equation of state (EoS) is written in terms of the Helmholtz free energy [10,11]. The different microscopic contributions that control the macroscopic properties of the fluid are explicitly considered when building the theory. The residual Helmholtz free energy for an n-component mixture of associating chain molecules can be expressed as a sum of three terms: a reference term, A^{ref}, including the repulsive and the attractive energies, a chain term, A^{chain}, and a perturbation term, A^{assoc}, which explicitly takes into account the contribution due to the association,

$$A^{res} = A - A^{ideal} = A^{ref}(m\rho, T, \sigma, \varepsilon) + A^{chain}(\rho, T, x_i, \sigma_i, \varepsilon_i, m_i) + A^{assoc}(\rho, T, x_i, \sigma_i, \varepsilon_i, \varepsilon^{\alpha_i\beta j}, k^{\alpha_i\beta j}) + ... \qquad (1)$$

where ρ is the (chain) molecular density, T the absolute temperature, and x_i the composition of species i in the mixture. Molecular parameters are m, the number of spherical segments forming a chain molecule, and the diameter σ and dispersive energy ε of the segments. The strength of the association bond between site α on species i and site β on species j depends on the energy $\varepsilon^{\alpha_i\beta j}$ and volume of association $k^{\alpha_i\beta j}$. The dots indicate that other terms can be added in a perturbation manner. A brief description of each of the terms follows. For more details, see references [10,11].

Ideal term. The form of A^{ideal} for the case of a multicomponent system is

$$A^{ideal} = RT \sum_{i=1}^{n} (x_i \ln \rho_m^{(i)} \Lambda_i^3) - 1 \qquad (2)$$

The sum is over all species i of the mixture, $x_i = N_m^{(i)}/N_m$ is the molar fraction, $\rho_m^{(i)} = N_m^{(i)}/V$ the molecular density, $N_m^{(i)}$ the number of molecules, Λ_i the thermal de Broglie wavelength, and V the volume of the system. ρ_m, the total number of chains divided by the volume, can be related to the total monomeric density by

$$\rho = \left(\sum_{i=1}^{n} m_i x_i \right) \rho_m = \sum_{i=1}^{n} m_i \rho^{(i)} \qquad (3)$$

being $\rho^{(i)} = x_i \rho_m$ the monomeric density of species i and m_i its chain length.

Lennard-Jones reference term. The reference term accounts for the repulsive and attractive interactions of the segments forming the chains. A^{LJ} is the Helmholtz free energy of a mixture of spherical Lennard-Jones. In this work we choose the Lennard-Jones EOS proposed by Johnson *et al.* [12]. This equation is an extended Benedict-Webb-Rubin equation of state that was fitted to simulation data for pure Lennard-Jones fluids over a broad range of temperatures and densities.

Chain term. Originally Wertheim [13] derived in an analytical way the energetic contribution (and thus the form of the corresponding EoS) that came about from the association of spherical particles. One of the successes of the theory came from the fact that, in the limit of infinitely strong bonding on an infinitely small association site placed at the edge of a given molecule, one can, in fact, account for polymerization of the monomers. The resulting equations are both reasonably simple and accurate.

The Helmholtz free energy due to the formation of chains from m_i spherical monomers is

$$A^{chain} = RT \sum_{i=1}^{n} x_i (1 - m_i) \ln g_{LJ}^{(ii)} (\sigma_{ii}) \tag{4}$$

where R is the ideal gas constant and $g_{LJ}^{ii}(\sigma_{ii})$ is the pair radial distribution function of the reference fluid for the interaction of two segments in a mixture of segments, evaluated at the segment contact σ.

Association term. The Helmholtz energy change due to association is calculated from

$$A^{assoc} = RT \sum_{i} x_i \left[\sum_{\alpha} \left(\ln X_i^{\alpha} - \frac{X_i^{\alpha}}{2} \right) + \frac{M_i}{2} \right] \tag{5}$$

where M_i is the number of association sites on each molecule of species i, $\Sigma\alpha$ represents a sum over all associating sites (on molecules of species i) and X_i^{α} is the fraction of nonbonded sites a of molecules i, defined as

$$X_i^{\alpha} = \frac{1}{1 + N_A \rho \sum_{j} x_j \sum_{\beta} X_j^{\beta} \Delta^{\alpha \beta_j}} \tag{6}$$

All the non-zero site-site interactions should be defined previously in order to solve the equation. $\Delta^{\alpha \beta_j}$ is defined as

$$\Delta^{\alpha_i \beta_j} = \int g_{LJ}^{ij} (12) f^{\alpha \beta_j} (12) d(12) \tag{7}$$

with $g_{LJ}^{ij}(12)$ the pair distribution function of the reference fluid, $f^{\alpha \beta_j}(12) = \exp(\varepsilon_{\mathrm{AB}}^{\mathrm{HB}}/k_{\mathrm{B}}T) - 1$ is the Mayer function of the association potential, and d(12) denotes an unweighted average over all orientations and an integration over all separations of molecules 1 and 2. The integration of equation 8 is not straightforward, since the pair distribution function is not readily available. In this work the pair distribution function of the Lennard-Jones chain fluid was substituted by the pair distribution function of the Lennard-Jones segment fluid, evaluated at the same temperature and segment density. In order to accurately calculate the integral, the expression from Muller *et al*. [14] for a particular position of the association site inside the Lennard-Jones sphere has been used. Different association schemes can be assumed including cross-association. For more detail on the equations to use in each case see reference [15].

The model is easily extended to mixtures using usual mixing rules. In fact, only the reference term needs to be extended to mixtures since the chain and association terms depend explicitly on composition and thus they are already applicable to mixtures. The van der Waals one fluid mixing rules were used. The corresponding expressions for the size and energy parameters of the conformal fluid are:

$$\sigma^3 = \frac{\sum_i \sum_j x_i x_j m_i m_j \sigma_{ij}^3}{\left(\sum_i x_i m_i\right)^2} \qquad (8)$$

$$\varepsilon\sigma^3 = \frac{\sum_i \sum_j x_i x_j m_i m_j \varepsilon_{ij} \sigma_{ij}^3}{\left(\sum_i x_i m_i\right)^2} \qquad (9)$$

The expressions 8 and 9 involve the mole fraction x_i and the chain length m_i of each of the components of the mixture of chains, denoted by the indices i and j, and the unlike ($j \neq i$) interaction parameters σ_{ij} and ε_{ij}, which are determined by means of combination rules. The Lorentz-Berthelot combining rules are commonly used and were also employed in this work

$$\sigma_{ij} = \eta_{ij}\frac{\sigma_{ii}+\sigma_{ij}}{2} \qquad (10)$$

$$\varepsilon_{ij} = \xi_{ij}\sqrt{\varepsilon_{ii}\varepsilon_{jj}} \qquad (11)$$

where the factors η_{ij} and ξ_{ij} modify the arithmetic and geometric averages, respectively, between components i and j.

RESULTS AND DISCUSSION

The pure component molecular parameters to be used in the soft-SAFT EoS were adjusted as usual [10] to experimental vapour pressure and density data for these compounds. In the case of radon, experimental VLE data was difficult to find. Only one value for the liquid density at 211 K was available in the literature [16]. This value was used as a reference to calculate radon liquid densities for a broader temperature range following the method of Rackett [17]. Table 1 compiles all the parameters for the compounds studied as well as the references from where experimental data used to fit the parameters were taken. The average absolute deviations observed in each case are also reported in Table 1.

Table 1. Optimized molecular parameters for the pure components.

Compound	m	σ (Å)	ε/k_B (K)	AAD (%) Density	AAD (%) P_{vap}	Ref.
Xe	1.000	3.953	226.6	0.64	0.79	18
Rn	1.460	3.606	233.6	0.47	8.52	16, 18
C_8F_{18}	3.522	4.521	245.1	0.09	3.66	19
1Br-C_8F_{17}	3.522	4.652	268.9	0.01	4.0	19
1H-C_8F_{17}	3.522	4.492	253.6	0.04	5.0	19
1H,8H-C_8F_{16}	3.522	4.456	267.8	0.03	5.0	8

Experimental vapour pressure and density data were taken from references.

Previous attempts to model the solubility of oxygen in linear perfluoroalkanes with the soft-SAFT EoS considering both oxygen and fluorinated compounds as non-interacting molecules, predicted a much weaker temperature dependence than that observed experimentally [9]. Meanwhile, evidences were found in the literature for a possible interaction between the oxygen and the CF_3 end group of perfluorocarbons. *Ab initio* calculations of the interaction potentials for the complex CF_4–O_2 show that an interaction between the oxygen and the positive carbon nucleus in CF_4 occurs, forming a very strong complex [20]. Also, through ^{19}F NMR techniques it was demonstrated that the terminal trifluoromethyl groups have a larger sensitivity to oxygen when compared with the CF_2 groups in molecules as 1Br-perfluoro-*n*-octane, perfluorotripropylamine and perfluorotributylamine [21]. In a previous work [8], it was found that the solubility of oxygen in substituted fluorinated compounds (1Br-perfluoro-*n*-octane, 1H-perfluoro-*n*-octane and 1H,8H-perfluoro-*n*-octane), decreases with increasing substitution of the CF_3 end group from the perfluoro-*n*-octane to the 1H,8H-perfluoro-*n*-octane. The enthalpies of solution and solvation also vary in this order clearly showing the existence of an interaction between the oxygen and the CF_3 end-groups.

It seems that, in order to correctly describe the temperature dependence of the solubility of oxygen in perfluoroalkanes, the free energy of cross-association between oxygen and the CF_3 end groups of the perfluoroalkane molecules must be taken into account. One of the main advantages of using an equation as the SAFT EoS comparing to simpler equations of state is that one can "adequate" the equation to the system under study by introducing or removing terms to the original equation. To model the interaction between solute and solvent, both molecular oxygen and perfluoroalkanes are here considered as associating molecules, the former with two association sites and the later with one association site on each CF_3 group. The magnitude of the site-site interaction between oxygen and perfluoroalkane molecules in the SAFT model depends on the two cross-association parameters, ε and k, that were taken as ε = 2000 K and k = 8000 Å^3, and were set constant for all mixtures. As reported by Kontogeorgis *et al*. [22] a direct relation can be established between the enthalpy of association and the energy of association. If a similar comparison is done it is possi-

ble to observe that value for the cross-association parameter, which corresponds to ≈ −16 kJ·mol⁻¹, agrees well with the experimental values for the enthalpies of interaction between oxygen and perfluoroalkanes [8]. Figure 1 shows the results obtained for the different systems studied when the proposed model is applied. Binary size, η, and energy, ξ, interaction parameters were fitted to experimental data for each mixture and are listed in Table 2. The approach used allows for a correct description of the solubility and consequently it is also able to quantitatively describe the solution enthalpy as shown in Table 3.
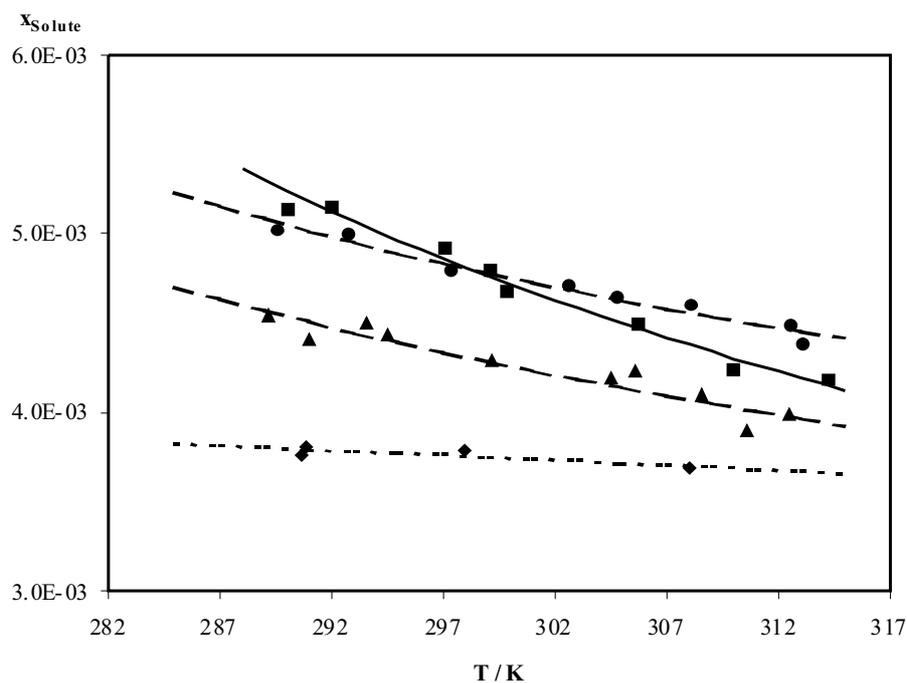

Figure 1. Solubility of oxygen in fluorinated compounds as a function of temperature: (■) perfluoro-*n*-octane, (●) 1Br-perfluoro-*n*-octane, (▲) 1H-perfluoro-*n*-octane and (◆) 1H,8H-perfluoro-*n*-octane. Lines represent correlations of the soft-SAFT EoS with two association sites (—), one association site (---) and no association point (···).

Table 2. Adjusted binary parameters for the solubility of oxygen in fluorinated perfluoroalkanes.

Compound	η	ξ	N⁰ of association sites
C_8F_{18}	1.90	1.17	2
$CF_3(CF_2)_6CF_2Br$	1.56	1.22	1
$CF_3(CF_2)_6CF_2H$	1.56	1.17	1
$CF_2H(CF_2)_6CF_2H$	1.26	1.11	0

Table 3. Experimental and calculated solution thermodynamic properties for saturated and substituted perfluoro-*n*-octane at the solute's partial pressure.

	ΔG	ΔH	ΔS
	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$J \cdot mol^{-1} \cdot K^{-1}$
C_8F_{18}			
Experimental	13.23 ± 0.62	-7.11 ± 0.44	-68.22 ± 1.45
soft-SAFT without association	13.26	−4.44	−59.35
soft-SAFT with association	13.23	−7.29	−68.81
$1Br\text{-}C_8F_{17}$			
Experimental	13.23 ± 0.35	-3.76 ± 0.25	-56.98 ± 0.83
soft-SAFT with association	13.24	−3.18	−55.08
$1H\text{-}C_8F_{17}$			
Experimental	13.49 ± 0.11	-4.14 ± 0.08	-59.16 ± 0.26
soft-SAFT with association	13.51	−3.72	−57.78
$1H,8H\text{-}C_8F_{16}$			
Experimental	13.85 ± 0.15	-1.06 ± 0.90	-49.99 ± 1.20
soft-SAFT without association	13.85	−1.09	−50.08

A similar study is carried out using the soft-SAFT EoS to describe solubility data for xenon and radon in perfluoroalkanes. Data for the solubility of xenon and radon in perfluoroalkanes were measured by Kennan and Pollack [23] and Lewis *et al.* [24], respectively. In both works, solubility data were presented in terms of Ostwald coefficient and solute molar fraction at a partial pressure of the gas equal to 1 atm. The equilibrium molar fractions of the liquid and gaseous phase were recalculated from these data following to the procedure for data reduction presented in a recent publication [25].

Previous studies have been done on the modelling of the solubility data of xenon in perfluoroalkanes, particularly perfluoro-*n*-hexane [26]. The authors used both molecular simulation and the SAFT-VR EoS to describe experimental data. They observed that in both cases a binary interaction parameter had to be introduced in order to reproduce the experimental results. This behaviour was expected since, in a previous work dealing with the phase diagram of xenon in lighter alkanes (C_1 to C_4) and perfluoroalkanes (C_1 to C_2) also using the SAFT-VR, they showed that while the behaviour of xenon correlated strongly with that of the *n*-alkanes (the experimental phase diagrams and excess volumes could be described accurately using simple Lorentz-Berthelot combining rules to determine the cross interaction parameters), for xenon in *n*-perfluoroalkanes the existing experimental data could only be reproduced by introducing a binary interaction parameter [27,28]. The energetic binary interaction parameter used by the authors was the same that they used in an earlier study of alkane + perfluoroalkanes binary mixtures [28], equal to 0.92. They stated that although this was not the best value and a slight improvement would be possible if the parameter were fitted to the specific system, they preferred to use the parameters in a transferable way giving importance to the predictive capability of the equation instead to look for the accuracy of the results given by the model.

In this work, both solutes and solvents are modelled as non associating molecules. As in the work of Filipe *et al*. [27] only the energetic parameter has to be included to correctly describe experimental data. It was adjusted for each mixture and is listed in Table 4. In the case of the solubility of xenon, the same energetic parameter is used for perfluoro-*n*-heptane and perfluoro-*n*-octane and a slightly different parameter had to be used to perfluoro-*n*-hexane to obtain a quantitative description. In the case of the solubility of radon, the same parameters are used for both systems. The results obtained for the correlation of the experimental data with the soft-SAFT model are presented in Figure 2. The higher deviations for radon are believed to be related to the less accurate adjustment of the molecular parameters for pure radon due to the lack of experimental data as described above. Nevertheless, it can be observed that in both cases the soft-SAFT model without any association can correctly describe the experimental solubility data. The temperature dependences for these systems are even higher than in the case of the oxygen in perfluoroalkanes and the model can still correctly describe them using just one adjusted parameter. No association between the gas and the pefluoroalkane was taken into account.

Table 4. Adjusted binary parameters for the solubility of xenon and radon in fluorinated compounds and AADs of the calculations by the soft-SAFT EOS with respect to experimental data.

Solvent	η	ξ	AAD (%)
Xenon			
C_6F_{14}	1	0.870	3
C_7F_{16}	1	0.860	2
C_8F_{18}	1	0.860	1
Radon			
C_6F_{14}	1	0.825	7
C_8F_{18}	1	0.825	4

The results obtained in this work strongly indicate the presence of a real interaction between the oxygen and the perfluoroalkanes. The fact that the soft-SAFT model is able to adequately correlate solubility data for systems of non interacting compounds, such as xenon and radon in perfluoroalkanes, even when they present large enthalpies of solution, clearly shows that the need to consider an interaction between oxygen and the perfluoroalkanes to correlate the solubility data reflects a real interaction between the solute and solvent and is not just another mathematical parameter to correct model failures. Moreover, the results obtained with the soft-SAFT model corroborate the experimental data that there is specific interaction between the oxygen and the CF_3 terminal groups of the perfluorcarbon molecules.
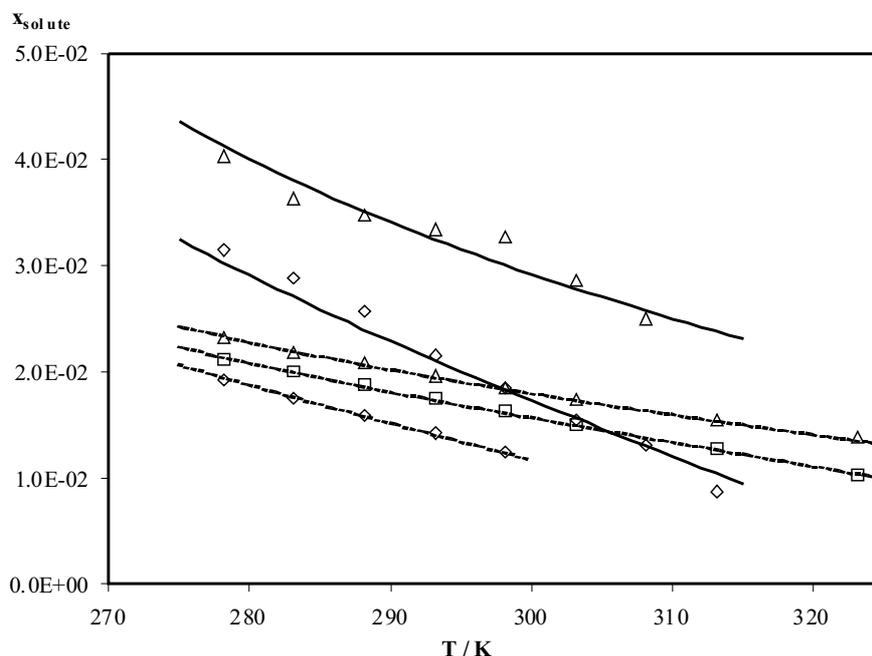
Figure 2. Solubility of xenon and radon in linear perfluoroalkanes. Symbols represent experimental data for perfluoro-*n*-hexane ($\Diamond$), perfluoro-*n*-heptane ($\square$), and perfluoro-*n*-octane ($\triangle$). Lines correspond to the results from the soft-SAFT EoS: full lines are the results for the solubility of radon and dashed lines for the solubility of xenon.

REFERENCES

1. Krafft M.P., *Advanced Drug Delivery Reviews*, **47**, 209 (2001).
2. Riess J.G., *Chem. Rev*., **101**, 2797 (2001).
3. Raveendran P. and Wallen S.L., *J. Am. Chem. Soc*., **124**, 12590 (2002).
4. Horvath I.T. and Rabai J., *Science*, **266**, 72 (1994).
5. Wallington T.J., Schneider W.F., Worsnop D.R., Nielsen O.J., Sehested J., Debruyn W.J. and Shorter J.A., *Environ. Sci. Technol.*, **28**, 320A–325A (1994).
6. Wasanasathian A. and Peng C.-A., *Artificial Cells, Blood Substitutes, & Immobilization Biotechnology*, **29**, 47 (2001).
7. Dias A.M.A., Freire M.G., Coutinho J.A.P. and Marrucho I.M., *Fluid Phase Equilibria*, **222–223**, 325 (2004).
8. Dias A.M.A., Coutinho J.A. and Marrucho I.M., *Fluid Phase Equilibria*, (2005), (in press).
9. Dias A.M.A., Pamies J.C., Coutinho J.A.P., Marrucho I.M. and Vega L.F., *J. Phys. Chem. B*, **108**, 1450 (2004).
10. Blas F.J. and Vega L.F., *Ind. Eng. Chem. Res*., **37**, 660 (1998).

11. Blas F.J. and Vega L.F., *Mol. Phys*., **92**, 135 (1997).
12. Johnson J.K., Zollweg J.A. and Gubbins K.E., *Mol. Phys.*, **78**, 591 (1993).
13. Wertheim M.S., *J. Chem. Phys*., **87**, 7323 (1987).
14. Muller E.A., Vega L.F. and Gubbins K.E., *Int. J. Thermophys*., **16**, 705 (1995).
15. Pamies J.C., *Ph. D. Thesis*, University Rovira i Virgili (2003).
16. Herreman W., *Cryogenics*, **20**, 133 (1980).
17. Rackett H.G., *J. Chem. Eng. Data*, **15**, 514 (1970).
18. NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. P.J. Linstrom and W.G. Mallard, March 2003, National Institute of Standards and Technology, Gaithersburg MD, 20899 (http//webbook.nist.gov).
19. Dias A.M.A., Gonçalves C.M., Caço A.I., Santos L.M.N.B.F., Piñeiro M.M., Vega L.F., Coutinho J.A.P. and Marrucho I.M., *J. Chem. Eng. Data*, 5**0**, 1328 (2005).
20. Mack H.G. and Oberhammer H., *J. Chem. Phys*., **87**, 2158 (1987).
21. Shukla H., Mason R., Woessner D. and Antich P., *J. Mag. Res. Series B*, **106**, 131 (1995).
22. Kontogeorgis G.M., Voutsas E.C., Yakoumis I.V. and Tassios D.P., *Ind. Eng. Chem. Res*., **35**, 4310 (1996).
23. Kennan R.P. and Pollack G.L., *J. Chem. Phys*., **89**, 517 (1988).
24. Lewis C., Hopke P.K. and Stukel J.J., *Ind. Eng. Chem. Res*., **26**, 356 (1987).
25. Dias A.M.A., Coutinho J.A.P., Piñeiro M., Gomes M.F.C. and Marrucho I.M., *Fluid Phase Equilibria*, **225**, 39 (2004).
26. Bonifácio R.P., Filipe E.J.M., McCabe C., Gomes M.F.C. and Pádua A.H.A., *Mol. Phys*., **100**, 2547 (2002).
27. Filipe E.J.M., Gomes de Azevedo E.J.S., Martins L.F.G., Soares V.A.M., Calado J.C.G., McCabe C. and Jackson G., *J. Phys. Chem. B*, **104**, 1315 (2000).
28. McCabe C., Dias L.M.B., Jackson G. and Filipe E.J.M., *Phys. Chem. Chem. Phys*., **3**, 2852 (2001).