

Modeling the Liquid–Liquid Equilibria of Water + Fluorocarbons with the Cubic-Plus-Association Equation of State

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Fluorocarbons (FCs) are a family of chemicals that are composed primarily of carbon and fluorine. They present weak intermolecular and strong intramolecular interactions, which confers them unusual thermophysical properties. They can also solubilize large amounts of gases such as oxygen and carbon dioxide, making them interesting for several biomedical applications. In most of these applications, water or aqueous systems are present for which the knowledge of the mutual solubilities between the fluorocarbons and the aqueous phases is important. In this work, the application of the cubic-plus-association equation of state (CPA EoS) has been extended to binary mixtures of water with several linear, cyclic, aromatic, and substituted fluorocarbons. The CPA EoS was successfully used to model the liquid–liquid equilibria of aqueous mixtures that contain FCs, while also being able to describe the cross-association phenomena between substituted and aromatic FCs and water. It is shown that, for aliphatic perfluorocarbons, CPA can be used without any mixture binary parameter to predict the water solubility.

1. Introduction

Fluorocarbons (FCs) are nonpolar highly fluorinated molecules that have found several applications in numerous fields, because of their stability, chemical and biochemical inertness,¹ and unusual physicochemical properties, which result from strong intramolecular and weak intermolecular forces.

The FCs can be used as substitutes for chlorinated solvents; as surfactants in supercritical solvents; as environmental surveys, to determinate the exchanges between the atmosphere and natural waters; as anticorrosive, antifriction, and flame-retardant components; and as water repellents.^{2–4}

They also have widespread use in the biomedical field, as, for example, components in blood substitutes, tissue oxygenation fluids, anti-tumoral agents, perfusates for isolated organs, gas carriers in eye surgery, diagnostic imaging agents, lubrication and cushioning for articular disorders, cell culture media, and drug delivery systems.^{5–8}

Some approaches to the modeling of perfluorocarbon systems can be found in the literature. The description of the solubility of gases such as oxygen, xenon, and radon in saturated and substituted perfluorocarbons^{9–11} and the modeling of the phase behavior of carbon dioxide–perfluorocarbon¹² and of linear perfluorocarbon–alkane¹³ mixtures, were already performed using the soft statistical associating fluid theory equation of state (soft-SAFT EoS). For this last type of mixture, the modified UNIFAC model was also applied.¹³

However, despite the increasing interest in fluorocarbon applications that involve contact with aqueous solutions, there is still a considerable lack of data for the mutual solubilities of FCs in water, and, thus, there is a need to develop an adequate model to describe these systems.

For water + alkane systems, associated perturbed anisotropic chain theory (APACT), SAFT and the cubic-plus-association equation of state (CPA EoS) have already been shown to be accurate models to describe both the solubility of water in the hydrocarbon phase and the hydrocarbon solubility in the aqueous phase.^{14–18} The CPA EoS was also successfully applied to cross-associating systems that contained water, alcohols, and glycols.^{19,20} However, the mutual solubilities of water and FCs are 1 order of magnitude less than their hydrocarbon homologues, making their description more difficult and a very stringent test of the capabilities of the models.

In this work, the ability of the CPA EoS to model the liquid–liquid equilibria (LLE) of FC + water systems was evaluated. This EoS combines the Soave–Redlich–Kwong (SRK) cubic EoS for the physical contribution with the association contribution proposed by Wertheim, which has been used in other associating equations of state, such as the different versions of SAFT.

LLE results are reported in this work for 11 FCs: 4 linear FCs (*n*-perfluorohexane, *n*-perfluoroheptane, *n*-perfluorooctane, and *n*-perfluorononane), 2 aromatic FCs (perfluorobenzene and perfluorotoluene), 2 cyclic FCs (perfluorodecalin and perfluoromethylcyclohexane) and 3 substituted FCs (1-Br-perfluorooctane, 1-H-perfluorooctane, and 1,8-H-perfluorooctane).

Although the aromatic perfluorocarbons are themselves non-self-associating, it is known that aromatic compounds are able to cross-associate (solvate) with polar compounds such as water,^{21,22} and therefore, a solvation scheme that involved combining rules for the cross-associating energy and volume parameters was used in this work, as recently suggested by Folas et al.²³

Similarly, through experimental measurements and ab initio calculations, it has recently been shown that, in systems that

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Table 1. Pure Component CPA Parameters

compound	a_0 (Pa m ⁶ /mol ²)	c_1	b ($\times 10^5$ m ³ /mol)	ϵ (J/mol)	β	AAD (%)	
						for P	for ρ_{liq}
C ₆ F ₆	2.18	0.99	9.78	0	0	0.77	1.63
C ₇ F ₈	2.90	1.04	12.40	0	0	0.42	2.05
C ₆ F ₁₄	2.99	1.20	15.90	0	0	5.04	1.90
C ₇ F ₁₆	3.82	1.21	18.90	0	0	2.83	2.01
C ₈ F ₁₈	4.37	1.32	20.60	0	0	0.92	3.58
C ₉ F ₂₀	5.23	1.42	24.20	0	0	1.18	2.38
C ₇ F ₁₄	3.50	0.96	16.29	0	0	7.28	0.64
C ₁₀ F ₁₈	8.64	1.38	42.90	0	0	0.56	4.66
1-Br-C ₈ F ₁₇	5.52	1.29	23.50	0	0	2.98	3.20
1-H-C ₈ F ₁₇	5.02	1.07	20.64	0	0	0.04	0.36
1,8-H-C ₈ F ₁₆	5.68	1.01	20.02	0	0	0.00	0.36
H ₂ O	0.12	0.67	1.45	16655	0.069	0.73	0.82

Table 2. AAD in xH₂O in the Aliphatic Fluorocarbon Phase, as Obtained from CPA^a

compound	AAD (%)
C ₆ F ₁₄	29.2
C ₇ F ₁₆	16.1
C ₈ F ₁₈	9.8
C ₉ F ₂₀	2.4
C ₇ F ₁₄	3.4
C ₁₀ F ₁₈	29.9

^a $k_{ij} = 0.0$ in all cases except for C₇F₁₄, for which $k_{ij} = 0.145$ for C₇F₁₄.

contain substituted n -fluoroalkanes, the water solubility in the hydrocarbon phase is greater, because of the stronger interaction between the water molecule and the substituted atom (H, Cl, or Br).²⁴ Thus, in this work, a similar solvation scheme to that used for water + aromatics was selected, where an optimization of the cross-association volume parameter from equilibrium data was involved.

In this work, we show that CPA can provide a good description of the water solubility in perfluorocarbons and, particularly for nonaromatic fluorocarbons, CPA provides very good prediction of the water solubility in the temperature range of the available data.

2. Model

The CPA EoS can be expressed in terms of the compressibility factor as the sum of two contributions: one that accounts for physical interactions (the SRK EoS), and another that accounts for chemical interactions due to association (the Wertheim association term).^{14,15,19,20,23,25–27}

$$Z = Z^{\text{phys}} + Z^{\text{assoc}} = \frac{1}{1 - b\rho} - \frac{a\rho}{RT(1 + b\rho)} - \frac{1}{2} \left(1 + \rho \frac{\partial \ln g}{\partial \rho} \right) \sum_i x_i \sum_{A_i} (1 - X_{A_i}) \quad (1)$$

where a is the energy parameter, b the co-volume parameter, ρ the density, g the simplified radial distribution function,²⁶ X_{A_i} the mole fraction of pure component i not bonded at site A, and x_i is the mole fraction of component i .

The pure component energy parameter of CPA is given by a Soave-type temperature dependency:

$$a(T) = a_0 \left[1 + c_1 (1 - \sqrt{T_r}) \right]^2 \quad (2)$$

where a_0 and c_1 are regressed (simultaneously with b) from selected pure-component vapor-pressure and liquid-density data. When CPA is extended to mixtures, the energy and co-volume

parameters of the physical term are calculated applying the conventional van der Waals one-fluid mixing rules:

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (3a)$$

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad (3b)$$

and

$$b_{ij} = \frac{b_i + b_j}{2} (1 - l_{ij}) \quad (4)$$

The co-volume binary interaction parameter (l_{ij}) is usually set to zero, resulting in a linear mixing rule for the mixture co-volume parameter.

X_{A_i} is related to the association strength $\Delta^{A_i B_j}$ between two sites belonging to two different molecules and is calculated by solving the following set of equations:

$$X_{A_i} = \frac{1}{1 + \rho \sum_j x_j \sum_{B_j} X_{B_j} \Delta^{A_i B_j}} \quad (5)$$

where

$$\Delta^{A_i B_j} = g(\rho) \left[\exp\left(\frac{\epsilon^{A_i B_j}}{RT}\right) - 1 \right] b_{ij} \beta^{A_i B_j} \quad (6)$$

and $\epsilon^{A_i B_j}$ and $\beta^{A_i B_j}$ are the association energy and the association volume, respectively.

The simplified radial distribution function ($g(\rho)$) is given by²⁶

$$g(\rho) = \frac{1}{1 - 1.9\eta} \quad (7)$$

where

$$\eta = \left(\frac{1}{4}\right) b\rho$$

For nonassociating components, CPA has three pure-component parameters (a_0 , c_1 , and b), whereas, for associating components, it has five (a_0 , c_1 , b , ϵ , β). In both cases, parameters are regressed simultaneously from vapor-pressure and liquid-density data.

For a binary mixture that contains a self-associating and an inert compound, such as a water + n -perfluoroalkane system, the binary interaction parameter k_{ij} is the only adjustable parameter and no combining rules are required for the association energy and volume.

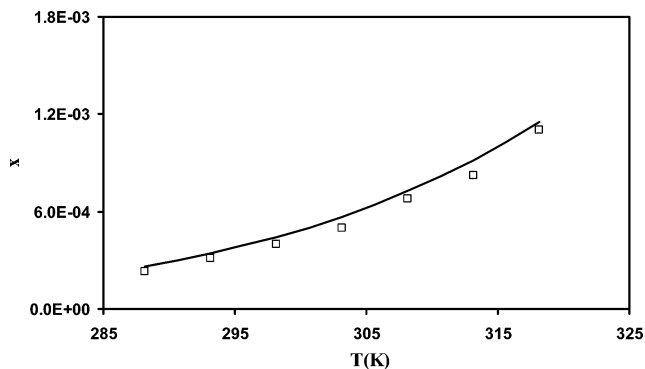


Figure 1. Water solubility in the C_8F_{18} phase: (□) experimental and (—) CPA results.

After CPA is applied to mixtures that contain cross-association, which is the case of the aromatic and substituted FCs + H_2O systems evaluated in this work, combining rules for the association energy and volume parameters are required.^{19,23,27}

In this work, we adopted the approach recently suggested by Folas et al.,²³ where the cross-association energy between water and aromatics or substituted FCs is equal to half the water association energy and the cross-association volume is left as an adjustable parameter from equilibrium data:

$$\epsilon^{A_{\text{aromatic}}B_{H_2O}} = \frac{\epsilon^{A_{H_2O}B_{H_2O}}}{2} \quad (8)$$

$$\beta^{A_{\text{aromatic}}B_{H_2O}} = \text{fitted} \quad (9)$$

For water, the four-site (4C) association scheme is selected, in which hydrogen bonding is considered to occur between the two H atoms and the two lone pairs of electrons in the oxygen of the water molecules. For the aromatics and substituted FCs that are cross-associating with water, a single association site is considered.

3. Results and Discussion

The required CPA pure-component parameters have been determined by a simultaneous regression of selected vapor-pressure and saturated liquid-density data.^{11,28–45} Results are presented in Table 1 for the studied FCs and water, where it can be observed that very good vapor-pressure and liquid-density results are obtained from CPA, with maximum deviations less than 8% and 5%, respectively. On average, both vapor-pressure and liquid-density data can be estimated with an average deviation of <2%.

Using these parameters, it was then possible to model the LLE for the linear and for one of the cyclic compounds (perfluorodecalin) with CPA, setting the k_{ij} binary interaction parameters to zero. Experimental data, at atmospheric pressure, were obtained from Freire and co-workers.^{24,46,47} As observed in Table 2 and in Figure 1, the water solubility in the hydrocarbon phases are well-described, with an average deviation of <30% for the aliphatic FCs. The inclusion of a binary interaction parameter had no significant improvement in the average deviation values, and, therefore, the prediction performance of this equation can be considered quite good for the aliphatic FCs. The dispersion of the average absolute deviation (AAD) values can be explained by the use of different sources, some of them rather old and of low quality, to obtain the thermophysical data required to estimate the parameters of the pure components.

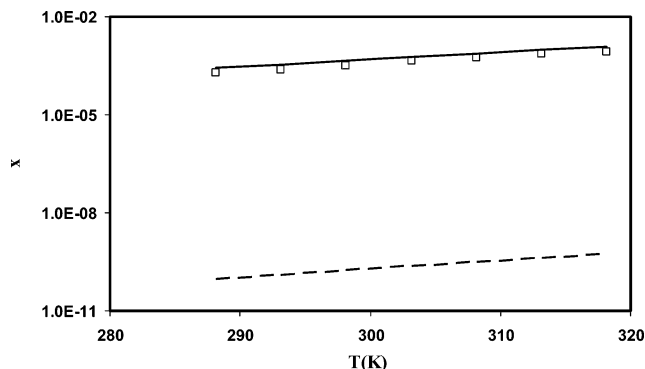


Figure 2. Liquid-liquid equilibria (LLE) for $C_6F_{14} + H_2O$: (□) experimental (hydrocarbon phase); (—) CPA results (hydrocarbon phase); and (- -) CPA results (aqueous phase).

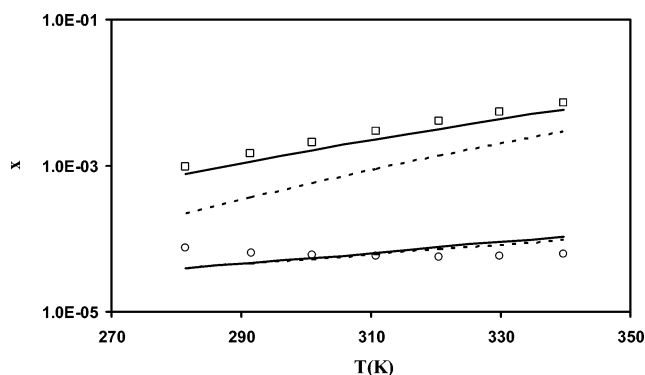


Figure 3. LLE for $C_6F_6 + H_2O$. Symbols represent experimental results ((□) (hydrocarbon phase and (○) aqueous phase), whereas lines represent CPA results ((- -) only k_{ij} fitted and (—) cross association).

Table 3. AAD in xH_2O in the Aromatic and Substituted Fluorocarbon Phase, as Obtained from CPA, and the Respective Cross-Association Volume and Binary Interaction Parameter Values

compound	AAD (%)	k_{ij}	β^{AiBj}
Aromatic Fluorocarbon Phase			
C_6F_6	68.9	-0.054	
C_7F_8	70.3	-0.098	
Cross-Association Values			
C_6F_6	21.8	-0.034	0.032
C_7F_8	22.5	-0.034	0.032
Substituted Fluorocarbon Phase			
Cross-Association Values			
1-Br- C_8F_{17}	6.6		0.012
1-H- C_8F_{17}	5.3		0.066
1,8-H- C_8F_{16}	1.7		0.138

Unfortunately, there is still a considerable lack of data for the solubility of aliphatic FCs in water, because these are very low and, thus, difficult to measure; therefore, no comparisons were made to the results obtained for the corresponding water-rich phases. Nevertheless, the predicted mutual solubilities are plotted in Figure 2 for perfluorohexane, where it can be seen, that, according to the model, these are, as expected, considerably lower than those from the corresponding linear alkane.

For the other cyclic FC (perfluoromethylcyclohexane), CPA was not able to predict the water solubility in the FC-rich phase satisfactorily, and an interaction coefficient was regressed from C_7F_{14} solubility data, which enabled a very good description of the LLE, with an average deviation of <4% (see Table 2).

Because stronger interactions are known to be present between aromatics and water,^{22,23} in this work, the LLE of perfluoroaromatics and water was correlated here, assuming that the aromatic FC + H_2O system is characterized by water self-

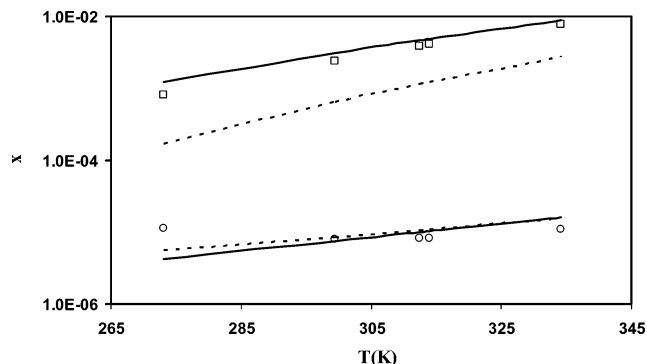


Figure 4. LLE for $C_7F_8 + H_2O$. Symbols represent experimental results (\square) (hydrocarbon phase and \circ) aqueous phase), whereas lines represent CPA results (---) only k_{ij} fitted and (—) cross association).

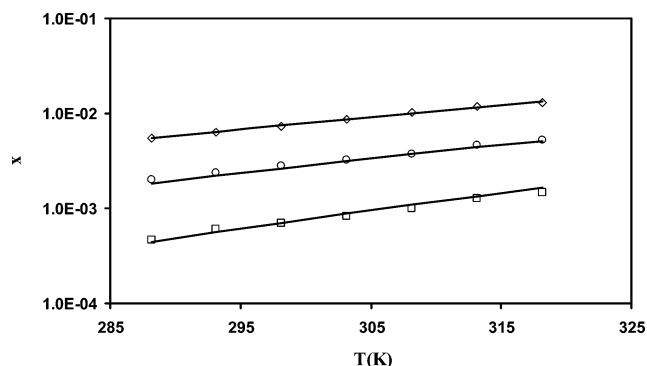


Figure 5. Water solubility in substituted perfluorocarbons. Symbols represent experimental data (\diamond) 1,8-H- C_8F_{16} , \circ) 1-H- C_8F_{17} , and \square) 1-Br- C_8F_{17}), and the solid lines represent CPA results.

association and water + aromatic cross-association (solvation), using the approach suggested recently by Folas et al.²³ As shown in Table 3, and in Figures 3 and 4, if this cross-association interaction is not taken into account and only a k_{ij} parameter is fitted to the experimental data, an adequate representation of the mutual solubilities is not possible. Although the solubility of aromatic perfluorocarbons in water is acceptably represented, except for the minimum at lower temperatures (which might be related to the hydrophobic effect²³ and cannot be described by the CPA EoS), high deviations are obtained for the water solubility in the hydrocarbon phase.

When the solvation is explicitly taken into account and both the k_{ij} and β^{A,B_j} parameters are optimized from equilibrium data, considerable improvements in the results were obtained, especially for the water solubility in the hydrocarbon phase. Because both the k_{ij} and β^{A,B_j} parameters for perfluorobenzene and perfluorotoluene are equal, similar aromatic compounds may be predicted with this set of interaction parameters. Thus, accounting for this solvation phenomena is essential for one to obtain a good correlation of the aromatic FC + water LLE, as found previously by Folas et al.²³ for aromatic hydrocarbons.

Having only the β^{A,B_j} parameter optimized from equilibrium data is sufficient to describe the substituted fluorocarbons. These exhibit a stronger interaction with polar molecules, such as water, because of the formation of a dipole with a positive charge on the new atom that increases the interaction between the solute and the solvent, as already shown experimentally and through ab initio calculations.²⁴ Very good modeling of the water solubility was obtained, as observed in Table 3 and Figure 5. Note that the value of β^{A,B_j} for 1-H-perfluorooctane is approximately half of that for 1,8-H-perfluorooctane. CPA could also demonstrate the increase in water solubility with decreasing

electronegativity of the heteroatoms included, according to the sequence $Br < H < 2H$.

4. Conclusions

In this work, the cubic-plus-association equation of state (CPA EoS) was applied to model the liquid–liquid equilibria (LLE) of fluorocarbon (FC) + water systems. Experimental solubility data from literature for several linear, aromatic, and substituted fluorocarbons were used for this purpose in this paper.

In the case of the aliphatic FCs, LLE calculations have been performed by setting the k_{ij} binary interaction parameters to zero. This approach provides excellent pure predictions for the water solubility in the FC phase, with average deviations of <30%. Unfortunately, no data are available on the FC solubility in the aqueous phase; however, the model predicts lower solubilities than those observed for the equivalent alkanes, as expected.

For the aromatic FCs, the model must explicitly take into account the cross-association between the self-associating molecule (water) and the non-self-associating molecule (aromatic FCs). Solvation between aromatic FCs and water cannot be ignored, as observed previously for aromatic hydrocarbons and water.

For the aliphatic FCs, where one or two of the F atoms are substituted by a H or Br atom, it was only necessary to fit β^{A,B_j} to the experimental data for a suitable modeling of the LLE. Thus, CPA is able to take into account the stronger polar interactions between the substituted fluoroalkane and water, which leads to increased water solubility in the hydrocarbon phase. It was also possible to describe the increase in water solubility with decreasing electronegativity of the heteroatoms, according to the sequence $Br < H < 2H$.

Here, it has been shown that CPA can adequately describe the water solubility in extremely hydrophobic compounds such as FCs, for which the very low solubility values are a stringent test of the capabilities of the models. CPA was successfully extended to mixtures that contained cross-associating compounds such as aromatic and substituted FCs with water, and it has been proven to be a flexible and reliable thermodynamic model to describe difficult systems and interactions between molecules of different types.

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Nomenclature

- a = energy parameter in the physical term
- a_0, c_1 = parameters used to calculate a
- A_i = site A in molecule i
- b = co-volume
- B_j = site B in molecule j
- g = radial distribution function
- k_{ij}, l_{ij} = binary interaction parameters
- P = vapor pressure
- R = real gas constant
- T = temperature
- x = mole fraction
- X_A = fraction of molecules not bonded at site A
- Z = compressibility factor

Greek Symbols

- β = association volume
 ϵ = association energy
 η = reduced fluid density
 ρ = mole density
 Δ = association strength

Superscripts

- assoc = association
 phys = physical

Subscripts

- i, j = pure component indexes
 liq = liquid
 r = reduced

List of Abbreviations

- AAD = average absolute deviation
 APACT = associated perturbed anisotropic chain theory
 CPA = cubic plus association
 EoS = equation of state
 FCs = fluorocarbons
 LLE = liquid–liquid equilibria
 SAFT = statistical associating fluid theory
 SRK = Soave–Redlich–Kwong
 UNIFAC = universal functional activity coefficient model

Literature Cited

- (1) Riess, J. G. Oxygen Carriers (“Blood Substitutes”)—Raison d’Etre, Chemistry, and Some Physiology. *Chem. Rev.* **2001**, *101*, 2797.
- (2) Millard, R. W. Oxygen Solubility, Rheology and Hemodynamics of Perfluorocarbon Emulsion Blood Substitutes. *Artif. Cells, Blood Substitutes, Immobilization Biotechnol.* **1994**, *22*, 235.
- (3) Lowe, K. C. Perfluorinated Blood Substitutes and Artificial Oxygen Carriers. *Blood Rev.* **1999**, *13*, 171.
- (4) Riess, J. G. Fluorocarbon-Based Oxygen-Delivery: Basic Principles and Product Development. In *Blood Substitutes: Principles, Methods, Products, and Clinical Trials*, Vol. II; Karger Landes Systems: Basel, Switzerland, 1998; p 101.
- (5) Wilhelm, E.; Battino, R.; Wilcock, R. J. Low-Pressure Solubility of Gases in Liquid Water. *Chem. Rev.* **1977**, *77*, 219.
- (6) Lowe, K. C. Perfluorochemical Respiratory Gas Carriers: Benefits to Cell Culture Systems. *J. Fluor. Chem.* **2002**, *118*, 19.
- (7) Ju, L. K.; Lee, J. F.; Armiger, W. B. Enhancing Oxygen-Transfer in Bioreactors by Perfluorocarbon Emulsions. *Biotechnol. Prog.* **1991**, *7*, 323.
- (8) Dias, A. M. A.; Pàmies, J. C.; Coutinho, J. A. P.; Marrucho, I. M.; Vega, L. F. Solubility of Oxygen in Liquid Perfluorocarbons. *J. Phys. Chem. B* **2004**, *108*, 1450.
- (9) Dias, A. M. A.; Pàmies, J. C.; Vega, L. F.; Coutinho, J. A. P.; Marrucho, I. M. Modelling the Solubility of Gases in Saturated and Substituted Perfluoroalkanes. *Pol. J. Chem.* **2006**, *80*, 143.
- (10) Dias, A. M. A.; Pàmies, J. C.; Coutinho, J. A. P.; Marrucho, I. M.; Vega, L. F. SAFT Modeling of the Solubility of Gases in Perfluoroalkanes. *J. Phys. Chem. B* **2006**, *108*, 1450.
- (11) Dias, A. M. A.; Caço, A. I.; Coutinho, J. A. P.; Santos, L. B.; Piñeiro, M. M.; Vega, L. F.; Gomes, M. F. C.; Marrucho, I. M. Thermodynamic Properties of Perfluoro-*n*-octane. *Fluid Phase Equilib.* **2006**, *225*, 39.
- (12) Dias, A. M. A.; Carrier, H.; Daridon, J. L.; Pàmies, J. C.; Vega, L. F.; Coutinho, J. A. P.; Marrucho, I. M. Vapor–Liquid Equilibrium of Carbon Dioxide–Perfluoroalkane Mixtures: Experimental Data and SAFT Modeling. *Ind. Eng. Chem. Res.* **2006**, *45*, 2341.
- (13) Pratas de Melo, M. J.; Dias, A. M. A.; Blesic, M.; Rebelo, L. P. N.; Vega, L. F.; Coutinho, J. A. P.; Marrucho, I. M. Liquid–Liquid Equilibrium of (perfluoroalkane + alkane) Binary Mixtures. *Fluid Phase Equilib.* **2006**, *242*, 210.
- (14) Yakoumis, I. V.; Kontogeorgis, G. M.; Voutsas, E. C.; Hendriks, E. M.; Tassios, D. P. Prediction of Phase Equilibria in Binary Aqueous Systems Containing Alkanes, Cycloalkanes, and Alkenes with the Cubic-plus-Association Equation of State. *Ind. Eng. Chem. Res.* **1998**, *37*, 4175.
- (15) Voutsas, E. C.; Boulougouris, G. C.; Economou, I. G.; Tassios, D. P. Water/Hydrocarbon Phase Equilibria Using the Thermodynamic Perturbation Theory. *Ind. Eng. Chem. Res.* **2000**, *39*, 797.
- (16) Blas, F. Aplicación de las Técnicas de Modelización Molecular al Cálculo del Equilibrio de Fases de Sistemas Multicomponentes e Caracterización de Materiales Adsorbentes. Ph.D. Thesis, Universitat Rovira et Virgili, Tarragona, Spain, 2000.
- (17) McCabe, C.; Galindo, A.; Cummings, P. T. Anomalies in the Solubility of Alkanes in Near-Critical Water. *J. Phys. Chem. B* **2003**, *107*, 12307.
- (18) Economou, I. G.; Donohue, M. D. Equation of State with Multiple Associating Sites for Water and Hydrocarbon Mixtures. *Ind. Eng. Chem. Res.* **1992**, *31*, 2388.
- (19) Folas, G. K.; Gabrielsen, J.; Michelsen, M. L.; Stenby, E. H.; Kontogeorgis, G. M. Application of the Cubic-Plus-Association (CPA) Equation of State to Cross-Associating Systems. *Ind. Eng. Chem. Res.* **2005**, *44*, 3823.
- (20) Derawi, S. O.; Kontogeorgis, G. M.; Michelsen, M. L.; Stenby, E. H. Extension of the Cubic-Plus-Association Equation of State Glycol–Water Cross-Associating Systems. *Ind. Eng. Chem. Res.* **2003**, *42*, 1470.
- (21) Brinkley, R. L.; Gupta, R. B. Hydrogen Bonding with Aromatic Rings. *AIChE J.* **2001**, *47*, 948.
- (22) Tarakeshwar, P.; Choi, H. S.; Lee, S. J.; Lee, J. Y.; Kim, K. S.; Ha, T. K.; Jang, J. H.; Lee, J. G.; Lee, H. J. A Theoretical Investigation of the Nature of the –H Interaction in Ethene–H₂O, Benzene–H₂O, and Benzene–(H₂O)₂. *Chem. Phys.* **1999**, *111*, 5838.
- (23) Folas, G. K.; Kontogeorgis, G. M.; Michelsen, M. L.; Stenby, E. H. Application of the Cubic-Plus-Association (CPA) Equation of State to Complex Mixtures with Aromatic Hydrocarbons. *Ind. Eng. Chem. Res.* **2006**, *45*, 1527.
- (24) Freire, M. G.; Gomes, L.; Santos, L. M. N. B. F.; Marrucho, I. M.; Coutinho, J. A. P. Water Solubility in Linear Fluoroalkanes Used in Blood Substitute Formulations. *J. Phys. Chem. B* **2006**, *110* (45), 22923–22929.
- (25) Queimada, A. J.; Miqueu, C.; Marrucho, I. M.; Kontogeorgis, G. M.; Coutinho, J. A. P. Modeling Vapor–Liquid Interfaces with the Gradient Theory in Combination with the CPA Equation of State. *Fluid Phase Equilib.* **2005**, *479*, 228–229.
- (26) Kontogeorgis, G. M.; Yakoumis, I. V.; Meijer, H.; Hendriks, E. M.; Moorwood, T. Multicomponent Phase Equilibrium Calculations for Water–Methanol–Alkane Mixtures. *Fluid Phase Equilib.* **1999**, *201*, 158–160.
- (27) Voutsas, E. C.; Yakoumis, I. V.; Tassios, D. P. Prediction of Phase Equilibria in Water/Alcohol/Alkane Systems. *Fluid Phase Equilib.* **1999**, *160*, 151.
- (28) Stiles, V. E.; Cady, G. H. Physical Properties of Perfluoro-Normal-Hexane and Perfluoro-2-Methylpentane. *J. Am. Chem. Soc.* **1952**, *74*, 3771.
- (29) Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A. Vapor Pressure, Heat Capacity, and Density Along the Saturation Line, Measurements for cyclohexanol, 2-cyclohexen-1-one, 1,2-dichloropropane, 1,4-di-*tert*-butylbenzene, (+/–)-2-ethylhexanoic acid, 2-(methylamino)ethanol, perfluoro-*n*-heptane, and sulfolane. *J. Chem. Eng. Data* **1997**, *42*, 1021.
- (30) Oliver, G. D.; Blumkin, S.; Cunningham, C. W. Some Physical Properties of Hexadecafluoroheptane. *J. Am. Chem. Soc.* **1951**, *73*, 5722.
- (31) Kennan, R. P.; Pollack, G. L. Solubility of Xenon in Perfluoroalkanes—Temperature-Dependence and Thermodynamics. *J. Chem. Phys.* **1988**, *89*, 517.
- (32) Haszeldine, R. N.; Smith, F. Organic Fluorides. 4. The Chemical and Physical Properties of Certain Fluorocarbons. *J. Chem. Soc.* **1951**, (Feb.), 603.
- (33) Hales, J. L.; Townsend, R. Liquid Densities from 293 to 490 K of 8 Fluorinated Aromatic-Compounds. *J. Chem. Thermodyn.* **1974**, *6*, 111.
- (34) Findlay, T. J. V. Vapor Pressures of Fluorobenzenes from 5 Degrees C to 50 Degrees C. *J. Chem. Eng. Data* **1969**, *14*, 229.
- (35) Dunlap, R. D.; Murphy, C. J.; Bedford, R. G. Some Physical Properties of Perfluoro-Normal-Hexane. *J. Am. Chem. Soc.* **1958**, *80*, 83.
- (36) Douslin, D. R.; Osborn, A. Pressure Measurements in 0.01–30 torr Range with an Inclined-Piston Gauge. *J. Sci. Instrum.* **1965**, *42*, 369.
- (37) Dias, A. M. A.; Goncalves, C. M. B.; Legido, J. L.; Coutinho, J. A. P.; Marrucho, I. M. Solubility of Oxygen in Substituted Perfluorocarbons. *Fluid Phase Equilib.* **2005**, *238*, 7.
- (38) Dias, A. M. A.; Goncalves, C. M. B.; Caco, A. I.; Santos, L. M. N. B. F.; Pineiro, M. M.; Vega, L. F.; Coutinho, J. A. P.; Marrucho, I. M. Densities and Vapor Pressures of Highly Fluorinated Compounds. *J. Chem. Eng. Data* **2005**, *50*, 1328.
- (39) Crowder, G. A.; Taylor, Z. L.; Reed, T. M.; Young, J. A. Vapor Pressures and Triple Point Temperatures for Several Pure Fluorocarbons. *J. Chem. Eng. Data* **1967**, *12*, 481.
- (40) Counsell, J. F.; Green, J. H. S.; Hales, J. L.; Martin, J. F. Thermodynamic Properties of Fluorine Compounds. 2. Physical and

Thermodynamic Properties of Hexafluorobenzene. *Trans. Faraday Soc.* **1965**, *61*, (506P), 212.

(41) Ambrose, D.; Ellender, J. H. The Vapor-Pressure of Octafluorotoluene. *J. Chem. Thermodyn.* **1981**, *13*, 901.

(42) Ambrose, D. Reference Values of Vapor-Pressure—The Vapor-Pressures of Benzene and Hexafluorobenzene. *J. Chem. Thermodyn.* **1981**, *13*, 1161.

(43) DIPPR, Thermophysical Properties Database, 1998.

(44) Kreglewski, A. Vapour Pressures and Molar Volumes of Liquid Perfluoro-*n*-Octane Trifluoroacetic Acid and its Anhydride. *Bull. Acad. Pol. Sci.* **1962**, *10*, 629.

(45) NIST Chemistry WebBook, <http://webbook.nist.gov/chemistry/fluid/>.

(46) Freire, M. G.; Santos, L. M. N. B. F; Marrucho, I. M.; Coutinho, J. A. P. Water Solubility in Fluorocarbons: Experimental Measurements and Modelling. To be submitted to *Ind. Eng. Chem. Res.*

(47) Freire, M. G.; Razzouk, A.; Mokbel, I.; Jose, J.; Marrucho, I. M.; Coutinho, J. A. P. Solubility of Hexafluorobenzene in Aqueous Salt Solutions from (280 to 340) K. *J. Chem. Eng. Data* **2005**, *50*, 237.

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