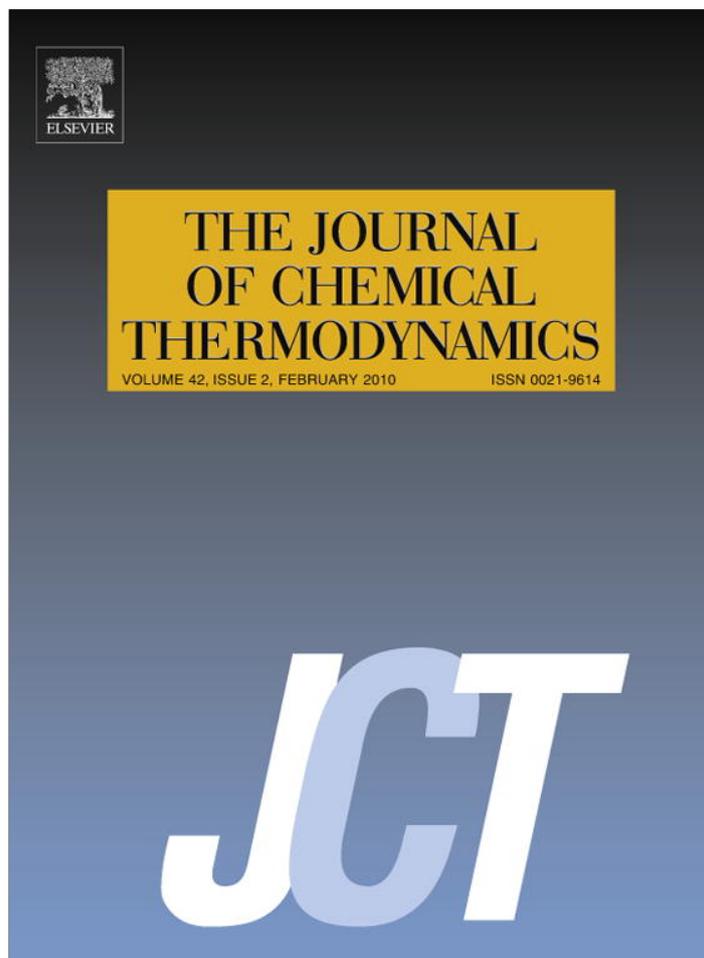


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Solubility of water in fluorocarbons: Experimental and COSMO-RS prediction results

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ABSTRACT

This work aims at providing experimental and theoretical information about the water–perfluorocarbon molecular interactions. For that purpose, experimental solubility results for water in cyclic and aromatic perfluorocarbons (PFCs), over the temperature range between (288.15 and 318.15) K, and at atmospheric pressure, were obtained and are presented. From the experimental solubility dependence on temperature, the partial molar solution and solvation thermodynamic functions such as Gibbs free energy, enthalpy and entropy were determined and are discussed. The process of dissolution of water in PFCs is shown to be spontaneous for cyclic and aromatic compounds. It is demonstrated that the interactions between the non-aromatic PFCs and water are negligible while those between aromatic PFCs and water are favourable. The COSMO-RS predictive capability was explored for the description of the water solubility in PFCs and others substituted fluoro compounds. The COSMO-RS is shown to be a useful model to provide reasonable predictions of the solubility values, as well as to describe their temperature and structural modifications dependence. Moreover, the molar Gibbs free energy and molar enthalpy of solution of water are predicted remarkably well by COSMO-RS while the main deviations appear for the prediction of the molar entropy of solution.

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1. Introduction

Perfluorocarbons (PFCs) are synthetic and completely fluorinated halocarbons while fluorocarbons (FCs) are partially fluorinated hydrocarbons. The substitution of hydrogen for fluorine in hydrocarbons has a dramatic influence on the compound's chemical and physical properties [1,2]. The high ionization potential of fluorine and relatively low polarizability lead to weak intermolecular forces [1,2]. By contrast, the carbon–fluorine bond creates strong intramolecular forces [1,2]. As a result, PFCs and FCs present unusual and interesting properties, as for example, large solubility for gases, exceptional chemical and biological inertness, excellent spreading characteristics, low surface tension and refractive index, density higher than water, and high isothermal compressibility [3–7]. Due to their intrinsic properties, PFCs and FCs are commonly used in the most diverse commercial and industrial applications ranging from cleaning solvents, fire suppression agents, heat transfer fluids, surfactants in supercritical solvents, in uranium enrichment, and as aerosol solvents [8]. On the other hand, PFCs and FCs are also exploited in biomedical purposes as aspirants for drug

delivery, anti-tumour, and diagnostic imaging agents, and particularly, as *in vivo* gas carriers in liquid ventilation or blood substitute formulations [9].

The determination of mutual solubilities between water and PFCs or FCs has a particular interest as the solubility determines their fate in biological, medical, industrial and environmental applications and provides useful information about the cross-contamination of (water + PFCs/FCs) systems. Furthermore, such solubility supports the PFC-in-water or reversed emulsion formation and preferred aging mechanisms [10,11] and the oxygen solubility decrease in PFC-based emulsions when compared to the oxygen solubility of the pure liquid phases [12]. In spite of the importance regarding the knowledge of the mutual solubilities between water and PFCs/FCs, such solubilities are so small that accurate experimental measurements are often limited by the experimental techniques available. So, the development of reliable correlations and predictive methods is the most viable way to overcome this lack of experimental results.

Experimental values for phase equilibrium covering PFCs/FCs and water systems are particularly scarce in the literature [13–17]. Adding to our previous contributions [16,17], in this work, new experimental results for the solubility of water in cyclic and aromatic PFCs are presented. Moreover, the experimental solubility values for water in saturated PFC-rich phases were obtained

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over a large temperature range allowing the determination of the thermodynamic functions associated with the water solvation.

Some approaches to the modelling of fluorocarbon (liquid + liquid) systems can be found in the open literature [18–21]. The description of the liquid–liquid phase behaviour of (fluorocarbon + alkane) [18,19] and (fluoroalcohol + perfluoroalkane) [20] mixtures was already performed using the soft-SAFT EoS and modified UNIFAC model. Recently, Oliveira *et al.* [21] applied with success the cubic-plus-association equation of state (CPA EoS) to the description of binary mixtures of water and several linear, cyclic, aromatic, and substituted PFCs. In spite of their interest, (water + PFCs/FCs) systems behaviour cannot be simply described by molecular modelling due to the extremely strong electrostatic and hydrogen-bonding interactions present in water, which in (water + organic) mixtures results in the water hydrogen-bonding network reorganization around non-polar surfaces. Thus, COSMO-RS, Conductor-like Screening Model for Real Solvents, a method for the prediction of thermophysical properties of fluids based on unimolecular quantum calculations [22–25], can be undoubtedly applied to predict the solubility of water in PFCs and FCs and its dependence with temperature. Klamt [26] already showed the high potential of COSMO-RS to predict mutual solubilities between water and hydrocarbons. Nevertheless, no reports for PFCs or FCs (liquid + liquid) phase equilibrium systems using COSMO-RS were previously attempted. Therefore, the performance of this predictive method is analyzed here for water solubility in PFCs/FCs showing to provide a satisfactory description of the experimental results.

2. Experimental

2.1. Materials

The PFCs studied with respect to their solubility of water were the cyclic perfluoromethylcyclohexane, C_7F_{14} , and perfluorodecalin (mixture of *cis* and *trans* isomers), $C_{10}F_{18}$, from Apollo Scientific and

from Flutec with mass fraction purities of 0.9998 and 0.9988, respectively. The aromatics hexafluorobenzene, C_6F_6 , and octafluorotoluene, C_7F_8 , were obtained from Fluorochem and Apollo Scientific with mass fraction purities of 0.9999 and 0.9990, respectively. All the perfluorocarbons, with the exception of perfluorodecalin, were used as received without any further purification. The perfluorodecalin was purified by passage through a silica column (*circa* 10 times) according to the suggestions of Gaonkar and Newman [27] and Goebel and Lunkenheimer [28]. The purity of each compound was analyzed by gas chromatography as previously described [17]. The molecular structure of the studied PFCs is presented in figure 1.

The water used was double distilled, passed by a reverse osmosis system and further treated with a Milli-Q plus 185 water purification apparatus. Hydranal[®] – Coulomat AG from Riedel-de Haën was used as the analyte in the coulometric Karl–Fischer titration.

2.2. Procedure

The solubility of water in the PFC-rich phase was determined for the cyclic and aromatic compounds described above over the temperature range from (288.15 to 318.15) K with a Metrohm Karl–Fischer (KF) coulometer, model 831. The two phases were placed in 22 cm³ glass vials, vigorously agitated, and allowed to reach equilibrium for a minimum of 24 h. This period was the minimum time period found for equilibration, where a complete separation of the two phases was achieved and no further variations in the water mole fraction solubility were observed. The temperature was kept constant within ± 0.01 K using an air bath. Further details can be found elsewhere [17]. Five precise independent PFC-rich phase extractions were carried for each compound at every temperature, and the respective mole fraction solubility and associated standard deviations were determined. The experimental methodology adopted was validated previously [17] with water solubility in *n*-heptane and respective comparison with the literature data.

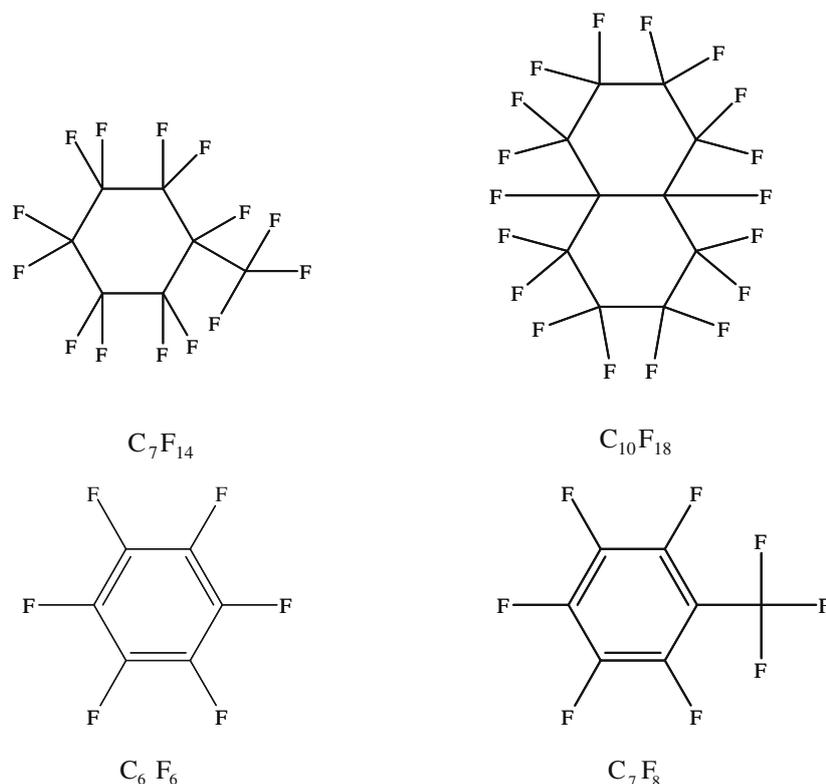


FIGURE 1. Molecular structure of the studied PFCs: C_7F_{14} (perfluoromethylcyclohexane); $C_{10}F_{18}$ (perfluorodecalin); C_6F_6 (hexafluorobenzene); and C_7F_8 (octafluorotoluene).

3. Thermodynamic functions

The solvation process and the dependency of the solvation equilibria with temperature, are associated with several variations in their thermodynamic functions, namely, the standard molar Gibbs free energy of solution, $\Delta_{sol}G_m^\circ(T)$, the standard molar enthalpy of solution, $\Delta_{sol}H_m^\circ(T)$, and the standard molar entropy of solution, $\Delta_{sol}S_m^\circ(T)$. These thermodynamic functions describing the solvation process can be obtained directly or from the temperature dependence of the experimental solute solubility values. The thermodynamic parameters noted above reflect the transference of the solute molecules to a hypothetical dilute ideal solution where the mole fraction of the solvent is equal to one (and thus the mole fraction of the solute is at infinite dilution), and can be calculated according to equations (1) to (3) [29]

$$\frac{\Delta_{sol}H_m^\circ(T)}{RT^2} = \left(\frac{\partial \ln x_i}{\partial T} \right)_p, \quad (1)$$

$$\Delta_{sol}G_m^\circ(T) = -RT \ln(x_i)_p, \quad (2)$$

$$\Delta_{sol}S_m^\circ(T) = R \left(\frac{\partial \ln x_i}{\partial T} \times T + \ln x_i \right), \quad (3)$$

where x_i is the mole fraction solubility of the solute i , R is the ideal gas constant, and T is the temperature at a constant pressure, p .

The integration of equation (1), assuming that $\Delta_{sol}H_m^\circ(T)$ over a specific temperature interval is temperature independent leads to equation (4), valuable for the correlation of the experimental data,

$$\ln(x_i/x_0) = A + \frac{B}{T}, \quad (4)$$

where x_0 is taken by convention as one unit mole fraction, and A and B are constants related with $\Delta_{sol}H_m^\circ(T)$, $\Delta_{sol}S_m^\circ(T)$, and the ideal gas constant (R).

On the other hand, the standard molar enthalpy of solution of the solute, $\Delta_{sol}H_m^\circ(T)$, can be split into two contributions: the standard molar enthalpy of vaporization of the solute, $\Delta_i^g H_m^\circ$, and the standard molar enthalpy of solvation, $\Delta_{svt}H_m^\circ(T)$,

$$\Delta_{sol}H_m^\circ(T) = \Delta_{svt}H_m^\circ(T) + \Delta_i^g H_m^\circ. \quad (5)$$

The standard molar Gibbs free energy of solvation, $\Delta_{svt}G_m^\circ(T)$, can be derived for a temperature T using the hypothetical reference state for water in the gas phase and at the pressure $p^\circ = 10^5$ Pa,

$$\Delta_{svt}G_m^\circ(T) = \Delta_{sol}G_m^\circ(T) + RT \ln \left(\frac{p(s_i, T)}{p^\circ} \right), \quad (6)$$

and therefore,

$$\Delta_{svt}S_m^\circ(T) = \frac{\Delta_{svt}H_m^\circ(T) - \Delta_{svt}G_m^\circ(T)}{T}, \quad (7)$$

where $p(s_i, T)$ is the vapour pressure of the solute i at the temperature T .

Another approach to define a standard state could be based on statistical mechanical methods as proposed by Ben-Naim [30]. The changes that occur in the solute neighbourhood during the dissolution process due to the transfer of one solute molecule from a fixed position in an ideal gas phase into a fixed position in the fluid, at a constant temperature, T , and constant pressure, p , with the composition of the system unchanged, are represented by the molar local standard Gibbs free energy, $\Delta_{svt}G_m^*(T)$, the molar local standard enthalpy, $\Delta_{svt}H_m^*(T)$, and the molar local standard entropy, $\Delta_{svt}S_m^*(T)$, of solvation [30–32]. Moreover, these local thermodynamic functions can be related to the conventional thermodynamic functions described in equations (5) to (7) using the following equations (8) to (10):

$$\Delta_{svt}G_m^*(T) = \Delta_{svt}G_m^\circ(T) - RT \ln \left(\frac{RT}{p^\circ V_{j,m}} \right), \quad (8)$$

$$\Delta_{svt}H_m^*(T) = \Delta_{svt}H_m^\circ(T) - RT(\alpha_j - 1), \quad (9)$$

$$\Delta_{svt}S_m^*(T) = \Delta_{svt}S_m^\circ(T) + R \ln \left(\frac{RT}{p^\circ V_{j,m}} \right) - R(T\alpha_j - 1), \quad (10)$$

where $V_{j,m}$ is the molar volume of the solvent j and α_j is the isobaric thermal expansibility of the solvent derived from experimental density data.

4. The model COSMO-RS

The COSMO-RS (Conductor-like Screening Model for Real Solvents) was proposed by Klamt and co-workers [22–26]. It combines the electrostatic advantages and the computational efficiency of the quantum chemical dielectric continuum solvation model, COSMO, with a statistical thermodynamic approach for local interaction of surfaces, where the local deviations from dielectric behaviour as well as hydrogen-bonding are considered. The standard procedure of COSMO-RS calculations consists essentially in two major stages: quantum chemical COSMO calculations for the molecular species involved and COSMO-RS statistical thermodynamic calculations performed within the COSMOtherm program [33,34].

In the COSMO calculations, the solute molecules are assumed to be in a virtual conductor environment, where the solute molecule induces a polarization charge density, σ , on the interface between the molecule and the conductor. In the quantum chemical self-consistency algorithm cycle, the solute molecule is converged to its energetically optimal state in a conductor with respect to electron density. The calculations end up with the self-consistent state of the solute in the presence of a virtual conductor that surrounds the solute outside the cavity. The polarization density distribution on the surface of each molecule X_i is converted into a distribution function, the σ -profile, $p_i^X(\sigma)$, that describes the polarity of each surface segment on the overall surface of the molecule. If a mixture is considered, the σ -profile of a solvent j , $p_j(\sigma)$, is the result of adding the individual $p_i^X(\sigma)$ weighed by their mole fractions, x_i , as expressed in the following equation:

$$p_j(\sigma) = \sum_{i \in j} x_i p_i^X(\sigma). \quad (11)$$

For the statistical thermodynamics, it is convenient to account with a normalized ensemble. The integral of $p_i^X(\sigma)$ over the entire σ -range is the total surface area, A^{X_i} , of a compound X_i . Thus the normalised σ -profile, $p_j'(\sigma)$, of the overall system is defined as follows:

$$p_j'(\sigma) = \frac{p_j(\sigma)}{A_j} = \frac{p_j(\sigma)}{\sum_{i \in j} x_i A^{X_i}}. \quad (12)$$

The electrostatic misfit energy (E_{misfit}) and hydrogen-bonding (E_{HB}) are described as functions of the polarization charges of two interacting segments, σ and σ' or σ_{acceptor} and σ_{donor} , if the segments are located in a hydrogen bond donor or acceptor atom, as described in equations (13) and (14). On the other hand, the van der Waals energy (E_{vdw}) is only dependent on the elements of the atoms involved (equation (15)):

$$E_{\text{misfit}}(\sigma, \sigma') = a_{\text{eff}} \frac{\alpha'}{2} (\sigma + \sigma')^2, \quad (13)$$

$$E_{\text{HB}} = a_{\text{eff}} c_{\text{HB}} \min(0; \min(0; \sigma_{\text{donor}} + \sigma_{\text{HB}}) \max(0; \sigma_{\text{acceptor}} - \sigma_{\text{HB}})), \quad (14)$$

$$E_{\text{vdw}} = a_{\text{eff}} (\tau_{\text{vdw}} + \tau'_{\text{vdw}}), \quad (15)$$

where α' is the coefficient for electrostatic misfit interactions, a_{eff} is the effective contact area between two surface segments, c_{HB} is the

coefficient for hydrogen bond strength, σ_{HB} is the threshold for hydrogen-bonding and τ_{vdW} and τ_{vdW}^* are element-specific vdWs coefficients.

The solubility of water in PFCs or FCs was studied as a function of temperature using the quantum chemical COSMO calculation performed in the Turbomole program package [33,34] using the BP density functional theory and the Ahlrichs-TZVP (triple- ζ valence polarized large basis set) [35–37]. The fully optimized geometries at the same level of theory for the lower energy conformers of the molecules (when several conformers exist) and with the parameter file BP_TZVP_C21_0105 were employed.

5. Results and discussion

The solubility of water in the cyclic (C_7F_{14} and $C_{10}F_{18}$) and in the aromatic (C_6F_6 and C_7F_8) PFCs was measured from $T = (288.15$ to $318.15)$ K at atmospheric pressure. Experimental values for the solubility of water in the studied PFCs and the respective standard deviations are reported in table 1 and, for a better perspective, presented in figure 2.

From the inspection of table 1, it is noticeable that the water solubility in PFCs, expressed in terms of water mole fraction, is strongly dependent on the temperature and only weakly dependent on the number of carbons within the same family. Moreover, within the same family, the available results suggest an increase of water solubility with the rise in the carbon atoms number of the PFC. They also point out that the water solubility rises from cyclic PFCs to n -perfluoroalkanes [17] to aromatic PFCs (considering structures of the type C_7F_n). In addition, a significant increase in the water solubility, of one order of magnitude, is verified for the aromatic PFC family that can be attributed to the interaction of water with the PFC π system [38] arising from the decrease of the π electron density in the perfluorinated aromatic ring.

In order to determine the associated thermodynamic functions of solution of water, equation (4) was used to correlate the temperature dependence of the solubility data for the systems studied (graphically represented in figure 2). The fitted parameters A and B , as well as their standard deviations [39], are reported in table 2. The conventional standard molar enthalpy, Gibbs free energy and entropy of solution and solvation of water were determined from equations (1) to (3) and from equations (5) to (7), respectively, and are reported in table 3. The conventional standard molar enthalpies of solvation, $\Delta_{solv}H_m^p(T)$, were derived using the reported standard molar enthalpy of vaporization of H_2O at $T = 298.15$ K of 43.99 $\text{kJ} \cdot \text{mol}^{-1}$ [40].

It has been previously demonstrated that the standard molar enthalpies of solution and solvation of water in n -perfluoroalkanes [17] do not show any dependence on the carbon number. This fact is additionally corroborated by the results obtained in this work with both aromatic and cyclic PFCs. Moreover, the standard molar enthalpies of solution of water in n -perfluoroalkanes, (39.3 ± 0.2) $\text{kJ} \cdot \text{mol}^{-1}$, were verified to be somewhat higher than in the corre-

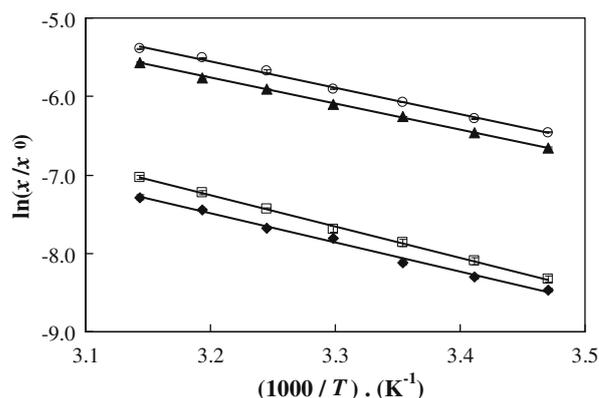


FIGURE 2. Plot of mole fraction of water (x) as a function of reciprocal temperature to illustrate solubility in the PFCs: \blacklozenge , C_7F_{14} ; \square , $C_{10}F_{18}$; \blacktriangle , C_6F_6 ; \circ , C_7F_8 . The solid lines represent the correlation of the experimental results using equation (4).

TABLE 2

Correlation parameters obtained from equation (4) for the mole fraction solubility of water in PFCs dependent on temperature.

PFC	$A \pm \sigma^a$	$10^{-3} (B \pm \sigma^a)/K$
C_7F_{14}	4.44 ± 0.60	-3.73 ± 0.18
$C_{10}F_{18}$	5.47 ± 0.21	-3.98 ± 0.06
C_6F_6	4.81 ± 0.22	-3.30 ± 0.06
C_7F_8	5.25 ± 0.35	-3.38 ± 0.11

^a Standard deviation.

sponding n -alkanes ((34.9 ± 0.5) $\text{kJ} \cdot \text{mol}^{-1}$ for n -heptane [17]). Nevertheless, a decrease in the standard molar enthalpy of solution of water in cyclic (31.0 and 33.1) $\text{kJ} \cdot \text{mol}^{-1}$ and aromatic (27.5 and 28.1) $\text{kJ} \cdot \text{mol}^{-1}$ PFCs was observed when compared with those of water in n -perfluoroalkanes (≈ 39.3 $\text{kJ} \cdot \text{mol}^{-1}$ [17]), the decrease being more pronounced for the aromatic family and close to the molar enthalpy of solution of water in the substituted fluoroalkanes (≈ 24.9 $\text{kJ} \cdot \text{mol}^{-1}$ [17]). These low molar enthalpies of solution/solvation indicate that the enthalpic energetic balance involved in the dissolution/solvation of water in an aromatic PFC is favourable, when compared with the cyclic PFC or with the n -perfluoroalkanes. The general low solubility of water in PFCs, arises mainly from the significant difference between the standard molar enthalpies of solvation, $\Delta_{solv}H_m^p(T = 298.15 \text{ K})$, between water–water (-43.99 $\text{kJ} \cdot \text{mol}^{-1}$) [40] and water–PFCs (-10 to -20 $\text{kJ} \cdot \text{mol}^{-1}$) [17].

The Ben-Naim standard quantities of solvation were derived using the molar volume and the isobaric thermal expansivity of the solvents derived from experimental density values [5,41]. The Ben-Naim local standard Gibbs free energy, enthalpy and entropy changes along with the molar volume and the thermal expansion coefficient of the liquids, at $T = 298.15$ K, are reported in table 4. The Ben-Naim local standard thermodynamic functions of solvation for the (water + water) system, as well as the molar volume and thermal expansion coefficient of water, at $T = 298.15$ K, are additionally reported in table 4 for comparison purposes [42]. The uncertainty interval quoted is the standard deviation of each independent function determination [39]. The values reported show that the standard molar Gibbs free energy of solvation is always negative, thus the solvation process is spontaneous at the Ben-Naim local standard conditions. In addition, regarding the enthalpies of solvation, at the Ben-Naim local standard conditions, this property shows itself to be less significant for the n -perfluoroalkanes (≈ -3.4 $\text{kJ} \cdot \text{mol}^{-1}$ [17]) and cyclic PFCs (≈ -10.5 $\text{kJ} \cdot \text{mol}^{-1}$) when compared with the values obtained for the aromatic

TABLE 1

Experimental mole fraction solubility of water in the studied PFCs.

T/K	C_7F_{14} $10^4 (x \pm \sigma^a)$	$C_{10}F_{18}$ $10^4 (x \pm \sigma^a)$	C_6F_6 $10^3 (x \pm \sigma^a)$	C_7F_8 $10^3 (x \pm \sigma^a)$
288.15	2.10 ± 0.05	2.41 ± 0.08	1.28 ± 0.01	1.57 ± 0.01
293.15	2.48 ± 0.06	3.04 ± 0.14	1.56 ± 0.01	1.86 ± 0.01
298.15	3.00 ± 0.09	3.84 ± 0.17	1.92 ± 0.01	2.30 ± 0.01
303.15	4.07 ± 0.07	4.58 ± 0.18	2.23 ± 0.02	2.72 ± 0.01
308.15	4.64 ± 0.09	5.94 ± 0.06	2.73 ± 0.01	3.42 ± 0.05
313.15	5.81 ± 0.07	7.27 ± 0.02	3.15 ± 0.07	4.06 ± 0.03
318.15	6.84 ± 0.09	8.84 ± 0.02	3.84 ± 0.03	4.54 ± 0.04

^a Standard deviation.

TABLE 3

Conventional thermodynamic properties of solution and solvation of water in the PFCs studied at $T = 298.15$ K determined from experimental results.

PFC	$\Delta_{sol}G_m^{\circ}(T) \pm \sigma^a$ (kJ · mol ⁻¹)	$\Delta_{sol}H_m^{\circ}(T) \pm \sigma^a$ (kJ · mol ⁻¹)	$\Delta_{sol}S_m^{\circ}(T) \pm \sigma^a$ (J · K ⁻¹ · mol ⁻¹)	$\Delta_{svt}G_m^{\circ}(T) \pm \sigma^a$ (kJ · mol ⁻¹)	$\Delta_{svt}H_m^{\circ}(T) \pm \sigma^a$ (kJ · mol ⁻¹)	$\Delta_{svt}S_m^{\circ}(T) \pm \sigma^a$ (J · K ⁻¹ · mol ⁻¹)
C ₇ F ₁₄	20.11 ± 0.08	31.0 ± 1.5	36.5 ± 5.3	11.55 ± 0.08	-13.0 ± 1.5	-82.3 ± 5.3
C ₁₀ F ₁₈	19.50 ± 0.11	33.1 ± 0.5	45.5 ± 2.1	10.94 ± 0.11	-10.9 ± 0.5	-73.3 ± 2.1
C ₆ F ₆	15.51 ± 0.01	27.5 ± 0.5	40.1 ± 1.9	6.95 ± 0.01	-16.5 ± 0.5	-78.7 ± 1.9
C ₇ F ₈	15.06 ± 0.01	28.1 ± 0.9	43.6 ± 2.9	6.51 ± 0.01	-15.9 ± 0.9	-75.2 ± 2.9

^a Standard deviation.

TABLE 4

Molar volume and isobaric thermal expansivity of the PFC solvents and experimental thermodynamic local standard properties of the solvation of water at $T = 298.15$ K determined from experimental data.

Fluid	10 ⁴ V _m (m ³ · mol ⁻¹)	10 ³ α/K ⁻¹	$\Delta_{svt}G_m^{\circ}(T) \pm \sigma^a$ (kJ · mol ⁻¹)	$\Delta_{svt}H_m^{\circ}(T) \pm \sigma^a$ (kJ · mol ⁻¹)	$\Delta_{svt}S_m^{\circ}(T) \pm \sigma^a$ (J · K ⁻¹ · mol ⁻¹)
H ₂ O	0.181 [42]	0.201 [42]	-26.468 [30]	-41.771 [30]	-51.33 [30]
C ₇ F ₁₄	1.96 [41]	1.44 [41]	-0.45 ± 0.08	-11.6 ± 1.5	-37.3 ± 5.3
C ₁₀ F ₁₈	2.39 [5]	1.28 [5]	-0.57 ± 0.11	-9.4 ± 0.5	-29.6 ± 2.1
C ₆ F ₆	1.16 [5]	1.43 [5]	-6.35 ± 0.01	-15.1 ± 0.5	-29.4 ± 1.9
C ₇ F ₈	1.42 [5]	1.29 [5]	-6.29 ± 0.01	-14.4 ± 0.9	-27.2 ± 2.9

^a Standard deviation.

PFCs (≈ -14.8 kJ · mol⁻¹) and previously with the α -(ω)substituted n -fluorooctanes (≈ -17.5 kJ · mol⁻¹ [17]). These results indicate that the interactions between the non-aromatic fully fluorinated

compounds and water are smaller than to those observed between the aromatic PFCs and water. Moreover, considering the results obtained for the molar enthalpies and entropies of solvation, the Ben-Naim local standard and in the standard state conditions, it is clear that the enthalpy contribution is ruling the increase of solubility of water in aromatic PFC systems.

The quantum chemical COSMO calculations for the water and the PFCs and FCs under study and those previously reported [17] were performed with the Turbomole program package [33,34] using the BP density functional theory and the triple- ζ valence polarized large basis set (TZVP) [35–37]. Water solubility experimental data and COSMO-RS predictions are presented in the form of $\ln(x/x_0) = f(1000/T)$ for each binary mixture experimentally investigated and the results obtained are compared in figures 3 to 5.

Analysing figure 3 it can be seen that the COSMO-RS results describe well the increasing solubility of water with the carbon number, although the predicted differences in solubility are much smaller than the observed experimentally. From figure 4 it is shown that, besides the carbon number dependence within the same family, COSMO-RS is also able to predict the solubility differences observed between the different FCs families. Figure 5 shows

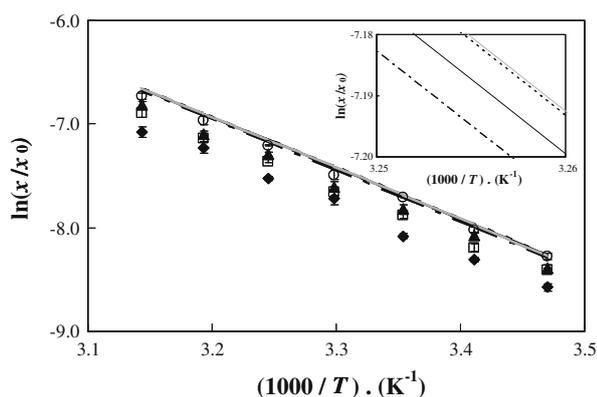


FIGURE 3. Plot of mole fraction of water (x) as a function of reciprocal to illustrate solubility in n -perfluoroalkanes: (♦) (---), C₆F₁₄; (□) (—), C₇F₁₆; (▲) (-----), C₈F₁₈; (○) (—), C₉F₂₀. The single symbols and the lines represent, respectively, the experimental results [17] and the COSMO-RS predictions.

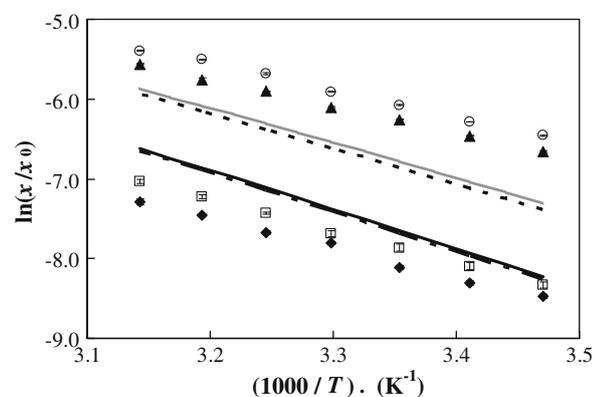


FIGURE 4. Plot of mole fraction of water (x) against reciprocal temperature to illustrate solubility in cyclic and aromatic PFCs: (♦) (---), C₇F₁₄; (□) (—), C₁₀F₁₈; (▲) (-----), C₆F₆; (○) (—), C₇F₈. The single symbols and the lines represent, respectively, the experimental results (this work) and the COSMO-RS predictions.

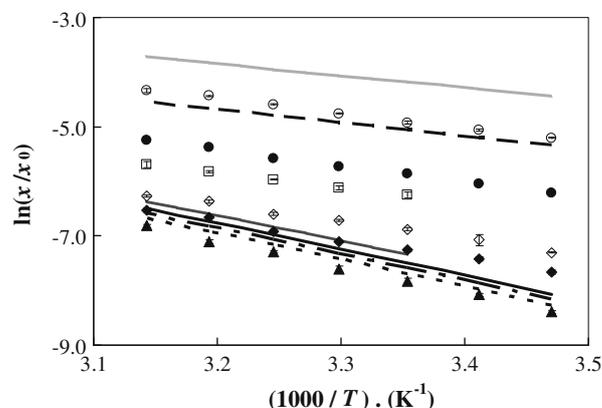


FIGURE 5. Plot of mole fraction of water (x) against reciprocal temperature to illustrate solubility in n -perfluorooctane and in α -(ω -) substituted n -fluorooctanes: (▲) (-----), C₈F₁₈; (♦) (---), C₈F₁₇Br; (□) (—), C₈F₁₇I; (●) (—), C₈F₁₇H; (○) (—), C₈F₁₆H₂; (◇) (—), C₈F₁₆Cl₂. The single symbols and the lines represent, respectively, the experimental results [17] and the COSMO-RS predictions.

TABLE 5

Mole fraction solubility, correlation parameters obtained from equation (4), thermodynamic conventional properties of solution predicted by COSMO-RS at 298.15 K, and respective deviation from the thermodynamic properties determined from experimental results.

PFC	10^4x	A	$10^{-3}B$	$\Delta_{sol}C_m^o(T) \pm \sigma^a$ (kJ · mol ⁻¹)	$\Delta_{sol}H_m^o(T) \pm \sigma^a$ (kJ · mol ⁻¹)	$\Delta_{sol}S_m^o(T) \pm \sigma^a$ (J · K ⁻¹ · mol ⁻¹)	$\Delta(\Delta_{sol}G_m^o(T))$ (kJ · mol ⁻¹)	$\Delta(\Delta_{sol}H_m^o(T))$ (kJ · mol ⁻¹)	$\Delta(\Delta_{sol}S_m^o(T))$ (J · K ⁻¹ · mol ⁻¹)
C ₇ F ₁₄ ^a	4.67	8.83	-4.92	19.01	40.9	73.4	-1.10	9.9	36.9
C ₁₀ F ₁₈ ^a	4.76	8.91	-4.94	19.96	41.1	74.1	-0.53	8.0	28.6
C ₆ F ₆ ^a	10.52	7.98	-4.42	17.00	36.8	66.3	1.49	9.3	26.2
C ₇ F ₈ ^a	11.36	7.94	-4.39	16.81	36.5	66.3	1.74	8.4	22.4
C ₆ F ₁₄ ^b	4.56	8.78	-4.91	19.07	40.9	73.1	-0.96	1.6	8.5
C ₇ F ₁₆ ^b	4.59	8.80	-4.92	19.05	40.9	73.2	-0.49	1.8	7.6
C ₈ F ₁₈ ^b	4.61	8.82	-4.92	19.04	40.9	73.3	-0.36	1.6	6.5
C ₉ F ₂₀ ^b	4.62	8.83	-4.92	19.04	40.9	73.4	-0.06	1.3	4.7
C ₈ F ₁₇ Br ^b	5.15	8.64	-4.84	18.77	40.2	71.9	0.78	11.4	35.5
C ₈ F ₁₇ H ^b	64.26	3.20	-2.46	12.51	20.4	26.6	-2.04	-4.2	-7.1
C ₈ F ₁₆ H ₂ ^b	153.12	3.20	-2.20	10.36	18.3	26.6	-1.85	-4.5	-8.8
C ₈ F ₁₆ Cl ₂ ^b	5.53	8.67	-4.82	18.59	40.1	72.1	1.55	14.1	42.0
C ₈ F ₁₇ ^b	6.51	8.26	-4.65	15.50	38.7	77.7	0.00	16.3	54.7

^a PFCs studied in this work.

^b FCs studied elsewhere [17].

that the overall trend in the solubility of water is also well predicted for all the substituted FCs, with their hydrophobic character increasing from C₈F₁₆H₂ < C₈F₁₆H < C₈F₁₇ < C₈F₁₆Cl₂ < C₈F₁₇Br < C₈F₁₈, as experimentally verified [17]. In spite of the deviations observed, it is unambiguous that the COSMO-RS predictive method can be used to predict the water solubility and the hydrophobic character of others α -(ω)-substituted fluoroalkanes and PFCs not experimentally available.

For water solubility in all the PFCs and FCs studied, it is further revealed that COSMO-RS is capable of predicting the correct temperature dependence, and intrinsically, a correct description of the molar enthalpies of solution of water in PFCs and FCs is attained, as shown in table 5. The COSMO-RS is also able to provide an acceptable description of the solubility values despite their extremely small values. The major deviations seem to be related to a poor description of the entropies of solution that may in turn be related to the combinatorial term used by COSMO-RS. In table 5, it is evident that the deviations between the molar functions of solution predicted from COSMO-RS and the determined from experimental results are higher for the molar entropy of solution, while the molar Gibbs free energy and the molar enthalpy of solution present small deviations. Curiously for the molar Gibbs free energy function, the COSMO-RS prediction results, either by excess or default, seem to be divided by PFCs/FCs families.

In general, the water solubility results obtained from COSMO-RS calculations show an acceptable agreement with the experimental data available, describing well the water solubility in both PFCs and FCs including the structural effects and temperature dependence, allowing thus a reasonable prediction of the molar enthalpy of solution of water.

6. Conclusions

Original experimental results for the solubility of water in cyclic and aromatic PFCs at temperatures ranging between (288.15 and 318.15) K and at atmospheric pressure are presented. From the temperature dependence of the water solubility, the thermodynamic properties of solution and solvation have been determined. The process of water dissolution in PFCs was found to be spontaneous under the Ben-Naim standard conditions as reported by negative standard local Gibbs free energy changes. In addition, the low values of local enthalpies of solvation indicate a weak interaction between water and the cyclic PFCs while the higher values observed for the aromatic PFCs indicate that favourable interactions are present.

Quantum chemical calculations based on the σ profiles of several PFCs, FCs and water were used for the prediction of the solubility of water in those organic compounds (both for literature values [17] and the ones presented in this work). The COSMO-RS and its implementation in the program COSMOtherm are capable of providing qualitative predictions of the solubility. The predicted values of water solubility correctly describe all the PFCs and FCs structural modifications and temperature dependence. This approach proved to be a potential alternative for providing values of the solubility of water and molar Gibbs free energy and enthalpies of solution of water in PFCs or FCs when no experimental values are available.

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