

# Solubility of oxygen in substituted perfluorocarbons

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## Abstract

The solubilities of oxygen in 1Br-perfluoro-*n*-octane, 1H-perfluoro-*n*-octane and 1H,8H-perfluoro-*n*-octane were measured using the saturation method at temperatures between 288 and 313 K and pressures close to atmospheric. The experimental data measured allows the calculation of derived properties as enthalpy and entropy of solution, which are not available in the literature, helping to elucidate about the solvation of oxygen in these fluorinated compounds. The study of the solubility of oxygen in linear-fluorinated molecules presenting different degrees of substitution on the terminal CF<sub>3</sub> groups seems to indicate the existence of strong interactions between the oxygen and those groups. New experimental density and vapor pressure data for 1H,8H-perfluoro-*n*-octane, needed for solubility data reduction, were also measured and correlated with appropriate equations. © 2005 Elsevier B.V. All rights reserved.

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## 1. Introduction

Perfluoroalkanes are being used in a wide variety of areas such as surfactants in supercritical solvents, environmental probes, anticorrosive and antifriction components, as flame retardants, water repellents, or sliding agents, in paints, coatings, polymer technology, metal working and uranium recovery process. However, the most relevant applications are found in the biomedical field. The solubility of respiratory gases in perfluoroalkanes is the largest known for liquids being almost twice that of their hydrocarbon counterparts [1]. Part of the difference of solubilities can be explained by the interaction energies between the solute and the different solvents. However, factors related to the structure of the liquid solvents seem to play an important role. The increased rigidity of the perfluorocarbon when compared to the analogous hydrocarbon at the same temperature probably means that larger cavities (at the molecular scale) are spontaneously present in the liquid perfluorocarbon than in the hydrocarbon as reported previously by Dias et al. [1] and Gomes and Pádua [2] when comparing the atom–atom radial distribution functions of oxygen and carbon dioxide in different

fluorinated and non-fluorinated solvents. This certainly has a significant incidence on the solubility of small gaseous molecules.

This property associated with biochemical inertness, low surface tensions and high fluidities of these compounds make them attractive solvents to be used in vivo oxygen delivery. Nowadays they are finding applications as tissue oxygenation fluids, as blood substitutes, anti-tumoral agents, perfusates for isolated organs, gas-carriers in eye surgery, diagnostic imaging agents and drug delivery [3]. Perfluoroalkanes behave like typical non-associated, non-polar liquids, with solubility for gases depending essentially on the molecule's shape [4]. For similar molecular weight, the differences in O<sub>2</sub> solubility can reach 20–25% for different molecular structures. Linear perfluoroalkanes, including those that have a double bond, an oxygen atom, or a terminal bromine atom, present higher O<sub>2</sub> solubility when compared to cyclic and polycyclic perfluoroalkanes [5]. Terminal alkyl chain resulted in slightly reduced O<sub>2</sub> solubility [6]. Although several hundreds of fluorinated compounds have been screened over the past 20 years, very few were found to meet the appropriate physicochemical and biological criteria for in vivo oxygen delivery. This includes high purity, rapid excretion, aptitude to form stable emulsions, absence of clinically significant side-effect, and large-scale cost-effective industrial feasibility [7]. Among the different studied fluorinated compounds that accomplish these requirements is 1Br-perfluorooctylbromide, as

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one of the best candidates. At the moment it is being investigated in Phase II for treatment of acute respiratory failure by liquid ventilation and as a red cell substitute in the emulsified form under the name of Oxygent® [8].

Besides the direct practical application that solubility measurements of respiratory gases in these compounds have, they can also provide important information about the solvation process of the small gas molecules and about the structure of the solutions. A formal two-step dissolution process, consisting on opening a cavity in the solvent large enough to fit the gas molecule and then introducing the gas in this cavity, is often postulated for the purpose of discussing and predicting solubility data.

Until now, the solubility of oxygen in perfluoroalkanes have been studied and compared at one single temperature, usually 298.15 or 310.15 K. However, the temperature dependence of the solubility data gives important information about the interactions between the solute and the solvent in solution.

In this work, the solubility of oxygen was measured in different fluorinated compounds with an apparatus based on the saturation method [9] in the temperature range between 288 and 313 K and at pressures close to the atmospheric. The oxygen solubility in 1Br-perfluoro-*n*-octane, 1H-perfluoro-*n*-octane and 1H,8H-perfluoro-*n*-octane was measured and compared with its solubility in the completely fluorinated perfluoro-*n*-octane in order to study the influence of the terminal groups on the solubility of oxygen including its temperature dependence.

## 2. Experimental

The apparatus and procedure used for the solubility measurements were described in detail in a previous paper [10]. The apparatus is based on the saturation method proposed by Ben-Naim and Baer [9], where the solubility is determined by measuring the quantity of gas dissolved in an accurately known volume of solvent, at constant pressure and temperature. It consists mainly of a mercury manometer, with a mercury reservoir, a calibrated dissolution cell and a gas line with a pre-saturator, where the gas phase is pre-saturated with the solvent.

The equilibrium cell is based on the design of Carnicer et al. [11] with two capillaries that improves the contact between the solute and the solvent by the formation of a very thin film of the solvent during the dissolution process. The cell was calibrated with mercury, by measuring the mercury levels in the cell capillaries and the corresponding weight of mercury. A relation between mercury levels and the cell volume is obtained being the cell volume approximately 7 cm<sup>3</sup>.

The cell is filled with the degassed solvent and the gas is introduced to the system until a pressure close to the atmospheric is reached. As the gas dissolves, the system pressure is maintained at initial pressure by allowing the mercury from the reservoir to displace the gas in the system. The displacement of the mercury level is measured with a cathetometer with a precision of ±0.01 mm. Direct reading of the mercury levels of mercury and solution levels in the equilibrium cell after equilibrium is reached are the only measurements required to calculate the volume of gas dissolved in a given volume of solution.

The entire apparatus is immersed in an air bath, capable of maintaining the temperature to within 0.1 K. The accuracy of the experimental data measured was estimated to be ±1% when solubility data measured for the oxygen/*n*-heptane system were measured and compared with data reported by Hesse et al. [12] following the data reduction presented by the authors.

Chemicals used for the measurements were 1Br-perfluoro-*n*-octane from ABCR, 1H-perfluoro-*n*-octane from Interchim and 1H,8H-perfluoro-*n*-octane from Apollo Scientific with a minimum stated purity of 99.97, 97 and 99%, respectively. The oxygen used was from Air Liquide with 99.999% mol/mol minimum stated purity. The purities of the solvents were confirmed by gas chromatographic analyses giving purities of 99.9, 97.1 and 99.1%, respectively. Solvents and gas were used with no further purification.

## 3. Results and discussion

### 3.1. Data reduction

The Ostwald coefficient is a convenient and frequently used measure of the solubility of a gas in a liquid. It can be defined, through the experimentally accessible quantities, as

$$L_{2,1}(T, P) = \frac{C_2^L}{C_2^V} = \frac{V^V}{V^L} \quad (1)$$

where  $V^V$  is the volume of gas solubilized,  $V^L$ , the volume of liquid solution after equilibrium is reached. As indicated,  $L_{2,1}(T, P)$  depends on both temperature and total pressure. However, for conditions well below the critical point of the solvent, the pressure dependence is usually very small.

Solubility data is also usually presented in terms of the solute molar fraction. The molar fraction of component 2 (the gaseous solute) in the liquid solution can be directly related to the Ostwald coefficient by

$$x_2 = \left[ \frac{Z_{12}RT}{P_2 L_{2,1}(T, P) V^L(T, P)} + 1 \right]^{-1} \quad (2)$$

which for the accuracy of most of the experimental methods can be approximated to [12]:

$$x_2 = \frac{L_{2,1}(T, p) P_2 V^L(T, p)}{Z_{12}RT} \quad (3)$$

where  $P_2$  is the partial pressure of the solute,  $V^L(T, P)$ , the molar volume of the liquid solution and  $Z_{12}$  is the compressibility factor of the gaseous mixture. In this work, the virial equation of state is used to calculate  $Z_{12}$  as following:

$$Z_{12} = 1 + \frac{P}{RT} B \quad (4)$$

where  $B$  is the second virial coefficient for the solvent–solute mixture and is given by

$$B = y_1 B_{11} + y_2 B_{22} + y_1 y_2 \delta_{12} \quad (5)$$

where  $B_{11}$  and  $B_{22}$  are the second virial coefficients for the pure solvent and the pure solute, respectively, and  $\delta_{12} = 2B_{12}$

Table 1

Experimental data for the solubility of oxygen in the studied fluoroalkanes between 288 and 313 K expressed as Ostwald coefficients and mole fraction solubilities at a solute partial pressure of 101,325 Pa

| $T$ (K)                           | $P$ (bar) | $L_{2,1}(T, P)$ | $x_2 (\times 10^{-3})$ |
|-----------------------------------|-----------|-----------------|------------------------|
| 1Br-perfluoro- <i>n</i> -octane   |           |                 |                        |
| 289.58                            | 1.020     | 0.463           | 5.02                   |
| 292.71                            | 1.017     | 0.466           | 5.01                   |
| 297.37                            | 1.015     | 0.453           | 4.82                   |
| 302.63                            | 1.021     | 0.449           | 4.73                   |
| 304.80                            | 1.010     | 0.450           | 4.72                   |
| 308.09                            | 1.020     | 0.446           | 4.64                   |
| 312.57                            | 1.032     | 0.435           | 4.49                   |
| 1H-perfluoro- <i>n</i> -octane    |           |                 |                        |
| 289.15                            | 1.014     | 0.462           | 4.54                   |
| 294.50                            | 1.012     | 0.459           | 4.43                   |
| 299.17                            | 1.012     | 0.451           | 4.29                   |
| 304.47                            | 1.018     | 0.446           | 4.19                   |
| 308.55                            | 1.017     | 0.444           | 4.10                   |
| 312.48                            | 1.016     | 0.440           | 3.99                   |
| 1H,8H-perfluoro- <i>n</i> -octane |           |                 |                        |
| 290.68                            | 1.010     | 0.399           | 3.76                   |
| 290.82                            | 1.019     | 0.400           | 3.80                   |
| 297.97                            | 1.011     | 0.409           | 3.78                   |
| 307.99                            | 1.009     | 0.411           | 3.69                   |

–  $B_{11}$  –  $B_{22}$ , being  $B_{12}$  the solute–solvent cross second virial coefficient. The second virial coefficient for the solute was obtained from the compilation of Dymond and Smith [13] and both the second virial coefficient for the solvent and the cross virial coefficient were estimated using the correlation proposed by Tsonopoulos [14].

The mole fractions of the vapor phase in equilibrium with the liquid solution,  $y_i$ , are calculated by an iterative process using the vapor liquid equilibrium equation [15]:

$$y_1 = (1 - x_2) \left( \frac{P_1^{\text{sat}}}{P} \right) \left( \frac{\Phi_1^{\text{sat}}}{\Phi_1} \right) \exp \left[ \frac{V_1^0 (P - P_1^{\text{sat}})}{RT} \right] \quad (6)$$

where  $P_1^{\text{sat}}$  is the vapor pressure of the solvent,  $V_1^0$ , the molar liquid volume of the pure solvent and  $\phi_1$  and  $\phi_1^{\text{sat}}$  are the fugacity coefficient and the standard state fugacity of the solvent, respectively. Table 1 presents experimental data for the solubility of oxygen in the studied perfluoroalkanes between 288 and 313 K expressed as Ostwald's coefficients and solute's mole fraction corrected to a partial pressure of the gas of 101,325 Pa.

Liquid densities were measured in our laboratory with a vibrating tube Antón Paar DSA-48 densimeter between 288.15 and 313.15 K at atmospheric pressure. The measuring principle is based on the calculation of the frequency of resonance of a mechanic oscillator with a given mass and volume, which is excited to be in resonance. The precision of the measurements is  $\pm 5 \times 10^{-5} \text{ g cm}^{-3}$ . The experimental data measured were correlated with an equation of the type:

$$\rho_{\text{calc}} = A - BT \quad (7)$$

where  $\rho_{\text{calc}}$  is the calculated density in  $\text{g cm}^{-3}$  and  $T$  is the temperature in K.

Table 2

Experimental and calculated liquid densities of 1H,8H-perfluoro-*n*-octane

| $T$ (K) | $\rho_{\text{exp}} (\text{g cm}^{-3})$ | $\rho_{\text{calc}} (\text{g cm}^{-3})$ | $\Delta\rho^a (\text{g cm}^{-3})$ |
|---------|--|---|-----------------------------------|
| 288.15  | 1.7753                                 | 1.7754                                  | –0.00009                          |
| 293.15  | 1.7644                                 | 1.7644                                  | 0.00004                           |
| 298.15  | 1.7534                                 | 1.7533                                  | 0.00010                           |
| 303.15  | 1.7424                                 | 1.7423                                  | 0.00010                           |
| 308.15  | 1.7313                                 | 1.7313                                  | 0.00004                           |
| 313.15  | 1.7202                                 | 1.7203                                  | –0.00009                          |

$$^a \Delta\rho = \rho_{\text{exp}} - \rho_{\text{calc}}$$

Vapor pressures were also measured in our laboratory using an apparatus based on the static method. This method consists mainly of a glass sample cell, a thermostatic water bath and a temperature and pressure measurement systems. The apparatus and the experimental method are described in more detail elsewhere. The accuracy of the apparatus was determined to be better than 0.1 kPa [16]. Experimental vapor pressure data measured were correlated with the Antoine equation:

$$\ln \left( \frac{P_1^{\text{sat}}}{\text{kPa}} \right) = A - \frac{B}{(T/\text{K}) + C} \quad (8)$$

Experimental density and vapor pressure data for 1Br-perfluoro-*n*-octane and 1H-perfluoro-*n*-octane were presented elsewhere [16]. In this work, the same procedure was used to measure liquid densities and vapor pressures for 1H,8H-perfluoro-*n*-octane and the experimental data are reported in Tables 2 and 3.

The coefficients  $A$  and  $B$  in the density Eq. (6) for 1H,8H-perfluoro-*n*-octane are 2.4106 and 2.2045E-03, respectively. The Antoine's coefficients adjusted for 1H,8H-perfluoro-*n*-octane are 14.686, 3500.361 and –59.499, respectively.

Solubilities of oxygen in the different studied solvents are presented in Fig. 1. Data for perfluoro-*n*-octane previously presented [10] and for *n*-octane [17] are also shown for comparison. It can be observed that the solubility decreases from the perfluoro-*n*-octane, with two completely fluorinated terminal  $\text{CF}_3$  groups, to 1H,8H-perfluoro-*n*-octane, where both extremities are substituted. The temperature dependence of the oxygen solubility also shows the same trend, meaning that it decreases from perfluoro-*n*-octane to 1H-perfluoro-*n*-octane and no dependence was found for 1H,8H-perfluoro-*n*-octane. In the case

Table 3

Experimental and calculated vapor pressures of 1H,8H-perfluoro-*n*-octane

| $T$ (K) | $P_{\text{exp}} (\text{kPa})$ | $P_{\text{calc}} (\text{kPa})$ | $\Delta P^a (\text{kPa})$ |
|---------|-------------------------------|--------------------------------|---------------------------|
| 289.31  | 0.55                          | 0.58                           | –0.03                     |
| 293.26  | 0.75                          | 0.75                           | 0.00                      |
| 298.2   | 0.99                          | 1.02                           | –0.03                     |
| 303.18  | 1.43                          | 1.38                           | 0.05                      |
| 308.17  | 1.92                          | 1.84                           | 0.08                      |
| 313.18  | 2.49                          | 2.43                           | 0.06                      |
| 318.14  | 3.12                          | 3.17                           | –0.05                     |
| 323.15  | 4.07                          | 4.10                           | –0.03                     |
| 328.15  | 5.26                          | 5.24                           | 0.02                      |
| 333.14  | 6.64                          | 6.65                           | –0.01                     |

$$^a \Delta P = P_{\text{exp}} - P_{\text{calc}}$$

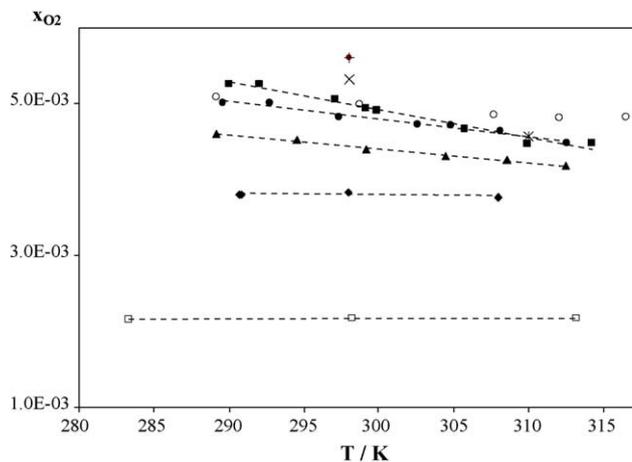


Fig. 1. Oxygen mole fraction solubility data for the studied systems at temperatures between 283 and 313 K and at partial pressure of the gas of 101325 Pa for (●) 1Br-perfluoro-*n*-octane, (▲) 1H-perfluoro-*n*-octane and (◆) 1H,8H-perfluoro-*n*-octane. Data for perfluoro-*n*-octane [10] (■) and for *n*-octane [17] (□) are also presented for comparison as well as literature data for 1Br-perfluoro-*n*-octane reported by (○) Gomes et al. [18], (×) Riess [7], (+) Wesseler et al. [20] and (\*) Skarts and Reese [19].

of the alkane, the solubility is approximately half that of the corresponding perfluoro-*n*-octane and also no noticeable temperature dependence is observed. Literature data concerning oxygen solubility as a function of temperature is scarce. No data was found for the solubility of oxygen in 1H-perfluoro-*n*-octane and 1H,8H-perfluoro-*n*-octane. For 1Br-perfluoro-*n*-octane, data measured in this work show more pronounced temperature dependence than data measured by Gomes et al. [18], which is almost temperature independent. Experimental values at the lowest temperature agree well with the ones measured in this work but, at higher temperatures, deviations are about 7%. However, the value reported by Skarts and Reese [19] at 310.15 K agrees with this work. The values reported by Wesseler et al. [20] and Riess [7] at 298.15 K are 14 and 9%, respectively, higher than the values measured in this work at the same temperature. The scatter of oxygen solubility data can be attributed both to the poor characterization of the samples used, since some authors do not state the purities of the samples used, and to the different techniques used to perform the measurements.

### 3.2. Thermodynamic functions

The dissolution of a gas into a liquid is associated with changes in thermodynamic functions namely standard Gibbs energy ( $\Delta G_2^*$ ), standard enthalpy ( $\Delta H_2^*$ ) and standard entropy ( $\Delta S_2^*$ ) of solution that can be calculated from experimental solubility results. These functions represent the changes that occur in the solute neighborhood during dissolution process due to the transference of one solute molecule from the pure perfect gas state to an infinitely dilute state in the solvent, at a given temperature  $T$  [21–23]. The thermodynamic functions were calculated from the temperature dependence of the molar fraction

according to the following equations:

$$\Delta G_2^* = \Delta G^0 - RT \ln \left( \frac{RT}{V_1^0} \right) \quad (9)$$

$$\Delta H_2^* = \Delta H^0 - RT(T\alpha_1 - 1) \quad (10)$$

$$\Delta S_2^* = \Delta S^0 + R \ln \left( \frac{RT}{V_1^0} \right) - R(T\alpha_1 - 1) \quad (11)$$

where  $R$  is the gas constant,  $\alpha_1$ , the isobaric thermal expansibility of the solvent, calculated from density data, and  $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$  are the thermodynamic functions associated with the hypothetical changes that happen in the solute neighborhood when the molecules are transferred from the gas phase to a hypothetical solution where the mole fraction of solute is equal to one [21,22], which are calculated from the temperature dependence of the experimental solubility data measured according to the following equations [21]:

$$\Delta G_2^0 = -RT(\ln x_2)_p \quad (12)$$

$$\Delta H_2^0 = -T^2 \left( \frac{\partial(\Delta G^0/T)}{\partial T} \right)_p \quad (13)$$

$$\Delta S_2^0 = - \left( \frac{\partial \Delta G^0}{\partial T} \right)_p \quad (14)$$

The values for the thermodynamic functions of dissolution of oxygen in the different compounds at 298.15 K are listed in Table 4. Data for perfluoro-*n*-octane and *n*-octane are also showed here for comparison.

The reported values for enthalpies of solvation show that they decrease from perfluoro-*n*-octane, with two completely fluorinated terminal  $\text{CF}_3$  groups, to 1H,8H-perfluoro-*n*-octane without any  $\text{CF}_3$  group for which solubility does not present any temperature dependence. It is interesting to notice that the enthalpies of solution for oxygen in 1H,8H-perfluoro-*n*-octane are similar to those obtained for *n*-octane, indicating that the solvation of oxygen is performed by the end groups. Note also that the presence of  $\text{CF}_3$  end groups enhances the solubility of oxygen in the perfluorocompound. The significant variation of the enthalpies of solution with the substitution of the  $\text{CF}_3$  end group shows that the interaction between oxygen and the  $\text{CF}_3$  group is stronger than between oxygen and other end groups.

To assess the validity of any assumption about special solute–solvent interactions, it is necessary to analyse the

Table 4  
Gibbs energy ( $\Delta G^*$ ), enthalpy ( $\Delta H^*$ ) and entropy ( $\Delta S^*$ ) of dissolution at 298.15 K calculated from experimental solubility data

| Compound   | $\Delta G^*$ (kJ mol <sup>-1</sup> ) | $\Delta H^*$ (kJ mol <sup>-1</sup> ) | $\Delta S^*$ (J mol <sup>-1</sup> K <sup>-1</sup> ) |
|--|--------------------------------------|--------------------------------------|---|
| C <sub>8</sub> F <sub>18</sub>                                     | 1.74                                 | -4.36                                | -20.44  |
| C <sub>8</sub> H <sub>18</sub>                                     | 2.76                                 | 1.73                                 | -3.46   |
| CF <sub>3</sub> (CF <sub>2</sub> ) <sub>6</sub> CF <sub>2</sub> Br | 1.92                                 | -2.06                                | -13.36  |
| CF <sub>3</sub> (CF <sub>2</sub> ) <sub>6</sub> CF <sub>2</sub> H  | 1.94                                 | -1.64                                | -12.00  |
| CF <sub>2</sub> H(CF <sub>2</sub> ) <sub>6</sub> CF <sub>2</sub> H | 2.21                                 | 1.22                                 | -3.31   |

Table 5

Enthalpies of cavity formation,  $H^{\text{cav}}$ , and solute–solvent interaction,  $H^{\text{int}}$  for oxygen in different fluorinated compounds at 298 K

| Compound   | $\sigma$ (Å) | $V_1^0$ (cm <sup>3</sup> mol <sup>-1</sup> ) | $H^{\text{cav}}$ (kJ mol <sup>-1</sup> ) | $H^{\text{int}}$ (kJ mol <sup>-1</sup> ) |
|--|--------------|--|--|--|
| C <sub>8</sub> F <sub>18</sub>                                     | 7.38         | 248.24                                       | 10.64 ± 0.04                             | -14.99 ± 0.39                            |
| C <sub>8</sub> H <sub>18</sub>                                     | 6.54         | 163.48                                       | 12.94 ± 0.04                             | -11.22 ± 0.38                            |
| CF <sub>3</sub> (CF <sub>2</sub> ) <sub>6</sub> CF <sub>2</sub> Br | 7.67         | 260.58                                       | 11.12 ± 0.03                             | -13.37 ± 0.30                            |
| CF <sub>3</sub> (CF <sub>2</sub> ) <sub>6</sub> CF <sub>2</sub> H  | 7.38         | 240.06                                       | 11.43 ± 0.05                             | -13.07 ± 0.12                            |
| CF <sub>2</sub> H(CF <sub>2</sub> ) <sub>6</sub> CF <sub>2</sub> H | 7.34         | 229.31                                       | 11.93 ± 0.05                             | -10.71 ± 0.40                            |

Also reported are the solvent's hard sphere diameter,  $\sigma$  and molar volume,  $V_1^0$ .

different contributions to the overall solubility process namely cavity formation, mixing and interaction. This can be done by using the appropriate expressions from the scaled particle theory applied to solutions of gases in liquids considering a two-step mechanism of the solution process [24]:

$$\Delta G_2^* = G^{\text{cav}} + G^{\text{int}} \quad (15)$$

where  $G^{\text{cav}}$  and  $G^{\text{int}}$  are the partial molar Gibbs energy of cavity formation and interaction, respectively. In this work,  $G^{\text{cav}}$  was calculated as suggested by Reiss et al. [25] as a function of parameters of the solute and the solvent, namely the hard sphere diameter (HSD) and the density of the solvent. The HSD for oxygen was taken from the work of Wilhelm and Battino [26] and is equal to 3.46 Å. For the solvents, the HSDs were calculated from enthalpy of vaporization and thermal expansivity data of the solvents, as suggested by Wilhelm and Battino [27], using the vapor pressure and density measured. Table 5 resumes the parameters for the different solvents studied along with the different enthalpic contributions.

The calculated enthalpies of cavity formation,  $G^{\text{cav}}$  are very similar for the different solvents within the uncertainty of the calculation. The enthalpies of cavity formation are also in agreement with the surface tensions measured for these compounds [28]. The results presented in Table 5 indicate that the differences observed in the enthalpies of dissolution reported in Table 4 are mainly caused by differences in the enthalpies of interaction. The interaction energy between oxygen and perfluoro-*n*-octane is significantly higher than the interaction energy between oxygen and substituted perfluoroalkanes. Worthwhile mentioning that the enthalpy of interaction for 1H,8H-perfluoro-*n*-octane at 298.15 K is similar to the one observed for *n*-octane. The results in Table 5 indicate that the interaction between O<sub>2</sub> and the CF<sub>3</sub> end groups is circa 2.1 kJ/mol higher than with the other end groups.

These results are supported by data previously presented by ourselves and others [18,29]. Values for the enthalpies of solution of oxygen in other linear perfluoroalkanes, namely perfluoro-*n*-hexane, perfluoro-*n*-heptane, perfluoro-*n*-nonane, are in same order of magnitude of perfluoro-*n*-octane while for perfluorodecalin [29] and perfluorocyclohexane [18] they are virtually zero. According to Mack and Oberhammer [30], ab initio calculations of the interaction potentials for the complex CF<sub>4</sub>–O<sub>2</sub> provide evidence that an interaction between the oxygen and the positive carbon nucleus in CF<sub>4</sub> occurs, forming a very strong complex. Unfortunately, no further work was done for higher fluorinated molecules to conclude if this favourable

interaction could also exist between the oxygen molecule and the terminals CF<sub>3</sub> groups. Using <sup>19</sup>F NMR, Shukla et al. [31] also showed that the terminal trifluoromethyl groups have the greatest sensitivity to oxygen when compared with the CF<sub>2</sub> groups in molecules as 1Br-perfluoro-*n*-octane, perfluorotripropylamine and perfluorotributylamine.

#### 4. Conclusions

The study of the solubility of oxygen in linear-fluorinated molecules presenting different degrees of substitution on the terminal CF<sub>3</sub> groups seems to indicate that the solvation of oxygen is carried by the end groups of the perfluorocarbons and the existence of interactions between the oxygen and the CF<sub>3</sub> group on the fluorinated molecules that is more than 2 kJ/mol higher than with other end groups.

#### List of symbols

|                                      |  |
|--------------------------------------|--|
| $B$                                  | second virial coefficient  |
| $C_2^{\text{L}}$                     | concentration of the solute in the liquid phase solution   |
| $C_2^{\text{V}}$                     | concentration of the solute in the coexisting vapor phase solution   |
| $\Delta G^0, \Delta H^0, \Delta S^0$ | standard Gibbs energy, enthalpy and entropy associated with the hypothetical changes that happen in the solute neighborhood when the molecules are transferred from the gas phase to a hypothetical solution where the mole fraction of solute is equal to one                                   |
| $\Delta G^*, \Delta H^*, \Delta S^*$ | standard Gibbs energy, enthalpy and entropy associated with the changes that occur in the solute neighborhood during dissolution process due to the transference of one solute molecule from the pure perfect gas state to an infinitely dilute state in the solvent, at a given temperature $T$ |
| $G^{\text{cav}}$                     | partial molar Gibbs energy of cavity formation   |
| $G^{\text{int}}$                     | partial molar Gibbs energy of interaction  |
| $L_{2,1}(T, P)$                      | Ostwald coefficient at temperature and total pressure of the system  |
| $P$                                  | total pressure of the system   |
| $P_1^{\text{sat}}$                   | vapor pressure of the solvent  |
| $P_2$                                | partial pressure of the solute   |
| $R$                                  | gas constant   |
| $T$                                  | temperature of the system  |
| $V^{\text{L}}$                       | volume of liquid solution after equilibrium is reached   |
| $V^{\text{V}}$                       | volume of gas solubilized in the liquid solution   |
| $V_1^0$                              | molar volume of the pure solvent   |
| $x_2$                                | solute molar fraction in the liquid phase  |

$y_2$  solute molar fraction in the vapor phase  
 $Z$  compressibility factor

#### Greek letters

$\alpha$  isobaric thermal expansibility of the solvent  
 $\rho$  liquid density

#### Subscripts

1, 2 solvent, solute

#### Superscripts

calc calculated  
 cav cavity  
 exp experimental  
 int interaction  
 L liquid phase  
 sat saturated  
 V vapor phase

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