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Ana M. Mainar, José F. Martínez-López, José S. Urieta, Juan I. Pardo

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Solubility of gases in fluoroorganic alcohols. Part III. Solubilities of several non-polar gases in water + 1,1,1,3,3,3-hexafluoropropan-2-ol at 298.15 K and 101.33 kPa

Ana M. Mainar[a,], José F. Martínez-López[b], José S. Urieta[a], and Juan I. Pardo[a]*

[a]Group of Applied Thermodynamics and Surfaces (GATHERS), Aragón Institute for Engineering Research (I3A), Universidad de Zaragoza, c/ Mariano Esquillor s/n, 50018 Zaragoza, Spain.

[b]Group of Applied Thermodynamics and Surfaces (GATHERS), AgriFood Institute of Aragon (IA2), Universidad de Zaragoza, Facultad de Ciencias, 50009 Zaragoza, Spain.

Email: ammainar@unizar.es. Fax: +34 976 761 202. Phone +34 976 761 195

ABSTRACT Solubilities of the non-polar gases H_2, N_2, O_2, CH_4, C_2H_6, C_2H_4, CF_4, SF_6, and CO_2 in the mixture (water + 1,1,1,3,3,3-hexafluoropropan-2-ol) at the temperature of 298.15 K and 101.33 kPa partial pressure of gas are reported. A polynomial dependence of the solubilities on the molar fraction of the binary liquid mixture is found. The Henry's constants at the vapor pressure of water, the standard changes in the Gibbs energy for the solution process and for the solvation process, and the so-called excess Henry's constant are calculated. The results have been compared with those obtained by scaled particle theory (SPT). A method to compare the solubility of a gas in different liquids is proposed and applied to 2,2,2-trifluoroethanol and 1,1,1,3,3,3-hexafluoropropan-2-ol.

Keywords: Gas solubility, Non-polar gases, 1,1,1,3,3,3-Hexafluoropropan-2-ol, Water, Scaled Particle Theory

1. Introduction

As gases can act as probes for certain features of the solvent into which they dissolve, the solubility of gases in liquids is worth to be determined. For example, solubilities provide information about the solvophobicity of the liquid solvent [1] and also allow an estimation of certain molecular parameters of the solvent, such as those of the Lennard-Jones potential [2]. For this reason, our research group has focused on measuring the solubility of a wide set of nonpolar gases (He, Ne, Ar, Kr, Xe, H_2, N_2, O_2, CH_4, C_2H_6, C_2H_4, CF_4, SF_6, and CO_2) in two fluoroorganic alcohols, namely, 2,2,2-trifluorethanol (TFE) and 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) [3-5] as well as in mixtures of water and TFE [6,7] and has also reported the solubility of noble gases in mixtures of water and HFIP [8].

The liquid mixtures are very interesting because they both have been used to modulate some of the properties having an influence on the kinetics of Diels-Alder reactions [9]. Besides, TFE and HFIP are very effective in stabilizing the α-helical structure of peptides and proteins in aqueous solutions [10,11] which is important for the study of these biological compounds. Actually, the relevance of mixtures (water + HFIP) has brought about structural studies [12-15] as well as molecular simulations [16-18]. But the importance of HFIP seems not only to remain unaffected but to grow in such a way that Colomer *et al*. [19] in a recent review about HFIP state that “1,1,1,3,3,3-Hexafluoroisopropanol (HFIP) has recently become a very popular solvent or additive with applications across the spectrum of chemistry” as is shown by its extensive role in synthesis reactions [19] or in solvolytic studies [20].

Then, this paper is aimed to complete the previous studies of solubilities of gases in mixtures of water and fluoroalcohol. Here we report the solubilities, expressed as mole fraction of gas dissolved and also as Henry’s constant, of the non-polar gases H_2, N_2, O_2, CH_4, C_2H_6, C_2H_4, CF_4, SF_6, and CO_2 in the mixture (water + HFIP) at a temperature of 298.15 K and 101.33 kPa partial pressure of gas. The ratio of fluoroorganic alcohol in the mixtures covers a range between 10 and 90 per cent in volume.

From the solubility data, the change in the standard Gibbs energy for both solution and solvation processes and the so-called excess Henry’s constant have been calculated and discussed. A method is proposed to compare solubilities of a given gas in different liquids and it is applied to elucidate if the solubility of several gases increases or decreases in TFE and HFIP with respect to other liquid solvents. In addition, the Scaled Particle Theory (SPT) [2,21-24] has been used to predict the solubilities with the aim of verifying the validity of the model in these ternary solutions. The results obtained for the mixture (water + HFIP) are compared with those of the mixture (water + TFE).

2. Experimental

2.1. Materials

The gases used were H_2, N_2, O_2, CH_4, C_2H_6, C_2H_4, SF_6, and CO_2 all supplied by Air Liquide España, along with CF_4 supplied by J.T. Baker. The liquids were 1,1,1,3,3,3-hexafluoropropan-2-ol provided by Fluorchem Ltd., and ultrapure water produced in our institution facilities using a Millipore device. All the chemicals were used without further purification and their descriptions appears in table 1.

2.2. Apparatus and procedure

The solubilities of gases in the liquids have been measured employing an equipment and procedure which have been described in detail elsewhere [25]. The equipment is an all-glass setup similar to that used by Ben-Naim and Baer [26] and is designed to perform a saturation method. A system of burettes allows the determination of the volume of wet gas (a mixture of the gas and the solvent vapor) dissolved in a known quantity of liquid solvent.

This solvent fills a vessel that is immersed in a thermostated water bath whose temperature is controlled within ±0.05 K. In turn, the whole apparatus is placed in an air bath whose temperature, greater than that of the water to prevent condensation of the solvent from the solution vessel, is also maintained constant to within ±0.2 K. The difference between the temperatures in the water bath and air bath is the main characteristic that distinguishes our apparatus from that of Ben-Naim and Baer. This particularity has the advantage of simplifying the handling but it must be taken into account in the treatment of the experimental data.

To verify the accuracy of the apparatus, the solubilities of argon in water were determined at temperatures near 298.15 K and then compared with the most reliable values in the literature [27]. The deviations of our values [6] from the bibliographic ones are below the mean values estimated for the relative expanded uncertainties in the solubility measurements, expressed as mole fractions, that were in all cases 0.01 (coverage factor $k = 2$).

The density of each mixture was obtained once the measurements had been completed. The densities were determined with an Anton Paar DMA-58 vibrating tube density meter with a repeatability of ±10^{-2} kg·m^{-3} whereas the relative standard uncertainty, taking into account the purity of HFIP, has been estimated to be ±0.6%. They can be found in table S.1 in the Supporting information.

2.3. Solubility Calculations

The solubility values, expressed as mole fraction of gas dissolved in a liquid binary mixture, were calculated using a reduction method described in detail elsewhere [6]. The method, which takes into account the specific features of our device mentioned above, is an extension of a trial-and-error approach to determine the solubility of a gas in a pure liquid [28].

To summarize, the calculation procedure involves two intertwined parts. The first focuses on the calculation of the phase equilibrium composition considering that the gas phase is a wet gas; consequently, the number of moles of component 3 (gas) dissolved is given by

$$n_3 = n_\mathrm{T} - n_1^\mathrm{V} - n_2^\mathrm{V}, \tag{1}$$

where n_3 is the effective mole number of pure gas dissolved, n_T is the total mole number of wet gas dissolved, and n_1^V and n_2^V are the mole numbers of the components of the liquid mixture in the gas phase. These mole numbers are calculated through a virial equation truncated after the second term at the temperature of the air bath. The initial values for the process are obtained from an arbitrary value of density near that of the final liquid mixture.

The second part of the reduction method is introduced to ensure the thermodynamic consistency of the gas-liquid equilibrium, expressed by the following equations

$$y_\mathrm{i} \cdot \phi_\mathrm{i}^\mathrm{V}(T,P,\{y\}) \cdot P = x_\mathrm{i} \cdot \gamma_\mathrm{i}(T,P,\{x\}) \cdot P_\mathrm{s,i} \cdot \phi_\mathrm{s,i}^{*\mathrm{V}} \cdot \wp(T,P) \quad \mathrm{i} = 1, 2, \tag{2}$$

$$y_3 \cdot \phi_3^\mathrm{V}(T,P,\{y\}) \cdot P = x_3 \cdot \gamma_3'(T,P,\{x\}) \cdot K_\mathrm{H3,12}(T,P), \tag{3}$$

where $\phi_\mathrm{i}^\mathrm{V}$ stands for the fugacity coefficient of solvent i, $\phi_\mathrm{s,i}^{*\mathrm{V}}$ for the fugacity coefficient of saturated pure component i, $P_\mathrm{s,i}$ for the vapor pressure of component i, $\wp$ for the Poynting correction, γ_i for the activity coefficient of liquid component i according to the Lewis-Randall rule, γ_3' for the activity coefficient of the gas according to Henry's law, and $K_\mathrm{H3,12}$ for the Henry's law constant for the gaseous component in the liquid mixture of 1 and 2.

To simplify equations (2) and (3), two assumptions are made:

a) We consider that the fugacity coefficients at the low pressures used in this work can be obtained from a virial equation truncated after the second term

$$\phi_\mathrm{i}^\mathrm{V} = \exp\left[\left(2\sum_{j=1}^{n} y_\mathrm{j} B_\mathrm{ij} - B_\mathrm{m(ter)}\right)\frac{P}{\mathrm{R}T}\right], \tag{4}$$

where B_ij and $B_\mathrm{m(ter)}$ are the cross second virial coefficient for a binary ij-mixture and the second virial coefficient (SCV) for the ternary mixture, respectively.

b) The activity coefficients for liquid components 1 and 2 were estimated from the excess Gibbs energies corresponding to their mixture. Given the small solubilities of the gases, the influence of component 3 on the activity coefficients of the liquids, γ_i, is considered negligible.

The whole procedure finishes when the density value of the final mixture provided by it coincides with the experimental one within the experimental error.

To implement the calculation method, values of molar volumes and vapour pressures are needed for water, HFIP as well as for their mixtures. Densities of pure solvents [4,6] and those of their mixtures [8] at 298.15 K and 101.33 kPa were previously reported. From these data the volumetric properties are derived straightforward. On his side, vapor pressures of pure water and HFIP at 298.15 K were taken from the literature [29,30]. The vapor pressure for liquid mixtures (water + HFIP) and the corresponding vapor composition, y_i, at 298.15 K were obtained from the work of Blandamer *et al.* [31]. Values of second virial coefficients are also necessary for the calculation. Then, second virial coefficients for pure components [4,32] and cross SVC for the binary mixtures (HFIP + gas) [4] and (water + gas) [6] were obtained from the literature. The cross SVC for the mixtures (HFIP + water) at several temperatures within the interval (268.15-308.15) K were calculated by the method proposed by Maris and Stiel [33] and fitted to the temperature by means of the equation

$$B_{12}\ (\mathrm{m^3 \cdot mol^{-1}}) = \mathrm{a}_0 + \mathrm{a}_1\, T + \mathrm{a}_2\, T^2 + \mathrm{a}_3\, T^3, \tag{5}$$

The coefficients a_i obtained in the fitting process were: $\mathrm{a}_0 = -0.17767\ \mathrm{m^3 \cdot mol^{-1}}$; $\mathrm{a}_1 = 1.7776 \cdot 10^{-3}\ \mathrm{m^3 \cdot mol^{-1} \cdot K^{-1}}$; $\mathrm{a}_2 = -6.014 \cdot 10^{-6}\ \mathrm{m^3 \cdot mol^{-1} \cdot K^{-2}}$; $\mathrm{a}_3 = 6.84 \cdot 10^{-9}\ \mathrm{m^3 \cdot mol^{-1} \cdot K^{-3}}$ and the squared regression coefficient $R^2 = 0.9977$.

The relative combined expanded uncertainties (coverage factor $k \approx 2$) in the mole fraction of gas dissolved have been estimated to be ±2% for the lower solubilities ($x_3 < 10^{-4}$) and to ±1% (or lower) for the remaining solubilities.

3. Results and Discussion

3.1. Solubility and Gibbs energies for the Solution and Solvation Processes

The solubilities of the nonpolar gases H_2, N_2, O_2, CH_4, C_2H_6, C_2H_4, CF_4, SF_6, and CO_2 in mixtures (water + HFIP), x_3, at 298.15 K and 101.33 kPa partial pressure of gas, expressed as mole fraction of gas dissolved, x_3, are reported in table 2 for different mole fractions of HFIP, x_2, in the binary solvent mixture. The solubilities expressed as the logarithm of the Henry's law constant, $\ln K_{\mathrm{H}3,12}$ (Pa), at the vapour pressure of water are also listed in table 2. These solubilities at 101.33 kPa partial pressure of gas were calculated from the solubilities obtained at the actual working pressures [6]. The actual total pressures along with the corresponding solubilities can be found in table S.1 in the Supporting information.

The mole fractions of gas dissolved, x_3, were fitted using the least-squares method to a polynomial of the type

$$x_3 \cdot 10^4 = A_0 + A_1 x_2 + A_2 x_2^2 + A_3 x_2^3, \tag{6}$$

The coefficients A_i are given in table 3 along with the corresponding standard deviations, σ. The solubilities and their corresponding fitting curves are shown in figure 1 along with detailed graphics for the zone rich in water. Solubilities of gases were taken from the literature for pure water [34] and pure pure HFIP [4].

From the solubility, the change in the Gibbs energy accompanying the hypothetical solution process

M (gas, T, 101.33 kPa) $\rightarrow$ M (T, P, hyp. solution, x_3= 1),

which is equal to the variation in the partial molar Gibbs energy for the solute, can be calculated through the equation

$$\Delta \overline{G}^{0}_{3,\mathrm{sol}} = \mathrm{R}T \ln K_{\mathrm{H}\,3,12}\,. \tag{7}$$

The values for this property have been included in table 2.

Closely related with the Gibbs energy for the solution process is the change in the Gibbs energy for the solvation process, $\Delta \overline{G}_{\mathrm{solv}}$, being the relationship between these two properties the one given by the following expression

$$\Delta \overline{G}_{\mathrm{solv}} = \Delta \overline{G}^{0}_{3,\mathrm{sol}} - \mathrm{R}T \ln\left(\frac{\mathrm{R}T}{V_{12}}\right), \tag{8}$$

where V_{12} is the molar volume of the liquid mixture of 1 and 2 (note that RT/V_{12} must be expressed in atm). Solvation is defined [35] as the process of transferring a molecule of solute from a fixed position in the gas phase into a fixed position in the liquid phase at a given pressure and temperature. $\Delta \overline{G}_{\mathrm{solv}}$ is a relevant quantity because it is related with the changes that occur when a molecule of solute is considered in the frame of its entire surroundings whereas those changes are not, in general, suitably described by $\Delta\overline{G}^{0}_{3,\mathrm{sol}}$. The values of the Gibbs energy for the solvation process can be found in figure 2 for the eight nonpolar gases.

The solubilities of the gases increase as the mole fraction of fluoroalcohol in the liquid solvent mixture increases although, as occurred with the noble gases [8], it can be seen that near pure water, the solubility scarcely increases until $x_2 \approx 0.07$ is reached, being the solubility at $x_2 \approx 0.02$ very similar to that of pure water. But no minimum in the solubility is observed as was the case with He and Ne. It is noticeable that the solubility curves of CF_4 and SF_6 cut those of other gases (included the noble ones). This is due to the fact that the fluorinated gases are the least soluble ones in water whereas they are quite soluble in HFIP. When considering the sequence of gases according to their solubility in pure HFIP, CF_4 reaches the same place in the mixture (water + HFIP) when $x_2 \approx 0.6$ and SF_6 when $x_2 \approx 0.3$. Referring to $\Delta\overline{G}^{0}_{3,\mathrm{sol}}$, its behavior with respect to the mole fraction of HFIP in the solvent mixture, as can be expected from its definition (Eq. 7), is very similar to that of the solubilities (x_3) but now the values are positive.

Finally, the general shape of the curves of $\Delta\overline{G}_{\mathrm{solv}}$ follows that of the corresponding $\Delta\overline{G}^{0}_{3,\mathrm{sol}}$. In agreement with the solubility values the curves of $\Delta\overline{G}_{\mathrm{solv}}$ for CF_4 and SF_6 cut those of other gases. As occurred with He, Ne and Xe, slight maxima in $\Delta\overline{G}_{\mathrm{solv}}$ are observed for the gases H_2, O_2 and CO_2 in the zone near pure water. From the values of $\Delta\overline{G}_{\mathrm{solv}}$ it can be concluded that the solvation of these gases is not favored (positive values over the whole composition range) except for C_2H_6 when $x_2 > 0.5$, C_2H_4 and SF_6 when $x_2 > 0.3$, and CO_2 when $x_2 > 0.05$. This is consistent with the higher solubility of these gases as was already stated for Xe [8] which has high solubility in the mixtures (water + HFIP) and also shows negative values of $\Delta\overline{G}_{\mathrm{solv}}$ in part of the composition range.

It must be said that there is a clear similarity between the solubilities and related properties of non-polar gases (noble gases included) in the mixtures (HFIP + water) and those determined in the mixtures (water + TFE). The solubilities are lower for the mixtures with TFE but in both cases there is not a noticeable increase in the solubility in the zone very rich in water. In fact, minimum values for the solubility are observed in this zone for Ne, Xe, H_2, N_2 and CF_4 when the fluoroalcohol is TFE and for He and Ne when it is HFIP.

The solubility curves of CF_4 and SF_6 in the mixtures (water + TFE) also cut those of the other gases and also for the same reason than in the mixtures (water + HFIP), although the effect was less pronounced, as CF_4 reached the same place in the sequence of gases according to their solubility in pure TFE when $x_2 \approx 0.7$ while SF_6 did it when $x_2 \approx 0.9$. It is clear that the chemical similarity enhances the solubility of these fluorinated gases in fluoroalcohols to the point that, for example, SF_6 is the most soluble gas, excepting CO_2, in both TFE and HFIP. Actually, CO_2 is the most soluble gas for both mixtures (fluoroalcohol + water) in the entire composition range. The high solubility of CO_2 in water is well known whereas its high solubility in the fluoroalcohols can be due, as was advanced in a previous paper [8], to the presence of the fluorine atoms. The high miscibility and solubitlity of fluorocarbons in supercritical CO_2 is a well established phenomenon [36] and the presumable affinity between CO_2 and fluorine atoms could act also at lower pressures. On the other hand, it is also possible that a hindered solubility of C_2H_4 and C_2H_6, which are usually the more soluble gases, would explain the highest solubility of CO_2.

In relation to $\Delta\overline{G}_{\mathrm{solv}}$, the solvation is lower, then more favored, in the mixtures (water + HFIP) than in the mixtures (water + TFE) as was to be expected from the higher solubility of gases in the former system. Nevertheless, negative values of $\Delta\overline{G}_{\mathrm{solv}}$ (solvation favored) are only reached for Xe, C_2H_4, C_2H_6, SF_6 and CO_2, that is, for the more soluble gases, in both mixtures (water + fluoroalcohol). Maximum values in $\Delta\overline{G}_{\mathrm{solv}}$ in the zone very rich in water can be observed for all of the gases, excepting C_2H_4 and SF_6 when solved in (water + TFE) [6] and for He, Ne, Xe, H_2, O_2 and CO_2, as stated above, when solved in (water + HFIP). Even when no maxima are observed, $\Delta\overline{G}_{\mathrm{solv}}$ decreases very slightly in that zone. This would indicate that the fluoroalcohols do not promote the structure of water when the mole fraction of fluoroalcohol is very low, at least at 298.15 K, although a promotion of the structure of water has been observed at the temperature of 283.15 K for the mixture (water + TFE) in that composition range [37] and the same could be expected to occur for the mixture (water + HFIP) at temperatures lower than 298.15 K.

The anomalous behavior of the solubilities and Gibbs energies for solution and solvation processes in the zone very rich in water can be related to the peculiar structure of the mixtures in this zone which has been brought to light by structural and simulation studies. The mixtures (water + HFIP) show microheterogeneities due to the formation of micelle-like clusters of HFIP when $x_2 < 0.07$ [12-15] whereas for the mixtures (TFE + water) several experimental studies [38,39] point to the presence of microheterogeneities and structural transitions at values of x_2 ranging from 0.15 to 0.2. Burakovski *et al.* [40]] have detected a discontinuity in the isentropic compressibility of the mixture (water + TFE) at $x_2 \approx 0.05$ that they attribute to the joining of weak hydrates of TFE leading to the formation of bigger and weaker hydrates, most probably containing TFE dimers instead of monomeric alcohol molecules, i.e., a micelle-like aggregation. In any case these studies indicate that the composition range for the existence of microheterogeneities is somewhat wider for TFE. The microheterogeneities would presumably decrease the solubility of the gases in that composition range.

3.2. A method for comparing the solubility of a gas in different liquids. Application to TFE and HFIP.

In the preceding section has been stated that the highest values of solubility obtained for CO_2 in the mixtures could be explained by an enhanced solubility of this gas or by a hindered one of C_2H_4 and C_2H_6. It would be interesting to elucidate which of these is the case. For this purpose, the definition of the following solubility ratio

$$r_i = \frac{x_i}{x_{Kr}} \tag{9}$$

is proposed where x_i is the solubility expressed as mole fraction of gas i and x_{Kr} is the solubility expressed as mole fraction for Kr, both in a given liquid solvent. Krypton has been chosen as the gas of reference. This gas of reference should not have especial characteristics either in size and shape nor differences in its interaction with chemically different solvents. Krypton is a noble gas of intermediate size and the solubility predictions of SPT for it are very good for many solvents, a sign that it does not establish especial interactions and has an “average” behavior among the gases.

The comparison of the values of the solubility ratio for a gas in different solvents would provide clues about their relative solubilities. Obviously, a direct relationship between solubilities of two gases likely supposes a simplification and, on the other hand, the utility of the ratio is dependent on the quality of the available measured solubilities. Nevertheless, it will be seen that the ratio performs well.

The values of the solubility ratios for several gases in different kinds of solvents are gathered in Table 4. The gases considered are C_2H_4, C_2H_6 and CO_2 which are those whose better or worse solubility is to be elucidated. Besides, CH_4, CF_4 and SF_6 have been also included: the fluorinated ones because of their especial behavior in the mixtures (water + fluoroalcohol) and CH_4 as point of comparison for CF_4. Referring to the solvents, a rather ample set of liquids have been considered in order to assess the reliability of the method. They include water [34], TFE [3] and HFIP [4] as well as benzene, toluene [41], halogenated benzenes [42,43], n-alkanes [44-47], cycloalkanes [43,48,49] and halogenated cyclohexanes [50-52] alkan-1-ols [53-55] and cycloketones [56-60] and carbon tetrachloride. The solubilities have been obtained from the literature and no consideration about their quality has been made.

A survey of table 4 shows that the ratios fulfill the expectations. For example, the ratios for all of the gases, excepting C_2H_4 and CO_2, are very similar for most of the liquids, excluding precisely water, TFE and HFIP. Then, for the hydrocarbons CH_4 and C_2H_6 the main feature would be the interaction with the hydrocarbon part of the molecules and the presence of a functional group would be of lesser importance. On the other hand, CF_4 and SF_6 exhibit low values of the ratios which are in agreement with the lipophobic character of fluorinated compounds. Ethylene shows a wider range of variability in such a way that their ratios are quite low for alkanes while they increase for alkanols, benzene and benzene derivatives and cycloketones. In all of these cases attractive interactions can be established between the π electronic density in the double bond of C_2H_4 and either the –OH group of alkanols or the π cloud of benzene and benzene derivatives or the π electronic density in the double bond of the carbonyl group.

Also CO_2 shows quite different values of the ratios for different solvents. They are low for alkanes and cycloalkanes but increase for alkanols and benzene and benzene derivatives reaching maximum values when the solvents are cycloketones. Again, the interaction between π electronic densities in double bonds or between between π electronic densities in the carbonyl group and π clouds would be responsible of the observed values. That the maximum ratios appear for cycloketones is not very surprising as they have double C=O bonds like those of CO_2.

Centering on the solvents of interest, it can be seen that most of the gases show clearly lower ratios, i.e, lower solubilities, in water, a fact which agrees with the hydrophobic character of the gases. The higher hydrophobicity of CF_4 and SF_6 lead to significantly low ratio values. The exception comes from CO_2 that is highly soluble in water and provides the highest value for a ratio in table 4, namely, 13.60. CF_4 and SF_6 show, as would be expected, higher solubilities in fluoroalcohols than in the remaining solvents, excepting the also fluorinated hexafluorobenzene whose ratio for CF_4 is identical to that of TFE. According to the ratios, CH_4 and C_2H_6 are less soluble in the fluoroalcohols than in most of the compounds and specifically than in alkanols whereas C_2H_4 seems to have a similar solubility in fluoroalcohols and alkanols. Finally, CO_2 clearly exhibit a high solubility in fluoroalcohols, only comparable with that of some cycloketones. This would support the especial affinity between CO_2 and fluorinated compounds. But it is noticeable that the ratio for CO_2 in hexafluorobenzene is very similar to that of benzene, then the question of the affinity remains open in absence of more data. In any case, it can be concluded that the highest solubility of CO_2 in TFE and HFIP is the result of an enhanced solubility of CO_2 together with a hindered solubility of C_2H_6.

3.3. Excess Henry's Constant and the SPT Theory

Another property worth to be considered when dealing with gas solubilities in liquid mixtures is the so-called excess Henry's constant, $\ln K^{\mathrm{E}}_{\mathrm{H3,12}}$, that is defined [61] by

$$\ln K^{\mathrm{E}}_{\mathrm{H3,12}} = \ln K_{\mathrm{H3,12}} - \sum_{\mathrm{i=1}}^{2} x_{\mathrm{i}} \cdot \ln K_{\mathrm{H3,i}} \ , \tag{9}$$

for a binary liquid solvent. The values for the solubilities of the non-polar gases in the pure components can be found in the literature [4,27] and the corresponding calculated excess Henry's constants in mixtures (HFIP + water) are listed in table 2. These values have been fitted to the mole fraction of fluoroalcohol according to the following rational adjusting equation [62]

$$\ln K_{\mathrm{H3,12}}^{\mathrm{E}} = \frac{x_2(1-x_2)\sum_{\mathrm{i}=0}^{\mathrm{p}} C_{\mathrm{i}}(1-2x_2)^{\mathrm{i}}}{1+\sum_{\mathrm{i}=0}^{\mathrm{q}} D_{\mathrm{i}}(1-2x_2)^{\mathrm{i}}}. \qquad (10)$$

The coefficients C_{i}, D_{i} and the standard deviations are gathered in table 5 while the graphics with the excess Henry's constant values and their fitting curves are shown in figure 3. The excess Henry's constants are negative for all the gases, except for H_2 and O_2 in the zone very rich in water ($x_2 < 0.02$) where they are slightly positive. These maxima were also observed for He, Ne and Xe. In that zone, most of the remaining gases exhibit a very slight decrease of $\ln K_{\mathrm{H3,12}}^{\mathrm{E}}$. Only CF_4 and SF_6 show a smooth trend. In general, the minimum values of $\ln K_{\mathrm{H3,12}}^{\mathrm{E}}$ are placed around $x_2 = 0.3$ except for H_2 and CO_2 which have the minima situated at $x_2 = 0.4$ and CF_4 and SF_6 whose minima appear at $x_2 = 0.2$. The minimum values range from -0.9271 for H_2 to -3.6649 for SF_6. Taking into account the noble gases, the module of the excess Henry's constants increase in the sequence

$H_2 < CO_2 <$ He $<$ Ne $<$ Ar $<$ Kr $< O_2 < CH_4 <$ Xe $< N_2 < C_2H_4 < C_2H_6 < CF_4 < SF_6$

Once again the behavior of $\ln K_{\mathrm{H3,12}}^{\mathrm{E}}$ for the mixtures (water + fluoroalcohol) is quite similar for TFE and HFIP. But the values are higher for the mixtures with TFE, a fact that leads to the main difference between both mixtures, namely, that positive values of $\ln K_{\mathrm{H3,12}}^{\mathrm{E}}$ appear for all of the gases when solved in mixtures (water + TFE) and their composition range increases until $x_2 < 0.07$ in most cases. This is in agreement with the structural data discussed above. Another difference is in the sequence of increase of the module of the excess Henry's constants because, in the mixtures (water + TFE) it is lower for He and Ne than for CO_2 and lower for O_2 than for Kr.

Negative excess Henry's constants imply that the solubilities are greater than those expected if the behavior of the gas in the mixtures is described by a linear variation of the logarithms of the Henry's constants when passing from one pure compound to the other. Then, except in the composition range near pure water, the solubility of the gases in the mixtures (water + fluoroalcohol) increases very rapidly, with the amount of fluoroalcohol in such a way that it is clearly higher in the mixtures than would be expected from the values for the pure solvents. This effect is most pronounced for the fluorinated gases in such a way that low proportions of fluoroalcohol increases the solubility of CF_4 and SF_6 much above the values expected from a linear variation.

Finally, to complete our study, the Scaled Particle Theory [2,21-24] has been applied to predict the solubilities of the gases in the mixture (water + HFIP). This theory assumes that the solution process can be divided in two steps: (a) creation of a cavity in the solvent to locate the solute molecule followed by (b) introduction of the solute molecule in that cavity and its interaction with the solvent. Then, the Gibbs energy for the solution process is given by

$$\Delta\overline{G}_{3,\mathrm{sol}}^{0,\mathrm{SPT}} = \Delta\overline{G}_c + \Delta\overline{G}_i + \mathrm{R}T\ln\frac{\mathrm{R}T}{V_{12}}, \tag{11}$$

where $\Delta\overline{G}_c$ and $\Delta\overline{G}_i$ are the changes in the partial molar Gibbs energy for the steps of formation of the cavity and of interaction, respectively. $\Delta\overline{G}_c$ corresponds to the creation of a cavity in a liquid binary mixture constituted by hard spheres and is related to the hard sphere diameter [23], σ_i, which is identified with the distance parameter of the Lennard-Jones potential. For non-polar gases, $\Delta\overline{G}_i$ is the sum of two terms [24], one accounting for dispersion-repulsion interaction and the other for dipole-induced dipole interaction. $\Delta\overline{G}_i$ is related with the energy parameters of the Lennard-Jones potential, ε_i / k .

The values of σ_i and ε_i / k, polarizabilities and dipole moments of the pure components which are necessary for the calculations have been obtained from the literature [4,24]. The values predicted by the theory for $\Delta\overline{G}_{3,\mathrm{sol}}^{0}$ along with the corresponding average deviation estimated by means of Eq (12) have been included in table 2.

$$\text{Average deviation} = \frac{1}{n} \cdot \sum_{i=1}^{n} \left| \frac{\Delta \overline{G}_{3,\text{sol}}^{0,\exp} - \Delta \overline{G}_{3,\text{sol}}^{0,\text{SPT}}}{\Delta \overline{G}_{3,\text{sol}}^{0,\exp}} \right| \times 100 . \tag{12}$$

The results are fairly good for most of the gases, being the exceptions CF_4, SF_6 and CO_2, i. e., those gases which would present especial interactions with both HFIP and water. Moreover, the solubilities predicted for CF_4, SF_6 and CO_2 as well as C_2H_4 are lower than the experimental ones whereas the opposite result is obtained for the remaining gases, noble ones included [8], a feature already observed in the SPT predictions for the mixture (TFE + water) [6,7]. The maximum deviation appears for CO_2. In any case, as was already observed for the noble gases, the deviations of SPT for the mixture (water + HFIP) significantly decrease in many cases with respect to those previously found when the gases are dissolved in pure HFIP [4]. The exceptions are for the gases N_2, C_2H_4 and, most notably, CO_2. When comparing the performance of SPT in the mixture with that in the pure fluoroalcohol, it can be seen that the results for the mixture (water + TFE) are somewhat different because the deviations are quite similar to those of pure TFE.

Another approach to the SPT is given by the values of the excess Henry's constants, calculated by applying Eq. (9) to the results obtained by SPT for both the mixed solvent and the pure liquids. The excess Henry's constants so determined are shown in the last column of table 2. As occurred for the noble gases [8], the excess Henry's constants predicted by SPT are always negative. The minima coincide fairly well with those obtained from the experimental values although the values predicted by the theory are always smaller in module, excepting CF_4 and SF_6 whose enhanced solubility leads SPT to underestimate their excess Henry's constants. Negative values of the excess Henry's constants predicted by SPT were also obtained for the mixtures (water + TFE) [6,7] and those values were usually also smaller than the experimental ones, but they were greater, in this case, for N_2, CH_4, C_2H_6, C_2H_4, CF_4 and SF_6. In general, a good qualitative agreement is obtained between the SPT and the experimental results, the shortcomings of the model to reproduce the behavior for the pure solvents being apparently the main source of the deviations. However, it is quite remarkable the performance of the model because the assumption that the properties of water and HFIP do not undergo any modification when passing from the pure to the mixed state is quite unrealistic.

4. Conclusion

In this paper the solubilities of the non-polar gases H_2, N_2, O_2, CH_4, C_2H_6, C_2H_4, CF_4, SF_6, and CO_2 in the mixture (water + HFIP) at a temperature of 298.15 K and 101.33 kPa partial pressure of gas have been reported for the entire composition range. The Gibbs energies for both the solution and the solvation processes have been calculated. The solubility of CF_4 and SF_6 highly rises as the mole fraction of HFIP increases due to the fact that they are very little soluble in water and very soluble in the chemically more similar HFIP. CO_2 is the most soluble gas in both the pure solvents and their mixtures. The solubility of the gases scarcely increases when $x_2 < 0.07$. The solvation of the gases is not favored except for C_2H_6 when $x_2 > 0.5$, C_2H_4 and SF_6 when $x_2 > 0.3$, and CO_2 when $x_2 > 0.05$ and, as occurred with solubilities, shows a quite anomalous behavior in mixtures very rich in water.

A method has been proposed to compare solubilities of a given gas in different liquids and has been applied to elucidate if the solubilities of CH_4, CF_4, C_2H_6, C_2H_4, SF_6 and CO_2 in TFE and HFIP are enhanced or hindered with respect to other kinds of compounds. The results indicate that the solubilities of the fluorinated gases as well as that of CO_2 is enhanced and those of CH_4 and C_2H_6 are hindered.

Furthermore, the so-called excess Henry's constants have been calculated showing that the solubilities in the mixture are greater than those expected if the behavior of the gas in the mixtures is described by a linear variation of the logarithms of the Henry's constants when passing from one pure compound to the other. In this property the peculiar behavior of the solubility of gases in the mixtures very diluted in HFIP can clearly observed. This behavior has been related to the presence of micelle-like microheterogeneities in the zone with $x_{HFIP} < 0.07$. The Scaled Particle Theory has been applied yielding quite acceptable results.

A comparison with the solubilities and related properties of the same set of non-polar gases and noble gases in the mixture (water + TFE) has been carried out. It shows that the aqueous mixtures of both fluoroalcohols share many features.

Acknowledgements

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FIGURE CAPTIONS

FIGURE 1. Solubility, x_3, versus mole fraction of HFIP, x_2, in the solvent liquid mixture {water (1) + HFIP (2)} at 298.15 K and 101.33 kPa partial pressure of gas for the gases: (a) (▽) hydrogen, (∗) nitrogen, and (△) oxygen. (b) (■) methane, (●) ethane, and (▲) ethylene. (c) (○) carbon tetrafluoride, (◇) sulphur hexafluoride, and (□) carbon dioxide. Fitting curves and a detail of the zone rich in water have been also drawn. Solubilities of gases were taken from the literature for pure HFIP [4] and pure water [34]

FIGURE 2. Gibbs energies for the solvation process, $\Delta\overline{G}_{solv}$, versus the mole fraction of HFIP, x_2, in the solvent liquid mixture {water (1) + HFIP (2)} at 298.15 K and 101.33 kPa partial pressure of gas.

FIGURE 3. Excess Henry's constant, $\ln K_{\mathrm{H}3,12}^{\mathrm{E}}$, versus mole fraction of HFIP, x_2, in the solvent liquid mixture {water (1) + HFIP (2)} at 298.15 K and 101.33 kPa partial pressure of gas for the gases: (a) (▽) hydrogen, (∗) nitrogen, and (△) oxygen. (b) (■) methane, (●) ethane, (▲) ethylene, (○) carbon tetrafluoride, (◇) sulphur hexafluoride, and (□) carbon dioxide. Fitting curves have been also drawn.

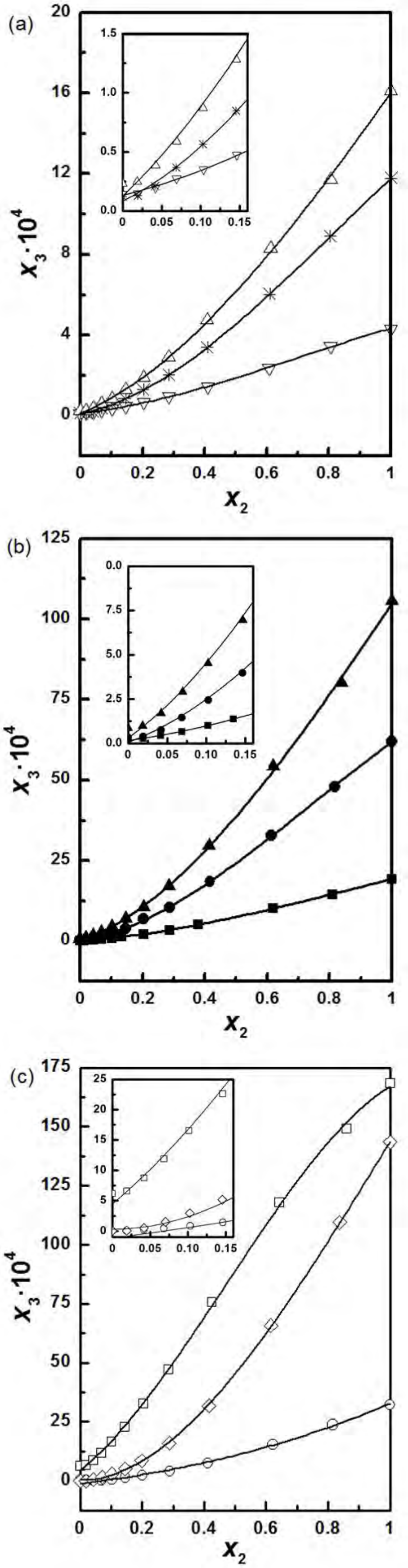
(a)
20
16
12
8
4
0
$x_3 \cdot 10^4$
0
0.2
0.4
0.6
0.8
1
x_2
1.5
1.0
0.5
0.0
0
0.05
0.10
0.15
(b)
125
100
75
50
25
0
$x_3 \cdot 10^4$
0
0.2
0.4
0.6
0.8
1
x_2
0.0
7.5
5.0
2.5
0.0
0
0.05
0.10
0.15
(c)
175
150
125
100
75
50
25
0
$x_3 \cdot 10^4$
0
0.2
0.4
0.6
0.8
1
x_2
25
20
15
10
5
0
0
0.05
0.10
0.15

FIGURE 1

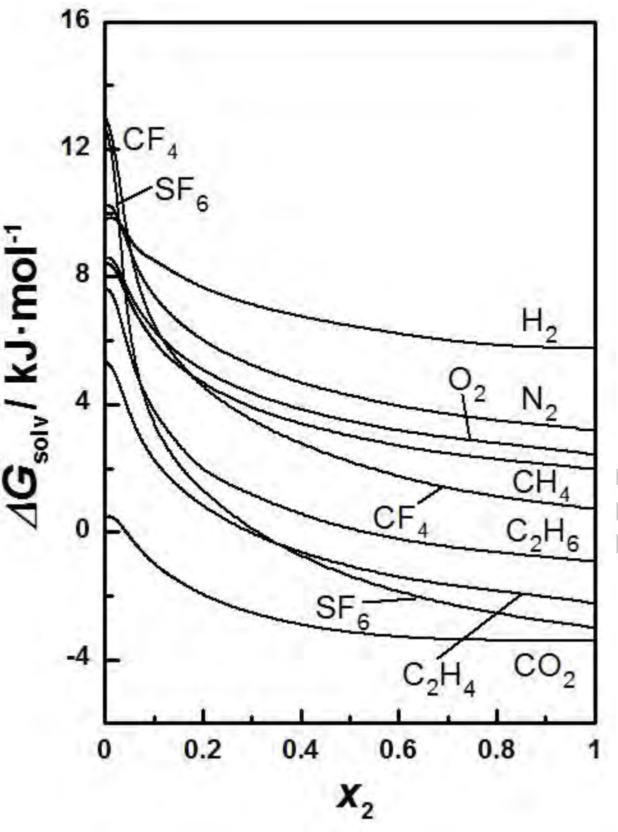
16
12
8
4
0
-4
$\Delta\overline{G}_{solv}$ / kJ·mol^{-1}
0
0.2
0.4
0.6
0.8
1
x_2
CF_4
SF_6
H_2
O_2
N_2
CH_4
CF_4
C_2H_6
SF_6
C_2H_4
CO_2

FIGURE 2

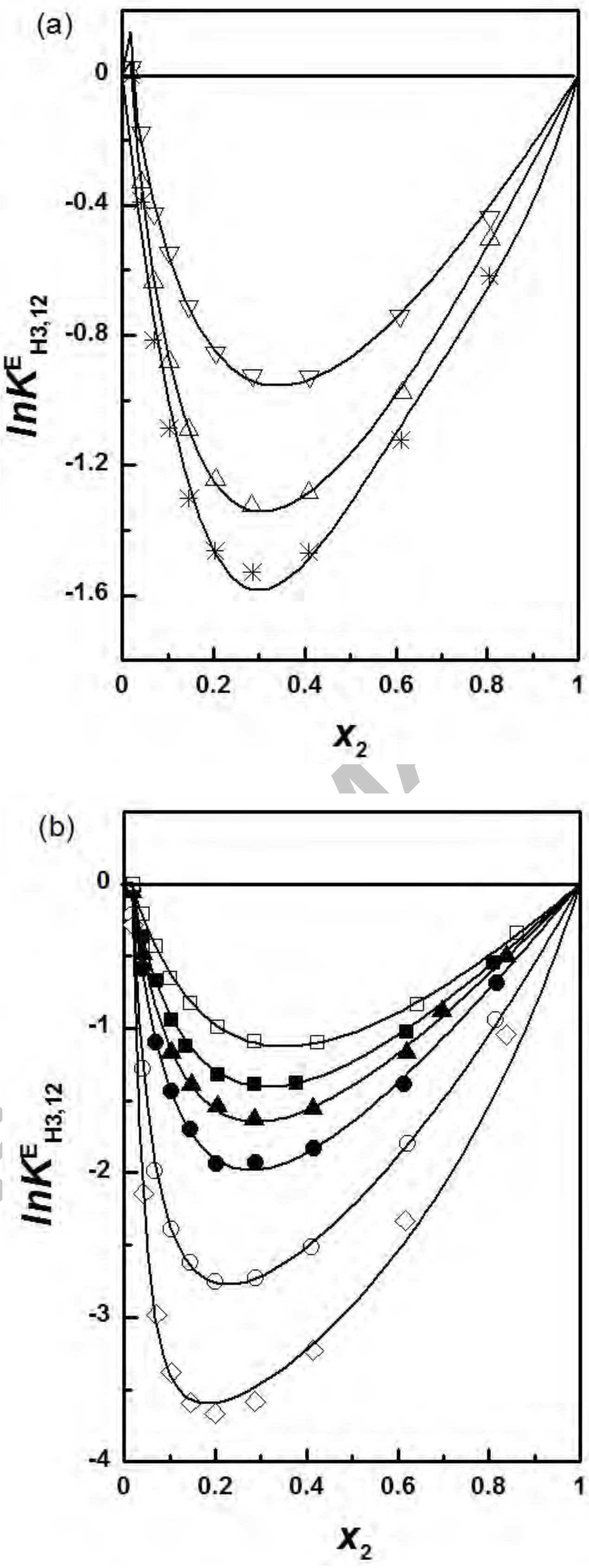
(a)
0
-0.4
-0.8
-1.2
-1.6
lnK^E_H3,12
0
0.2
0.4
0.6
0.8
1
x2
(b)
0
-1
-2
-3
-4
lnK^E_H3,12
0
0.2
0.4
0.6
0.8
1
x2

FIGURE 3

TABLE 1

Sample Description

Chemical Name	Source	Purity	Purification Method	Analysis Method
Water	laboratory	Milli-Q [a]	Filtration and deionization	Resistivity
HFIP [b]	Fluorchem Ltd.	0.99 [c]	None	GC [d]
Hydrogen	Air Liquide	0.9999 [e]	None	-
Nitrogen	J.T. Baker	0.99998 [e]	None	-
Oxygen	Air Liquide	0.9998 [e]	None	-
Methane	Air Liquide	0.9995 [e]	None	-
Ethane	Air Liquide	0.990 [e]	None	-
Ethylene	Air Liquide	0.9990 [e]	None	
Carbon tetrafluoride	J.T. Baker	0.99 [e]	None	
Sulphur hexafluoride	Air Liquide	0.995 [e]	None	
Carbon dioxide	Air Liquide	0.9998 [e]	None	

[a] 18.2 MΩ·cm

[b] HFIP = 1,1,1,3,3,3-hexafluoroisopropan-2-ol

[c] Mole fraction purity. Provided by the supplier.

[d] Gas-liquid chromatography.

[e] Mass fraction purity. Provided by the supplier.

TABLE 2

Solubility of the gases, x_3 and $\ln K_{\mathrm{H3,12}}$, in the mixtures {water (1) + HFIP (2)} at 298.15 K and 101.33 kPa partial pressure of gas, Gibbs energy for the solution process, $\Delta\overline{G}^{0}_{3,\mathrm{sol}}$, and experimental excess Henry's constant, $\ln K^{\mathrm{E}}_{\mathrm{H3,12}}$, at each mole fraction of HFIP in the liquid solvent, x_2 (bin). Also, predicted SPT Gibbs energy, $\Delta\overline{G}^{0,\mathrm{SPT}}_{3,\mathrm{sol}}$, and excess Henry's constant, $\ln K^{\mathrm{E,SPT}}_{\mathrm{H3,12}}$. The average deviations correspond to the SPT predictions for the Gibbs energy.

x_2 (bin)	$10^4 \cdot x_3$	$\ln K_{\mathrm{H3,12}}$	$\Delta\overline{G}^{0}_{3,\mathrm{sol}}$ (kJ · mol^{-1})	$\ln K^{\mathrm{E}}_{\mathrm{H3,12}}$	$\Delta\overline{G}^{0,\mathrm{SPT}}_{3,\mathrm{sol}}$ (kJ · mol^{-1})	$\ln K^{\mathrm{E,SPT}}_{\mathrm{H3,12}}$
			Hydrogen			
0.0194	0.1474	22.65	27.58	0.0264	27.00	-0.3657
0.0419	0.1959	22.37	26.87	-0.1767	26.45	-0.4993
0.0690	0.2749	22.03	25.95	-0.4240	25.85	-0.6352
0.1035	0.3503	21.79	25.43	-0.5460	25.16	-0.7783
0.1460	0.4740	21.48	24.68	-0.7107	24.42	-0.9102
0.2038	0.6682	21.14	23.83	-0.8530	23.54	-1.0386
0.2858	0.9527	20.79	22.95	-0.9226	22.53	-1.1247
0.4102	1.456	20.36	21.90	-0.9271	21.33	-1.1211
0.6082	2.376	19.87	20.69	-0.7400	19.99	-0.8855
0.8057	3.463	19.50	19.75	-0.4345	19.05	-0.4905
					1.9 %	
			Nitrogen			
0.0191	0.1294	22.78	27.90	-0.0021	27.42	-0.5754
0.0415	0.2118	22.29	26.68	-0.3891	26.70	-0.7523
0.0685	0.3668	21.74	25.32	-0.8149	25.90	-0.9382
0.1028	0.5652	21.31	24.25	-1.0871	25.00	-1.1274
0.1453	0.8488	20.90	23.24	-1.3016	24.02	-1.3072
0.2036	1.305	20.47	22.17	-1.4634	22.88	-1.4715
0.2848	2.030	20.03	21.08	-1.5299	21.60	-1.5762
0.4091	3.386	19.52	19.81	-1.4681	20.10	-1.5512
0.6104	6.029	18.94	18.38	-1.1222	18.43	-1.2043
0.8047	8.918	18.55	17.41	-0.6184	17.33	-0.6629

					1.8 %	
			Oxygen			
0.0185	0.2473	22.13	26.29	0.0084	25.36	-0.5260
0.0422	0.3844	21.69	25.20	-0.3311	24.64	-0.7046
0.0691	0.5872	21.27	24.15	-0.6370	23.91	-0.8721
0.1032	0.8681	20.88	23.18	-0.8824	23.08	-1.0460
0.1457	1.280	20.49	22.22	-1.0922	22.17	-1.2125
0.2045	1.910	20.09	21.23	-1.2429	21.11	-1.3626
0.2844	2.891	19.67	20.20	-1.3241	19.93	-1.4615
0.4088	4.755	19.18	18.97	-1.2867	18.54	-1.4351
0.6137	8.293	18.62	17.59	-0.9779	16.95	-1.1094
0.8055	11.73	18.28	16.73	-0.5047	15.94	-0.6116
					2.0 %	
			Methane			
0.0194	0.2727	22.03	26.05	-0.0154	23.97	-0.5821
0.0417	0.4280	21.58	24.93	-0.3682	23.33	-0.7346
0.0688	0.6565	21.16	23.87	-0.6700	22.60	-0.9006
0.1026	0.9953	20.74	22.84	-0.9427	21.79	-1.0672
0.1347	1.366	20.42	22.06	-1.1227	21.10	-1.1934
0.2046	2.250	19.92	20.82	-1.3179	19.83	-1.3744
0.2864	3.482	19.49	19.74	-1.3913	18.63	-1.4708
0.3777	5.114	19.10	18.79	-1.3832	17.57	-1.4656
0.6187	10.25	18.41	17.06	-1.0225	15.64	-1.1019
0.8082	14.54	18.06	16.20	-0.5462	14.65	-0.6031
					6.3 %	
			Ethane			
0.0189	0.3890	21.67	25.17	-0.0415	22.37	-0.7867
0.0420	0.7635	21.00	23.50	-0.5912	21.62	-0.9636
0.0688	1.454	20.35	21.90	-1.1016	20.82	-1.1406
0.1028	2.440	19.84	20.62	-1.4344	19.90	-1.3268
0.1462	3.970	19.35	19.41	-1.6983	18.86	-1.5102
0.2028	6.840	18.81	18.06	-1.9434	17.71	-1.6662
0.2876	10.46	18.38	17.01	-1.9316	16.31	-1.7697
0.4167	18.54	17.81	15.59	-1.8290	14.70	-1.7169
0.6132	32.94	17.23	14.17	-1.3852	13.02	-1.3257
0.8175	47.99	16.86	13.24	-0.6908	11.84	-0.6903
					6.1 %	

Ethylene						
0.0186	0.9909	20.74	22.85	-0.0603	22.32	-0.7124
0.0420	1.699	20.20	21.52	-0.4876	21.56	-0.8967
0.0696	2.901	19.67	20.19	-0.8845	20.75	-1.0791
0.1023	4.506	19.23	19.10	-1.1669	19.89	-1.2550
0.1467	6.952	18.79	18.02	-1.3929	18.89	-1.4383
0.2040	10.60	18.37	16.98	-1.5367	17.74	-1.5904
0.2848	17.05	17.89	15.80	-1.6273	16.45	-1.6883
0.4135	29.60	17.34	14.43	-1.5569	14.90	-1.6405
0.6192	54.36	16.74	12.93	-1.1655	13.21	-1.2464
0.8376	80.17	16.35	11.96	-0.5028	12.02	-0.5843
					2.9 %	
Carbon Tetrafluoride						
0.0186	0.0538	23.66	30.08	-0.2146	29.47	-0.8106
0.0419	0.1813	22.44	27.06	-1.2776	28.52	-1.0125
0.0682	0.4395	21.55	24.87	-1.9903	27.54	-1.2033
0.1030	0.8373	20.91	23.27	-2.3958	26.37	-1.4045
0.1461	1.403	20.39	21.99	-2.6253	25.11	-1.5775
0.2008	2.324	19.89	20.74	-2.7566	23.75	-1.7006
0.2890	4.102	19.32	19.33	-2.7321	21.98	-1.7285
0.4116	7.523	18.71	17.83	-2.5158	20.15	-1.5129
0.6230	15.39	18.00	16.05	-1.8010	18.01	-0.7315
0.8154	23.84	17.56	14.97	-0.9442	16.73	0.2490
					11.1 %	
Sulfur Hexafluoride						
0.0191	0.0674	23.42	29.52	-0.2853	27.74	-1.1671
0.0418	0.5183	21.38	24.46	-2.1414	26.74	-1.4325
0.0701	1.509	20.31	21.81	-2.9822	25.58	-1.7284
0.1024	2.939	19.65	20.16	-3.3806	24.38	-2.0161
0.1452	5.150	19.09	18.77	-3.5939	22.97	-2.3247
0.1994	8.505	18.58	17.52	-3.6649	21.45	-2.6083
0.2870	16.00	17.95	15.96	-3.5853	19.46	-2.8785
0.4147	31.66	17.27	14.27	-3.2309	17.30	-2.9735
0.6158	65.72	16.54	12.46	-2.3320	15.02	-2.6706
0.8376	109.6	16.03	11.19	-1.0454	13.39	-1.9796
					18.2 %	

			Carbon Dioxide			
0.0193	6.550	18.85	18.17	-0.0061	23.58	-0.6710
0.0421	8.723	18.57	17.46	-0.2106	22.83	-0.8550
0.0684	11.84	18.26	16.70	-0.4336	22.05	-1.0330
0.1014	16.51	17.93	15.88	-0.6544	21.17	-1.2164
0.1460	22.58	17.61	15.10	-0.8267	20.13	-1.4040
0.2041	32.54	17.25	14.20	-0.9944	18.99	-1.5618
0.2856	47.18	16.88	13.28	-1.0947	17.69	-1.6624
0.4251	75.51	16.41	12.11	-1.1029	16.03	-1.6067
0.6429	117.8	15.96	11.01	-0.8320	14.30	-1.1720
0.8605	149.2	15.73	10.42	-0.3417	13.16	-0.5004
					31.5 %	

Standard uncertainties *u* are $u(T) = \pm0.05$ K and $u(P) = \pm7$ Pa, the combined expanded uncertainty U_c is $U_c(x_2) = \pm0.02$ with 0.95 level of confidence ($k \approx 2$) and the relative combined expanded uncertainty U_r is $U_r(x_3) = \pm0.02$ ($x_3 \leq 10^{-4}$) and $\pm0.01\%$ ($x_3 > 10^{-4}$) with 0.95 level of confidence ($k \approx 2$)

TABLE 3

Fitting coefficients, A_i, and standard deviations, σ, according to Eq. (6) for the solubilities of noble gases in mixtures {water + HFIP} at 298.15 K and 101.33 kPa partial pressure of gas.

Gas	A_0	A_1	A_2	A_3	$\sigma\cdot 10^4$
H_2	0.1338	1.621	4.933	-2.345	0.026
N_2	0.0835	3.281	14.07	-5.642	0.023
O_2	0.1248	6.288	13.42	-3.797	0.10
CH_4	0.1600	6.309	20.92	-8.085	0.066
C_2H_6	0.0429	17.24	80.05	-35.29	0.29
C_2H_4	0.3080	31.85	106.9	-34.03	0.90
CF_4	0.0566	2.295	45.79	-15.94	0.088
SF_6	0.3031	-0.4437	218.2	-74.31	0.44
CO_2	4.427	104.9	198.6	-140.7	1.5

TABLE 4

Solubility ratios, $r_{x,i}$, as defined by Eq. (9) for several gases i in different solvents at 298.15 K

Solvent	$r_{x,i}$						Refs.
	CH_4	CF_4	C_2H_6	C_2H_4	SF_6	CO_2	
Water	0.56	0.09	0.74	1.91	0.10	13.60	40
TFE	0.67	0.77	2.42	3.01	3.25	6.77	3
HFIP	0.69	1.15	2.23	3.79	5.15	5.92	4
Benzene	0.76	0.21	5.43	4.50	0.96	3.55	41
Toluene	0.72	0.21	4.61	4.37	1.01	3.03	41
Chlorobenzene[a]	0.72	0.17	5.50	4.52	0.85	3.79	42,43
Bromobenzene[a]	0.72	0.13	5.66	4.72	0.62	3.69	42,43
Hexafluorobenzene	0.65	0.77				3.73	41
Hexane	0.72	0.33	4.34	2.25	1.52	1.69	44-47
Heptane	0.71	0.30	4.47	2.41	1.43	1.66	44-47
Octane	0.72	0.28	4.78	2.62	1.39	1.72	44-47
Nonane	0.73	0.28	4.96	2.75	1.31	1.58	44-47
Decane	0.73	0.26	4.95	2.91	1.22	1.72	44-47
Dodecane	0.72	0.24	4.56	2.85	1.10	1.69	44-47
Cyclohexane	0.70	0.22	5.05	3.21	1.16	1.63	41,48
Cyclooctane[b]	0.80	0.20			0.86	1.99	49
Chlorocyclohexane[a]	0.70	0.17	4.08	5.29	0.84	3.22	50,51
Bromocyclohexane[a]	0.70	0.14	4.23	5.43	0.66	3.16	50,52
Methanol	0.78	0.29	3.77	4.09	0.97	6.07	53-55
Ethanol	0.74	0.28	4.15	3.61	1.10	4.38	53-55
Propan-1-ol	0.74	0.25	4.22	3.50	1.08	3.19	53-55
Butan-1-ol	0.73	0.24	4.31	3.44	1.02	2.84	53-55
Pentan-1-ol	0.73	0.22	4.39	3.43	0.97	2.81	53-55
Hexan-1-ol	0.72	0.21	4.42	3.35	0.90	3.34	53-55
Heptan-1-ol	0.74	0.20	4.55	3.37	0.90	3.36	53-55
Octan-1-ol	0.72	0.20	4.60	3.37	0.87	2.49	53-55
Cyclopentanone	0.74	0.19	4.60	5.12	0.82	8.40	56

Cyclohexanone		0.18	4.73	4.58	0.78	7.08	57
Cycloheptanone	0.72	0.16	4.73	4.82	0.72	6.63	58
2-Methylcyclohexanone	0.72	0.19	4.69	4.40	0.88	5.55	59
2,6-Dimethylcyclohexanone	0.72	0.21	4.71	4.10	0.97	4.65	60

[a] at $T = 293.15$ K

[b] at temperatures between 298.21 and 298.26 K.

TABLE 5

Fitting coefficients and standard deviations according to Eq. (10) for the excess Henry's constants in mixtures {water + HFIP} at 298.15 K and 101.33 kPa partial pressure of gas.

Gas	C_0	C_1	D_1	D_2	D_3	σ
H_2	-3.483	3.620	-1.590	0.5814		0.028
N_2	-5.298	5.492	-1.756	0.5460		0.034
O_2	-4.644	4.819	-1.729	0.7276		0.014
CH_4	-4.930	5.106	-1.696	0.6898		0.027
C_2H_6	-6.588	6.811	-1.788	0.7858		0.041
C_2H_4	-5.588	5.787	-1.759	0.7557		0.026
CF_4	-8.912	9.193	-1.747	0.5781	0.1701	0.024
SF_6	-11.57	11.97	-1.691	0.7038	0.2884	0.071
CO_2	-4.129	4.272	-1.591	0.5885		0.019

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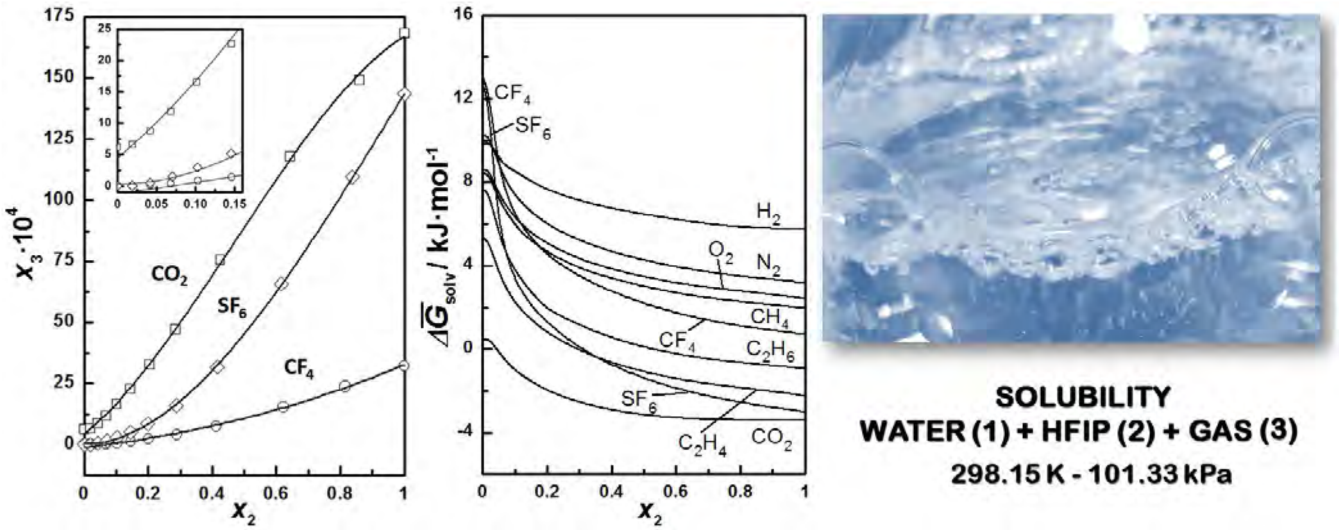

Highlights

Solubility of gases in fluoroorganic alcohols. Part III. Solubilities of several non-polar gases in water+1,1,1,3,3,3-hexafluoropropan-2-ol at 298.15 K and 101.33 kPa

Ana M. Mainar[a,]*, José F. Martínez-López[b], José S. Urieta[a], Juan I. Pardo[a]

[a] Group of Applied Thermodynamics and Surfaces (GATHERS), Aragón Institute for Engineering Research (I3A), Universidad de Zaragoza, c/ Mariano Esquillor s/n, 50018 Zaragoza, Spain.

[b] Group of Applied Thermodynamics and Surfaces (GATHERS), AgriFood Institute of Aragon (IA2), Universidad de Zaragoza, Facultad de Ciencias, 50009 Zaragoza, Spain.

- Solubility of H_2, N_2, O_2, CH_4, C_2H_6, C_2H_4, CF_4, SF_6, and CO_2 in water+HFIP at 298.15 K and 101.33 kPa was determined
- Changes in the Gibbs energies of the solution and solvation processes were calculated
- $\ln K^{E}_{H3,12}$ values at $x_{HFIP} < 0.07$ has been related to the presence of microheterogeneities
- A method has been proposed to compare solubilities of a given gas in different liquids
- SPT yields quite acceptable results despite its simplicity