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Interactions of Fluorinated Gases with Ionic Liquids: Solubility of CF$_4$, C$_2$F$_6$, and C$_3$F$_8$ in Trihexyltetradecylphosphonium Bis(trifluoromethylsulfonyl)amide

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The interactions between ionic liquids and totally fluorinated alkanes are investigated by associating gas solubility measurements with molecular simulation calculations. Experimental values for the solubility of perfluoromethane, perfluoroethane, and perfluoropropane in one ionic liquid—trihexyltetradecylphophonium bis(trifluoromethylsulfonyl)amide [P$_{6,6,6,14}$][Ntf$_2$]—are reported between 303 and 343 K and close to atmospheric pressure. All mole fraction solubilities decrease with increasing temperature. From the variation of Henry's law constants with temperature, the thermodynamic functions of solvation were calculated. The precision of the experimental data, considered as the average absolute deviation of the Henry's law constants from appropriate smoothing equations, is always better than ±3%. By the analysis of the differences between the solute−solvent radial distribution functions of perfluoromethane and perfluoropropane obtained by molecular simulation, it was possible to explain why solubility increases with the size of the perfluoroalkane. The trend of solubility is explained on the basis of the location of the solute with respect to the solvent ions as well as on the differences in the solute−solvent energies of interaction.

1. Introduction

One possible way of assessing the importance of the interactions between two families of chemical species is to measure their mutual solubility.[1] Solubility is directly proportional to the Gibbs energy of solution, and from its variation with temperature, the enthalpy and entropy of solution can be calculated. When one of the chemical species is a low-pressure gas at the pressure and temperature conditions at which the solution is equilibrated, the solubility can be related directly to the Gibbs energy of solvation, usually defined as the variation of the Gibbs energy when the solute is transferred from an ideal gas at the standard pressure into the infinitely dilute solution.[2] The variation of the Gibbs energy of solvation with temperature, in this case, provides values for the enthalpy of solvation, that are related to the importance of solute−solvent interactions in solution, and for the entropy of solvation, which is related to the structuring of the solvent surrounding the solute. The Gibbs energy of solvation is also accessible by models of statistical thermodynamics and can be directly calculated by molecular simulation, provided that realistic intermolecular force fields are available both for the solvent and for the solute. The link between the macroscopic properties and the microscopic interactions can then be established, and the molecular mechanisms of solvation can be investigated by molecular simulation.[3]

In the present work, we have studied the interactions between a phosphonium-based ionic liquid and fluorinated molecules. Fully or partially fluorinated organic molecules, and in particular

fluorinated gases, are important for a number of industrial applications ranging from medicine to semiconductor production.[4] Organic species in which the hydrogen atoms have been replaced by fluorine can serve as basis for alternative reaction or extraction schemes because they are poorly miscible with both hydrocarbons and water[5−8] and, due to their extraordinary affinity with carbon dioxide, can improve the solubility of chemicals in supercritical reaction or extraction media.[9,10] Ionic liquids join up a number of properties that make them good candidates as environmentally friendly solvents,[11] namely, their negligible vapor pressure, their thermal stability, and their ability to partially dissolve different families of chemicals.[12] The study of the solubility of fluorinated gases in ionic liquids can be of great importance both in the investigation of the interactions of these two classes of chemicals in view of their industrial applications and to improve the understanding of the molecular mechanisms underlying their mutual solubility. Liquid phase solubilities of fluorinated compounds[13] and of partially fluorinated organic species[14] in different ionic liquids have been investigated with the same objectives.

Yokozeki, Shiflett, and co-workers have studied the solubility of different industrially relevant fluorinated gases in ionic liquids.[15−18] In their work, the solubilities were quite large since the gases studied are only partially fluorinated and therefore exhibit large dipole moments and are then able to interact specifically with charged species such as ionic liquids. Nevertheless, the trends found in the solubility of several partially fluorinated methanes[15] and ethanes[18] do not correlate with the hydrofluorocarbon dipole moments. These authors argue that the molecular mechanisms involved in the solvation of the fluorinated gases are not simple and are still not very clear. Molecular dynamics simulations were proposed[19] as a possible source of supporting information that might shed some light into the solvation mechanisms. As far as we are aware, only

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one paper was published on the solubility of gaseous perfluorinated alkanes in ionic liquids. Kumelan et al.[20] measured the solubility of perfluoromethane in 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and successfully correlated the data using two procedures, one based on an equation of state and the other on an extended Henry's law approach. However, these authors did not interpret the data at a molecular level. Therefore, no mechanism to explain the solvation of fluorinated gases was purposed.

Herein, we have measured the solubility of three perfluorinated gases with increasing molecular size in a common alkylphosphonium-based ionic liquid. As the measurements were made at different temperatures, the enthalpy and entropy of solution were determined. Molecular simulation tools were used to assess the molecular mechanisms responsible for the macroscopic properties, namely, the solubility trend observed with the three solutes. The solubility of perfluoromethane was also measured in 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, and the data obtained were compared with that previously published by Kumelan et al.[20] in order to have an estimate of the uncertainty of the present measurements.

2. Experimental Section

2.1. Materials. The sample of the ionic liquid used—trihexyltetradecylphosphonium bis(trifluoromethylsulfonylamide) $[P_{6,6,6,14}][Ntf_2]$—was synthesized at the QUILL Centre, Belfast, according to procedures found elsewhere.[21] The sample was washed thoroughly with water to remove the undesired LiCl salt formed in the reaction and any potential water-soluble impurity that might be present and that could affect the accuracy of the gas solubility measurements.[22]

The ionic liquid was kept under vacuum for 15 h at 303 K before each measurement. A coulometric Karl Fisher titration (Mettler Toledo DL31) was performed before and after each series of measurements, and it was found that there was no variation of the water quantity in the samples. After all the gas solubility measurements were finished, the water quantity measured in the degassed sample of ionic liquid was 54 ± 5 ppm.

The ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethyl)sulfonylamide $[C_6C_1Im][Ntf_2]$ was also synthesized at the QUILL Centre, Belfast, according to procedures described elsewhere.[23] Similar procedures to those described above were followed to condition the ionic liquid before the gas solubility measurements. In this case, the water quantity measured in the degassed sample of ionic liquid after the gas solubility measurements were finished was 83 ± 5 ppm.

The gases used for this study were all supplied by Linde Gas with mole fraction purities of 99.995% for CF_4 (R14), 99.95% for C_2F_6 (R116), and 99.95% for C_3F_8 (R218). All gases were used as received from the manufacturer.

2.2. Experimental Procedure. The experimental method used for these gas solubility measurements is based on an isochoric saturation technique and has been described in previous publications.[24–27] In this technique, a known quantity of gaseous solute is put in contact with a precisely determined quantity of degassed solvent at a constant temperature inside an accurately known volume. When thermodynamic equilibrium is attained, the pressure above the liquid solution is constant and is directly related to the solubility of the gas in the liquid.

The quantity of ionic liquid introduced in the equilibration cell, V_{liq}, is determined gravimetrically. The amount of solute present in the liquid solution, n_2^{liq} (subscripts 1 and 2 stand for solvent and solute, respectively), is calculated by the difference

between two pVT measurements: first when the gas is introduced in a calibrated bulb with volume V_{GB} and second after thermodynamic equilibrium is reached:

$$n_2^{liq} = \frac{p_{ini}V_{GB}}{[Z_2(p_{ini}, T_{ini})RT_{ini}]} - \frac{p_{eq}(V_{tot} - V_{liq})}{[Z_2(p_{eq}, T_{eq})RT_{eq}]} \quad (1)$$

where p_{ini} and T_{ini} are the pressure and temperature in the first pVT determination and p_{eq} and T_{eq} the pressure and temperature at the equilibrium. V_{tot} is the total volume of the equilibration cell, and Z_2 is the compression factor for the pure gas. The solubility can then be expressed in mole fraction

$$x_2 = \frac{n_2^{liq}}{n_1^{liq} + n_2^{liq}} \quad (2)$$

or as Henry's law constant

$$K_H = \lim_{x_2 \to 0} \frac{f_2(p, T, x_2)}{x_2} \cong \frac{\varphi_2(p_{eq}, T_{eq})p_{eq}}{x_2} \quad (3)$$

where f_2 is the fugacity of the solute and ϕ_2 is its fugacity coefficient.

2.3. Molecular Simulation. The experimental data were interpreted from a molecular perspective using simulation results. Molecular dynamics runs at 298 K were performed using the DL_POLY package.[28] An all-atom force field based on a version of the AMBER/OPLS-AA framework extended to encompass ionic liquids like $[P_{6,6,6,14}][Ntf_2]$[29–31] was used to describe the liquid solvent studied here. An OPLS-AA parametrization was used for perfluoroalkanes.[32] The liquid solutions were modeled in boxes with about 400 ions and 5 solute molecules (CF_4 or C_3F_8), cutoff distances of 1.2 nm, and the usual Ewald summation technique to account for long-range interactions. More details on this type of simulation, involving small concentrations of solute molecules in ionic liquids, can be found elsewhere.[33] The simulation data were obtained in production runs of 400 ps that were started only after an equilibration period of 1.5 ns.

3. Results and Discussion

For each system studied, multiple experimental data points were obtained in the temperature interval between 303 and 343 K in steps of approximately 10 K. The experimental solubilities of the three gases in $[P_{6,6,6,14}][Ntf_2]$ are reported in Table 1 and depicted in Figure 1, as mole fraction solubilities and Henry's law constants as a function of temperature. Henry's law constants can be calculated from the experimental values and are used to determine the mole fraction solubility assuming a partial pressure of the gaseous solute equal to 0.1 MPa. The necessary relative atomic masses used are the ones recommended by IUPAC,[34] and the values of the second virial coefficients for the gases, necessary for the calculation of the compressibility factor, were taken from the compilation by Dymond and Smith.[35] The density of the ionic liquid $[P_{6,6,6,14}][Ntf_2]$ had been previously determined as a function of temperature:[36]

$$\ln(\rho_{[P_{6,6,6,14}][Ntf_2]}/kg\ m^{-3}) = 7.34466 -$$

$$1.75418 \times 10^{-3}(T/K) + 1.69333 \times 10^{-6}(T/K)^2 \quad (4)$$

The raw experimental data were correlated as a function of temperature by an empirical equation of the type

TABLE 1: Experimental Values of the Solubility of Three Perfluorinated Gases in the Ionic Liquid $[P_{6,6,6,14}][Ntf_2]$ Expressed Both as Henry's Law Constants, K_H, and as Mole Fraction, x_2, Corrected for a Partial Pressure of Solute of 0.1 MPa

T/K	$p/10^2$ Pa	$K_H/10^5$ Pa	$x_2/10^{-3}$	dev %
CF_4				
303.41	1053.56	374.25	2.67	−6.7
303.41	1095.30	341.13	2.93	+2.4
303.43	1045.89	337.23	2.97	+3.6
313.38	1131.44	370.43	2.70	+0.0
313.41	1088.30	388.70	2.57	−4.7
313.45	1080.41	347.77	2.88	+6.6
323.39	1167.77	407.90	2.45	+2.5
323.42	1123.13	409.76	2.44	+2.1
323.46	1115.28	431.75	2.32	−3.1
333.42	1204.43	524.25	1.91	−5.3
333.42	1149.74	488.34	2.05	+1.6
343.44	1150.29	612.93	1.63	+0.2
343.49	1241.01	605.45	1.65	+1.6
C_2F_6				
303.19	1156.68	183.62	5.45	+0.6
303.52	1055.40	184.57	5.42	+0.4
313.20	1195.90	210.35	4.75	−0.2
313.52	1091.18	207.85	4.81	−0.5
323.22	1234.99	234.31	4.27	+1.1
323.42	1126.58	235.09	4.25	+1.1
333.23	1274.28	280.25	3.57	−0.2
343.23	1313.48	338.18	2.96	−0.3
C_3F_8				
303.43	1035.75	86.07	11.6	+2.0
303.43	1048.77	87.73	11.4	+0.1
303.64	696.38	88.58	11.3	−0.7
304.45	411.99	89.50	11.2	−1.1
313.44	1072.20	95.17	10.5	+1.1
313.44	1086.07	97.89	10.2	−1.7
323.47	1123.25	108.72	9.20	−0.7
333.53	1160.42	121.07	8.26	+2.1
343.50	1181.49	144.88	6.90	−1.0
343.70	1198.36	143.88	6.95	+0.0

[a] p is the experimental equilibrium pressure, and the percent deviation, dev %, is relative to the correlations of the data reported in Table 2.

$$\ln[K_H/10^5 \text{ Pa}] = \sum_{i=0}^{n} A_i(T/K)^{-i} \quad (5)$$

The coefficients A_i are listed in Table 2 together with the average absolute deviations obtained for each solute. These deviations can be regarded as an estimation of the precision of the experimental data, which is, in the present case, always better than 3%. The uncertainty of the solubility results obtained for CF_4 in $[P_{6,6,6,14}][Ntf_2]$ was higher than in previous gas solubility measurements[24−27,37,38] due to unexplained difficulties encountered with this system, the consequences being a larger than usual scatter of the experimental results.

In order to estimate the overall uncertainty associated with the experimental data reported here, the solubility of CF_4 was also measured between 303 and 343 K, in steps of approximately 10 K, in the ionic liquid $[C_6C_1Im][Ntf_2]$ and was compared with the values recently reported by Kumelan et al.[20] Multiple experimental data points were obtained and are listed in Table 3. The density of the ionic liquid, necessary to calculate Henry's law constants from the experimental values, was determined for the sample used
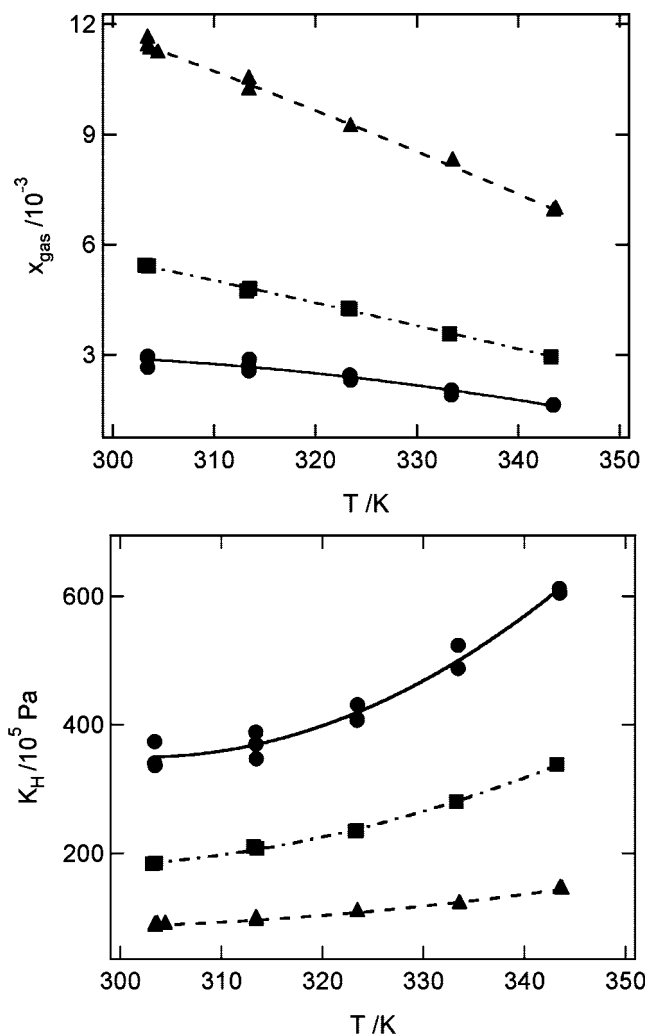

Figure 1. Gas solubilities of perfluorinated alkanes in $[P_{6,6,6,14}][Ntf_2]$ as a function of temperature at 0.1 MPa. Upper plot: mole fraction solubilities. Lower plot: Henry's law constants. ●, CF_4; ■, C_2F_6 and ▲, C_3F_8. Lines represent the smoothed data.

TABLE 2: Parameters of Eq 5 Used to Fit the Experimental Results of K_H from Tables 1 and 2 along with the Percent Average Absolute Deviation of the Fit (AAD %)

gas	A_0	A_1	A_2	AAD %
	$[P_{6,6,6,14}][Ntf_2]$			
CF_4	+41.92	-2.167×10^4	$+3.253 \times 10^6$	3.1
C_2F_6	+28.65	-1.338×10^4	$+1.902 \times 10^6$	0.8
C_3F_8	+22.88	-1.046×10^4	$+1.480 \times 10^6$	1.0
	$[C_6C_1Im][Ntf_2]$			
CF_4	+16.24	-5.278×10^3	$+7.052 \times 10^5$	0.4

$$\ln(\rho_{[C_6C_1Im][Ntf_2]}/\text{kg m}^{-3}) = 7.43749 - 7.11481 \times 10^{-4}(T/K)$$

$$(6)$$

The precision of the low-pressure solubility of CF_4 in $[C_6C_1Im][Ntf_2]$ measured in this work, calculated as the average absolute deviation of the experimental data (or of the calculated Henry's law constants) from the appropriate smoothing function, is 0.4%, as indicated in Table 2. The comparison of our data to those recently published shows that, in the lower temperatures studied in this work, the Henry's law constants obtained by the two research teams agree to within a few percent, the present data showing a slightly different dependence with the temperature. The deviations found at 333 K between the two sets of

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TABLE 3: Experimental Values of the Solubility of Perfluoromethane in the Ionic Liquid [C_6C_1Im][Ntf_2] Expressed Both as Henry's Law Constants, K_H, and as Mole Fraction, x_2, Corrected for a Partial Pressure of Solute of 0.1 MPa[a]

T/K	$P/10^2$ Pa	$K_H/10^5$ Pa	$x_2/10^{-3}$	dev %
CF_4				
303.42	1146.54	665.69	1.50	+0.2
313.40	1184.57	721.00	1.39	−0.4
323.44	1222.83	783.18	1.28	−0.3
333.45	1260.93	849.06	1.18	+0.8
343.44	1299.08	946.33	1.06	−0.4

[a] p is the experimental equilibrium pressure, and the percent deviation, dev %, is relative to the correlations of the data reported in Table 3.
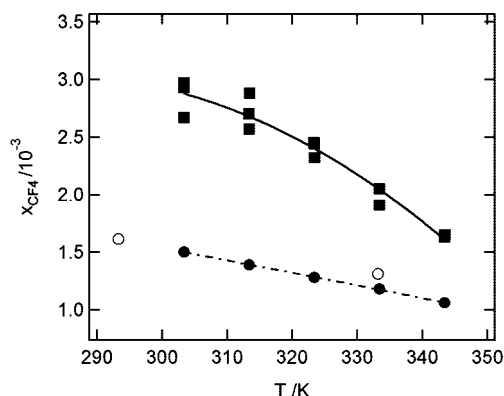

Figure 2. Mole fraction solubility of CF_4 in two ionic liquids based on the bis(trifluorosulfonyl)imide [Ntf_2] anion. ●, CF_4 in [C_6C_1Im][Ntf_2], this work; ○, CF_4 in [C_6C_1Im][Ntf_2], Kumelan et al. (ref 20); ■, CF_4 in [$P_{6,6,6,14}$][Ntf_2], this work. Lines represent the smoothed data.

data reach a higher value of 10%, the mole fraction solubility being higher in the work of Kumelan et al.[20]

These deviations are illustrated in Figure 2, where the mole fraction solubility of CF_4 in the two ionic liquids studied in this work is represented. It is observed that the solubility of the fluorinated gas is significantly higher in [$P_{6,6,6,14}$][Ntf_2] (ca. 2 times higher in mole fraction at the low-temperature end) than in the imidazolium-based ionic liquid. This difference is surprising at first sight, as it is expected that the fluorinated gas would present unfavorable interactions with the longer alkyl chains of the [$P_{6,6,6,14}$] cation, leading to a lower solubility in this ionic liquid.[39]

In order to get an insight on the molecular mechanisms controlling the gas solubilities, we have calculated the thermodynamic properties of solution. The variation with temperature of the solubility of the gases studied in the ionic liquids, expressed in Henry's law constant, is directly related to the thermodynamic properties of solvation which, as explained above, in the case of gaseous solutes at low pressures is practically identical to the thermodynamic properties of solution (the latter corresponding to an initial state of a pure substance at T and $p°$). The Gibbs energy of solvation is given by

$$\Delta_{solv}G^\infty = RT \ln(K_H/p^0) \quad (7)$$

where p^0 is the standard-state pressure. The partial molar differences in enthalpy and entropy between the ideal gas and solution states can be obtained by calculating the corresponding partial derivatives of the Gibbs energy with respect to temperature

TABLE 4: Thermodynamic Functions of Solvation for the Fluorinated Gases in the Studied Ionic Liquids at Several Discrete Temperatures between 303 and 343 K[a]

T/K	$\Delta_{solv}G^\infty$/kJ mol^{-1}	$\Delta_{solv}H^\infty$/kJ mol^{-1}	$\Delta_{solv}S^\infty$/J mol^{-1} K^{-1}
CF_4 in [$P_{6,6,6,14}$][Ntf_2]			
303	14.74	−2.90	−58.2
313	15.39	−7.24	−72.3
323	16.19	−12.1	−87.7
333	17.15	−17.6	−104
343	18.28	−23.6	−122
C_2F_6 in [$P_{6,6,6,14}$][Ntf_2]			
303	13.14	−7.43	−67.9
313	13.86	−10.1	−76.5
323	14.67	−13.0	−85.8
333	15.58	−16.3	−95.8
343	16.59	−19.9	−106
C_3F_8 in [$P_{6,6,6,14}$][Ntf_2]			
303	11.27	−6.19	−57.6
313	11.87	−8.27	−64.4
323	12.55	−10.6	−71.6
333	13.31	−13.1	−79.3
343	14.14	−15.9	−87.6
CF_4 in [C_6C_1Im][Ntf_2]			
303	16.38	−5.38	−71.8
313	17.11	−6.38	−75.1
323	17.88	−7.48	−78.5
333	18.68	−8.68	−82.2
343	19.52	−9.99	−86.0

[a] $\Delta_{solv}G^\infty$ is the Gibbs energy of solvation, $\Delta_{solv}H^\infty$ is the enthalpy of solvation, and $\Delta_{solv}S^\infty$ is the entropy of solvation. The values are consistent with $p^0 = 0.1$ MPa.

$$\Delta_{solv}H^\infty = -T^2 \partial/\partial T(\Delta_{solv}G^\infty/T) = -RT^2 \partial/\partial T[\ln(K_H/p^0)] \quad (8)$$

$$\Delta_{solv}S^\infty = (\Delta_{solv}H^\infty - \Delta_{solv}G^\infty)/T = -RT\partial/\partial T[\ln(K_H/p^0)] - R \ln(K_H/p^0) \quad (9)$$

The values for the Gibbs energy, enthalpy, and entropy of solvation are given in Table 4 for the three gases in the two ionic liquids, at discrete temperatures between 303 and 343 K, and are represented in Figure 3.

The thermodynamic properties of solvation provide valuable information both about the solute−solvent interactions and about the molecular structure of the solutions. The enthalpy of solution is closely related to the cross gas−ionic liquid molecular interactions, and the entropy of solvation gives indications about the structure of the solvent molecules surrounding the solute.[2,3] In the present case, the solubility of perfluoromethane is much higher in the phosphonium-based ionic liquid than in the imidazolium-based counterpart due to a favorable enthalpic term: the enthalpy of solvation is more negative for CF_4 in [$P_{6,6,6,14}$][Ntf_2] than for [C_6C_1Im][Ntf_2] and permits us to explain the larger solubility of the gas in the former ionic liquid, even if in the latter the entropy contributes more favorably to the Gibbs energy of solvation. This result confirms that dispersive-type intermolecular forces, often responsible for the properties of solutions involving fluorinated species,[40] determine the solubility of perfluoromethane in these ionic liquids. So, the larger the nonpolar domains in the ionic liquid,[41] the larger will be the solubility of nonpolar gases,[24,25,42] even of fluorinated nonpolar gases, although these last solutes probably interact less favorably than hydrocarbons with the alkyl chains constituting the ions of the ionic liquid. The values for the enthalpy and for
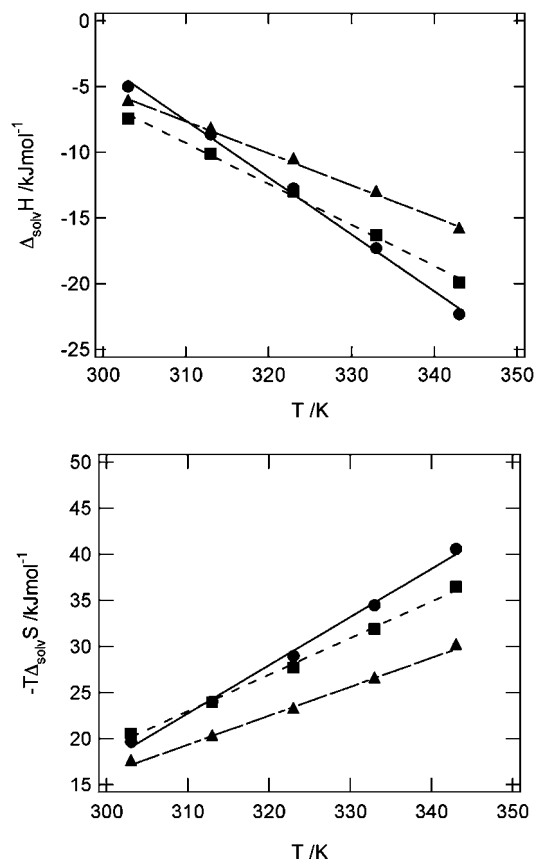
Figure 3. Enthalpy and entropy of solvation as a function of temperature of CF_4, C_2F_6, and C_3F_8 in $[P_{6,6,6,14}][Ntf_2]$: ●, CF_4; ■, C_2F_6; ▲, C_3F_8.
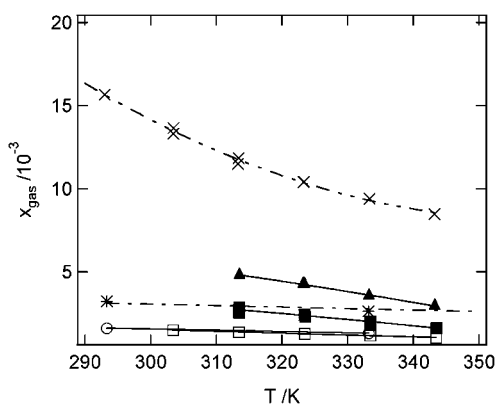
Figure 4. Mole fraction solubility of CF_4, C_2F_6, CH_4, and C_2H_6 in the ionic liquids $[C_6C_1Im][Ntf_2]$ and $[P_{6,6,6,14}][Ntf_2]$: ■, CF_4 in $[P_{6,6,6,14}][Ntf_2]$, this work; ▲, C_2F_6 in $[P_{6,6,6,14}][Ntf_2]$, this work; □, CF_4 in $[C_6C_1Im][Ntf_2]$, this work; ○, CF_4 in $[C_6C_1Im][Ntf_2]$, Kumelan et al. (ref 20); ∗, CH_4 in $[C_6C_1Im][Ntf_2]$, Kumelan et al. (ref 43); ×, C_2H_6 in $[C_6C_1Im][Ntf_2]$, Costa Gomes (ref 38). Solid lines are used for perfluorinated solutes and dashed lines for alkanes.

the entropy of solvation obtained in this work for CF_4 in $[C_6C_1Im][Ntf_2]$ at 298 K, −4.9 kJ mol^{-1} and −70.2 J mol^{-1} K^{-1}, respectively, agree with the ones reported by Kumelan et al.[20] ($\Delta_{solv}H^\infty$ = −4.5 kJ mol^{-1} and $\Delta_{solv}S^\infty$ = −68.8 J mol^{-1} K^{-1}, respectively).

In Figure 4 are represented the solubilities of low molecular weight alkanes and perfluoroalkanes in the imidazolium and in the phosphonium-based ionic liquids studied in this work. The values for the solubility of CF_4 in $[C_6C_1Im][Ntf_2]$[20] and for CH_4 in $[C_6C_1Im][Ntf_2]$[43] obtained by Kumelan et al. are also included. It is observed that the alkanes are more soluble than the

perfluoroalkanes in $[C_6C_1Im][Ntf_2]$ but the difference on the solubility of C_2H_6 and CH_4 is much larger than the difference of the solubility of CH_4 and CF_4. Perfluoromethane is significantly more soluble in $[P_{6,6,6,14}][Ntf_2]$ than in $[C_6C_1Im][Ntf_2]$. No data were found on the solubility of alkane gases in $[P_{6,6,6,14}][Ntf_2]$, but it is expected, by the analysis of the existing data on the solubility of liquid alkanes[44,45] and fluorinated alkanes[13,14] in phosphonium-based ionic liquids, that these gases will also be more soluble in the phosphonium-based ionic liquid.

The variation of the solubility with the molecular size of the fluorinated gases in $[P_{6,6,6,14}][Ntf_2]$, cannot be explained by the differences found in the enthalpic contributions to the Gibbs energy of solvation. In fact, the enthalpy of solvation is very similar for the three gases studied, being more negative for CF_4 and C_2F_6 (the average value in the temperature range studied is −13.2 and −13.3 kJ mol^{-1}, respectively) than for C_3F_8 (average value of −10.8 kJ mol^{-1}) although the solubility follows the inverse order. It is in fact the less negative entropy of solvation for C_3F_8 (−72 J mol^{-1} K^{-1}) than for C_2F_6 (−86 J mol^{-1} K^{-1}) or CF_4 (−90 J mol^{-1} K^{-1}) that explains that the solubility in $[P_{6,6,6,14}][Ntf_2]$ increases with the size of the fluorinated solute.

Molecular simulations were used to interpret, at the microscopic level, these surprising results. The solute−solvent site−site radial distribution functions (RDFs) obtained by molecular simulation are represented in Figure 5 and give a first clue concerning the unexpected behavior of the ionic liquid solutions. The RDFs clearly show that the locations of the CF_4 and C_3F_8 solutes in the ionic liquid solvent are very different: the small CF_4 molecules are able to be much closer to the phosphorus atom of the cation or the oxygen atoms of the anion than the C_3F_8 molecule. Thus, the smaller solutes are found over a larger volume of the solvent. This is probably due to the highly stereochemically constrained environment around the phosphorus atoms of the tetraalkylphosphonium cations, not only due to the four alkyl chains meeting at the central P atom, but also due to the presence of the $[Ntf_2]$ anion that will always tend to occupy a position near the region of the tetraalkylphosphonium cation where charge density is highest.

The present ionic liquid can be considered, as in the case of imidazolium-based ionic liquids,[41] as a nanoseggregated liquid where there coexist nonpolar regions—mainly composed of the alkyl chains of the cation plus the perfluoromethyl groups of the anion—dominated by dispersive intermolecular interactions and others where the charges of the cation and of the anion that constitute the ionic liquid interact by electrostatics—mainly the phosphorus plus the central part of the anion. If this nanoseggregated nature of the ionic liquid is also taken into account (as shown in Figure 6), it can be assumed that different solutes can be solvated in different regions of the same ionic liquid and so be exposed to completely different molecular environments.[33] In the present case, the C_3F_8 molecules will be restricted to the nonpolar, aliphatic regions of the ionic liquid, whereas the CF_4 molecules will also be found near the polar, high-charged density regions. This means that the enthalpy and entropy contribution to the solvation energy will be extremely difficult to compare—as if the two solutes were being dissolved in two different solvents—and explains the different slopes of the $\Delta_{solv}H(T)$ and $\Delta_{solv}S(T)$ functions obtained here for CF_4 and C_3F_8.

This point can be further discussed if the intensity of the solute−solvent interactions is taken into account. These interactions can be estimated by calculating the difference, for each molecular dynamics configuration, between the total configurational energy of the system (solvent + solute) and the sum of
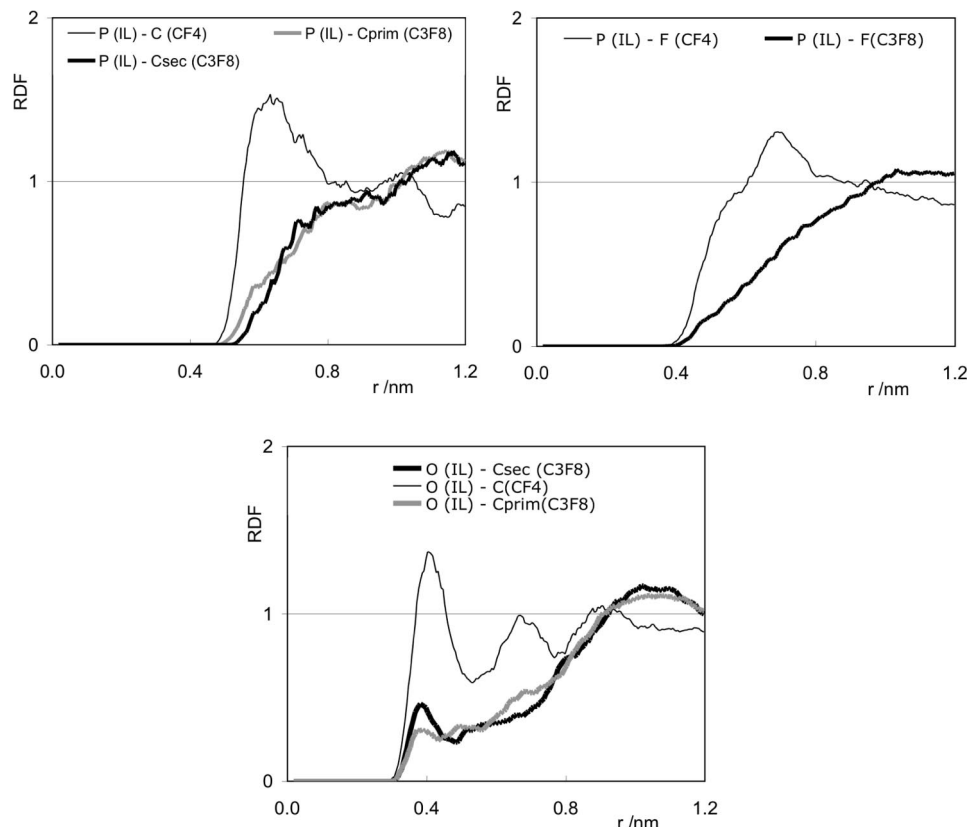
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Figure 5. Solvent−solute site−site radial distribution functions, RDF, as a function of the distance between sites, r, for solutions CF_4 (light lines) and C_3F_8 (bold lines) in $[P_{6,6,6,14}][Ntf_2]$.

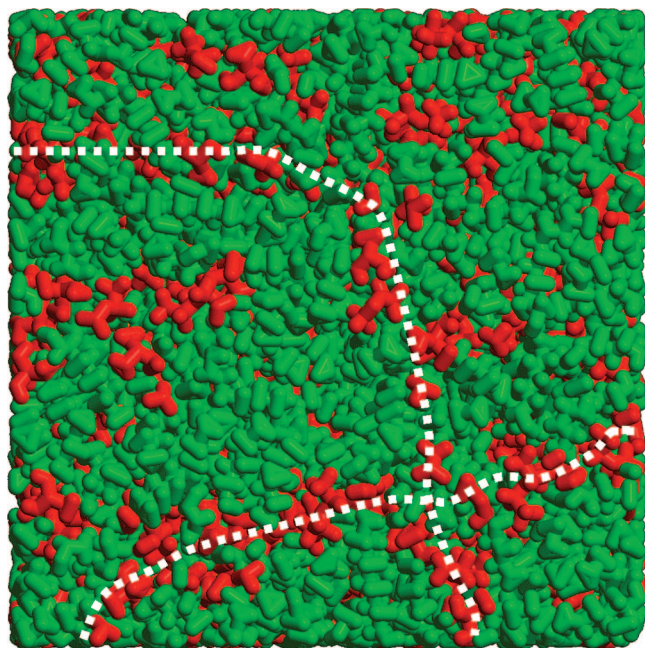**Figure 6.** Snapshot of an equilibrated simulation box of (pure) $[P_{6,6,6,14}][Ntf_2]$. The color codes of the atoms emphasize the nanosegregated nature of the ionic liquid, with the polar network shown in red and the nonpolar domains in green. In this case the volume occupied by the latter regions is much larger than that of the polar domains, which means that the polar network will exhibit a threadlike (albeit continuous) structure, exemplified by the dotted white lines.

the total configurational energies of systems where the solute and solvent molecules were removed in turn, leaving the remaining molecules in the same positions:

$$E_{conf}(\text{solute−IL interactions}) = E_{conf}(\text{solute} + \text{IL}) -$$
$$(E_{conf}(\text{IL} + \text{cavities}) + E_{conf}(\text{solute}))(10)$$

If this calculation is repeated for all configurations obtained during one production run, values of $E_{conf}(CF_4\text{−IL interactions})$ $= -26 \pm 1$ kJ mol^{-1} and $E_{conf}(C_3F_8\text{−IL interactions}) = -48$ ± 2 kJ mol^{-1} are obtained. Both quantities refer to molar quantities of solute and show (as expected) that the interactions of the ionic liquid with C_3F_8 are more intense than those with CF_4. It is important to note that these values can be compared to the cohesive energies of the solvent or of the pure solutes but are heavily dependent on the molecular model used during the simulations (including the combining rules to obtain the solute−solvent cross interactions) and should be analyzed more as relative quantities (the interactions are more intense in C_3F_8−IL than in CF_4−IL) than in absolute terms. The calculations have also shown that van der Waals dispersion forces account for most of the interactions present in both cases: in spite of CF_4 being closer to the charged parts of the ionic liquid, the neat contribution of the electrostatic forces for the solute−solvent interactions is almost null, revealing a possible cancelation of effects.

At a first glance these results seem to be perfectly obvious and consistent with the experimental solubility data: C_3F_8 interacts more with the solvent and consequently has a larger solubility. The thermodynamic quantities derived from the same experimental data and depicted in Figure 3 seem, however, to point to different solvation mechanisms. The difference between the solvation enthalpies of CF_4 and C_3F_8 is small, and the sign of that difference even changes when temperature is varied. At this point, all these facts can be brought into (qualitative) agreement if it is considered that the solvation enthalpy must be regarded as the sum of the energy involved during the

formation of solute−solvent interactions plus the energy concerning the solvent−solvent interactions that are broken or rearranged during the solvation process—the energy required for cavity formation. This last process is endothermic, is larger for C_3F_8 than for CF_4 (larger cavities in the former case), and will cancel partially the difference found for the solute−solvent interactions. Moreover, the different trends with temperature can also be justified by the formation of cavities of different size in different environments of the ionic liquid.

It should be noted that, as the fluorinated solutes become larger (and thus liquid at normal atmospheric conditions), their solubility in room temperature liquid salts tend to decrease as the perfluoroalkyl chain increases. This has been observed for the series $C_6−C_8$ perfluoroalkanes in $[P_{6,6,6,14}][Ntf_2]$[14] and is in agreement with the behavior observed in (alkane + perfluoroalkane) liquid systems. For instance, while the liquid−liquid critical temperature, T_c, of demixing in $C_6H_{14} + C_6F_{14}$ is $T_c \approx$ 295 K, it increases to $T_c \approx 310$ K for $C_6H_{14} + C_8F_{18}$.[7,8] Similarly, the solubility of $C_6−C_9$ perfluoroalkanes in a perfluoroalkylalkane-1-ol compound[46] markedly decreases with the increase of the number of carbon atoms.

The distinct trend presented by the solubility of gases as compared to that of the liquid state counterpart has a twofold origin: (i) the enthalpy of vaporization has to be taken into account if one wished to reach results' transferability as far as the magnitude and sign of interactions are concerned[2,3] and (ii) steric effects related to the small size of the solute are no longer to be equated for (larger molecule) solute liquids.

4. Conclusions

It has been shown in this work that the intrinsic complexity of ionic liquids—their nature as nanosegregated fluids—must always be taken into account when dealing with apparently simple processes like their ability to dissolve different gases, even when these are similar in molecular terms. If it is proven that the different solutes tend to be solvated in different regions of the ionic liquid, as in the present case, then it should always be kept in mind that in fact we will be dealing not only with different solutes but also with (pseudo) different solvents (corresponding to the different domains of the ionic liquid structure).

The new data obtained in this work contribute to the study of the properties of ionic liquids as solvents for fluorinated molecules. Not only the solubility of perfluorinated alkanes was obtained for the first time in phosphonium-based ionic liquids, but also the molecular mechanism of solvation was understood by complementing the experimental data with molecular simulation calculations.

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