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Solubility of carbon dioxide, ethane, methane, oxygen, nitrogen, hydrogen, argon, and carbon monoxide in 1-butyl-3-methylimidazolium tetrafluoroborate between temperatures 283 K and 343 K and at pressures close to atmospheric

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Abstract

Experimental values for the solubility of carbon dioxide, ethane, methane, oxygen, nitrogen, hydrogen, argon and carbon monoxide in 1-butyl-3-methylimidazolium tetrafluoroborate, [bmim][BF₄] – a room temperature ionic liquid – are reported as a function of temperature between 283 K and 343 K and at pressures close to atmospheric. Carbon dioxide is the most soluble gas with mole fraction solubilities of the order of 10^{−2}. Ethane and methane are one order of magnitude more soluble than the other five gases that have mole fraction solubilities of the order of 10^{−4}. Hydrogen is the less soluble of the gaseous solutes studied. From the variation of solubility, expressed as Henry's law constants, with temperature, the partial molar thermodynamic functions of solvation such as the standard Gibbs energy, the enthalpy, and the entropy are calculated. The precision of the experimental data, considered as the average absolute deviation of the Henry's law constants from appropriate smoothing equations is of 1%.

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1. Introduction

The main objective of this work is to investigate the interactions between room temperature ionic liquids and a variety of small gaseous molecules. In the current paper we present the study of the solubility of eight different gases in one ionic liquid as a function of temperature and at pressures close to atmospheric. Low pressure gas solubilities can constitute an important source of information about the molecular mechanisms involved in dissolution processes as they are directly related to the thermodynamic properties of solution. The knowledge

of the solubility of gases in ionic liquids is also of practical interest as it is useful in the calculation of (vapour + liquid) equilibria in systems of potential technological interest namely in solvents for reaction systems or for the development of new separation processes.

The room temperature ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate, [bmim][BF₄], was selected for this study. Imidazolium based ionic liquids are amongst the most widely used at present as they seem to be promising solvents for technological applications exhibiting properties that enable their use as reaction media. Although [bmim][BF₄] is commercially available at reasonable prices with a low level of impurities, there is still a lack of solubility data on this particular ionic liquid. Most of the studies described in the literature concerning the solubility of gases in ionic

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liquids are dedicated to systems involving carbon dioxide as solute. This can be explained first by its practical interest especially in separations processes [1]. Furthermore, as it is highly soluble in most room temperature ionic liquids (typical values of the Henry's law constant below 10 MPa) [2], its solubility is relatively easy to measure with a good precision using common experimental techniques.

Our research group has previously studied the solubility of carbon dioxide, oxygen [3] and argon [20] as a function of temperature in [bmim][BF₄]. Carbon dioxide was found to be much more soluble in the ionic liquid than the other two gases for temperatures ranging from $T = 303$ K to $T = 343$ K. The reported solubility decreases with temperature in the former case and increases in the latter. The experimental technique previously used is essentially the same as the one reported here but significant improvements were made both in the experimental apparatus and in the procedure followed so it was chosen to study again the solubility of these gases in addition to other five gaseous solutes measured for the first time in the present work.

Cadena *et al.* [2] have determined the solubility of carbon dioxide in [bmim][BF₄] at three temperatures between $T = 283$ K and $T = 323$ K using a gravimetric microbalance for measurements at pressures up to 1.4 MPa. The Henry's law constants calculated from these measurements increase with temperature (exothermic solvation) and vary from 4.08 MPa to 8.89 MPa. These values agree with our previous measurements at $T = 298$ K, to within the mutual uncertainties, but a significant difference is found at the higher temperature end. These results have been recently recalculated by the same authors and the new Henry's law constant values also increase with temperature varying now from 4.18 MPa to 8.86 MPa. These new values are reported by Anthony *et al.* [5] together with original data on the solubility of gases in several ionic liquids that also include the study of carbon monoxide in [bmim][BF₄] for which the concentration in solution was non detectable. The same research group has studied several systems involving gases and ionic liquids at pressures not far from atmospheric but also at higher pressures using a stoichiometric phase equilibrium apparatus. For example, nine different gases were studied in 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF₆], at low pressures as a function of temperature [5], and it was observed that carbon dioxide is much more soluble than the other gases, closely followed by ethane and ethylene. Carbon monoxide, hydrogen and nitrogen were observed to be much less soluble and were not detected by the experimental technique used. The same authors found that gas solubilities decrease as a function of temperature except in the case of oxygen and argon for which an endothermic solubilization was observed (the solubility increases with temperature). Other studies

by the same authors were devoted to the influence of the nature of the ionic liquid on the solubility of carbon dioxide both experimentally [2,6,7] and by molecular simulation [2]. The two approaches seem to indicate that it is the anion that has the greatest impact on the solubility of the carbon dioxide.

In connection with the study of catalytic hydrogenation in ionic liquid-phase, Berger *et al.* [8] have reported the solubility of hydrogen in [bmim][BF₄] (and in [bmim][PF₆]). Their experimental method was based on the measurement of a pressure drop (at total pressures below 5 MPa), at constant temperature and constant volume. It was found that hydrogen was significantly more soluble in [bmim][BF₄] (Henry's law coefficient of 180 MPa at room temperature) than in [bmim][PF₆]. A much higher value of 580 MPa for the Henry's law constant (corresponding to a lower solubility) was found by Dyson *et al.* [9] using high-pressure ¹H NMR spectroscopy. The same authors used ¹³C high pressure NMR to determine the solubility of carbon monoxide in a series of different ionic liquids including [bmim][BF₄] and [bmim][PF₆] finding values of 337 MPa and 327 MPa for the Henry's law constant at 295 K, respectively [10]. The last value is much higher than the experimental value of 197 MPa at 293 K published by Kumelan *et al.* [11] for the solubility of carbon monoxide in [bmim][PF₆] which should not be significantly different from that in [bmim][BF₄].

Kroon *et al.* [12] have published the high-pressure phase behaviour (pressure above $p = 0.6$ MPa) of the binary system (carbon dioxide + [bmim][BF₄]) between $T = 278$ K and $T = 368$ K using a synthetic method. The Henry's law constants obtained by extrapolation of the experimental results on bubble-point pressures increase with temperature (the solubility decreases) and vary between $K_H = 6.5$ MPa at $T = 323.2$ K and $K_H = 10.4$ MPa at $T = 333.2$ K. These results are in agreement with the ones published by other authors in references [2] and [4] (a value of $K_H = 90.1$ MPa at $T = 323.2$ K was found by extrapolation of the data of [12] and $K_H = 88.9$ MPa, 1.3% lower, and $K_H = 88.6$ MPa, 1.7% lower, are reported in references [2] and [4], respectively).

The solvation of small molecules in ionic liquids has also been studied by molecular simulation [2,13–16] but the particular case of the interactions between gaseous solutes and the ionic liquid [bmim][BF₄] has only been addressed by our research group [15,16]. The molecular simulations reproduce the order of magnitude of the experimental data and give the correct relative solubility for carbon dioxide and oxygen. The temperature dependence of the solubility of oxygen and argon obtained by simulation is, however, opposite to the published experimental trends: the simulated mole fractions always decrease with temperature [16] whereas the experimental solubility of oxygen [3] and argon [20]

increases with temperature. Molecular simulations further indicate that the solubility of gases in [bmim][BF₄] should be lower than in, for example, [bmim][PF₆]. This observation is difficult to confirm experimentally as although it seems in accord with some experimental solubility evidence [17,18], other studies pointing to similar solubilities in both ionic liquids [3,5,19].

In this paper, experimental solubilities of eight gases in one ionic liquid [bmim][BF₄] were measured as a function of temperature from $T = 283$ K to $T = 343$ K near 1 bar using a high precision isochoric saturation method [3,20]. From the solubility data, the Henry's law constants were calculated and directly related to the Gibbs energy of solvation corresponding to the change in partial molar Gibbs energy when the solute is transferred at constant temperature from the pure perfect gas at standard pressure to the infinitely dilute state in the solvent. From the variation of the solubility with temperature, the standard enthalpy and entropy of solvation were also calculated.

The drive for studying the eight gaseous solutes chosen was threefold. First, we have decided to confirm the data previously obtained for carbon dioxide and oxygen (and the preliminary values for argon) as some differences (larger than the overall experimental uncertainties) were found between our previous results and those from other research groups. Second, the gases chosen are frequently used in mixtures of industrial importance as it is the case of carbon dioxide, carbon monoxide, oxygen, hydrogen, methane and ethane. Third, we have tried to cover different families of gases that could illustrate several solute effects on the solubility like the size of the molecule (ethane *versus* methane) or its polarity (nitrogen, carbon dioxide, carbon monoxide).

2. Experimental

2.1. Method

The experimental apparatus used during the gas solubility measurements reported here is based on an isochoric saturation technique and has been described briefly in previous publications [3,20]. A significant number of important modifications were introduced both in the apparatus and in the experimental technique. These alterations have improved considerably both the precision and the accuracy of the data obtained and for that reason, it was found useful to include here a detailed description of the experimental procedure followed during these experiments.

In the saturation technique at constant volume, 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 experimental apparatus used is schematically represented in figure 1. The equilibrium cell EC, together with the precision manometer M and the glass bulbs limited by valves V2 and V3, constitute the equilibrium section of the apparatus. The simple design of the equilibrium cell is very appropriate for the study of relatively viscous liquid solvents like the ionic liquid measured in this work. It permits to handle volumes of liquid solvent varying from (2 to 6) mL and an appropriate gas/liquid contact is guaranteed by means of good agitation using a glass coated magnetic bar. The whole equilibrium section is maintained inside a 45 L water bath at constant temperature to within ± 0.01 K using a PID temperature controller and accurately measured with a calibrated 100 Ω platinum resistance thermometer from Hart Scientific (Secondary Reference Temperature Standard, model 5612, accuracy of ± 0.018 °C at 0 °C).

The solubility measurement starts with the introduction of a known quantity of gas solute in one or both of the calibrated glass bulbs limited by valves V2 and V3. The exact amount of gas is determined by measuring its pressure in the manometer M (Druck RPT 2005, (10 to 1800) mbar, precision of 0.01% full scale) at constant temperature, correcting for gas imperfections. The exact volume of both bulbs, which is significantly different

FIGURE 1. Solubility apparatus used in this work: VP vacuum pump; TP, cold trap; VG, vacuum gauge; M, precision manometer; TB, thermostated liquid bath; EC, equilibrium cell; V1, V2, V3, constant volume glass valves; C1, C2, vacuum O-ring connections.

($VGB_{V2} = (64.10 \pm 0.02) \text{ cm}^3$ and $VGB_{V3} = (15.54 \pm 0.02) \text{ cm}^3$ at 342.65 K), was previously calibrated with a precision better than $\pm 0.1\%$ at two different temperatures in order to appropriately take into account for the corrections due to thermal expansion (the value for the gas bulbs thermal expansion coefficient determined experimentally equals those of Pyrex glass found in the literature [27]: $\alpha = 2.76 \times 10^{-5}$). The gas is isolated from the rest of the installation by closing the glass valves V2 and V3.

The ionic liquid is then introduced in the equilibrium cell through connection C2 by means of a syringe. The mass of ionic liquid introduced, which varies from (4 to 5) g in the present case, is determined gravimetrically with a precision of 1×10^{-4} g. The ionic liquid is degassed and dried by keeping it under vacuum (approximately 1 Pa) for 8 h to 15 h at a temperature above 303 K.

The equilibrium process starts by bringing into contact the solute and the solvent by closing valve V1 and opening valve V2 or V3 (constant volume valves). The total volume of the equilibrium section was previously calibrated by gas expansions from the gas bulbs at different temperatures in order to appropriately take into account the thermal expansion corrections ($V_{\text{tot}} = (107.9 \pm 0.2) \text{ cm}^3$ at $T = 323.22 \text{ K}$ with a thermal expansion coefficient $\alpha = 1.05 \times 10^{-4}$ and $V_{\text{tot}} = (156.0 \pm 0.2) \text{ cm}^3$ at $T = 303.89 \text{ K}$ with $\alpha = 1.39 \times 10^{-4}$ in the two cells used during these measurements). The pressure and temperature during the equilibration process are recorded in a computer until constant values are reached which means that thermodynamic equilibrium is attained.

The determination of the solubility at different temperatures is simply done by changing the liquid thermostat set point and waiting for a new thermodynamic equilibrium at a different temperature. With a single loading it is thus possible to make measurements over a large temperature range, $T = 283 \text{ K}$ to $T = 343 \text{ K}$ in this study. For each system, several runs were performed: first using the same ionic liquid sample and the two gas samples contained in the bulbs limited by V2 and V3 (by degassing the ionic liquid before opening each one of the valves) and then using both a fresh sample of ionic liquid and of gaseous solute.

2.2. Materials

The gases used have the following specifications: carbon dioxide from AGA/Linde Gaz, mole fraction purity of 0.99995; ethane from AGA/Linde Gaz, mole fraction purity of 0.995; methane from AGA/Linde Gaz, mole fraction purity of 0.99995; oxygen from AGA/Linde Gaz, mole fraction purity of 0.99999; nitrogen from SAGA, mole fraction purity 0.9998; hydrogen from AGA/Linde Gaz, mole fraction purity of 0.999997; argon from AGA/Linde Gaz, mole fraction purity of 0.999997; and carbon monoxide from AGA/Linde

Gaz, mole fraction purity of 0.99997. All gases were used as received from the manufacturer.

The sample of 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF₄] used was purchased from Sigma–Aldrich with a minimum stated mole fraction purity of 0.97. Before using it for the gas solubility measurements, the chloride and water contents were carefully determined as these impurities seem to influence significantly the thermodynamic and thermophysical properties of the ionic liquid [21].

The chloride content was measured using two different techniques: the Mohr method [22] and ionic chromatography [23]. In both cases a similar chloride content was found: 100 ppm using Mohr's method and 165 ppm by ion chromatography. The chloride content can significantly change for different samples of the same ionic liquid. The sample of [bmim][BF₄] used in the previous measurements [3] was also analysed by ion chromatography and a chloride content of less than 5 ppm was found. This observation proves that the two samples of ionic liquid were probably synthesized and purified using different paths.

The water content of the ionic liquid was determined before and after the solubility measurements by Karl–Fisher titration (Volumetric titrator from Mettler Toledo DL31). A reference value of 690 ppm was found after drying the liquid for 15 h at $T = 343 \text{ K}$ under vacuum. Several tests were done to check the time and the conditions for drying and degassing the ionic liquid sample – it is considered that, in the case of [bmim][BF₄] the liquid is appropriately degassed and dried after pumping it under a pressure of 1 Pa for 8 h at a temperature between $T = 303 \text{ K}$ and $T = 343 \text{ K}$.

2.3. Data reduction

The method of data reduction was reported in previous publications [3,20]. The solubility of the gaseous solute in the ionic liquid can be expressed in mole fraction which is calculated from

$$x_2 = n_2^{\text{liq}} / (n_1^{\text{liq}} + n_2^{\text{liq}}), \quad (1)$$

where n_2^{liq} is the amount of solute dissolved in the ionic liquid and $n_1^{\text{liq}} = n_1^{\text{tot}}$ is the total amount of ionic liquid.

The quantity of solute in the liquid solution is determined by the difference between two pVT measurements: first when the gas is initially introduced in the equilibrium cell and second after thermodynamic equilibrium is reached

$$n_2^{\text{liq}} = p_{\text{ini}} V_{\text{GB}} / [Z_2(p_{\text{ini}}, T_{\text{ini}}) RT_{\text{ini}}] - p_{\text{eq}} (V_{\text{tot}} - V_{\text{liq}}) / [Z_2(p_{\text{eq}}, T_{\text{eq}}) RT_{\text{eq}}], \quad (2)$$

where V_{GB} is the volume of the bulb initially filled with the gaseous solute at temperature T_{ini} , V_{tot} is the total volume of the equilibrium cell (calibrated by gas

expansions) and V_{liq} the volume occupied by the liquid solution at the equilibrium temperature T_{eq} . This volume can be measured accurately enough in the present experimental arrangement (by a gas expansion followed by a pVT measurement after equilibrium) but in the present case it was obtained by considering the density of the solution as equal to that of the pure solvent. p_{ini} is the initial pressure of gaseous solute present in the gas bulb and p_{eq} the equilibrium pressure. Z_2 is the compression factor for the pure gas.

Henry's law constants, considered in the present case as independent of pressure, can be calculated from the mole fraction solubilities given by equation (1) above as

$$K_{\text{H}} = \lim_{x_2 \rightarrow 0} f_2(p, T, x_2)/x_2 \cong \phi_2(p_{\text{eq}}, T_{\text{eq}})p_{\text{eq}}/x_2, \quad (3)$$

where f_2 is the fugacity of the solute and ϕ_2 its fugacity coefficient calculated in the usual way. In the present case, the fugacity coefficient was considered as unity as it does not affect significantly the solubility data.

The Henry's law constants can be exactly converted to the Gibbs energy of solvation, corresponding to the change in partial molar Gibbs energy when the solute is transferred, at constant temperature, from the pure perfect gas state at the standard pressure to the infinitely dilute state of the solute in the solvent

$$\Delta_{\text{sol}}G^\infty = RT \ln(K_{\text{H}}/p^\circ), \quad (4)$$

where p° is the standard state pressure. For the case of gaseous solutes at low pressure this free energy of solvation can be regarded as a good approximation for the Gibbs energy of solution.

The partial molar differences in enthalpy and entropy between the two states can be obtained by calculating the corresponding partial derivatives of the Gibbs energy with respect to temperature

$$\Delta_{\text{sol}}H^\infty = -T^2 \partial/\partial T (\Delta_{\text{sol}}G^\infty/T) = -RT^2 \partial/\partial T [\ln(K_{\text{H}}/p^\circ)], \quad (5)$$

$$\Delta_{\text{sol}}S^\infty = (\Delta_{\text{sol}}H^\infty - \Delta_{\text{sol}}G^\infty)/T = -RT \partial/\partial T [\ln(K_{\text{H}}/p^\circ)] - R \ln(K_{\text{H}}/p^\circ). \quad (6)$$

3. Results and discussion

For each gaseous solute studied, multiple experimental data points were obtained in the temperature interval between $T = 283$ K and $T = 343$ K in steps of approximately 10 K. The experimental solubilities of carbon dioxide, ethane, methane, oxygen, nitrogen, hydrogen, argon, and carbon monoxide in [bmim][BF₄] are reported in table 1. The solubility results are given in terms of mole fractions of solute and Henry's law constants. The relative atomic masses were taken from the IUPAC tables [24]. The values of the second virial coefficients for all the gases were taken from the compilation

of Dymond and Smith [25]. The density of the sample of [bmim][BF₄] was measured in our laboratory using an Anton Paar densitometer (model DMA 512 P), with a precision of 0.01%, before and after the solubility measurements and were adjusted to the function [26]

$$\rho_{[\text{bmim}][\text{BF}_4]}/\text{kg m}^{-3} = 1218.53 - 7116.23 \times 10^{-4} \{(T/\text{K}) - 273\}. \quad (7)$$

No remarkable differences were found in the density of the liquid solvent before and after the solubility measurements. The density of the ionic liquid was also measured at $T = 303$ K and $T = 313$ K using a 3 mL pycnometer calibrated with high purity degassed water. The largest deviations between the two sets of data were found at 313 K and amounted to 0.16%. In light of these observations, we consider that the densities of [bmim][BF₄] described by equation (7) are accurate to within 0.2%.

To get representative values of the solubility, the raw experimental data were correlated as a function of temperature by an empirical equation of the type

$$\ln\{K_{\text{H}}(T)/10^5 \text{ Pa}\} = \sum_{i=0}^n A_i (T/\text{K})^{-i}. \quad (8)$$

The coefficients A_i obtained in the fit are listed in table 2 together with the average absolute deviations obtained for each solute. These values can be regarded as an estimation of the precision of the experimental data which is in the present case less than 1% (except for the case of methane as a solute for which a value of 1.5% was found).

In figure 2 are represented the solubility data, expressed in mole fraction corrected for a 0.1 MPa partial pressure of solute, for the gases in the ionic liquid as a function of temperature. As it can be observed in the upper plot, carbon dioxide is the most soluble gas (almost one order of magnitude) followed by ethane, and the six other gases. In the lower plot of figure 2 are represented the data for the less soluble gases. It can be seen that the variation of the solubility with temperature is not similar for all the solutes. A larger variation is observed for methane, similar behaviours are found for hydrogen, nitrogen and argon with almost parallel curves depicted in the lower plot of figure 2. The solubility of oxygen and carbon monoxide is practically constant in the temperature range covered. The absolute values of the mole fraction are very similar in the six gases, methane being slightly more soluble in the lower temperature end and hydrogen being the less soluble gas.

The solubility of gases in [bmim][BF₄] has been studied by different research groups. Besides our previous results on the solubility of carbon dioxide and oxygen [3], three other sets of experimental data concerning the solubility of carbon dioxide contain a sufficient number of values to allow for a reliable comparison [2,4,12].

TABLE 1

Experimental values of gas solubilities in bmimBF₄ 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, p is the experimental equilibrium pressure and deviations are relative to the correlation of the data reported in table 2

T/K	$p/10^2$ Pa	$K_H/10^5$ Pa	$x_2/10^{-4}$	$10^2(K_H^{\text{exp}} - K_H^{\text{exp}})/K_H^{\text{exp}}$
CO₂				
303.38	777.97	61.60	162.3	+0.5
303.90	765.76	62.50	160.0	+0.0
303.93	215.88	62.86	159.1	−0.5
313.99	797.91	75.06	133.2	+0.4
323.19	846.66	88.78	112.6	−0.2
324.06	860.92	90.56	110.4	−0.7
324.18	824.70	90.58	110.4	−0.5
334.15	890.28	104.8	95.46	+1.5
342.96	910.46	122.4	81.73	−0.1
343.83	263.87	125.8	79.48	−1.5
344.27	920.00	123.4	81.01	+1.0
C₂H₆				
283.02	793.44	257.6	38.83	+0.1
292.98	821.84	286.0	34.97	−0.5
303.40	798.23	318.1	31.44	+0.0
303.43	423.57	316.7	31.57	+0.5
313.28	879.51	354.2	28.23	+0.4
315.76	831.30	366.2	27.31	−0.1
323.22	851.22	399.0	25.06	+0.0
323.26	452.02	398.4	25.10	+0.1
333.08	935.88	449.4	22.25	−0.3
333.14	877.74	451.9	22.13	−0.8
343.07	904.02	505.0	19.80	+0.0
343.22	480.32	502.6	19.90	+0.6
CH₄				
283.05	818.37	794.1	12.59	+1.4
292.95	846.06	842.8	11.87	+0.4
303.38	465.28	972.9	10.28	−2.5
303.38	875.48	946.1	10.57	+0.3
303.40	865.18	976.0	10.25	−2.8
313.27	479.89	1117	8.955	−0.7
313.29	892.81	1110	9.012	−0.1
323.19	494.57	1315	7.607	+2.3
323.20	920.57	1311	7.628	+2.5
333.06	959.60	1667	6.000	+0.6
333.15	509.48	1643	6.085	+2.3
343.04	976.49	2216	4.513	−3.1
343.09	524.35	2160	4.630	−0.4
O₂				
283.25	765.38	1505	6.644	+0.3
293.18	791.18	1552	6.445	+0.3
303.40	817.71	1621	6.170	−0.8
303.40	440.13	1604	6.234	+0.2
303.40	823.04	1623	6.161	−0.9
313.32	848.76	1651	6.056	+0.5
313.32	453.29	1659	6.028	+0.0
323.16	466.32	1726	5.794	−0.8
323.23	868.93	1712	5.842	+0.1
323.24	874.50	1712	5.842	+0.1
333.15	900.10	1737	5.757	+1.8
333.28	479.58	1758	5.689	+0.6
343.10	925.84	1824	5.483	+0.1
343.30	492.74	1854	5.394	−1.5
N₂				
283.20	810.39	1578	6.338	−0.2
293.21	837.99	1646	6.076	+0.1

(continued on next page)

TABLE 1 (continued)

T/K	$p/10^2 \text{ Pa}$	$K_{\text{H}}/10^5 \text{ Pa}$	$x_2/10^{-4}$	$10^2(K_{\text{H}}^{\text{exp}} - K_{\text{H}}^{\text{exp}})/K_{\text{H}}^{\text{exp}}$
303.38	866.11	1789	5.590	−0.2
303.38	454.34	1773	5.639	+0.7
303.40	842.69	1788	5.592	−0.1
313.27	468.19	1980	5.052	+0.4
313.31	869.32	2001	4.998	−0.6
323.24	482.11	2242	4.460	+0.9
323.25	895.99	2277	4.393	−0.6
333.21	496.04	2610	3.831	+0.5
333.28	922.91	2664	3.754	−1.4
343.14	509.83	3064	3.264	+0.6
H_2				
278.20	766.95	1990	5.026	+0.1
283.29	780.36	1941	5.152	+0.3
285.25	785.52	1940	5.156	+0.1
288.30	793.57	1939	5.158	+0.2
290.37	799.02	1947	5.136	+0.2
293.36	806.92	1974	5.065	−0.2
298.34	820.10	2036	4.911	−0.3
303.33	433.57	2144	4.664	−1.0
303.41	802.30	2143	4.666	−0.9
313.25	859.61	2391	4.183	+0.4
313.30	827.57	2413	4.144	−0.5
323.22	460.10	2802	3.569	+0.9
323.24	852.90	2780	3.598	+1.7
333.17	878.29	3437	2.910	+0.1
343.06	486.58	4318	2.316	−0.6
343.11	903.62	4318	2.316	−0.5
Ar				
283.01	803.86	1341	7.455	−0.3
293.47	846.91	1402	7.131	+0.1
303.37	859.58	1515	6.602	+0.7
313.29	886.81	1698	5.890	+0.5
323.17	913.97	1983	5.042	−1.5
323.33	930.37	1962	5.097	−0.2
333.11	941.16	2269	4.408	+0.5
342.96	968.08	2679	3.732	+0.6
343.02	985.32	2707	3.694	−0.3
CO				
283.18	798.86	1717	5.825	+0.1
293.16	825.82	1726	5.825	−0.1
303.39	802.03	1742	5.740	−0.5
303.39	853.42	1734	5.740	+0.0
313.27	879.97	1742	5.768	+0.0
313.28	826.96	1724	5.740	+1.0
323.20	852.03	1765	5.800	−0.7
333.09	876.86	1758	5.665	+0.3
343.04	901.82	1775	5.687	−0.1

As it is shown in figure 3, the present results agree, to within 1%, with the data reported by Cadena *et al.* [2], their agreement being slightly worse with the data of Anthony *et al.* [4] (our Henry's law constants extrapolated at 298 K, $K_{\text{H}} = 55.9 \text{ MPa}$, are 5.5% lower than $K_{\text{H}} = 59.0 \text{ MPa}$ [4] and only 1.1% lower than $K_{\text{H}} = 56.5 \text{ MPa}$ [2]). The results of Kroon *et al.* [12] are also represented in figure 3. A pressure extrapolation is necessary in this case to calculate the Henry's law constants but even so the agreement with the present

values, systematically lower, is satisfactory. The largest discrepancy is found at $T = 303.2 \text{ K}$ between the present value for the Henry's law constant of 61.7 MPa which is 5% lower than in reference [12] where a value of 64.9 MPa was calculated by extrapolation of the high pressure experimental results. At the lower temperature end a good agreement with our earlier results [3] is also observed with deviations at $T = 303 \text{ K}$ of the order of 3% which is the precision claimed in the previous set of data (at $T = 303.72 \text{ K}$ we had reported [3] a value

TABLE 2

Parameters of equation (8) used to smooth the raw experimental results from table 1 along with the per cent average absolute deviation of the fit (AAD)

Gas	A_0	A_1	A_2	AAD
CO ₂	+10.671	-2.2081×10^3	$+6.7431 \times 10^4$	0.6
C ₂ H ₆	+14.780	-4.4594×10^3	$+5.2295 \times 10^5$	0.3
CH ₄	+36.456	-1.6711×10^4	$+2.3452 \times 10^6$	1.5
O ₂	+9.4429	-9.5643×10^2	$+1.0053 \times 10^5$	0.6
N ₂	+26.101	-1.0419×10^4	$+1.4477 \times 10^6$	0.5
H ₂	+36.847	-1.6779×10^4	$+2.4041 \times 10^6$	0.5
Ar	+26.933	-1.0978×10^4	$+1.5263 \times 10^6$	0.5
CO	+8.0560	-3.1704×10^2	$+4.1109 \times 10^4$	0.3

of $K_H = 60.0$ MPa compared with the $K_H = 62.3$ MPa found here). These deviations become however much larger at higher temperatures and are significant at $T = 343$ K. We believe that our previous results clearly overestimate the solubility at the higher temperatures studied, this statement being confirmed by the agree-

FIGURE 3. Henry's law constants for CO₂ in [bmim][BF₄]: —, present results; — —, data from reference [3]; ■, data from reference [2]; ▲, data from reference [4] ○, data from reference [12]; - - -, values from reference [3] calculated with $\alpha = 1.4 \times 10^{-4}$; ···, data from reference [3] calculated with $\alpha = 2.3 \times 10^{-4}$.

FIGURE 2. Gas solubilities in [bmim][BF₄] expressed as mole fraction and as a function of temperature: □, carbon dioxide; ○, ethane; ■, methane; ●, oxygen; ▲, nitrogen; ◇, hydrogen; ▼, argon; ◆, carbon monoxide. Lines represent the smoothed data using the parameters in table 2. In the lower plot are represented the data for the six less soluble gases in an expanded scale.

ment found between the present results and those reported by other research groups [2,4,12].

The differences encountered in the carbon dioxide solubility between the present study and our previous measurements can have two explanations: on one hand, the improvements in the apparatus and in the experimental technique and on the other hand, the use of a different sample of the ionic liquid [bmim][BF₄]. The alterations in the equipment used mainly increase the precision of the measurements and the present results exhibit an imprecision better than $\pm 1\%$ compared with the 3–4% reported earlier. The three more important modifications in the equipment concern: first, the improvement in the accuracy of the total volume of the equilibrium cell with the use of constant volume valves (V1, V2 and V3 in figure 1) in substitution of the variable capacity stopcocks used before; second, the accurate determination of the quantity of ionic liquid which is now done gravimetrically instead of volumetrically by means of a micropipette; and third, the temperature and pressure are now continuously measured and so the approach to thermodynamic equilibrium is more accurately determined. All these changes lead to more precise and more accurate values of the gas solubility and can certainly explain the 3% deviations found, near $T = 303$ K, between the present and previous data. They cannot, however, account for the increasingly higher deviations found at the upper temperatures.

A compatible explanation was found by analysing the new volume calibration procedures used at present to determine the volume of the glass bulbs limited by valves V2 and V3 in figure 1 and of the total volume of the equilibrium cell. In our previous work, the volumes of the bulbs were calibrated at an accurate temperature

TABLE 3

Partial molar thermodynamic functions of solution for the gases in [bmim][BF₄] at several discrete temperatures between $T = 283$ K and $T = 343$ K

T/K	$\Delta_{\text{sol}}G^\infty/\text{kJ mol}^{-1}$	$\Delta_{\text{sol}}H^\infty/\text{kJ mol}^{-1}$	$\Delta_{\text{sol}}S^\infty/\text{J mol}^{-1} \text{K}^{-1}$
CO₂			
283	8.750	−13.9	−80.1
293	9.557	−14.3	−81.3
303	10.38	−14.6	−82.3
313	11.20	−14.8	−83.0
323	12.03	−14.9	−83.5
333	12.87	−15.0	−83.7
343	13.71	−15.0	−83.8
C₂H₆			
283	13.06	−6.77	−70.1
293	13.77	−7.51	−72.6
303	14.51	−8.31	−75.3
313	15.28	−9.16	−78.1
323	16.07	−10.1	−81.0
333	16.90	−11.0	−83.9
343	17.75	−12.1	−86.9
CH₄			
283	15.72	−3.24	−67.0
293	16.44	−6.28	−77.5
303	17.27	−9.71	−89.1
313	18.23	−13.6	−102
323	19.31	−17.9	−115
333	20.53	−22.6	−130
343	21.90	−27.8	−145
O₂			
283	17.22	−2.06	−68.1
293	17.91	−2.23	−68.7
303	18.60	−2.40	−69.3
313	19.29	−2.59	−69.9
323	19.99	−2.78	−70.5
333	20.70	−2.99	−71.1
343	21.42	−3.20	−71.8
N₂			
283	17.30	−2.92	−71.5
293	18.05	−4.80	−78.0
303	18.87	−6.92	−85.1
313	19.75	−9.28	−92.8
323	20.72	−11.9	−101
333	21.78	−14.8	−110
343	22.92	−18.0	−119
H₂			
283	17.82	−0.09	−63.3
293	18.50	−3.24	−74.2
303	19.30	−6.83	−86.3
313	20.23	−10.9	−99.4
323	21.30	−15.4	−114
333	22.51	−20.4	−129
343	23.88	−26.0	−145
Ar			
283	16.92	−3.14	−70.9
293	17.66	−5.07	−77.6
303	18.47	−7.24	−84.9
313	19.36	−9.66	−92.7
323	20.33	−12.4	−101
333	21.39	−15.3	−110
343	22.54	−18.6	−120

TABLE 3 (continued)

T/K	$\Delta_{\text{sol}}G^\infty/\text{kJ mol}^{-1}$	$\Delta_{\text{sol}}H^\infty/\text{kJ mol}^{-1}$	$\Delta_{\text{sol}}S^\infty/\text{J mol}^{-1} \text{K}^{-1}$
CO			
283	17.53	−0.25	−62.8
293	18.16	−0.31	−63.0
303	18.79	−0.37	−63.2
313	19.42	−0.44	−63.5
323	20.06	−0.52	−63.7
333	20.70	−0.60	−63.9
343	21.34	−0.69	−64.2

$\Delta_{\text{sol}}G^\infty$ is the partial molar Gibbs energy of solution, $\Delta_{\text{sol}}H^\infty$ the partial molar enthalpy and $\Delta_{\text{sol}}S^\infty$ the partial molar entropy. The values are based on the ideal gas state at 0.1 MPa.

of approximately $T = 303$ K by weighing them filled with a liquid of known density (water and/or mercury). The equilibrium cell was calibrated by gas expansion at the same temperature. Thermal expansion coefficients for Pyrex glass were then used to take into account for the volumetric thermal expansion up to $T = 343$ K [27]. In the present case, the volumetric thermal expansion coefficients for the bulbs and for the equilibrium cell were determined experimentally by calibrating the volume at least at two different temperatures in the range under study. It was found that, for the case of the total volume of the equilibrium cell, the experimental value was much higher than the one previously considered. This observation can be explained by the fact that the connexion between C2 and the manometer in the equilibrium cell (see figure 1) is made in stainless steel and is quite long (disposed as a spiral to facilitate the temperature control).

In figure 3 are also represented our previous data calculated using two different values for the thermal expansion coefficient: $\alpha = 1.4 \times 10^{-4}$ which is the thermal expansion coefficient for the equilibrium cell used to obtain most of the gas solubility data reported in the present paper; and $\alpha = 2.3 \times 10^{-4}$, the average value of the thermal expansion coefficients of the different cells built in our laboratory. It is observed that when our previous results are calculated with the first value of α , the deviations between the two sets of data are always lower than 15% and when the second realistic value for the thermal expansion coefficient is used the data agree to within 5%.

It seems thought that the differences due to the use of two different samples of ionic liquid should be minor compared with those discussed before. It is still noteworthy that the analysis of the chloride content done by ion chromatography in the two samples of [bmim][BF₄] (the one used here and that used to obtain the data published before [3]) reveal huge differences in the quantity of halide indicating that the ionic liquid was probably synthesised and/or purified in distinct ways [21].

It appears clearly that the previous values should be disregarded in relation with the present ones and that

the differences in the two data sets are due to two main reasons: one is the considerable improvements of the experimental apparatus that have led to a better precision and accuracy of the solubility; the other reason is the erroneous thermal expansion coefficient used to correct the total volume of the equilibrium cell in the previous version of the experimental equipment. These two factors are even more significant in the case of oxygen as the solubility in this case is much lower than in the case of carbon dioxide and so significantly more affected by the corrections described above.

A comparison is also possible between the values for the solubility of hydrogen obtained here and those reported by other authors. The value of 180 MPa for the Henry's law constant [8], reported for hydrogen in [bmim][BF₄] at room temperature, is in satisfactory agreement with the present value of 203.6 MPa at $T = 298.34$ K. Another result of 580 MPa at 295 K [9] seems to clearly underestimate hydrogen solubility in the ionic liquid.

In the case of carbon monoxide, an Henry's law constant of 337 MPa at 295 K [10] has been reported. By comparison with the data obtained here ($K_H = 172.6$ MPa at $T = 293.16$ K), these measurements also seem to underestimate the solubility of this gas in the ionic liquid which was reported as non detectable by other authors [4]. Our results seem coherent with the solubility of carbon monoxide in a similar solvent, [bmim][PF₆], for which a Henry's law constant of $K_H = 197.4$ MPa is measured at $T = 303.38$ K [11].

The variation with temperature of the solubility for the eight gases studied, expressed in Henry's law constant, is directly related with the thermodynamic properties of solvation through equations (4)–(6) and constitute a reasonable approximation, for the case of gaseous solutes at low pressure, for the thermodynamic properties of solution [28]. The values for the partial molar Gibbs energy, enthalpy and entropy of solvation are given for the eight gases in [bmim][BF₄] in table 3.

As can be observed in figure 4, the partial molar Gibbs energy of solvation behaves with temperature in a similar manner for all the gases studied, being directly proportional to the logarithm of the Henry's law constants. The variation with temperature of the enthalpy and entropy of solution is depicted in figure 5. All the gases exhibit negative enthalpies of solution corresponding to an exothermic solvation. At around $T = 283$ K, the lower temperature of this study, carbon dioxide and ethane exhibit the more negative enthalpies of solvation. In both cases the values do not vary significantly with temperature. Oxygen and carbon monoxide also exhibit enthalpies of solvation which are constant in the temperature range covered but in these cases they are close to zero. For all the other gases, the enthalpy of solution varies more significantly with temperature

FIGURE 4. Partial molar Gibbs energy of solution of the gases in [bmim][BF₄] as a function of temperature: □, carbon dioxide; ○, ethane; ■, methane; ●, oxygen; ▲, nitrogen; ◇, hydrogen; ▼, argon; ◆, carbon monoxide.

and approaches zero in the lower temperature end. For the case of hydrogen, it is observed that the enthalpy of solution is very close to zero at the lower temperatures. This indicated the existence of an *extremum* in the solubility, which first increases at the lower temperatures and then decreases at the higher temperatures. In the case of the entropy of solvation, the gases have a similar behaviour. All values are negative and decrease with temperature except in the case of carbon dioxide, ethane, oxygen and carbon monoxide for which constant values with temperature are observed.

Because the solubility data obtained are sufficiently precise, the thermodynamic properties of solvation, can be used to infer about the molecular mechanisms pertaining to the solvation of the different gases in [bmim][BF₄]. By the analysis of figures 2 and 4 it can be concluded that, except for hydrogen at the lower temperature end, the solubility of the gases in the ionic liquid decreases with temperature (almost constant with temperature in the cases of oxygen and carbon monoxide). This means that we are in presence of exothermic processes of solvation for all the gases in the temperature range covered.

Furthermore, these properties provide valuable information both about the solute–solvent interactions and about the molecular structure of the solutions: the enthalpy of solution is closely related with the crossed gas–ionic liquid molecular interactions and the entropy of solvation gives indications about the structure of the solvent molecules surrounding the solute. The behaviour observed for the enthalpy of solution probably means that the solute–solvent interactions are of different nature in the gases studied. Two different patterns can be identified corresponding to two groups of gases: one being constituted of carbon dioxide, ethane, oxygen and carbon monoxide and the other of

FIGURE 5. Partial molar enthalpy of solution (left) and partial molar entropy of solution (right) of the gases in [bmim][BF₄] as a function of temperature: $\square$, carbon dioxide; $\circ$, ethane; $\blacksquare$, methane; $\bullet$, oxygen; $\blacktriangle$, nitrogen; $\diamond$, hydrogen; $\blacktriangledown$, argon; $\blacklozenge$, carbon monoxide.

methane, nitrogen, hydrogen and argon. The same distinct behaviour is found in the entropy of solvation with also the same two patterns of behaviour but not as clearly marked as the previous ones.

4. Conclusions

We report the solubility of eight different gases in one ionic liquid: 1-butyl-3-methylimidazolium tetrafluoro-

FIGURE 5 (continued)

borate as a function of temperature. The results could be compared with reliable literature data on the solubility of carbon dioxide and the experimental technique could be validated. We assume that the solubilities determined here are precise to within $\pm 1\%$ and have an accuracy better than $\pm 3\%$. This last value was found after a care-

ful analysis of the present data, considering all sources and order of magnitude of the uncertainties during our experiments (referred during the text), and their confrontation with the existing literature data. The solubility of the different gases varies significantly in the temperature range covered. Carbon dioxide is the most

soluble gas with mole fraction solubilities of the order of 10^{-2} . Ethane and methane are one order of magnitude more soluble than the other five gases which have solubilities of the order of 10^{-4} in mole fraction, hydrogen exhibiting the lower concentration in the ionic liquid.

The solubility of all the gases decrease with temperature except for the case of hydrogen in the lower temperature end. This observation is contrary to that made previously for a number of low solubility gases like oxygen and argon [3,5,20] for which a slight increase with temperature was observed in the solubility. It is our opinion that, for the reasons explained before, the previous values should be disregarded and the solvation of all the gases studied here should be considered as exothermic.

The data obtained makes it possible to analyse the thermodynamic properties of solvation which can provide some tools to assess the molecular interactions in solution. It was observed that the enthalpy and the entropy of solvation can vary significantly for the eight gases studied and two groups of solutes could be identified, probably corresponding to two different mechanisms of solvation.

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