Functionalized Imidazolium Bis(trifluoromethylsulfonyl)imide Ionic Liquids for Gas Sensors: Solubility of H_2, O_2 and SO_2

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Abstract

Gas solubilities of non-polar (hydrogen and oxygen) and polar (sulphur dioxide) gases in a set of functionalized alkyl imidazolium ionic liquids with the bis(trifluoromethylsulfonyl)imide ($[NTf_2]^-$) anion are reported between 303 and 333 K at 1 bar. The alkyl side-chains in the imidazolium cations include different functional groups, such as –OH, –CN and benzyl; their effects on gas solubilities were studied. The solubility decreases with temperature for all gases, as expected for an exothermic dissolution. Sulphur dioxide is by far the most soluble gas, with mole fractions between 0.29 and 0.41 in the ionic liquids at 313 K and 1 bar, approximately 2-3 orders of magnitude higher than the two other gases studied. Oxygen is generally more soluble in the ionic liquids than hydrogen with mole fractions ranging from 9×10^{-4} to 21×10^{-4} and 5×10^{-4} to 15×10^{-4} at 313 K and 1 bar for oxygen and hydrogen, respectively. In the case of hydrogen, the solubility increases when the molar volume of the ionic liquid increases, whereas for oxygen, the presence of polar groups in the cation causes a reduction in the solubility. None of the three gases is chemically absorbed in the ionic liquids.

Keywords: Ionic Liquids, Gas solubility, Hydrogen, Oxygen, Sulphur Dioxide

1. Introduction

The need for highly sensitive and robust gas sensors is a main research focus in the area of gas monitoring for environmental, industrial and health purposes. A broad variety of systems are available, however the requirements of low cost, small and mobile sensors that have high robustness in extreme conditions are not often fulfilled.

Room-temperature ionic liquids (RTILs) are drawing more and more attention for application as electrolytes in gas sensors [1] due to their unique characteristics like low volatility, high conductivity, large electrochemical window, good solvent properties as well as high chemical and thermal stability [2]. It has been shown that the high thermal stability up to approximately 350°C of certain ionic liquids makes it possible to detect volatile organic compounds (VOCs) up to 200°C [3]. By far, the most attractive property of RTILs is the possibility of tuning their properties by appropriately combining cations and anions or by introducing chemical functionalities in their structures [4]. This allows the adjustment of the physicochemical properties towards certain requirements such as low or high viscosities, high gas absorption or increased selectivity towards certain analytes. This concept is present in the preparation of task-specific ionic liquids (TSILs) initially prepared to increase the selectivity in gas absorption and improve sensitivity towards trace analyte capture and detection.

Bates and co-workers introduced the idea of TSIL with an amine-functionalized imidazolium-based IL with increased carbon dioxide capacity due to the reversible formation of a carbamate [5].To avoid the increase of the viscosity of the RTIL solution after the gas absorption, further developments have been proposed by Gurkan *et al.*[6] who designed ionic liquids based on suitably substituted aprotic heterocyclic anions capable of selectively and reversely absorbing carbon dioxide while maintaining the liquid fluidity. Polymerized ionic liquids (PILs) and amino-acid-based polymerized ionic liquids (AAPILs) have also been used for enhanced carbon dioxide sorption [7].

In the case of sulphur dioxide (SO_2), little research has been performed so far compared to CO_2 especially with regards to SO_2/O_2 or SO_2/H_2 separation in mixed gas streams. Anderson *et al.*[8] measured Henry constants, K_H, for sulphur dioxide and carbon dioxide in two commercially available ionic liquids based on the $[NTf_2]^-$ anion. They showed a significantly higher K_H and therefore lower solubility at 25°C for CO_2 (around 32 bar) compared to SO_2 (approximately 1.6 bar) for both RTILs, explained by a pure physical absorption mechanism. Shiflett *et al.*[9] studied SO_2 absorption in imidazolium-based ionic liquids with different anions and suggested a chemical absorption mechanism. Yuan *et al.*[10] studied the impact of the chemical modification of ammonium ionic liquids with hydroxyl groups and measured high, reversible SO_2 capacities explained by the reaction of the gas at the –NH group in the hydroxyl ammonium cation to form N–S bonds. Under vacuum conditions or at elevated temperatures, this reaction can be reversed to release SO_2, which makes these RTILs reusable. Jin *et al.*[11] compared SO_2 absorptions in conventional 1-butyl-3-methylimidazolium tetrafluoroborate, $[C_4mim][BF_4]$, and hexafluorophosphate, $[C_4mim][PF_6]$, and in the

TSILs 1,1,3,3-tetramethylguanidinium lactate and monoethanolaminium lactate, and concluded that both ILs can absorb SO_2 effectively at high partial pressures, but only TSILs exhibit high sulphur dioxide capacities at low partial pressures of SO_2. A comparison of solubility isotherms revealed that the proposed TSILs absorb SO_2 chemically as well as physically in contrast to a pure physical absorption mechanism in RTILs.

Several researchers have measured the solubilities of non-polar and small gases like hydrogen and oxygen in commercially available RTILs such as $[C_4mim][BF_4]$, $[C_4mim][PF_6]$ or 1-butyl-3-methylimidazolium bis(trifluoromethyl)sulfonylimide, $[C_4mim][NTf_2]$. For O_2, some work showed no change in the solubility with temperature [12] whereas others noted increasing solubility with increased temperature [13], not coherent with the common exothermal gas dissolution observed in RTILs [14-16]. Even if for hydrogen, an 'inverse' temperature effect, i.e. hydrogen solubility increases with increasing temperature in $[C_4mim][PF_6]$ [16] and $[C_4mim][NTf_2]$ [17] has been reported, the temperature has only a small influence on the solubility of light, non-polar gases in RTILs, supported by enthalpy of solvation ($\Delta_{solv}H^{\infty}$) values only slightly negative. The mole fraction solubility of light gases in RTILs are in general 1–2 orders of magnitude lower than that of CO_2 [18].

It has been first established by Anthony *et al.*[14] that dissolved gases mainly interact with the anion of the RTILs. More recently, it is assumed that gas solvation mechanisms are more complex and, depending on the structure of the RTIL might be controlled by functionalization of the cations as clearly seen when the cation side chains are fluorinated [19, 20]. Blesic *et al.*[21] studied also the phase behaviour of mixtures of ionic liquids and fluorinated and non-fluorinated benzenes, observing that the competition of the solute interaction with the polar and non-polar nanoregions determines the solubility in this case. When the solubility of gases is not controlled by specific interactions with RTIL ions, it increases with the size and flexibility of the ions or, in other words, when the molar volume (V_m) of the RTIL increases [22]. However, for gases that have strong interactions with ionic liquids, the segregation of the liquid into a polar and non-polar region has to be taken into account [23]. Therefore, modification of the domain in which the analyte is mainly distributed is one way to increase the solubility of different gases, i.e. CO_2 and SO_2 in the polar region and H_2 and O_2 in the non-polar domain of the RTIL.

This work focusses on chemically modifying imidazolium cations by functionalizing with different moieties and quantify how they influence the absorption and selectivity of different gases namely SO_2/H_2 and SO_2/O_2. The anion was kept identical, *i.e.* bis(trifluoromethylsulfonyl)imide $[NTf_2]^-$, and the alkyl side-chains in the imidazolium cations were functionalised to change the non-polar nanoregion probably affecting the gas solubilities of analytes that dissolve in the non-polar regions.

Based on these results obtained herein, the developed systems could be used as electrolytes to study their suitability for electrochemical gas sensing experiments. Several researchers showed that ionic liquids form alternating cation- and anion-rich layers next to a charged surface, with a thickness that depends on the applied potential [24-27].For electrochemical sensing applications, analytes can be either locally retained from or accumulated in the electric double layer by choosing an appropriate cation and anion combination that more effectively solubilizes the analyte, or one that chemically binds the analyte reversibly to influence

the diffusion towards or away from the electrode. If there is no chemical interaction between the gas and the ionic liquid, the application of an external electrical field can restructure the polar and non-polar ionic liquid domains to change the solubility of the gas.

In this paper, the experimentally measured solubilities of hydrogen, oxygen and sulphur dioxide in a series of functionalized and non-functionalized imidazolium based ionic liquids with the $[NTf_2]^-$ anion, are reported at temperatures between 303 and 333 K using the well-established isochoric saturation method [28]. A set of functionalised ionic liquids was synthesized, and their densities and viscosities were determined in a temperature range of 293 to 353 K. Additionally, the selectivity is discussed based on the experimentally determined gas solubilities.

2. Experimental

2.1 Chemical Reagents

All commercially available RTILs were obtained at the highest purity level possible. 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_2mim][NTf_2]$, 99.5%, IoLiTec) and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_4mim][NTf_2]$, 99.5%, IoLiTec) were used without further purification. 1-(2-hydroxyethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_2OHmim][NTf_2]$), 1-methylnitrile-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[CCNmim][NTf_2]$) and 1-methylbenzyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl)imide ($[CBenzmim][NTf_2]$) were synthesised and characterised according to standard literature procedures (see details in the supporting information). The structures of the RTILs studied are shown in Figure 1. All RTILs were dried overnight at 60°C under reduced pressure to remove traces of water as well as dissolved gases before experiments.

Oxygen 5.0 (99.999% pure) was purchased from Messer, nitrogen 5.0 (99.999% pure) and hydrogen 5.0 (99.999%) were purchased from Linde Gas and sulphur dioxide 4.0 (99.99%) was purchased Air Liquide. All gases were used as supplied without further purification.

2.2 Density and viscosity measurements

Densities were measured at atmospheric pressure and within a temperature range from 293 to 353 K with a U-shaped vibration-tube densimeter (Anton Paar, model DMA™ 5000 M). The temperatures were kept constant within 0.001 K and measured with an accuracy of 0.01 K. The precision was determined as 10^{-5} g cm^{-3}. The densimeter was calibrated before the measurements with air and the Anton Paar certified ultra-pure water. The measured values were corrected for viscosity using the inbuilt full range viscosity correction option from Anton Paar.

Dynamic viscosities were measured with a rolling ball viscosimeter (Anton Paar, Lovis 2000 ME) within a temperature range from 293 to 353 K. The temperatures were controlled within 0.005 K. The

experiments were performed with a capillary tube (1.59 mm diameter) and a steel ball. Calibration experiments were performed as a function of temperature and angle with appropriate standard viscosity oils from Paragon Sci. The overall uncertainty was estimated as 0.5%. Samples were dried overnight at 333 K under reduced pressure before measurements were performed.

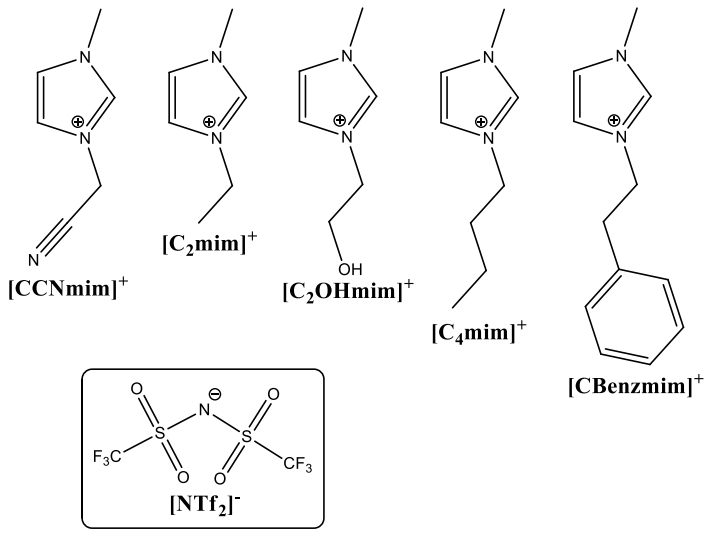

Figure 1. *Chemical structures and abbreviations of the commercial and synthesised ionic liquid cations and the anion, $[NTf_2]^-$, used in this work.*

2.3 Gas absorption measurements

Gas absorption was measured at four temperatures between 303 and 333 K with an in-house built apparatus which is based on an isochoric saturation method as described elsewhere in detail [28].

A precisely calibrated bulb with volume V_{GB} is filled with the respective gas at a known pressure and constant temperature thus allowing the calculation of the quantity of gas in the equilibration cell. After bringing the gas in contact with the dried and degassed ionic liquid, the constant temperature and pressure above the liquid at the equilibrium can be used to calculate the solubility of the respective gas in the liquid phase. The quantity of ionic liquid present in the equilibrium cell, n_1, is determined gravimetrically with a precision of ±0.1 mg. The volume occupied by the liquid solution, V_{liq}, is determined through the knowledge of the density of the pure ionic liquid, assuming that it does not change significantly upon the dissolution of the gas. The gas content in the ionic liquid, n_2^{liq}, is calculated by the difference of the two *pVT* measurements – one when bulb is filled with gas and the other when the vapour-liquid equilibrium is attained:

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

with p_{ini} and T_{ini} as initial pressure and temperature respectively and p_{eq} and T_{eq} after reaching the equilibrium. V_{tot} is the total volume of the equilibration cell and Z_2 is the compressibility factor of the respective pure gas. The gas solubility can be expressed as mole fraction x_2 according to eq 2 or as Henry's law constant K_H (eq 3):

$$x_2 = \frac{n_2^{liq}}{n_2^{liq} + n_1^{liq}} \tag{2}$$

$$K_H = \lim_{x \to 0} \frac{f_2\left(p, T, x_2\right)}{x_2} \approx \frac{\phi_2\left(p_{eq}, T_{eq}\right) p_{eq}}{x_2} \tag{3}$$

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

For the calculation of the compressibility factor, the fit function for the second virial coefficient B_2 of hydrogen from 273 to 400 K was taken from the compilation by Dymond and Smith [29] and for oxygen and sulphur dioxide from Dymond *et al.*[30] (eq 4 - 6) for temperature ranges from 270 to 373 K and 270 to 470 K respectively.

$$B_{H_2} = -1.03725 \times 10^{-4} T^2 + 8.27777 \times 10^{-2} T - 8.36008 \times 10^{-1} \tag{4}$$

$$B_{O_2} = -4.64968 \times 10^{-4} T^2 + 4.92052 \times 10^{-2} T - 1.21657 \times 10^{+2} \tag{5}$$

$$B_{SO_2} = -8.26060 \times 10^{+9} T^3 - 4.97860 \times 10^{+6} T^2 - 2.3892 \times 10^{+2} T + 2.47940 \times 10^{+1} \tag{6}$$

3 Results and Discussion

3.1. Density and Viscosity

The experimentally measured densities are listed in Table S2 and were fitted as a function of temperature according to the following equation (see Table 1):

$$\rho = \rho_0 - AT \tag{7}$$

The linear density dependence on temperature perfectly describes the experimental data.

The results were compared to the literature, when data were available, and the densities are in good agreement with reported values (see supporting information Figure S1-S4). For [C_2mim][NTf_2] a huge dataset of experimentally measured densities has already been published. The deviation from most of the literature values is less than 0.1%. The negative deviation of 0.05% — *i.e.* lower experimental densities in our case — can be explained by the fact that other groups prepared the ionic liquids in their laboratory (at least the anion exchange steps) whereas the sample that was used for this study was obtained commercially with the highest purity available sample, i.e. 99.5%. Residues of the salts used for the anion exchange can cause a higher RTIL density. For [C_4mim][NTf_2], very good agreement with literature data was achieved. The datasets for which large deviations were founds were obtained for less pure salts or containing large amounts of water. For [CCNmim][NTf_2] and [C_2OHmim][NTf_2] (two of the synthesised samples), only a limited number of density values are reported and significant differences in these values can be observed. In the case of synthesised

ionic liquids, unreacted precursors can still be present after purification steps [31]. The densities measured herein (eq 7 and Table 1) were necessary for the calculation of the gas solubility.

Table 1. *Parameters of eq. 7 used to fit the experimental density ρ as a function of the temperature in* K.

Ionic Liquid	ρ_0 / kg m^{-3}	A / 10^{-4} K
[CCNmim][NTf$_2$]	1899.7	696.27
[C$_2$mim][NTf$_2$]	1814.3	892.53
[C$_2$OHmim][NTf$_2$]	1866.9	980.36
[C$_4$mim][NTf$_2$]	1717.3	405.52
[CBenzmim][NTf$_2$]	1727.3	871.57

Viscosity data (see Table S3) were fitted via the Vogel-Fulcher-Tammann (VFT) equation:

$$\eta = \eta_0 e^{\frac{B}{T - T_{VF}}} \tag{8}$$

where η and T are the experimentally determined viscosity and temperature values respectively, η_0 and B are temperature dependent variables and T_{VF} is a temperature that is approximately 50 K below the glass transition temperature of the substance.

Comparison of experimentally determined viscosities with previously published data are shown in the supporting information (Figures S1-S4). Positive and negative deviations of our data to that previously reported, indicates that our results do not present systematic errors. However, even if the viscosities of [C$_2$mim][NTf$_2$] and [C$_4$mim][NTf$_2$] are in good agreement with literature (within 2%), the glass transition temperatures (T_g) — which should be approximately 50 K above the T_{VF} values — are in accordance to published ones for the cation with a shorter alkyl side-chain (T_g = 195 K) but not for the cation with a longer chain (T_g = 186 K) [32] (see Table 2).

Table 2. *Parameters of eq. 8 used to fit the experimental viscosity η as a function of the temperature in* K.

Ionic Liquid	η_0 / mPa s	B / K	T_{VF} / K
[CCNmim][NTf$_2$]	0.25	696.27	200.48
[C$_2$mim][NTf$_2$]	0.12	892.53	139.12
[C$_2$OHmim][NTf$_2$]	0.08	980.36	159.74
[C$_4$mim][NTf$_2$]	0.59	405.52	207.84
[CBenzmim][NTf$_2$]	0.13	871.57	147.11

Table 3 summarizes the densities and viscosities at 313.15 K of the ionic liquids studied herein. In general, attaching more polar functional groups such as –OH or –CN, increases the molecular weight as well as intermolecular forces like dipole-dipole interactions and hydrogen bonding. As can be seen in Table 3, increased densities are observed for functionalised imidazolium based ionic liquids. The density at 313 K

follows the order [C_4mim][NTf_2] < [C_2Benzmim][NTf_2] < [C_2mim][NTf_2] < [C_2OHmim][NTf_2] < [CCNmim][NTf_2]. The viscosity trend at 313 K is as follows: [C_2mim][NTf_2] < [C_4mim][NTf_2] < [C_2OHmim][NTf_2] < [C_2Benzmim][NTf_2] < [CCNmim][NTf_2]. The different trends can be explained by different water contents, which has to be taken into account, especially with the attachment of polar groups.

Table 3. *Overview of experimentally measured densities ρ and viscosities η for the studied ionic liquids at 313.15 K.*

Ionic Liquid	ρ / g cm^{-3} [a]	η / mPa s [b]
[CCNmim][NTf_2]	1.59335	126.6
[C_2mim][NTf_2]	1.50276	20.2
[C_2OHmim][NTf_2]	1.56222	47.3
[C_4mim][NTf_2]	1.42200	28.5
[CBenzmim][NTf_2]	1.44206	98.5

[a] ± 10^{-5} g cm^{-3} [b] ± 0.5%

Oliveira *et al.*[33] studied the effect of water on the physical chemical properties of RTILs and concluded that the presence of water is more crucial to explain the variations in the viscosity than those of the density, due to the fact that viscosity is highly dependent on intermolecular interactions. Generally, this could explain the higher variations between experimental and literature data in the case of viscosity, and also the different trend for both viscosity and density. The study [33] also revealed that the relative density difference between 'water saturated' and 'dried' pyridinium-based ionic liquid is less than 1%. It is noted that the viscosity only affects the time to reach thermodynamical equilibrium, whereas the variation in density directly affects the determination of gas solubility. Due to the fact that comparison of our data with literature data did not show significant differences, no further drying of the samples was performed before the measurements. For gas solubility determinations, the ionic liquid was degassed and kept under vacuum for several hours while the pressure was continuously measured to ensure that no volatile compounds were present in the cell before the equilibration of the gas with the ionic liquid was performed.

3.3. Gas Solubilities

Experimentally measured temperatures, T, and pressures, p, the measured mole fraction gas solubilities x_2, calculated Henry's law constants, K_H, mole fraction, x_2 (1 bar), corrected for a partial pressure of 1 bar and molarity, c, are reported in supporting information Tables S4-S6.

The precision (u) was calculated via error propagation for each measurement based on the uncertainty of the gravimetrically determined mass (± 0.001 g) and the volume of the glass bulb cell, as well as the variation of the pressure (approximately ± 0.02 mbar) and temperature (approximately ± 0.003 K) measurements. The precision of the mole fraction solubility for all measurements is within ± 2 × 10^{-4} to ± 4

$\times 10^{-4}$ for all samples and temperatures which also indicates the limits for the gas solubility values with this kind of setup.

The gas solubilities for all studied gases decrease with increasing temperature and therefore, especially for the less soluble hydrogen and oxygen, the experimental data shows a much larger relative error for the higher temperatures studied here (*e.g.* a relative error of more than 100% is reported for the very low solubility of H_2 in [C_2mim][NTf_2] at 333.15 K). For SO_2 gives the measured absorptions are several orders of magnitude higher, therefore the contribution of the precision of the experimental setup affects the overall error much less, the reported values are being affected with errors within 0.2%. The uncertainty introduced by the experimental method has to be taken into account for the following discussion and hence the gas absorptions at the lower temperatures (*i.e.* 313 K), with generally lower relative errors, were used for comparison between the solutes.

Table 4 lists the mole fraction solubility of the three gases, hydrogen, oxygen and sulphur dioxide, in the functionalised and non-functionalised imidazolium ionic liquids at 313 K. As can be seen, the solubilities of hydrogen and oxygen are approximately 2-3 orders of magnitude lower than for SO_2, in general H_2 being slightly less soluble than O_2 in the RTILs studied.

The differences in solubility can be rationalised by the Hildebrandt solubility parameters, δ, which take the cohesive energy density into account [34]. Hydrogen and oxygen are considered as non-polar gases with small solubility parameters, δ, e.g. 5.08 $MPa^{½}$ for H_2 and 14.64 $MPa^{½}$ for O_2 [35]. For CO_2, a value of 19.10 $MPa^{½}$ has been reported, and it can be assumed that SO_2, which is also a polar and heavy gas, has an equally high δ even in the absence of literature data. Solubility parameters for imidazolium based RTILs were calculated by Bara *et al.*[36] based on a modified Kapustinskii equation [37], they are between 38.4 $MPa^{½}$ for [C_2mim][NTf_2] and 50.9 $MPa^{½}$ for 1-ethyl-3-methylimidazolium dicyanamide, [C_2mim][DCA]. According to the regular solution theory, gases with higher, *i.e.* more similar, solubility parameters to ionic liquids are more easily dissolved.

As can be seen in Figure 2, the trend of increasing gas solubility for all ionic liquids is $H_2 < O_2 < SO_2$, as predicted by the regular solution theory. Furthermore, the solubility of the non-polar gases mainly follows the trend of increasing molar volume, V_m, of the ionic liquid, even if the errors for these low solubilities are significant (see Tables S4-S6). This means that the solubility is dominated by the free volume of the ionic liquid – *i.e.* non-specific interactions between the gas and the liquid. However, in the case of oxygen, it can be seen that non-functionalised ionic liquids show slightly higher oxygen solubilities when compared to the functionalised ones. As previously mentioned, the solubility of light gases is mainly defined as physical absorption in the non-polar region of the ionic liquid, therefore the solubility is assumed to decrease with the addition of more polar groups in the side-chain, keeping the molar volume, V_m, the same. This effect can be seen for [C_2mim][NTf_2] (V_m = 260.30 $cm^3\ mol^{-1}$) and [C_2OHmim][NTf_2] (V_m = 260.72 $cm^3\ mol^{-1}$) where the synthesised sample shows smaller gas solubilities even if the molar volumes are approximately the same.

This assumption can only be confirmed for oxygen as for hydrogen, the molar volume is more decisive taking into account that the relative error of the solubility data.

Table 4. *Overview of molar volumes, V_m, calculated from the experimental densities of the RTILs and mole fraction gas solubilities, x, corrected for a 1 bar partial pressure of gas in the studied ionic liquids at 313 K.*

Ionic Liquid	V_m / cm^3 mol^{-1}	$x(H_2)$ / 10^{-4}	$x(O_2)$ / 10^{-4}	$x(SO_2)$ / 10^{-4}
[CCNmim][NTf$_2$]	252.48	4.7	9.3	2913
[C$_2$mim][NTf$_2$]	260.39	9.8	15	3727
[C$_2$OHmim][NTf$_2$]	260.72	7.3	13	3077
[C$_4$mim][NTf$_2$]	294.91	7.6	20	3017
[CBenzmim][NTf$_2$]	323.87	13	15	3626

It has been reported that the ionic liquid anion-gas interaction is an important factor that contributes to the solubility of polar gases like CO_2, the cation having only a small effect [38-40]. Greater flexibility in the anion structure such as in the $[NTf_2]^-$ anion, supports the presence of a larger free volume in the polar region of the RTIL where polar gases are absorbed [41-43]. As in our study the anion was kept the same for all samples, the modifications on the cation are the reasons for the change in solubility. Table 4 shows that the solubilities are significantly higher for the more polar SO_2 by more than two orders of magnitude, in comparison to the non-polar gases. No evidence is found of a chemical absorption of SO_2. Apart from [C$_2$mim][NTf$_2$], which has an unexpectedly high SO_2 solubility, ionic liquids with more polar functional groups in their side chain, such as –CN or –OH, give markedly lower mole fraction solubility values compared to less polar benzyl or alkyl side chains.

Both chemical and physisorption has been reported for SO_2 in RTILs, depending on the cation and anion [8, 18, 44]. Huang *et al.*[45] observed a purely physical absorption of SO_2 in several imidazolium and 1,1,3,3-tetramethylguanidinium-based ionic liquids with $[BF_4]^-$ and $[NTf_2]^-$ as anion. Anderson *et al.*[8] calculated the partial molar enthalpy and entropy of dissolution of SO_2 and CO_2 in [C$_6$mim][NTf$_2$] and reported a significantly stronger interaction between the solvent and solute (SO_2) with an enthalpy of dissolution ($\Delta_{solv}H^{\infty}$) value of approximately −20 kJ/mol compared to −11 kJ/mol for CO_2. The entropic contribution is also ($\Delta_{solv}S^{\infty}$) is also twice as high for SO_2. These values suggest a purely physical absorption mechanism favoured for the sulphur dioxide compared with carbon dioxide.

Table 5 shows the calculated molar enthalpy and entropy values of solvation for SO_2, calculated from the experimental data for the synthesised and commercially available imidazolium-based ionic liquids. As can be seen, $\Delta_{solv}H^{\infty}$ is within the experimental error (around −20 kJ mol^{-1}) for all samples, which is the same as reported by Anderson *et al.*[8] for [C$_6$mim][NTf$_2$] and for physical absorption of CO_2 in [C$_4$mim][TFA], by Carvalho *et al.*[46]. Furthermore, similar molar entropy values for all ionic liquids indicate that the effect of

the solute in the structure of the liquid phase is similar for all gases, also pointing towards physical absorption of the gas.

Table 5. *Molar enthalpy of solvation ($\Delta_{solv}H^{\infty}$) and molar entropy of solvation ($\Delta_{solv}S^{\infty}$) of SO_2 at a pressure of 0.1 MPa in the five ionic liquids averaged over the temperature range from 304 to 333 K.*

Ionic Liquid	$\Delta_{solv}H^{\infty}$ / kJ mol^{-1}	$\Delta_{solv}S^{\infty}$ / J mol^{-1} K^{-1}
[CCNmim][NTf_2]	−20 ± 2	−75 ± 5
[C_2mim][NTf_2]	−20 ± 2	−71 ± 5
[C_2OHmim][NTf_2]	−21 ± 2	−75 ± 5
[C_4mim][NTf_2]	−19 ± 2	−70 ± 5
[CBenzmim][NTf_2]	−20 ± 2	−71 ± 5

Based on the calculated molar enthalpies and entropies of dissolution, there is no indication of chemical binding of SO_2, as has been confirmed previously for CO_2 by several groups [46-49] in the case of an ionic liquid anion, such as acetate, which is able to deprotonate an acidic hydrogen from the ionic liquid cation [49, 50]. The bis(trifluoromethylsulfonyl)imide anion is known to be a weak base that cannot deprotonate the most acidic hydrogen atom from the imidazolium ring and thus not allowing the reaction with carbon dioxide or sulphur dioxide.

For applications where these ionic liquids are used in electrochemical gas sensors, the spontaneous, irreversible chemical binding of an analyte is undesirable. A chemically bound analyte could accumulate in the electrolyte and the establishment of a calibration curve over a broad concentration range would not be reliable. However, sensing of trace concentrations of toxic gases like SO_2 could be improved. The gas analyte should be absorbed reversibly, and the electrolyte must be electrochemically stable, preferably over a wide electrochemical window.

For gas sensors based in RTILs for use in real world environments, it is also desired to have a high selectivity towards certain gases that are toxic or dangerous at low concentrations. Therefore, the selectivities of SO_2/H_2 and SO_2/O_2 were calculated based on the molar fraction solubility of the respective gases and corrected for a partial pressure of 1 bar at 313 K (see supporting information Tables S4 – S6). Air is mainly composed of nitrogen which is electrochemically inert, and oxygen, which can be electrochemically reduced at similar potentials to SO_2. Therefore, a high SO_2/O_2 selectivity is desired for the sensing of low concentrations of sulphur dioxide.

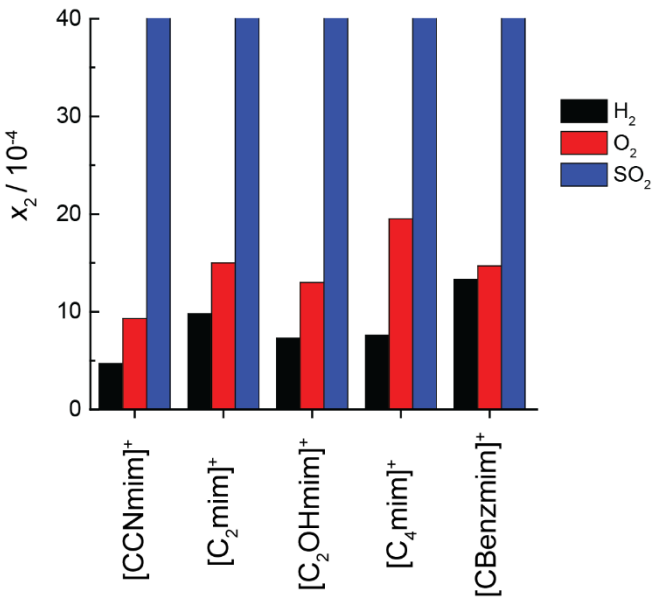

Figure 2. *Comparison of solubility of hydrogen, oxygen and sulfur dioxide in the studied RTILs corrected for a partial pressure of 1 bar at 313 K ($x_2 \times 10^4$). For simplification, only the abbreviation for the cation was used. SO_2 solubilities are significantly higher (as listed in Table 4) but are caped in this Figure at $x(SO_2) = 40 \times 10^{-4}$).*

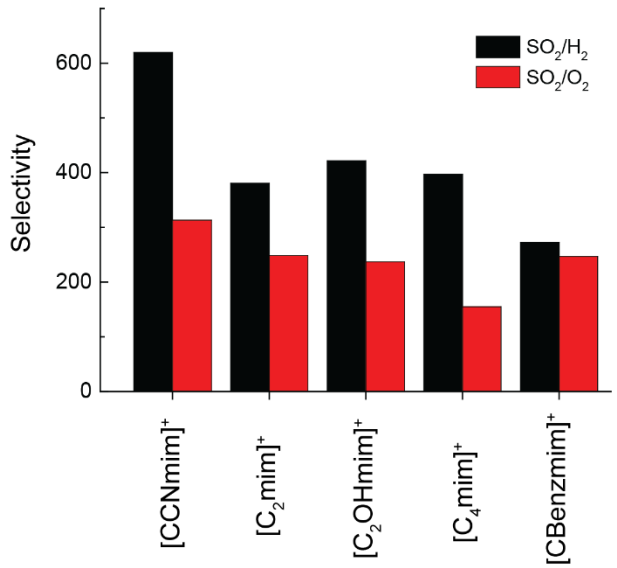

Figure 3. *Gas selectivities, SO_2/H_2 and SO_2/O_2, calculated from the ratio of the mole fraction solubility at 313 K.*

Figure 3 illustrates the SO_2/H_2 and SO_2/O_2 selectivities of the different ionic liquids at 313 K calculated from the experimental mole fractions ordered from the lowest V_m (left) to the highest (right). As can be seen, for the SO_2/H_2 selectivity, high sulphur dioxide selectivities can be achieved in [CCNmim][NTf_2] due to a low hydrogen and reasonably high SO_2 solubility. As previously discussed, hydrogen is mainly dissolved in the non-polar domains formed by the ionic liquid structure, whereas sulphur dioxide can act as a linker between the cation and the anion in certain RTILs, and so strongly interacts with the ring hydrogen atoms in the imidazolium cation [51]; therefore it is mainly present in the polar region of the ionic liquid structure. For the

selectivity of sulphur dioxide and oxygen, the trends are not as obvious. In general, a similar trend as for hydrogen could be observed, however taking into account that relative error on the measured solubilities of the non-polar gases, it may be concluded that there is no significant improvement in the selectivity towards sulphur dioxide is achieved by attaching polar functional groups to the side chain of the imidazolium cation.

Conclusions

The density, viscosity and gas solubilities of hydrogen, oxygen and sulphur dioxide in a set of functionalised and non-functionalised imidazolium based room-temperature ionic liquids with the same bis(trifluoromethylsulfonyl)imide anion, are reported. In general, the trend of increasing solubility is $H_2 < O_2 < SO_2$, with the solubility values for oxygen approximately twice as high as for hydrogen. For SO_2, the solubility is 2-3 orders of magnitude higher. No chemical binding of the gases was observed, confirmed by the calculation of the molar enthalpy and entropy of SO_2 solvation. The attachment of polar groups to the imidazolium side chain appears to have only minor effects on the solubility of sulphur dioxide, whereas the change of the molar volume V_m that occurs because of the functionalisation explains the hydrogen solubility. For oxygen, a competing effect between improved solubility with increased V_m and decreased solubility with increased polarity in the side chain could be observed.

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