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Influence of an Oxygen Functionalization on the Physicochemical Properties of Ionic Liquids: Density, Viscosity, and Carbon Dioxide Solubility as a Function of Temperature

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ABSTRACT: The physicochemical properties (density, viscosity, and carbon dioxide solubility) of ionic liquids based on pyridinium, pyrrolidinium, and ammonium cations were studied at atmospheric pressure and as a function of temperature between (293 and 343) K. The influence of the inclusion of oxygen functional groups (hydroxyl and ester) in the cations was assessed by comparing their behavior with that of similar nonfunctionalized ionic liquids. We observed that the presence of oxygen groups does not affect the density significantly. The inclusion of an ester group in the alkyl-side chain of pyridinium or ammonium cations greatly increases the viscosity of bis(trifluoromethylsulfonyl)imide ionic liquids (5 times for pyridinium, 2 times for ammonium-based ionic liquids at 293 K), while the presence of hydroxyl groups only slightly increases their viscosity (16 % increase for ammonium at 293 K). Carbon dioxide solubilities are not significantly influenced by the introduction of oxygen functional groups in the cations for the ammonium-based ionic liquids. In the case of the pyridinium-based ionic liquids, the solubility of carbon dioxide significantly decreases (up to a 48 % decrease in mole fraction) due to a defavorable entropic contribution to the Gibbs energy of solvation.

INTRODUCTION

Ionic liquids (ILs) are candidates to substitute the classic volatile organic solvents, due to their interesting properties. Mainly because of their negligible vapor pressure, they are often presented as components with a low environmental impact. However, recent research has demonstrated that they can be toxic[1−8] and resistant to biodegradation.[9−12] It has been reported that the introduction of polar oxygenated functions (hydroxyl, ester, or ester plus ether groups), which are susceptible to enzymatic hydrolysis, in the alkyl side chains of imidazolium and pyridinium-based ILs can greatly improve their biodegradability.[9]

The chemical modification introduced to increase the biodegradability of these components will surely modify their physicochemical properties. So far, there is a lack of information about the physicochemical properties of functionalized ILs. Therefore, prior to considering these ILs for further studies or applications, a systematic and sufficiently accurate data set of physicochemical properties is required. Understanding the relationship between the molecular structures and properties is essential for pursuing the aim of designing and synthesizing ILs possessing interesting properties as well as low environmental impact.

Density and viscosity are relevant properties for the development of chemical processes, being related to mass transfer and power requirements for stirring. The insertion of ether groups in the alkyl chain on the sulfate anion of an imidazolium-based IL has been shown to decrease the viscosities of ILs. For example the viscosity of 3-methyl-1-ethyl imidazolium octylsulfate is divided by 4 with the substitution of two CH_2 groups by two O-atoms.[13] This observation has been explained by an increasing flexibility of the functionalized alkyl chains and by the interactions between the oxygen atoms and the positively charged imidazolium core. Higher densities for ILs containing anions with oxygen functionalized side chains compared to the nonfunctionalized anions have been measured and explained by the formation of intra- and intermolecular O···H bonds leading to a more compact arrangement of the ions per volume unit.[13] In a previous work,[14] our group has noticed no major effect on the density by the introduction of oxygenated functions (ether and/or ester) on the alkyl chain of the cation of imidazolium-based ILs.

The influence of oxygen functional groups on CO_2 solubility has been previously studied.[14−16] For example, to increase the solubility of this gas, Muldoon et al.[15] have introduced an ester group on pyridinium based ILs. Carbonyl groups are expected to be CO_2-philes, because the oxygen is, in principle, able to take part in specific molecular interactions with CO_2.[17] In fact, it has been proven, both experimentally[14,15] and by molecular simulation,[16] that ester groups do not introduce a significant change in the carbon dioxide or ethane solubility of pyridinium- and imidazolium-based ILs. The presence of ether functionalities is also expected to affect favorably the carbon dioxide solubility, because it increases the free volume and the oxygen interacts with the carbon of CO_2.[17] In fact, almost no differences in solubility were

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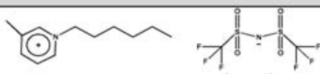
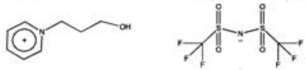
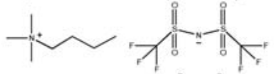
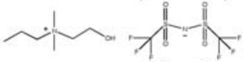
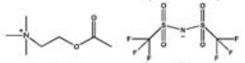
Table 1. Abbreviations, Structures, Cation Names, and Molecular Weight of the Studied Ionic Liquids

Abbreviation	Structure	Name of cation	Molecular weight g.mol^{-1}
[C$_6$mPy][Tf$_2$N]		1-hexyl-3-methylpyridinium	458.44
[C$_3$OHPy][Tf$_2$N]		1-(3-hydroxypropyl)pyridinium	418.33
[C$_1$COOC$_2$Py][Tf$_2$N]		1-(2-ethoxy-2-oxoethyl) pyridinium	446.34
[N$_{4111}$][Tf$_2$N]		Trimethylbutylammonium	396.37
[N$_{1132OH}$][Tf$_2$N]		2-hydroxyethyl-dimethylpropyl ammonium	412.37
[N$_{1112OOCCH3}$][Tf$_2$N]		2-acetoxyethyl-trimethylammonium	426.35
[C$_4$mPyr][Tf$_2$N]		1,1-butyl-methylpyrrolidinium	422.41

detected experimentally both in imidazolium-based ILs (with bis(trifluoromethylsulfonyl)imide)[14] and in ammonium-based ILs (with alkylsulfate anions) modified with the introduction of ether groups.[15]

Herein, we have decided to study the density, the viscosity, and the carbon dioxide solubility of bis(trifluoromethylsulfonyl)-imide, [Tf$_2$N], ILs associated with pyridinium, pyrrolidinium, or ammonium cations with alkyl side chains on the cation non-functionalized or having hydroxyl or ester moieties. Because our aim is to understand the effect of the functionalization on the physicochemical properties of several families of ILs, we have chosen cations with aromatic rings, aliphatic rings, and noncyclic groups. The anion [Tf$_2$N] was chosen because it contributes to the reduction of the viscosity of the ILs[18] and increases their capacity to dissolve CO$_2$.[19] No oxygen-functionalized pyrrolidinium-based IL in the temperature range of the present study was available commercially, which is the reason why only one pyrrolidinium-based IL is studied.

EXPERIMENTAL SECTION

Materials. The structures and abbreviations of the ILs used in this study are listed in Table 1. Two pyridinium-based ILs ([C$_1$COOC$_2$Py][Tf$_2$N], [C$_3$OHPy][Tf$_2$N]) were purchased from Iolitec (Germany), their purity (estimated by ^{1}H NMR) claimed to be higher than 98 %. One ammonium-based IL ([N$_{1112OOCCH_3}$][Tf$_2$N]) was purchased from Solvionic (France) with a stated purity higher than 98 % (estimated by ^{1}H NMR). The other ILs ([C$_6$mPy][Tf$_2$N], [C$_4$mPyr][Tf$_2$N], [N$_{4111}$][Tf$_2$N] and [N$_{1132OH}$][Tf$_2$N]) were supplied by Queen's University (Belfast, UK). Their purity is above 99 % as confirmed by ^{1}H NMR.

All of the samples were dried and degassed under primary vacuum (pressure lower than 1 Pa) for at least 10 h before use. Their water content was measured by coulometric Karl Fisher titration (model Mettler Toledo DL32) and was found to be less than 150 ppm (w/w) in all samples.

Density Measurements. The densities (ρ) of the samples at atmospheric pressure were measured using a U-shape vibrating tube densimeter (Anton Paar DMA 512P) as a function of temperature between (293 and 343) K in steps of 10 K. The temperature was maintained to within ± 0.01 K by means of a circulating bath equipped with a PID temperature controller (Julabo model F25-HE) and was measured using a 100 Ω platinum resistance thermometer calibrated against a secondary reference standard with a resolution of 0.001 K and an accuracy of ± 0.009 K. The calibration of the densimeter was done using *n*-heptane, bromobenzene, and 2,4-dichlorotoluene, as reference fluids as described in detail in a previous publication.[20] Due to the high viscosities of the ILs studied, a correction factor was applied to all of the density values measured. As recommended by the manufacturer for the densimeter DMA 512P, the following equation was used:[21]

$$\frac{\Delta\rho}{\rho} = (-0.5 + 0.45\sqrt{\eta})\cdot 10^{-1} \qquad (1)$$

where ρ is the density value obtained from the densimeter calibration and the measured periods, $\Delta\rho$ is the difference between this ρ value and the "corrected" density value due to the effect of viscosity, and η is the dynamic viscosity of the sample in mPa·s. Only the corrected densities are presented in this paper.

The statistical analysis of the results yielded an estimated uncertainty of the density of 0.01 %.

Viscosity Measurements. The dynamic viscosity (η) was determined using an Anton Paar microviscosimeter (AMVn) based on the falling-ball principle.[22] The time, t_1, taken by a ball to fall a given distance in a capillary tube of calibrated diameter filled with the liquid, is detected optically. The viscosity of the ILs is calculated from the values of t_1, the capillary calibration constant, K, and the densities of the ball and of the IL, ρ_b and ρ_{IL}, respectively:

$$\eta = K(\rho_{IL} - \rho_b)\cdot t_1 \qquad (2)$$

Two capillaries of 3.0 mm and 1.8 mm nominal diameters were chosen. They were calibrated using appropriate viscosity standards (Cannon Oil). For each IL at each temperature, 12 measurements were made using at least 2 different tilt angles of the capillary. The temperature of the apparatus was controlled within ± 0.01 K using a built-in Peltier device. The statistical analysis of the results yielded an estimated uncertainty of the viscosity of 2 %.

Carbon Dioxide Solubility Measurements. A method based on an isochoric saturation technique was used to measure carbon

Table 2. Experimental Densities (ρ) of the Studied Ionic Liquids as a Function of Temperature and at Atmospheric Pressure

T	ρ	T	ρ	T	ρ	T	ρ
K	$kg \cdot m^{-3}$	K	$kg \cdot m^{-3}$	K	$kg \cdot m^{-3}$	K	$kg \cdot m^{-3}$
$[C_6mPy][Tf_2N]$		$[C_3OHPy][Tf_2N]$		$[C_1COOC_2Py][Tf_2N]$		$[N_{4111}][NTf_2]$	
293.14	1356.1	293.15	1551.0	293.20	1532.2	293.26	1396.5
303.17	1347.1	303.24	1541.7	302.68	1522.5	303.22	1387.6
313.14	1338.4	313.14	1532.1	313.17	1512.1	313.03	1379.0
323.13	1329.7	323.15	1522.9	323.04	1501.9	323.13	1370.0
333.22	1321.0	333.16	1513.8	333.25	1492.2	333.17	1361.3
343.00	1312.9	343.13	1504.7	343.19	1482.1	343.18	1352.8
$[N_{1132OH}][Tf_2N]$		$[N_{1112OOCCH3}][Tf_2N]$		$[C_4mpyr][Tf_2N]$			
293.16	1453.6	293.18	1486.9	293.09	1398.0		
303.16	1444.5	303.19	1477.3	302.89	1389.2		
313.11	1435.7	313.21	1468.0	313.59	1379.8		
323.14	1426.8	323.16	1458.8	323.38	1371.3		
333.16	1418.1	333.19	1449.7	332.57	1363.1		
343.14	1408.7	343.21	1440.5	342.84	1354.6		

Table 3. Parameters a and b of Equation 3 and Standard Deviation (σ) from the Experimental Data of Table 2

	a	b	σ
ILs	$kg \cdot m^{-3} \cdot K^{-1}$	$kg \cdot m^{-3}$	%
$[C_6mPy][Tf_2N]$	−0.86662	1609.9	0.02
$[C_3OHPy][Tf_2N]$	−0.92768	1822.9	0.03
$[C_1COOC_2Py][Tf_2N]$	−1.00007	1825.3	0.06
$[N_{4111}][Tf_2N]$	−0.87662	1653.4	0.03
$[N_{1132OH}][Tf_2N]$	−0.89202	1715.0	0.03
$[N_{1122OOCCH_3}][Tf_2N]$	−0.92571	1758.1	0.04
$[C_4mPyr][Tf_2N]$	−0.87416	1654.0	0.02

dioxide solubility in all of the ILs between (303 and 343) K and close to atmospheric pressure. The apparatus and the experimental method have been described in previous publications.[14,23] In this technique, a known amount 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 at a given temperature, the pressure above the liquid solution is constant and is directly related to the solubility of the gas in the liquid. The total uncertainty associated with Henry's law constants calculated from the present experimental solubility is estimated to be 3 %.

■ RESULTS AND DISCUSSION

Density. *Experimental Results.* The experimental values obtained for the density of the ILs, at atmospheric pressure and between (293 and 343) K, are reported in Table 2.

The densities were fitted to the following equation:

$$\rho/kg \cdot m^{-3} = a(T/K) + b \tag{3}$$

The parameters a and b, together with the standard deviation of the fit are given in Table 3.

The densities of some of the ILs studied herein ($[N_{4111}][Tf_2N]$,[18,24−26] $[C_4mPyr][Tf_2N]$[19,26−28]) have been measured by other authors. The density of another sample of $[N_{1132OH}][Tf_2N]$[29] has been previously measured by our group. For these three ILs, the present results show relative deviations with literature generally lower than ± 1 %. This is illustrated in Figure 1 for $[C_4mPyr][Tf_2N]$. The small deviations observed can be explained by the presence of traces of impurities in the samples used, namely, water, that can be difficult to eliminate in certain cases. Differences in the sample handling and experimental procedure can also contribute to these small deviations. To the best of our knowledge, the volumetric properties of the functionalized ILs studied here were not measured by other groups.

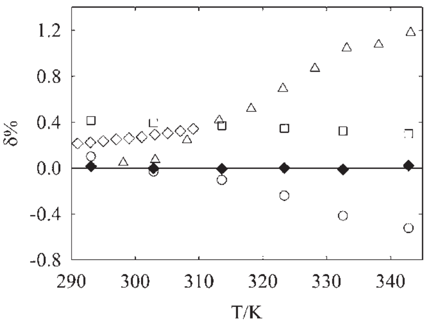


Figure 1. Relative deviations of the density for $[C_4mPyr][Tf_2N]$ from our fitted data: △, Kato and Gmehling;[27] □, Tokuda et al.;[26] ○, Anthony et al.;[19] ◇, Kumełan et al.;[28] ◆, this work.

Group-Contribution Models. Group-contribution models have been developed for the prediction of the volumetric properties of ILs as a function of temperature[30] and pressure.[31] These models are based on the assumption that the molar volume of an IL can be calculated as the sum of the effective molar volumes of the component ions at a given temperature.[32] For the calculation, the cation is considered as the addition of several groups. For example, the molar volume of $[C_1COOC_2Py][Tf_2N]$, $V_{[C_1COOC_2Py][Tf_2N]}$, can be decomposed as:

$$V_{[C_1COOC_2Py][Tf_2N]} = V_{pyridinium} + 3V_{CH_2} + V_{COO} + V_{[Tf_2N]^-} \tag{4}$$

where $V_{\mathrm{pyridinium}}$, $V_{\mathrm{CH_2}}$, V_{COO}, and $V_{[\mathrm{Tf_2N}]^-}$ are the contribution of the pyridinium, the CH_2 group, the ester group, and the anion $[Tf_2N]^-$, respectively. The effective molar volume of each ion or group is calculated, according to Jacquemin et al.,[30] as:

$$V_{\mathrm{group}}(T) = \sum_{i=0}^{2} C_i (T = 298)^i \qquad (5)$$

the parameters C_i for different groups being reported in literature.[14,30]

From the measured densities of $[C_3OHPy][Tf_2N]$, the coefficients C_i for the hydroxyl group were calculated. They are presented in Table 4, along with the parameters necessary for the prediction of the molar volumes of the considered ILs. Using these coefficients, it was possible to predict the molar volumes of all the ILs studied herein, as a function of temperature. An average absolute deviation of 0.3 % between the predicted and the experimental molar volume was obtained. This value is coherent with the uncertainty of 0.5 % claimed by Jacquemin et al.[30] To develop the use of functionalized ILs, the possibility to precisely predict their volumetric properties without having to synthesize them is a powerful tool. It will indeed help in the design of ILs possessing interesting properties and in the understanding of the relationships between their molecular structure and their physicochemical properties.

Viscosity. The dynamic viscosities as a function of temperature from (293 to 343) K are listed in Table 5 and are presented in Figure 2.

The Vogel−Fulcher−Tamman (VFT) equation was used to correlate the experimental viscosities as a function of temperature of ILs:[33]

$$\eta = \eta_0 T^{-1/2} \exp[B/[T - T_0]] \qquad (6)$$

where η_0 is a pre-exponential constant proportional to the viscosity coefficient, B is the pseudoactivation energy for viscous behavior, and T_0 is the ideal glass transition temperature. The values for fitting parameters are given in Table 6 along with the standard deviation associated to the fit. The viscosity dependence with temperature of most of the ILs studied follows the VFT equation ($\sigma \leq 2$ %). Similar values of the three correlation parameters are obtained for all of the nonfunctionalized ILs and for those modified with a hydroxyl group. The presence of an ester function has a noticeable effect on these parameters. It slightly decreases the value of T_0 and decreases by a factor 6 the pre-exponential constant η_0, while it increases by a factor of 2 the B parameter.

Table 4. Parameters C_i Associated with Equation 5 Used to Predict the Effective Molar Volume of Ions as a Function of Temperature at 0.1 MPa

		C_0	$10^3\ C_1$	$10^6\ C_2$
group		$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1} \cdot K^{-1}$	$cm^3 \cdot mol^{-1} \cdot K^{-2}$
$[Tf_2N]^-$	from ref 30	157.597	104.3	50.52
$[C_0Py]^+$	from ref 30	60.547	24.16	90.13
$[C_4C_1Pyr]^+$	from ref 30	145.033	99.95	−66.00
$[N_{4111}]^+$	from ref 30	126.642	94.94	−60.06
$[N_{1132OH}]^+$	from ref 30	126.736	72.67	64.01
$-CH_2-$	from ref 30	16.967	13.99	−1.946
$-COO-$	from ref 14	21.680	31.01	−433.2
$-OH$	this work	1.463	−4.521	−125.3

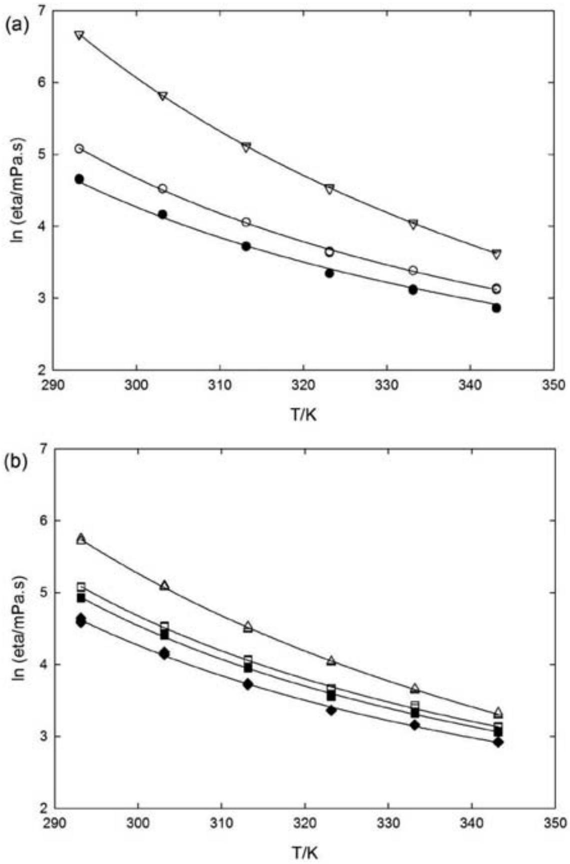


Figure 2. Viscosities as a function of temperature: (a) pyridinium-based ILs: ●, $[C_6mPy][Tf_2N]$; ○, $[C_3OHPy][Tf_2N]$; ▽, $[C_1COOC_2Py]$-$[Tf_2N]$. (b) Nonaromatic ILs: ■, $[N_{4111}][Tf_2N]$; □, $[N_{1132OH}][Tf_2N]$; △, $[N_{1112OOCCH_3}][Tf_2N]$; ◆, $[C_4mPyr][Tf_2N]$. The lines represent the VFT fit.

Table 5. Experimental Viscosities (η) in mPa·s of the ILs Studied in This Work as a Function of Temperature between (293 and 343) K at Atmospheric Pressure

ILs	293.15 K	303.15 K	313.15 K	323.15 K	333.15 K	343.15 K
$[C_6mPy][Tf_2N]$	105	64.2	41.2	28.3	22.5	17.5
$[C_3OHPy][Tf_2N]$	160	92.2	57.7	38.2	29.4	22.8
$[C_1COOC_2Py][Tf_2N]$	786	338	167	93.0	56.8	37.6
$[N_{4111}][Tf_2N]$	138	82.3	52.2	35.5	27.9	21.5
$[N_{1132OH}][Tf_2N]$	160	92.7	58.1	38.7	30.3	22.9
$[N_{1112OOCCH3}][Tf_2N]$	309	162	90.7	56.8	38.5	27.5
$[C_4mPyr][Tf_2N]$	101	63.8	41.8	28.9	23.5	18.6

Table 6. Correlation Parameters of the VFT Equation (η_0, B, and T_0) with the Standard Deviation of the Fit (σ)

	η_0/ mPa·s	B/K	T_0/K	σ
[C_6mPy][Tf_2N]	26.2	309	220	2 %
[C_3OHPy][Tf_2N]	29.7	318	223	2 %
[C_1COOC_2Py][Tf_2N]	3.94	709	206	1 %
[N_{4111}][Tf_2N]	32.0	303	223	2 %
[N_{1132OH}][Tf_2N]	28.2	332	221	2 %
[$N_{1112OOCCH_3}$][Tf_2N]	6.47	622	200	2 %
[C_4mPyr][Tf_2N]	30.4	301	219	2 %

A drastic decrease of the viscosity is observed as temperature increases as expected. At 293.15 K, the lowest temperature measured in this study, the viscosities range from (101 to 786) mPa·s, and at 343.15 K, they are much closer, ranging from (17 to 38) mPa·s. Other research groups have studied the viscosities of some of the ILs of this work: [C_4mPyr][Tf_2N][33−35,41] and [C_6mPy][Tf_2N].[37] As illustrated in Figure 3, in the case of [C_4mpyr][Tf_2N], the deviations encountered are less than 5 % for temperatures up to 320 K. At higher temperatures, more important deviations were calculated. For [$N_{1112OOCCH_3}$][Tf_2N], the viscosity reported in the literature (measured using a rolling-ball viscosimeter)[23] is similar to the one measured in this paper at 313 K (2 % deviation) but higher at elevated temperature (30 % higher at 343 K) and lower at low temperatures (41 % lower at 293 K). The deviations found for other ILs measured by the same authors are much smaller. For this reason, the measurement (calibration, procedure, temperature measurement) is probably correct, and then the deviations observed are most probably explained by the sample (purity, handling).

The viscosities of the ILs studied in this work, at 303 K, are compared in Figure 4, and as it can be observed, they increase in the order: [C_4mPyr][Tf_2N] < [C_6mPy][Tf_2N] < [N_{4111}][Tf_2N] < [C_3OHPy][Tf_2N] < [N_{1132OH}][Tf_2N] < [$N_{1112OOCCH_3}$][Tf_2N] < [C_1COOC_2Py][Tf_2N]. The introduction of oxygen functionalities in the ILs based on the pyridinium or ammonium cations increases the viscosity, the ester functions having a larger effect that the hydroxyl functionalities. The same conclusions have been drawn by Branco et al.[36] who have determined the viscosity of ILs with an hydroxyl group on the side chain of imidazolium cations associated to either PF_6^- or BF_4^- anions; by Crosthwaite et al.,[37] who studied the viscosity of pyridinium-based ILs containing ester functionalities on the alkyl side chain of the cation; and by Okoturo and VanderNoot[33] who concluded that the ILs with higher molar mass cations containing ester or hydroxyl functional group present higher viscosities. The increase of the viscosity of ILs containing oxygen functionalities (hydroxyl and ester) has been attributed to the additional hydrogen bonding involving these functional groups. It is interesting to note that the introduction of another oxygenated function, namely, an ether function on the anion of the IL, has the opposite effect, decreasing the viscosity of the liquid. This could be explained by the increased flexibility of the alkyl chains.[36] For example, the viscosity of [*N*-methoxymethyl-*N*-methylpyrrolidinium][Tf_2N] (41 mPa·s at 298.15 K[37]) is lower than that of [*N*-methyl-*N*-propylpiperidinium][Tf_2N] (60 mPa·s[38] or 63 mPa·s[39] at 298.15 K).

Carbon Dioxide Solubility. Multiple experimental data points of CO_2 solubilities were obtained for [C_3OHPy][Tf_2N], [C_1COOC_2Py][Tf_2N], [N_{4111}][Tf_2N], and [$N_{1112OOCCH_3}$][Tf_2N] between (303 and 343) K in steps of approximately 10 K and close to atmospheric pressure. The low pressure CO_2 solubility of the pyrrolidinium-based IL and of [N_{1132OH}][Tf_2N] were already measured by our group.[29] The experimental solubilities in the different ILs are reported in Table 7. They are expressed as Henry's law constants (K_H):

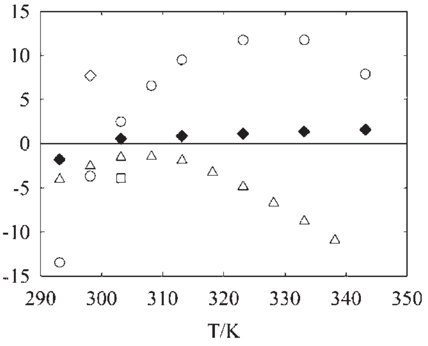


Figure 3. Relative deviations of the viscosity for [C_4mPyr][Tf_2N] from our fitted data: △, Pereiro et al.;[34] □, Tokuda et al.;[35] ○, Okoturo and VanderNoot;[33] ◇, MacFarlane et al.;[41] ◆, this work.

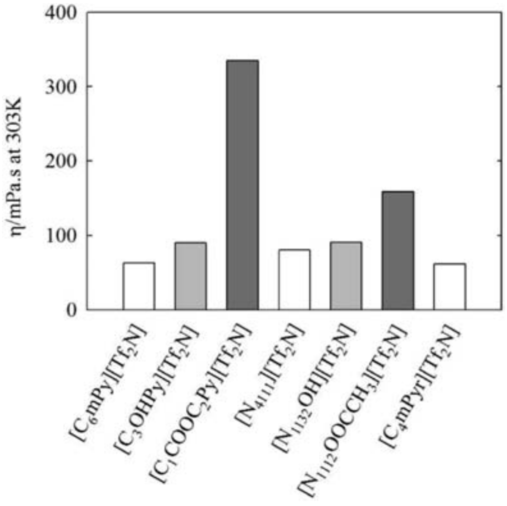


Figure 4. Experimental viscosities of the ILs studied at 303 K.

$$K_H \equiv \lim_{x_2 \to 0} \frac{f_2(p, T, x_2)}{x_2} \cong \frac{\phi_2(p_{eq}, T_{eq})p_{eq}}{x_2} \qquad (7)$$

where f_2 is the fugacity of the solute and ϕ_2 its fugacity coefficient. The fugacity coefficient, which is very close to unity in the present cases, was included in the calculation of the Henry's law constants for all of the gases. The second virial coefficients were taken to calculate the compressibility factor and of the fugacity coefficient of the carbon dioxide from the compilation by Dymond and Smith.[40]

In Table 7, the results are also given as mole fractions of solute (x_2). These last values are calculated from the experimental data of K_H (at slightly different total pressures) assuming a partial pressure of the gaseous solute equal to 0.1 MPa:

$$x_2 = \frac{n_2^{liq}}{(n_1^{liq} + n_2^{liq})} \qquad (8)$$

with n_2^{liq} the amount of solute present in the liquid solution and n_1^{liq} the amount of IL in the liquid phase.

Table 7. Experimental Values of Carbon Dioxide Solubility in ILs Expressed as Both Henry's Law Constants K_H and as CO_2 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	T/K	$p/10^2$ Pa	$K_H/10^2$ Pa	$x_2/10^{-3}$	dev
		$[C_3OHPy][Tf_2N]$					$[N_{4111}][Tf_2N]$		
303.58	643.2	84.71	11.75	+0.8 %	303.55	637.5	36.21	27.49	+0.2 %
303.59	597.0	84.97	11.71	+0.5 %	303.57	642.1	36.47	27.29	−0.5 %
313.55	622.5	115.1	8.649	−0.6 %	303.59	666.0	36.3	27.41	+0.0 %
313.55	616.1	116.3	8.559	−1.7 %	313.53	669.2	43.89	22.69	−0.3 %
323.47	699.6	172.2	5.784	−2.5 %	313.54	434.1	43.24	23.03	+1.2 %
323.50	648.0	166.9	5.969	+0.8 %	323.47	693.7	52.00	19.16	−0.3 %
333.42	726.3	264.0	3.775	+0.7 %	323.52	695.4	52.11	19.12	−0.4 %
333.45	672.7	258.8	3.851	+2.9 %	333.43	745.6	60.79	16.39	−0.3 %
333.46	665.7	262.4	3.797	+1.5 %	333.48	720.7	60.33	16.52	+0.5 %
343.40	752.3	459.0	2.172	−2.4 %	343.41	770.5	69.83	14.28	+0.1 %
343.45	689.4	449.3	2.219	−0.2 %	343.48	745.5	70.05	14.23	−0.1 %
		$[C_1COOC_2Py][Tf_2N]$					$[N_{1112OOCCH3}][Tf_2N]$		
303.59	668.3	73.61	13.52	+0.7 %	303.58	598.0	37.73	26.38	+0.3 %
303.60	666.6	73.38	13.56	+1.1 %	303.68	635.2	38.11	26.11	−0.5 %
313.54	695.5	101.6	9.801	−2.0 %	313.43	661.1	45.32	21.97	−0.6 %
313.55	693.3	101.2	9.842	−1.6 %	313.45	626.0	44.73	22.26	+0.8 %
323.48	721.9	144.8	6.880	−1.1 %	323.44	687.0	53.65	18.57	−0.8 %
323.50	719.2	142.5	6.991	+0.6 %	323.46	653.4	52.57	18.95	+1.2 %
333.44	747.6	215.1	4.634	+1.3 %	333.39	712.4	63.47	15.70	−2.1 %
333.48	744.6	210.7	4.730	+3.6 %	333.39	679.8	61.24	16.27	+1.4 %
343.44	773.0	355.2	2.807	−2.2 %	343.29	736.3	72.47	13.76	−0.9 %
343.50	769.7	349.6	2.851	−0.3 %	343.35	705.6	70.94	14.05	+1.3 %

[a] Dev corresponds to the relative deviation between the experimental and calculated Henry's law constant.

To correlate the solubility as a function of temperature, the Henry's law constants obtained from the experimental data were adjusted to a power series in $1/T$:

$$\ln(K_H/10^5\text{Pa}) = \sum_{i=0}^{n} A_i (T/\text{K})^{-i} \tag{9}$$

The coefficients A_i are collected in Table 8. The average deviation of the fit (presented in Table 7) characterizes the precision of the data, which is of the order of 1 %. In Figure 5 are represented the solubility data expressed in mole fraction as a function of temperature. The solubility decreases with increasing temperature in the range covered by this work. The solvation takes place preferentially at low temperature, which corresponds to an exothermic process.

The CO_2 solubility in another $[N_{4111}][Tf_2N]$ sample has been previously measured by our group[24] using the same experimental technique. The results are is in good agreement with the present data, as observed in Figure 6, with deviations lower than ± 1 %. The value reported by Kilaru et al.[43] for the CO_2 solubility (not presented in Figure 6), measured using the lag-time technique, in the same IL at 303 K only is 40 % lower ($x_{CO_2} = 0.0165$) than those reported in this work.

Also represented in Figure 5 are the solubilities of CO_2 in other previously studied ILs: $[C_4mPy][Tf_2N]$,[45] $[C_6mPy][Tf_2N]$,[46] $[N_{1132OH}][Tf_2N]$,[29] and $[C_4mPyr][Tf_2N]$.[29] The CO_2 mole fraction solubilities for these ILs are listed, at five discrete temperatures between (303 and 343) K, in Table 9. These solubilities are compared in Figure 7, at 325 K, with the ones reported herein. All ILs are able to dissolve CO_2 with mole fractions of the order of 10^{-2} at temperatures from room temperature up to 343 K and at partial pressures of gas of the order of 0.1 MPa. The pyridinium-, ammonium-, and pyrrolidinium-based ILs are capable of dissolving similar quantities of gas, and except for the pyridinium-based ILs, the presence of hydroxyl or ester functions does not affect significantly the CO_2 mole fraction solubility. In the case of the pyridinium-based ILs, the presence of OH or COO groups significantly lowers the capacity of the IL to dissolve CO_2.

Table 8. Parameters of Equation 9 Used to Smooth the Raw Experimental Results from Table 7

IL	A_0	A_1/K	A_2/K^2
$[C_3OHPy][Tf_2N]$	72.296	$-3.8988 \cdot 10^4$	$5.5830 \cdot 10^6$
$[C_1COOC_2Py][Tf_2N]$	59.931	$-3.1419 \cdot 10^4$	$4.4166 \cdot 10^6$
$[N_{4111}][Tf_2N]$	6.9363	$-2.2302 \cdot 10^2$	$-2.4052 \cdot 10^5$
$[N_{1112OOCCH_3}][Tf_2N]$	9.0170	$-1.5831 \cdot 10^3$	$-1.5512 \cdot 10^4$

For example, the CO_2 solubility in $[C_1COOC_2Py][Tf_2N]$ is almost 50 % lower than in $[C_6mPy][Tf_2N]$. Muldoon et al.[15] have reported similar solubilities of CO_2 in the ester-functionalized IL $[C_1COOC_4Py][Tf_2N]$ and in $[C_6mPy][Tf_2N]$ at atmospheric pressure, even if larger solubilites were expected in the former due to the presence of a longer alkyl-side chain in the cation. The differences found between the influence on the CO_2 solubility of the ester groups associated with imidazolium, ammonium, or pyridinium cations are difficult to explain. The negligible effect in imidazolium and ammonium-based ILs has been attributed to the dominant effect of the anion $[Tf_2N]$ or to the proximity of the cation core that lowers the electronegativity of the oxygen of the carbonyl group.[15]

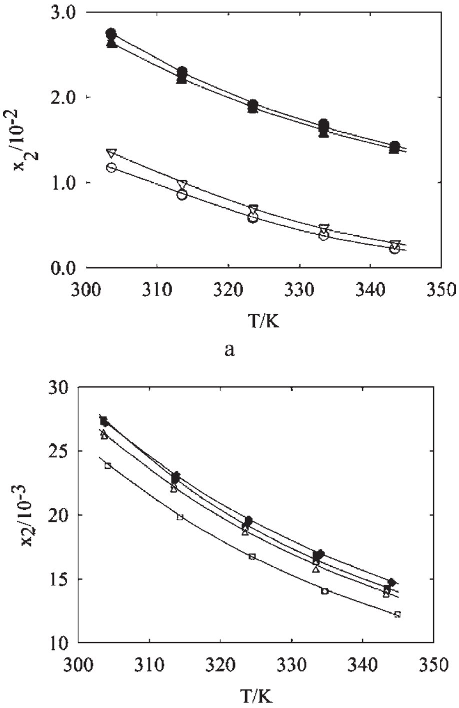


Figure 5. Mole fraction solubility of carbon dioxide in ILs as a function of temperature: (a) pyridinium-based ILs: ▲, [C$_4$mPy][Tf$_2$N];[45] ●, [C$_6$mPy][Tf$_2$N];[46] ○, [C$_3$OHPy][Tf$_2$N]; ▽, [C$_1$COOC$_2$Py][Tf$_2$N]. (b) Nonaromatic ILs: ■, [N$_{4111}$][Tf$_2$N]; □, [N$_{1132OH}$][Tf$_2$N];[29] △, [N$_{1112OOCCH_3}$][Tf$_2$N]; ◆, [C$_4$mPyr][Tf$_2$N].[29]

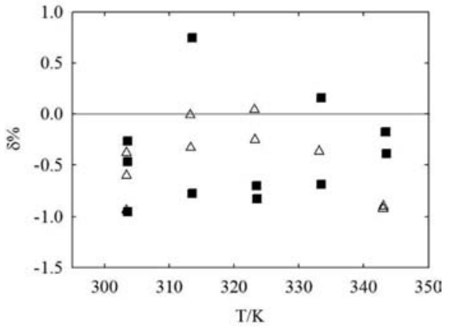


Figure 6. Deviations of the literature values to the correlation of mole fraction solubilities obtained in this work for carbon dioxide in [N$_{4111}$][Tf$_2$N]: ■, this work; △, Jacquemin et al.[24]

CO_2 solubility in [C$_3$OHPy][Tf$_2$N] is even 15 % lower than that measured in [C$_1$COOC$_2$Py][Tf$_2$N]. The decrease of CO_2 solubility caused by the presence of a hydroxyl group has also been observed in [N$_{1112OH}$][Tf$_2$N][15] and in [C$_2$OHmIm]-[BF$_4$].[42] Free volume arguments as well as weaker interactions between the solute and the IL due to the presence of hydroxyl groups have been advanced as possible explanations for this lowering of CO_2 solubility.[15,45] These explanations do not account for the observations that the presence of hydroxyl groups imidazolium-based ILs with the anions PF_6^- or $CF_3SO_3^-$ causes an increase on the CO_2 solubilities whereas they are comparable in [C$_2$OHmIm][Tf$_2$N] and [C$_2$mIm][Tf$_2$N].[48]

The thermodynamic properties of solvation provide valuable information about the mechanisms of solvation of the carbon dioxide in the different ILs. The variation of the solubility, expressed in Henry's law constant, with temperature is directly

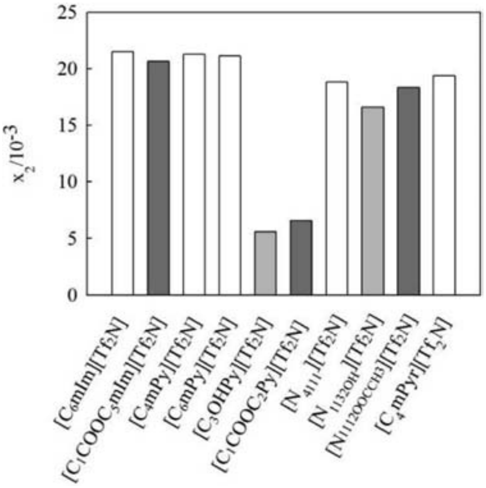


Figure 7. CO_2 mole fraction solubilities in the ILs at 325 K corrected for a partial pressure of solute of 0.1 MPa. [C$_6$mIm][Tf$_2$N];[47] [C$_4$mPy]-[Tf$_2$N];[48] [C$_6$mPy][Tf$_2$N];[49] [N$_{1132OH}$][Tf$_2$N];[29] [C$_4$mPyr][Tf$_2$N].[29]

Table 10. Average Values of the Thermodynamic Functions of Solvation of CO_2 in the Four Ionic Liquids in the Temperature Range (303 to 343) K

	$\Delta_{sol}H^\infty$	$\Delta_{sol}S^\infty$
	kJ·mol^{-1}	J·mol^{-1}·K^{-1}
[C$_3$OHPy][Tf$_2$N]	−38	−159
[C$_1$COOC$_2$Py][Tf$_2$N]	−35	−147
[N$_{4111}$][Tf$_2$N]	−14	−77
[N$_{1112OOCCH_3}$][Tf$_2$N]	−14	−76

Table 9. CO_2 Solubilities in ILs Reported in the Literature

T	[C$_4$mPy][Tf$_2$N][45]		[C$_6$mPy][Tf$_2$N][46]		N$_{1132OH}$][Tf$_2$N][29]		[C$_4$mPyr][Tf$_2$N][29]	
K	K_H/bar	$x_2/10^{-3}$	K_H/bar	$x_2/10^{-3}$	K_H/bar	$x_2/10^{-3}$	K_H/bar	$x_2/10^{-3}$
303	35.48	28.18	35.39	28.25	40.78	24.52	36.16	27.66
313	40.61	24.63	40.72	24.56	49.04	20.39	42.77	23.38
323	45.96	21.76	46.20	21.65	58.29	17.16	50.05	19.98
333	51.51	19.42	51.76	19.32	68.58	14.58	57.98	17.25
343	57.22	17.48	57.37	17.43	79.92	12.51	66.57	15.02

related to the thermodynamic properties of solvation, which, in the case of gaseous solutes at low pressures, are practically identical to the thermodynamic properties of solution.[44] The Gibbs energy of solvation is given by:

$$\Delta_{\mathrm{sol}}G^{\infty} = RT\,\ln(K_{\mathrm{H}}/p^0) \tag{10}$$

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

$$\Delta_{\mathrm{sol}}H^{\infty} = -T^2\partial/\partial T(\Delta_{\mathrm{sol}}G^{\infty}/T) = -RT^2\partial/\partial T[\ln(K_{\mathrm{H}}/p^0)] \tag{11}$$

$$\begin{aligned}\Delta_{\mathrm{sol}}S^{\infty} &= (\Delta_{\mathrm{sol}}H^{\infty} - \Delta_{\mathrm{sol}}G^{\infty})/T \\ &= -RT\partial/\partial T[\ln(K_{\mathrm{H}}/p^0)] - R\,\ln(K_{\mathrm{H}}/p^0)\end{aligned} \tag{12}$$

The average values for the Gibbs energy, enthalpy, and entropy of solvation in the temperature range studied are given in Table 10. It can be observed that the larger CO_2 solubility in the ammonium-based ILs cannot be explained by more favorable solute−solvent interactions that would lead to more negative enthalpies of solvation. The more negative enthalpies of solvation are observed in the pyridinium-based ILs, in which the gas is not as soluble as in the ammonium-based ILs. It is a more favorable (less negative) entropy of solvation that explains the larger solubility in the ammonium-based ILs, probably meaning that in these ILs the solute is more mobile, its dissolution leading to a significant increase on the entropy. The oxygen-functionalized ILs present, in general, more favorable enthalpies of solvation but less favorable entropic contributions to the Gibbs energy of solvation. The two terms tend to compensate, and so the solubility of CO_2 is comparable in functionalized and nonfunctionalized ILs. In the case of pyridinium-based ILs, associated with the $[Tf_2N]$ anion, the entropic term is very defavorable leading to significantly lower CO_2 solubilities in hydroxyl or carbonyl functionalized ILs.

■ CONCLUSION

The presence of carbonyl or hydroxyl groups in the alkyl side chains of ILs based on the pyridinium, pyrrolidinium, or ammonium cations can affect their physicochemical properties. In previous works[14,16] we have concluded that, for imidazolium-based ILs, the chemical modification of the alkyl side chain does not result in a significant change of the solubility of different families of gases.

Herein, we have studied the influence of the same chemical modifications in pyridinium and ammonium-based ILs. We conclude that the introduction of oxygen functionalities in the ILs based on the pyridinium or ammonium cations increases the viscosity, ester functions having a larger effect than the hydroxyl functionalities. The carbon dioxide solubility is not influenced by the presence of the ester and hydroxyl groups in the cation except for the case of pyridinium-based ILs in which the gas is much less soluble when the cation is functionalized. This can be explained by a much less favorable entropic contribution to the Gibbs energy of solvation that largely counterbalances the strong solute−solvent interactions characterized by a relatively large negative enthalpy of solvation.

The study of ILs including other functional groups, either in the cation or the anion, can be regarded as a possible perspective of the present work. Prior to the study of the solvation properties of these IL, it is important to check whether the insertion of this new function will modify physicochemical properties like the density or the viscosity which are important parameters to control the mass transfer. The authors find that the introduction of nitrile or vinyl groups, namely, in the cation of the IL, can lead to ILs with interesting solvation properties that could be successfully used, namely, as electrolytes for dye-sensitized solar cells.[44]

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