Prediction of Ionic Liquid Properties. I. Volumetric Properties as a Function of Temperature at 0.1 MPa

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The prediction of molar volumes and densities of several ionic liquids has been achieved using a group contribution model as a function of temperature between (273 and 423) K at atmospheric pressure. It was observed that the calculation of molar volumes or densities could be performed using the "ideal" behavior of the molar volumes of mixtures of ionic liquids. This model is based on the observations of Canongia Lopes et al. (*J. Phys. Chem. B* **2005**, *109*, 3519–3525) which showed that this ideal behavior is independent of the temperature and allows the molar volume of a given ionic liquid to be calculated by the sum of the effective molar volume of the component ions. Using this assumption, the effective molar volumes of ions constituting more than 220 different ionic liquids were calculated as a function of the temperature at 0.1 MPa using more than 2150 data points. These calculated results were used to build up a group contribution model for the calculation of ionic liquid molar volumes and densities with an estimated repeatability and uncertainty of 0.36 % and 0.48 %, respectively. The impact of impurities (water and halide content) in ionic liquids as well as the method of determination were also analyzed and quantified to estimate the overall uncertainty.

Introduction

Over the past decade, interest in ionic liquids as novel solvents and materials with negligible vapor pressure at normal temperature and pressure has increased significantly[1–4] with the vast majority of research concentrated on their implementation as new reaction media.[5] In that context, the knowledge of their thermophysical properties, in particular their transport properties, is still limited despite its importance if the use of ionic liquids as solvents is to become widespread commercially. Experimental data have been reported for a large range of properties with density and viscosity being the most widely examined.[5] A considerable amount of experimental data have been measured for the density as a function of the temperature for a range of imidazolium, pyridinium, ammonium, phosphonium, and pyrrolidinium based ionic liquids. However, due to the number of possible combinations of ionic liquids, predictive models are essential if ionic liquids are to realize their potential as "designer solvents".

A number of models for the calculation of the density at atmospheric pressure have been reported. Rebelo et al.[6,7] defined the effective molar volumes of ions at 298.15 K and used the "ideal behavior" of the molar volumes of mixtures of ionic liquids for the determination of the molar volume of ionic liquids at 298 K. Yang et al.[8] used a theory based on the "interstice model" which was established by correlating the density and the surface tension of a single ionic liquid. Unfortunately, the limited data set reported is insufficient to assess the uncertainty of the method although the repeatability of the density as a function of the temperature between (278 and 328) K is within 0.5 %. Group contribution models have been reported by Kim et al.[9,10] for the calculation of the density and CO_2 gas solubility for 1-alkyl-3-methylimidazolium based ionic liquids as a function of the temperature and the CO_2 gas pressure. The prediction of the density model was close to 0.6 % over the temperature range (293 to 343) K. However, in this study, no anion dependence was determined thus limiting the general applicability of this model for designer solvents. Deetlefs et al.[11] focused on the determination of refractive index, surface tension, and density at 298 K for a range of ionic liquids using a parachor function defined by Knotts et al.[12] Therein, the estimated uncertainty of this model was approximately 1.0 % for the determination of the density of ionic liquids at 298 K. Recently, Ye and Shreeve[13] reported that there was a linear relationship between the density in solid and liquid states of ionic liquids. Therefore, by using a group contribution model for the calculation of the density in solid state coupled with a linear regression, the density in the liquid state could be calculated. In this study, previously reported values of ionic liquid densities were used, and these had been measured at different temperatures between (291 and 303) K. However, over this range of temperatures, the density of ionic liquids varies by ≈ 0.8 %, and therefore, the uncertainty of this model cannot be better than this value. More recently, Gardas and Coutinho[14] extended the Ye and Shreeve group contribution method for the estimation of the density over a wide range of temperatures and pressures with an uncertainty determined as 0.6 %. Nevertheless, in this study, the calculation of ionic liquid density was determined from a prior knowledge of their mechanical coefficients again limiting the general applicability of this methodology. This methodology is only applicable where the calculations are performed for ionic

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liquids with a common anion, as it is only in this situation that there is a small variation in their mechanical coefficients.[15]

In general, many of the current models available are not effective at predicting ionic liquid density over a range of temperatures at atmospheric pressure. To date, only the models reported by Kim et al.[9,10] and by Gardas and Coutinho[14] have been able to predict density as a function of the temperature; however, these models are limited by a nonanion dependence and by the prior knowledge of the mechanical coefficients used in their calculations, respectively. Density, viscosity, and specific conductivity of 23 ionic liquids have been correlated using a volume based approach at (293 to 295) K, and using empirical relationships, good agreement with the experimental values was found.[16]

In this paper, the focus has been to examine the extent to which group contribution models may be used to predict the molar volume and the density of ionic liquids as a function of the temperature at atmospheric pressure. Herein, the model used is based on the assumption that the molar volume of the ionic liquid may be obtained from the effective molar volumes of the ions as an "ideal" mixture as proposed by Rebelo et al.[6,7] The development of the group contribution model reported has been achieved using a large amount of density data (2150 data points) taken from both reported values as well as new measurements performed in our laboratory. This model has enabled the uncertainty of the densities of ionic liquids to be quantified. This uncertainty may be attributed to two groups of errors, those caused by the apparatus and those due to the impurities present in the ionic liquids.

The densities of pure ionic liquids have been measured using a range of experimental techniques, mainly at atmospheric pressure and as a function of temperature. The majority of these data (around 64 % of the published values) is measured using indirect methods, predominantly the vibrating-tube densitometer. This apparatus relies on calibration as a function of temperature and pressure using appropriate reference fluids[17,18] whose density is similar to that of the sample. In the case of very dense fluids, such as ionic liquids, the calibration curve normally has to be extrapolated, and the use of three reference fluids is recommended; however, in most cases, this is not done.[17] The densities of ionic liquids measured with vibrating tube densitometers have a standard uncertainty to within 0.1 %. The low uncertainty (and repeatability) of the densities measured and the fact that only small quantities of fluid are required, have rendered this experimental method very popular. It should be noted that for the case of viscous fluids, such as ionic liquids (η > 100 mPa·s), a correction for the effect of viscosity should also be included.[19–21] Furthermore, due to the large effect of the temperature on the viscosity, this correction is only valid for short temperature ranges close to room temperature. Other indirect methods have been used for the measurement of the density of ionic liquids. It is possible to calculate the density of ionic liquids through speed of sound measurements[22] or piezometric methods[17] both of which have a standard uncertainty around 0.2 %. Both approaches are relatively complex technically but have the advantage of providing additional data on the thermodynamic properties of the fluids. Pycnometric methods or hydrostatic weighing techniques are also used extensively; however, the use of pycnometers requires a large sample of fluid and extensive volume calibration procedures with a reference fluid to obtain very accurate values of the density (typically 0.05 % uncertainty).[17] Hydrostatic weighing methods can be used in an absolute manner as the density of the fluid is determined by direct application of the Archimedes principle to a buoy immersed in the test fluid and have an uncertainty to within 0.1 %.[23] The major inconvenience of these methods is the transmission of the buoyancy force through the walls of the container, especially in the case of high-pressure vessels.[17,23]

As many ionic liquids inherently contain impurities which can have a significant impact on physical data,[24–27] it is vital to quantify the effect of the impurities on the uncertainty of the measured physical properties. The main impurities in ionic liquids are water, halides, and unreacted reagents of which water and halides are the most common. Some detailed studies have examined the effect of water on ionic liquids; for example, Jacquemin et al.[25] studied six hydrophobic and hydrophilic ILs (five imidazolium and one ammonium based ionic liquid) as a function of temperature up to 343 K and at atmospheric pressure. The densities of the water-saturated IL samples were found to be lower when compared with the dried samples with the differences found between (1 and 2) % for hydrophobic ionic liquid samples containing a mole fraction of water close to 30 %.

For the majority of densities reported to date, the ionic liquids examined contained a water mass fraction content ≤ 10^{-3} and a halide mass fraction content ≤ 10^{-4}. One important aspect of this work is to quantify the real impact of these impurities on ionic liquid density measurements.

In this paper, the chemical structures, molar mass, CAS registry numbers, and abbreviated notations (AN) of ions used in the present work are described in the Supporting Information.

Experimental

Materials. Ionic liquids (ILs) containing the anion bis{(trifluoromethyl)sulfonyl}imide ($[NTf_2]^-$) were prepared in house from the appropriate chloride or bromide salt using the procedure described by Bonhôte et al.,[28] except for 1-cyanomethylpyridinium bis{(trifluoromethyl)sulfonyl}imide ($[CNPy][NTf_2]$) and 1-cyanomethyl-1-methylpyrrolidinium bis{(trifluoromethyl)sulfonyl}imide ($[CNmPyrro][NTf_2]$), which were obtained from IoLiTec (98 %). Ionic liquids based on the trispentafluoroethyltrifluorophosphate ($[FAP]^-$) anion were also obtained from Merck (98 %). 1-Butyl-3-methylimidazolium trifluoromethanesulfonate, $[C_4mim][OTf]$, was prepared via a metathesis reaction between $[C_4mim]Cl$ and the lithium trifluoromethanesulfonate. 1-Ethyl-3-methylimidazolium ethyl sulfate, $[C_2mim][EtSO_4]$, was prepared by reacting 1-methylimidazole with diethyl sulfate according to previously reported procedures by Xu et al.[29] Two samples of 1-butyl-3-methylimidazolium hexafluorophosphate, $[C_4mim][PF_6]$, from Acros Organics, denoted $[C_4mim][PF_6]^{AO}$ (≥ 99.9 %), and from Solvionic, $[C_4mim][PF_6]^{solv}$ (≥ 99.9 %), were used. Two samples of 1-butyl-3-methylimidazolium tetrafluoroborate, $[C_4mim][BF_4]$, from Sigma Aldrich, denoted $[C_4mim][BF_4]^{SA}$ (≥ 98 %), and from Solvionic, $[C_4mim][BF_4]^{solv}$ (≥ 98 %), were used. 1,3-Dimethylimidazolium thiocyanate, $[C_1mim][SCN]$, was supplied by the group of P. Wasserscheid (University of Erlangen-Nurnberg, Germany) (≥ 99 %). Prior to use, the halide and water contents were determined to estimate their influence on the density measurements. The halide content of ionic liquids was determined using suppressed ion chromatography (IC).[30] The lithium content of those samples prepared via lithium salt metathesis was determined by inductively coupled plasma analysis (ICP). The water content was determined before and after measurements by volumetric Karl Fischer titration using a Mettler Toledo DL31 titrator. The source, molar mass, and halide, lithium, and water content of the ionic liquids measured in this study, after drying under a pressure of 1 Pa at temperature 323.15 K for 15 h, are summarized in Table 1.

Table 1. Molar Mass (M^{IL}), Halide Mass Fraction Content (w_h), Lithium Mass Fraction Content (w_{Li^+}), Water Content in Mass Fractions (w_w), and Mole Fractions (x_w) of ILs Measured in This Study

ionic liquid	$M^{IL}/g \cdot mol^{-1}$	source	$w_w \cdot 10^3$	$x_w \cdot 10^3$	$w_h \cdot 10^6$	$^f w_{Li^+} \cdot 10^6$
$^d[P_{66614}][NTf_2]$	764.01	QUILL	0.15	6.32	$<50^a$	0.45
$^{c,d}[C_2mim][NTf_2]$	391.31		0.05	1.09	$<5^b$	2.59
$^c[C_4mim][NTf_2]$	419.37		0.05	1.16	$<5^b$	0.74
$^d[C_4mim][NTf_2]$	419.37		0.24	5.57	$<5^b$	0.74
$^d[C_6mim][NTf_2]$	447.42		0.05	1.24	$<5^b$	0.79
$^d[C_8mim][NTf_2]$	475.47		0.05	1.32	$<5^b$	0.67
$^d[C_{10}mim][NTf_2]$	503.53		0.05	1.40	$<5^b$	1.37
$^d[C_2mim][EtSO_4]$	236.29		0.28	3.66	$-^e$	$-^g$
$^d[C_4mim][OTf]$	288.29		0.28	4.46	$<11^a$	5.65
$^d[CNPy][NTf_2]$	399.29	IoLiTec	<0.10	<2.14	$<100^a$	1.56
$^d[CNmPyrro][NTf_2]$	405.34	IoLiTec	<0.10	<2.17	$<100^a$	2.59
$^d[C_4mPyrro][FAP]$	587.27	Merck	<0.10	<3.25	$<100^a$	$-^g$
$^d[C_4Py][FAP]$	581.22	Merck	<0.10	<3.22	$<100^a$	$-^g$
$^d[C_6mim][FAP]$	612.28	Merck	<0.10	<3.39	$<100^a$	$-^g$
$^c[C_1mim][SCN]$	155.22	Erlangen	0.07	0.60	$-^e$	$-^g$
$^c[C_4mim][PF_6]$	284.18	Acros Organics	0.19	2.99	100^a	$-^g$
		Solvionic	0.19	2.99	20^a	$-^g$
$^c[C_4mim][BF_4]$	226.03	Sigma Aldrich	0.70	8.71	165^a	$-^g$
		Solvionic	0.70	8.71	20^a	$-^g$

[a] Cl^- measured using IC. [b] Br^- measured using IC. [c] LTSP measurements. [d] QUILL measurements. [e] Halogen-free sample. [f] Li^+ measured using ICP. [g] Lithuim-free sample.

Method. Two methods of measuring the density were employed during the study, both based upon the vibrating-tube densitometer. A U-shaped vibrating-tube densitometer (Anton Parr, model DMA 512, located at the Laboratoire de Thermodynamique des Solutions et des Polymères, denoted LTSP, in France), operated in the static mode, was used at atmospheric pressure with the temperature being maintained to within 0.01 K by means of a recirculation bath equipped with a PID temperature controller (Julabo FP40-HP). The temperature was determined using a 100 Ohm platinum resistance thermometer (repeatability 0.02 K, uncertainty 0.04 K) calibrated by comparison with a 100 Ohm platinum resistance Hart Scientific model 1502A. An analogous apparatus (Anton Paar, model DMA 4500 operating in a static mode at the Queen's University Ionic Liquid Laboratories, denoted QUILL, Belfast) was also used to measure the densities at atmospheric pressure. This instrument was fully automated, and therefore, the resonant frequency was automatically determined. The temperature in the cell was regulated to ± 0.01 K with a solid state thermostat. Independent measurements were made in each of the laboratories.

The measured period of vibration (τ) of the U tube is related to the density (ρ) according to

$$\rho = A\tau^2 + B \tag{1}$$

where A and B are parameters that are a function of both temperature and pressure. The method described by Lagourette et al.[31] was used to calibrate densitometers between (293 and 363) K, every 10 K, at atmospheric pressure using vacuum, air, nitrogen, triply distilled water, and aqueous solutions of NaCl (molalities of 1 $mol \cdot L^{-1}$ and 3 $mol \cdot L^{-1}$).

After treating the ILs for 15 h at 323 K under vacuum, the samples were considered as nominally "dry" and were stored under a nitrogen atmosphere. To avoid any contact of the sample with water, a Schlenk tube and a syringe equipped with a Luer-Lock valve were used to load the samples into the densitometer. To study the impact of water on the density, all the water contaminated samples were artificially contaminated with triply distilled water using a Schlenk technique. Prior to use, the water was first degassed and then introduced under the vapor pressure of pure water into the Schlenk tube containing the ionic liquid by gravity. The mass fraction of water was fixed at 10^{-3}, and the composition was determined before and after the density measurement by volumetric Karl Fischer titration. At least three independent values were obtained for each temperature. The effect of the viscosity on the density measurement was analyzed to validate the density measurements. In the case of $[C_4mim][PF_6]$, for which this effect will be greatest, the density was found to vary by < 0.1 % and, therefore, was considered to be negligible. The repeatability of the density measurements was 10^{-4} $g \cdot cm^{-3}$, and the results have an uncertainty to 10^{-3} $g \cdot cm^{-3}$, a value determined by comparing the two data sets obtained in the two laboratories using the same ionic liquid sample.

Results and Discussion

Density Measurements. Density measurements of pure ionic liquids were carried out at temperatures ranging from (293.15 to 363.15) K at 0.1 MPa. The experimental data obtained are reported in Table 2 for all the pure ILs studied. For the pure ILs, the values vary typically from (1.05 to 1.64) $g \cdot cm^{-3}$ at 293 K and from (1.01 to 1.57) $g \cdot cm^{-3}$ at 363 K. As expected, the densities are closely related to the molar mass of the ions with ILs containing heavy atoms found to be most dense, in general. In addition, the density is found to decrease with increasing length of the alkyl chain on the imidazolium cation, as expected. Such trends are in good agreement with the variation in density with the ionic liquid structure previously reported.[7–16,20,21,24–78] The variation of the density with temperature for the ionic liquids studied is illustrated in Figure 1. A quadratic equation was used to fit the variation with temperature at 0.1 MPa of the form

$$\rho_{IL}(T) = \sum_{i=0}^{2} (a_i \cdot T^i) \tag{2}$$

with the parameters, a_i, given in Table 3.

To examine the consistency of measuring the density, the same samples of $[C_2mim][NTf_2]$ and of $[C_4mim][NTf_2]$ were measured independently by both research groups (LTSP and QUILL), and the data are reported in Table 2. For $[C_2mim][NTf_2]$, the values obtained agree to within 0.04 %, a value compatible with the 0.1 % uncertainty claimed for these density measurements. In the case of $[C_4mim][NTf_2]$, higher deviations of up to 0.15 % were found which may be attributed

Table 2. Experimental Densities, ρ, of Dried ILs as a Function of Temperature at Atmospheric Pressure

	ρ/g·cm^{-3}			
T/K	[a][C$_4$mim] [BF$_4$]$^{\mathrm{solv},c}$	[a][C$_4$mim] [BF$_4$]$^{\mathrm{SA},d}$	[a][C$_4$mim] [PF$_6$]$^{\mathrm{solv},c}$	[a][C$_4$mim] [PF$_6$]$^{\mathrm{AO},e}$
293.15	1.2049	1.2038	1.3698	1.3681
298.15	1.2011	1.2000	1.3657	1.3641
303.15	1.1974	1.1962	1.3616	1.3600
308.15	1.1938	1.1924	1.3574	1.3557
313.15	1.1901	1.1889	1.3533	1.3518
318.15	1.1865	1.1854	1.3492	1.3475
323.15	1.1827	1.1813	1.3451	1.3435
328.15	1.1790	1.1779	1.3410	1.3394
333.15	1.1753	1.1741	1.3369	1.3352
338.15	1.1717	1.1705	1.3327	1.3311
343.15	1.1680	1.1669	1.3286	1.3270

	ρ/g·cm^{-3}			
T/K	[a][C$_2$mim] [NTf$_2$]	[b][C$_2$mim] [NTf$_2$]	[a][C$_4$mim] [NTf$_2$]	[b][C$_4$mim] [NTf$_2$]
293.15	1.5229	1.5234	1.4427	1.4402
298.15	1.5179	-	1.4379	-
303.15	1.5129	1.5134	1.4331	1.4307
308.15	1.5079	-	1.4283	-
313.15	1.5029	1.5034	1.4235	1.4212
318.15	1.4979	-	1.4188	-
323.15	1.4929	1.4934	1.4140	1.4118
328.15	1.4880	-	1.4093	-
333.15	1.4830	1.4835	1.4045	1.4024
338.15	1.4780	-	1.3997	-
343.15	1.4730	1.4737	1.3950	1.3930
353.15	-	1.4638	-	1.3836
363.15	-	1.4540	-	1.3743

	ρ/g·cm^{-3}			
T/K	[b][C$_6$mim] [NTf$_2$]	[b][C$_8$mim] [NTf$_2$]	[b][C$_{10}$mim] [NTf$_2$]	[b][P$_{666\ 14}$] [NTf$_2$]
293.15	1.3751	1.3245	1.2824	1.0676
303.15	1.3660	1.3158	1.2738	1.0603
313.15	1.3569	1.3070	1.2653	1.0529
323.15	1.3479	1.2982	1.2568	1.0457
333.15	1.3388	1.2895	1.2483	1.0386
343.15	1.3298	1.2808	1.2399	1.0315
353.15	1.3209	1.2721	1.2314	1.0244
363.15	1.3119	1.2635	1.2231	1.0173

	ρ/g·cm^{-3}			
T/K	[b][CNPy] [NTf$_2$]	[b][CNmPyrro] [NTf$_2$]	[b][C$_4$mim] [OTf]	[a][C$_1$mim] [SCN]
293.15	1.6362	1.5454	1.3013	1.1607
298.15	1.6312	1.5378	-	1.1574
303.15	1.6262	1.5331	1.2934	1.1542
313.15	1.6162	1.5238	1.2856	1.1478
323.15	1.6064	1.5145	1.2777	1.1414
333.15	1.5968	1.5055	1.2699	1.1352
343.15	1.5873	1.4967	1.2623	1.1291
353.15	1.5777	1.4878	1.2545	1.1231
363.15	1.5683	1.4790	1.2469	1.1172

	ρ/g·cm^{-3}			
T/K	[b][C$_6$mim] [FAP]	[b][C$_4$mPyrro] [FAP]	[b][C$_4$Py] [FAP]	[b][C$_2$mim] [EtSO$_4$]
293.15	1.5571	1.5881	1.6385	1.2423
298.15	1.5518	-	1.6330	-
303.15	1.5464	1.5773	1.6276	1.2356
313.15	1.5357	1.5668	1.6166	1.2289
323.15	1.5250	1.5564	1.6056	1.2221
333.15	1.5143	1.5459	1.5947	1.2155
343.15	1.5036	1.5355	1.5838	1.2088
353.15	1.4930	1.5251	1.5729	1.2022
363.15	1.4824	1.5147	1.5620	1.1956

[a] LTSP measurements. [b] QUILL measurements. [c] ILs purchased from Solvionic. [d] IL purchased from Sigma Aldrich. [e] IL purchased from Acros Organics.

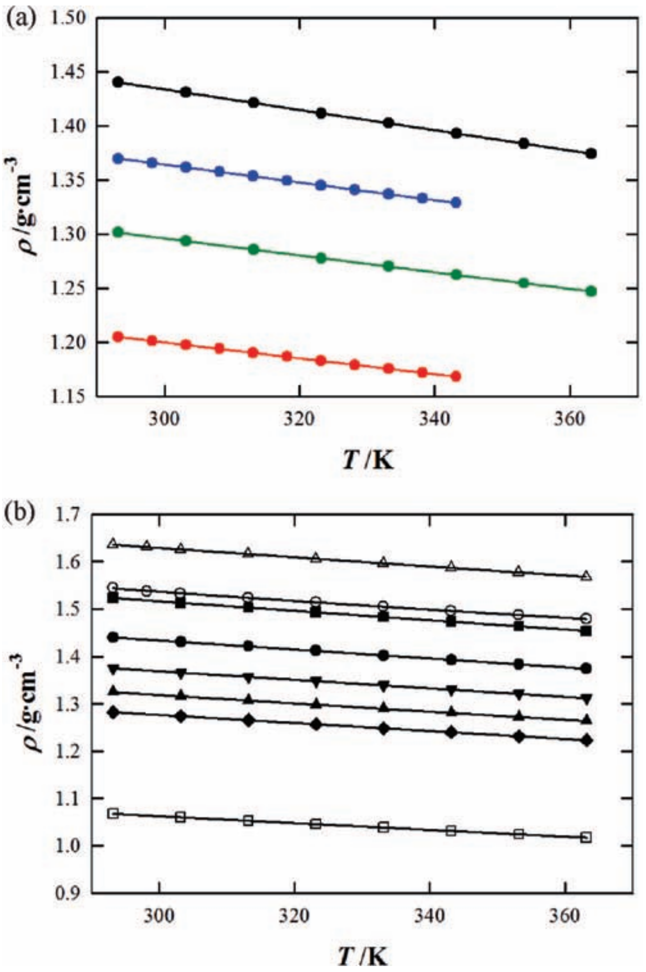

Figure 1. Experimental densities of dried ionic liquids as a function of the temperature at 0.1 MPa. (a) Effect of the anion on the densities of [C$_4$mim]$^+$ based ionic liquids: black ●, [NTf$_2$]$^-$; blue ●, [PF$_6$]$^-$; green ●, [OTf]$^-$; red ●, [BF$_4$]$^-$. (b) Effect of the cation on the densities of [NTf$_2$]$^-$ based ionic liquids: ■, [C$_2$mim]$^+$; ●, [C$_4$mim]$^+$; ▼, [C$_6$mim]$^+$; ▲, [C$_8$mim]$^+$; ♦, [C$_{10}$mim]$^+$; Δ, [CNPy]$^+$; ○, [CNmPyrro]$^+$; □, [P$_{66614}$]$^+$. The lines correspond to the fit of the data by eq 2 reported in Table 3.

to a difference in the water mass fraction contents of the ionic liquid samples measured in the two laboratories, 240·10^{-6} (QUILL) vs 50·10^{-6} (LTSP). This large difference in density illustrates the significant impact that small amounts of water has on the volumetric properties of ionic liquids.

To quantify this effect in detail, [C$_4$mim][BF$_4$]$^{\mathrm{solv}}$ ($^{\mathrm{solv}}$: ionic liquid from Solvionic), [C$_4$mim][PF$_6$]$^{\mathrm{solv}}$, [C$_2$mim][NTf$_2$], [C$_4$mim][NTf$_2$], [C$_{10}$mim][NTf$_2$], and [P$_{66614}$][NTf$_2$] were contaminated with a mass fraction of water fixed to 10^{-3}, and their densities were measured at 298.15 K and are reported in Table 4. The values obtained, ρ, may be compared with those in Table 2, and an average 0.2 % deviation is found. As expected, those ionic liquids which contained higher water contents were found to be systematically less dense than the dried samples. A similar deviation is also observed when the density of the contaminated ionic liquids is determined as a function of temperature. Table 5 summarizes the density data up to 343 K for [C$_4$mim][PF$_6$]$^{\mathrm{solv}}$, [C$_2$mim][NTf$_2$], and [C$_4$mim][NTf$_2$]. It should be noted that higher temperatures were not used to avoid uncertainties in the composition of the (IL + water) mixtures due to evaporative losses. Table 4 also quantifies the differences found in the molar volume of the ionic liquid when containing 10^{-3} of water in mass fraction (up to 4 % mole fraction, depending on the ionic liquid molar mass). This

Table 3. Correlation Parameters a_i and Absolute Average Deviation (AAD) for the Density of Dried and Water-Contaminated ILs ($w_w = 1 \cdot 10^{-3}$) as a Function of Temperature Determined from Measurements between (293 and 363) K for the Dried Samples and between (293 and 343) K for the Water-Contaminated Samples[a]

	a_0	$10^4 a_1$	$10^9 a_2$	AAD
ionic liquid	$g \cdot cm^{-3}$	$g \cdot cm^{-3} \cdot K^{-1}$	$g \cdot cm^{-3} \cdot K^{-2}$	%
$[C_4mim][BF_4]^{\text{solv},d}$	1.42374	−7.5489	+27.972	0.003
$[C_4mim][BF_4]^{\text{SA},e}$	1.44608	−9.0321	+261.07	0.007
[b]$[C_4mim][PF_6]^{\text{solv},d}$	1.61084	−8.2085	−4.6620	0.002
[c]$[C_4mim][PF_6]^{\text{solv},d}$	1.62571	−9.2571	+153.85	0.004
$[C_4mim][PF_6]^{\text{AO},f}$	1.60574	−7.9954	−37.296	0.004
$[C_4mim][OTf]$	1.55206	−9.1804	+214.29	0.003
[b]$[C_4mim][NTf_2]$	1.73011	−10.274	+130.95	0.001
[c]$[C_4mim][NTf_2]$	1.73075	−10.250	+111.89	0.001
[b]$[C_2mim][NTf_2]$	1.83432	−11.164	+190.48	0.002
[c]$[C_2mim][NTf_2]$	1.82177	−10.484	+65.268	0.002
$[C_6mim][NTf_2]$	1.65432	−9.9259	+136.90	0.002
$[C_8mim][NTf_2]$	1.59295	−9.5051	+119.05	0.002
$[C_{10}mim][NTf_2]$	1.54728	−9.4895	+154.76	0.002
$[CNPy][NTf_2]$	1.97741	−13.210	+535.85	0.003
$[CNmPyrro][NTf_2]$	1.98062	−19.469	+1560.2	0.011
$[P_{66614}][NTf_2]$	1.30524	−8.8572	+255.95	0.004
$[C_2mim][EtSO_4]$	1.45075	−7.4576	+119.05	0.002
$[C_4mPyrro][FAP]$	1.91771	−11.873	+214.29	0.003
$[C_4Py][FAP]$	1.96654	−11.399	+71.429	0.002
$[C_6mim][FAP]$	1.88050	−11.314	+96.639	0.001
$[C_1mim][SCN]$	1.40028	−9.7498	+538.35	0.003

[a] Unless otherwise denoted, the samples are considered as dry. [b] Dried ionic liquids. [c] Water contaminated ionic liquids. [d] ILs purchased from Solvionic. [e] IL purchased from Sigma Aldrich. [f] IL purchased from Acros Organics.

calculation is made by considering the mole fraction concentration, the molar volume of pure water,[34] and assuming ideal mixing between the ionic liquid and water. It is important to note that this is an approximation, and to adjust for nonideal mixing, a more rigorous calculation needs to include the excess molar volumes as non-negligible positive values. This effect is small and has been determined by Jacquemin for several hydrophobic ionic liquids: $[C_2mim][NTf_2]$, $[C_4mim][NTf_2]$, $[C_4mim][PF_6]$, $[N_{1114}][NTf_2]$, and $[C_4mPyrro][NTf_2]$.[35]

Table 2 also reports the densities of two different samples of the same ionic liquids, $[C_4mim][BF_4]$ and $[C_4mim][PF_6]$, measured under exactly the same experimental conditions. As reported in Table 1, each sample set had a constant water content but differing halide concentration. The density data obtained in both cases show that an increase in chloride mass fraction content from $(20 \text{ to } 165) \cdot 10^{-6}$ and from $(20 \text{ to } 100) \cdot 10^{-6}$ decreased the density of $[C_4mim][BF_4]$ and $[C_4mim][PF_6]$ by 0.1 %, respectively. Bromide is also found to have a similar effect in decreasing the density. For example, density measurements on samples of $[C_8mim][NTf_2]$ and $[C_{10}mim][NTf_2]$ containing $50 \cdot 10^{-6}$ (mass fraction) of water and either $(5 \text{ or } 100) \cdot 10^{-6}$ mass fraction content of bromide showed a deviation of 0.1 %. The density was found to decrease from (1.3158 to 1.3143) $g \cdot cm^{-3}$ for the two samples of $[C_8mim][NTf_2]$ and from (1.2738 to 1.2724) $g \cdot cm^{-3}$ for $[C_{10}mim][NTf_2]$ at 303.15 K and 0.1 MPa. This general trend of decreasing density with increasing halide content is in good agreement with previous reports by Seddon et al.[24] and Troncoso et al.[27] For small halide mass fraction contents, up to $150 \cdot 10^{-6}$, a decrease of ≈ 0.1 % on average when compared with halide free ILs is observed. In light of this analysis, which quantifies the effect of water and halide impurities on the density of ionic liquids, it is possible to estimate the accuracy of the existing data. A statistical analysis of 1800 data points from the literature associated with a critical examination of both the accuracy of the experimental techniques used and of the quantification of the impurities permits us to establish 0.4 % as a realistic estimation of the uncertainty of the published data on ionic liquid density as demonstrated for $[C_4mim][PF_6]$ in Figure 2.

Development of Predictive Methods

Empirical Method Based on the "Ideal" Volumetric Behavior of ILs. The experimentally determined densities of a series of imidazolium based ILs[6,7,27,32,36–40] indicate that, for a range of anions, the molar volumes vary linearly as a function of the number of carbons in the alkyl chain, and a constant variation of the molar volume is found with the addition of two carbon atoms on this alkyl chain, irrespective of the anion.[6,7,41] This observation has been verified by a number of studies[16,42,43] and was used as a starting point for the model described herein.[15,35] A slope ($\partial V_m / \partial(2x)$), for the variation of the molar volume per addition of two carbon atoms, $(\partial V_m / \partial(2x)) = (34.4 \pm 0.5)\ cm^3 \cdot mol^{-1}$, is obtained for the $[C_nmim]^+$ based ILs at 298.15 K.[6,7,35,41] Furthermore, the densities of IL mixtures have been measured previously to calculate their excess molar volume.[32,44] For every reported case, the excess molar volumes of the binary IL mixtures were small and independent of the temperature and pressure. From these observations, and from a comparison of the excess molar volume and the molar mass of the pure ILs, an "ideal" volumetric behavior of the IL may be obtained, assuming that the excess molar volume of binary IL mixtures may be considered to be zero. This ideality forms the foundation of a simple and precise methodology for the prediction of the molar volume of any ionic liquid from the combination (sum) of the effective volumes occupied by the constituent cations, V^*_c, and anions, V^*_a, ($V_m = V^*_c + V^*_a$) described by Rebelo et al.[6,7,41] and used in other models at 298.15 K.[15,35,42]

The algorithm initially fixes a priori the effective volume of a given ion; for example, Rebelo et al.[6,7,41] chose the $[PF_6]^-$ anion. Therein, its effective molar volume was calculated using the P−F bond length[45] and the van der Waals radius of the fluoride ion[45] giving a $V^*_{PF_6}$ of 73.71 $cm^3 \cdot mol^{-1}$ at 298.15 K and at 0.1 MPa using the following equation (eq 3)

$$V^*_{[PF_6]^-} = N_A \cdot \left(\frac{4\pi r^3}{3}\right) \tag{3}$$

where N_A and r are, respectively, the Avogadro constant ($N_A = 6.022 \cdot 10^{23}\ mol^{-1}$) and radius of the $[PF_6]^-$ hard sphere (r = P−F bond length + the van der Waals radius of the fluorine ion = (1.73 + 1.35) = 3.08 Å[45]).

Using this algorithm ($V_m = V^*_c + V^*_a$),[6,7,41] this model has been extended by Jacquemin and co-workers to predict the density as a function of temperature for 1,3-dialkylimidazolium based ILs with $[NTf_2]^-$, $[PF_6]^-$, $[BF_4]^-$, and $[EtSO_4]^-$ anions[15,35] using a small set of experimental density data.[15,25,35,46–52] The contribution of two $-CH_2-$ groups to the molar volume was obtained from the difference between the molar volume of $[C_2mim][NTf_2]$ and $[C_4mim][NTf_2]$ as a function of temperature. The variation of the molar volume of the anion and of the cation as a function of temperature was calculated using the experimental density of $[C_4mim][NTf_2]$ and fitted with a set of quadratic equations. This fit relies on the assumption that the density change with temperature is the same for the anion and for the cation.[15,35] The uncertainty was then calculated from a comparison of 250 previously reported density data points with those calculated using this extended model and indicated an average absolute deviation of 0.24 % for 1,3-dialkylimidazolium based ILs with alkyl chains containing between 1 and 14 carbon atoms and $[NTf_2]^-$, $[PF_6]^-$, $[BF_4]^-$, and $[EtSO_4]^-$ anions.[15,35]

Table 4. Experimental Densities, ρ, of Selected Ionic Liquids Contaminated by a Mass Fraction of Water of $w_w = 1 \cdot 10^{-3}$ at 298.15 K at 0.1 MPa[a]

ionic liquid	ρ / $g \cdot cm^{-3}$	V_m / $cm^3 \cdot mol^{-1}$	$10^2 \cdot x_w$	$M^{mixture}$ / $g \cdot mol^{-1}$	V_m^R / $cm^3 \cdot mol^{-1}$	ΔV_m / %
$[C_4mim][BF_4]^{solv,b}$	1.1975	188.76	1.24	223.44	186.59	−1.2
$[C_4mim][PF_6]^{solv,b}$	1.3634	208.44	1.55	280.06	205.41	−1.5
$[C_2mim][NTf_2]$	1.5150	258.29	2.13	383.37	253.05	−2.0
$[C_4mim][NTf_2]$	1.4351	292.22	2.27	410.25	285.87	−2.2
$[C_{10}mim][NTf_2]$	1.2755	394.77	2.72	490.32	384.41	−2.6
$[P_{66614}][NTf_2]$	1.0601	720.70	4.07	733.65	692.06	−4.0

[a] Standard deviations (ΔV_m) obtained between the calculation of the molar volumes, V_m, were evaluated directly using the experimental densities, ρ, and the molar mass of pure ILs (excluding the water content) and the calculation of the molar volumes, V_m^R, calculated by using the experimental densities, ρ, and the molar mass of the mixtures (IL + water), $M^{mixture}$ (accounting the water content), determined from the mole fraction, x_w, obtained for each component at 298.15 K and at atmospheric pressure. [b] ILs purchased from Solvionic.

Table 5. Experimental Densities, ρ, of Dried and Water Contaminated ($w_w = 1 \cdot 10^{-3}$) ILs as a Function of Temperature at Atmospheric Pressure

	$\rho/g \cdot cm^{-3}$								
	$[C_4mim][NTf_2]$			$[C_2mim][NTf_2]$			$[C_4mim][PF_6]^{solv,a}$		
T/K	dried	cont.	$\Delta\rho$/%	dried	cont.	$\Delta\rho$/%	dried	cont.	$\Delta\rho$/%
293.15	1.4427	1.4399	−0.19	1.5229	1.5200	−0.19	1.3698	1.3675	−0.17
298.15	1.4379	1.4351	−0.19	1.5179	1.5150	−0.19	1.3657	1.3634	−0.17
303.15	1.4331	1.4303	−0.20	1.5129	1.5100	−0.19	1.3616	1.3592	−0.18
308.15	1.4283	1.4255	−0.20	1.5079	1.5049	−0.20	1.3574	1.3552	−0.16
313.15	1.4235	1.4207	−0.20	1.5029	1.4998	−0.21	1.3533	1.3510	−0.17
318.15	1.4188	1.4160	−0.20	1.4979	1.4948	−0.21	1.3492	1.3468	−0.18
323.15	1.4140	1.4112	−0.20	1.4929	1.4898	−0.21	1.3451	1.3424	−0.20
328.15	1.4093	1.4065	−0.20	1.4880	1.4848	−0.22	1.3410	1.3385	−0.19
333.15	1.4045	1.4017	−0.20	1.4830	1.4797	−0.22	1.3369	1.3344	−0.19
338.15	1.3997	1.3969	−0.20	1.4780	1.4747	−0.22	1.3327	1.3303	−0.18
343.15	1.3950	1.3922	−0.20	1.4730	1.4697	−0.22	1.3286	1.3262	−0.18

[a] IL purchased from Solvionic.

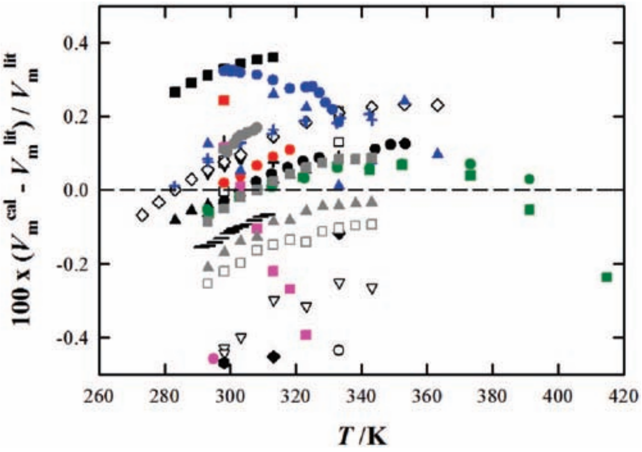

Figure 2. Deviation from the literature values and measured data in this work to the correlation of the molar volumes calculated from all described data sets for $[C_4mim][PF_6]$ (see the Supporting Information). ●, Kabo et al.;[53] ■, Tokuda et al.;[54] ▲, Tronsoco et al.;[27] ▼, Pereiro and Rodriguez;[55] ♦, Aki et al.;[56] black outlined □, Canongia Lopes et al.;[32] ○, Blanchard et al.;[57] Δ, Chun et al.;[58] ▽, Gu and Brennecke;[59] ◇, Harris et al.;[60] ⬢, Huddleston et al.;[61] blue +, Jacquemin et al.;[47] −, Kumelan et al.;[62] black +, Tomida et al.;[63] |, Wang et al.;[64] red ●, Zafarani-Moattar and Shekaari;[65] red ■, Zhong et al.;[66] blue ▲, Seddon et al.;[67] blue ●, Gomes de Azevedo et al.;[37] pink ●, Ohlin et al.;[68] pink ■, Dzyuba and Bartsch;[69] green ●, Jacquemin et al.;[25] green ■, Jacquemin et al.;[15] gray ●, Navia et al.[44] This work: C_4mimPF_6 from Solvionic: gray ■, dried; gray outlined □, contaminated with a water mass fraction content of 10^{-3}. From Acros Organics: gray ▲, dried. Due to a large deviation from the correlation, values published by Suarez et al.[70] and Branco et al.[71] were not used.

Table 6. Examples of Parameters Associated with Equation 10 Used to Predict the Effective Molar Volume of Ions Calculated in This Study as a Function of the Temperature at 0.1 MPa (Complete List Available in the Supporting Information)

ion	M / $g \cdot mol^{-1}$	C_0 / $cm^3 \cdot mol^{-1}$	$10^3 \cdot C_1$ / $cm^3 \cdot mol^{-1} \cdot K^{-1}$	$10^6 \cdot C_2$ / $cm^3 \cdot mol^{-1} \cdot K^{-2}$
$[BF_4]^-$	86.80	53.656	+24.04	+29.68
$[PF_6]^-$	144.96	73.710	+45.42	−58.03
Cl^-	35.45	27.003	+1.865	+5.873
$[NO_3]^-$	62.00	40.169	+14.43	−67.20
$[NTf_2]^-$	280.15	157.597	+104.3	+50.52
$[FAP]^-$	445.00	226.020	+148.3	+186.8
$[OTf]^-$	149.07	87.472	+52.78	−15.82
$[C_2mim]^+$	111.17	100.017	+69.55	+29.96
$[C_4mim]^+$	139.22	134.260	+88.90	+43.04
$[C_5mim]^+$	153.25	151.068	+80.30	+705.8
$[C_6mim]^+$	167.27	168.801	+115.2	+68.69
$[C_{10}mim]^+$	223.38	236.367	+159.6	+83.75
$[N_{1114}]^+$	116.23	126.642	+94.94	−60.06
$[P_{66614}]^+$	483.86	560.514	+390.4	+118.4

Using these assumptions, a range of other ions, including chloride, Cl^-; trispentafluoroethyltrifluorophosphate, $[FAP]^-$; nitrate, $[NO_3]^-$; *N*-alkylphosphonium, $[C_nPy]^+$; and *N*-tertraalkylammonium $[N_{nnnn}]^+$ have also been calculated. Ions were chosen where ionic liquid combinations containing these ions exist and where density data as a function of temperature are also known. The calculation of the molar volumes of a range of ILs using this methodology showed a large average deviation of 0.9 % compared with the experimentally determined values for temperatures up to 423.15 K. For example, using effective molar volumes previously reported[15,35] to calculate the molar volume as a function of temperature, deviations up to 0.9 %, 1.0 %, and 1.3 % for $[C_1mim][NTf_2]$, $[C_6mim][PF_6]$, and $[C_8mim][PF_6]$ were found, respectively. Furthermore, calculated effective molar volumes for Cl^-, $[FAP]^-$, $[C_4Py]^+$, and $[N_{4448}]^+$, using these parameters, were found to have uncertainties of ≈ 1.0 %, ≈ 1.1 %, ≈ 1.0 %, and ≈ 1.5 %, respectively, when compared with literature data for ionic liquids containing these ions, as a function of temperature. Two main reasons contribute to the large deviations observed in these calculations. First, the initial model reported by Jacquemin et al.[15,35] was calculated with only a small density data set compared with the current study. Second, these calculations were based on the assumption that the effective molar volume for $[\mathrm{C_4mim}]^+$ and $[\mathrm{NTf_2}]^-$ had the same temperature dependence. The latter was corrected by performing iterative calculations, by using an iterative Excel macro file, to obtain the smallest absolute deviation. An optimized temperature relationship was found to be proportional to the effective molar volume fraction of ions constituting the $[\mathrm{C_4mim}][\mathrm{NTf_2}]$ as a function of the temperature at 0.1 MPa as described in eqs 4 to 8

$$V_{\mathrm{m}[\mathrm{C_4mim}][\mathrm{NTf_2}]}(T) = \sum_{i=0}^{2} (A_i \cdot \delta T^i) \tag{4}$$

where δT is defined by the following relationship: $\delta T = (T - 298.15\ \mathrm{K})$ and A_i are the coefficients obtained by this fit. The coefficient A_0 corresponds to the molar volume of the $[\mathrm{C_4mim}][\mathrm{NTf_2}]$ at T^* (298.15 K) and 0.1 MPa

$$V_{\mathrm{m}[\mathrm{C_4mim}][\mathrm{NTf_2}]}(T^*) = V^*_{[\mathrm{C_4mim}]^+}(T^*) + V^*_{[\mathrm{NTf_2}]^-}(T^*) \tag{5}$$

where $V^*_{[\mathrm{C4mim}]^+}$ and $V^*_{[\mathrm{NTf2}]^-}$ are the effective molar volumes of ions constituting the ionic liquid $[\mathrm{C_4mim}][\mathrm{NTf_2}]$ at $T^* = 298.15$ K and 0.1 MPa and

$$V^*_{[\mathrm{C_4mim}]^+}(\delta T) = V^*_{[\mathrm{C_4mim}]^+}(\delta T) + \Phi_{[\mathrm{C_4mim}]^+} \cdot \left(\sum_{i=1}^{2} A_i \cdot (\delta T)^i \right) \tag{6}$$

$$V^*_{[\mathrm{NTf_2}]^-}(\delta T) = V^*_{[\mathrm{NTf_2}]^-}(\delta T) + \Phi_{[\mathrm{NTf_2}]^-} \cdot \left(\sum_{i=1}^{2} A_i \cdot (\delta T)^i \right) \tag{7}$$

where A_i are the coefficients obtained by eq 4 and $\Phi_{[\mathrm{C4mim}]^+}$ and $\Phi_{[\mathrm{NTf2}]^-}$ are the effective molar volume fraction at 298.15 K of ions constituting the $[\mathrm{C_4mim}][\mathrm{NTf_2}]$ defined by the following equation

$$\Phi_{[\mathrm{NTf_2}]^-} = \frac{V^*_{[\mathrm{NTf_2}]^-}(T^*)}{V^*_{[\mathrm{NTf_2}]^-}(T^*) + V^*_{[\mathrm{C_4mim}]^+}(T^*)} = 1 - \Phi_{[\mathrm{C_4mim}]^+} \tag{8}$$

As before, the $[\mathrm{C_4mim}]^+$ effective molar volume was calculated from the $[\mathrm{PF_6}]^-$ effective molar volume and the $[\mathrm{C_4mim}][\mathrm{PF_6}]$ molar volume at 298.15 K; however, in this case *all* density data sets measured herein as well as those reported previously[15,25,27,32,37,44,47,53–72] were used to obtain the IL molar volume. Using this approach, the molar volume of $[\mathrm{C_4mim}][\mathrm{PF_6}]$ was found equal to 207.97 $\mathrm{cm^3 \cdot mol^{-1}}$ (calculated from eq 9 using all previously presented densities as a function of the temperature at 0.1 MPa).

$$V_{\mathrm{mIL}}(T) = \sum_{i=0}^{2} (B_i \cdot T^i) \tag{9}$$

where T is the temperature (T/K) and B_i are the coefficients obtained by this fit (see Supporting Information in the case of $[\mathrm{C_4mim}][\mathrm{PF_6}]$). Therefore, the effective molar volume of $[\mathrm{C_4mim}]^+$ was calculated as 134.26 $\mathrm{cm^3 \cdot mol^{-1}}$ at 298.15 K and 0.1 MPa. From this value and the available density data for $[\mathrm{C_4mim}][\mathrm{NTf_2}]$, both were measured herein (Table 2) and reported previously[15,25,27,28,32,38,49,54,56,61,68,69,73–78] at 298.15 K and 0.1 MPa, and the effective molar volume of the $[\mathrm{NTf_2}]^-$ anion was calculated as 157.60 $\mathrm{cm^3 \cdot mol^{-1}}$. Using eq 4, a quadratic fit was determined at δT ($T - 298.15$ K, see the Supporting Information) from previously reported and current experimentally determined density data for $[\mathrm{C_4mim}][\mathrm{NTf_2}]$ and from which the effective molar volume of $[\mathrm{C_4mim}]^+$ and $[\mathrm{NTf_2}]^-$ were obtained as a function of temperature from (273 to 423) K at 0.1 MPa (reported in Table 6) using eqs 5 to 8.

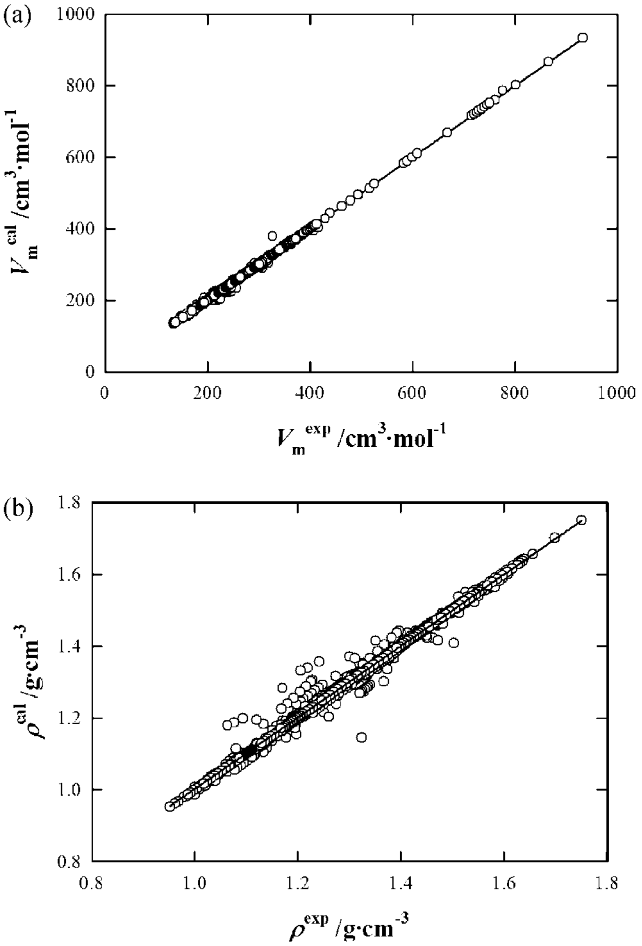

Figure 3. Experimental versus predicted molar volumes (a) and predicted densities (b) for all ionic liquids measured in the current study using the empirical method based on the "ideal" volumetric behavior of ILs.

This simple prediction method was used to calculate the effective molar volumes of a wide range of ions. In this present work, effective molar volumes of different ions (V^*_{ion}) were calculated from the large set of previously reported data[33] and also those measured herein (Table 2) as a function of the temperature at 0.1 MPa and using eq 10.

$$V^*_{\mathrm{ion}}(\delta T) = \sum_{i=0}^{2} (C_i \cdot \delta T^i) \tag{10}$$

The coefficients C_i obtained to fit 44 anions and 102 cations are listed in the Supporting Information and exemplified in Table 6. The repeatability of this model was found to be 0.36 % using more than 2150 data points (see Figure 3). It is interesting to observe that the precision of this model is close to the value expected for the uncertainty for the IL density as described above. The uncertainty of this methodology may be attributed to two errors: those caused by the experimental uncertainty of density (reflecting the repeatability of this model) and those due to the assumption that the excess molar volume equals zero. To date,[32,44] the maximum excess molar volume observed for

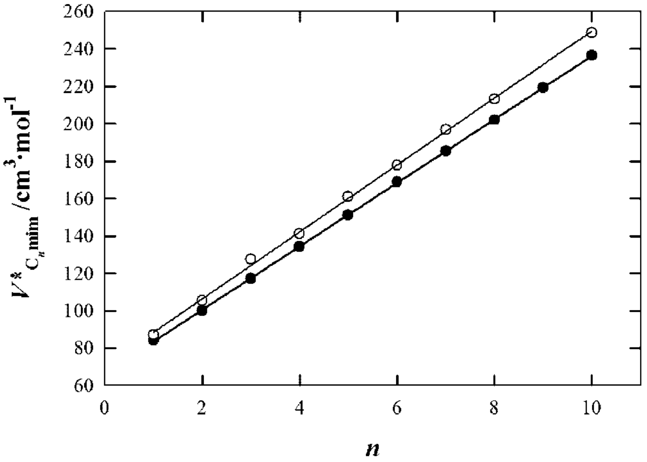

Figure 4. Effective molar volume as a function alkyl chain length, *n*, for a series of [C$_n$mim][NTf$_2$] ionic liquids: ●, 298.15 K; ○, 373.15 K.

binary mixtures containing exclusively ILs is ≈ 0.3 cm^3·mol^{-1}. When using this value as the deviation from ideal behavior, the average deviation of the molar volume was found to be 0.12 % as calculated from the average IL molar volume of 252.72 cm^3·mol^{-1} over the 2150 values used in this study. The predictive capability of this model cannot exceed the sum of these errors and, therefore, is found to be 0.48 % (0.36 % + 0.12 %). The accuracy of this methodology can also be estimated from a comparison of the calculated and experimental values of the density for an ionic liquid not used within the data set for the model. Using this approach with a data set containing 750 densities, the expected inaccuracy is 0.48 %.

An analysis of the 1-alkyl-3-methylimidazolium effective molar volumes, as a function of the alkyl chain at fixed temperature, showed a linear trend with the alkyl chain at (298.15 and 373.15) K (Figure 4), as predicted by Rebelo et al.[6,7] A new relationship was calculated and expressed as a function of δT using eqs 11 and 12

$$V^*_{[\mathrm{C}_n\mathrm{mim}]^+}(\delta T) = V^*_{[\mathrm{C}_0\mathrm{mim}]^+}(\delta T) + n \cdot a^* \qquad (11)$$

where a^* is the contribution to the molar volume of a $-\mathrm{CH}_2-$ group on the alkyl chain and n is the number of $-\mathrm{CH}_2-$ groups in the alkyl chain. Using eq 10 and the effective molar volume of [C$_n$mim]$^+$ cations calculated as a function of the temperature, the effective molar volume of the [C$_0$mim]$^+$ and the contribution of a $-\mathrm{CH}_2-$ group in the alkyl chain as a function of temperature (parameters D_i and E_i) have been calculated. Quadratic equations were found adequate for fitting the variation of these parameters with temperature (eq 12).

$$V^*_{[\mathrm{C}_n\mathrm{mim}]^+}(\delta T) = \left(\sum_{i=0}^{2} (D_i \cdot \delta T^i)\right) + n \cdot \left(\sum_{i=0}^{2} (E_i \cdot \delta T^i)\right) \qquad (12)$$

The parameters D_i and E_i, determined from the [C$_n$mim]$^+$ calculated effective molar volumes, are summarized in Table 7.

A major advantage of predicting the effective molar volume of ions constituting ILs is that it allows an assessment to be made of the impact of each ion on the IL volumetric properties. For example, using the data reported herein, it is straightforward to show that the molar volumes of [C$_n$mim]$^+$ based ILs increase with the alkyl chain length and that [C$_4$mim]$^+$ based ILs have lower molar volumes than the trihexyl-tetradecylphosphonium based ILs, denoted [P$_{66614}$]$^+$, by comparison of the effective molar volumes of the cations only. Within the present study, 16 ionic liquids were measured experimentally, many of which do not have a common cation or anion. Therefore, the effect of varying the ions on the volumetric properties of ionic liquids cannot be analyzed directly from the experimental data. However, by comparing the effective molar volumes of given cations or anions only, it is possible to determine the relative molar volumes for a common anion or cation, respectively. Furthermore, using the molar mass of ions and the same methodology allowed a simple evaluation of the change in density as a function of the ion. More than 4000 IL densities (molar volumes) at 298.15 K and 600 IL densities (molar volumes) as a function of temperature up to 423 K (depending on the temperature ranges described in the literature) at 0.1 MPa were calculated using this method. Therefore, calculation of binary or ternary IL mixtures is also possible, significantly increasing the impact of the method described herein. As a consequence, new effective molar volumes may be more easily calculated (or recalculated) knowing new/revised volumetric properties of pure ILs.

Table 7. Parameters Associated with Equation 12 Used to Predict the Effective Molar Volume of the Imidazolium Cation as a Function of Temperature from (293 to 423) K

	D_0 / cm^3·mol^{-1}	$10^2 \cdot D_1$ / cm^3·mol^{-1}·K^{-1}	$10^4 \cdot D_2$ / cm^3·mol^{-1}·K^{-2}
[C$_0$mim]$^+$	66.509	+1.249	+5.529
	E_0 / cm^3·mol^{-1}	$10^2 \cdot E_1$ / cm^3·mol^{-1}·K^{-1}	$10^6 \cdot E_2$ / cm^3·mol^{-1}·K^{-2}
[C$_n$mim]$^+$	16.967	+1.399	−1.946

It is also possible, by using this methodology together with the linear relationship between the density of the liquid and solid states as defined by Ye and Shreeve,[13] to calculate the density (molar volume) of ionic liquids in the solid state. The group contribution model described herein relies on the assumption that the material under investigation is a liquid. Given this limitation, it may be useful to combine such calculations with melting point calculations when investigating unknown ILs.[79–84] For binary and ternary ionic liquids, for the method described herein to be applicable, the component ionic liquids must be fully miscible. Using this methodology, the calculated volumetric properties of totally miscible binary (ternary) systems containing exclusively ILs show good agreement with the literature as shown in Figure 5. For example, 108 densities of the binary mixtures containing ([C$_4$mim][BF$_4$] + [C$_6$mim][BF$_4$]) as a function of the temperature from (298.15 to 308.15) K and mole fraction were calculated and found to have an absolute average deviation of 0.14 % from the experimental data reported by Navia et al.[44] Although many ILs are totally miscible, this cannot always be guaranteed as shown by examination of ([P$_{66614}$][NTf$_2$] + [C$_2$mim][NTf$_2$]) and ([P$_{666\ 14}$][NTf$_2$] + [C$_2$Py][NTf$_2$]) binary IL systems which have recently been shown to show a two-phase region.[85]

Conclusions

The prediction of molar volume and density of several ILs based on group contribution models (GCMs) has been shown to be highly effective over a wide range of ionic liquid types and temperatures. From a collection of densities (molar volumes) for several ILs, a detailed quantitative understanding of the influence of the impurities (water, halide content) was obtained. The GCMs presented here have been shown to predict the density (molar volumes) of the ILs as function of temperature, between (273 and 423) K at 0.1 MPa, with a predictive capability of approximately 0.48 % which compares well with

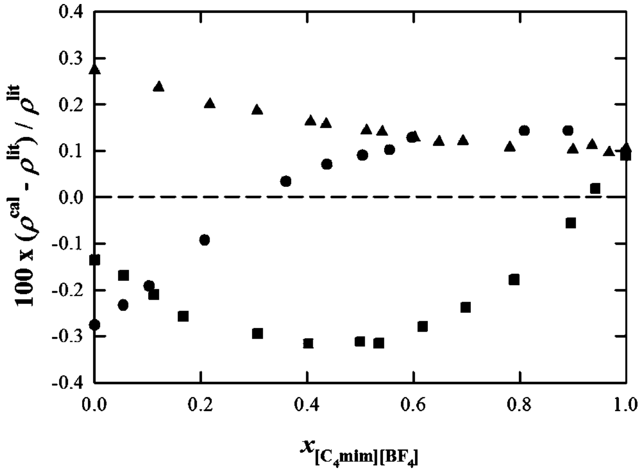

Figure 5. Deviation from the literature values and calculated density of totally miscible binary systems containing the $[C_4mim][BF_4]$ and ●, $[C_6mim][BF_4]$; ■, $[C_4mim][PF_6]$; and ▲, $[C_4mim][CH_3SO_4]$ as a function of the mole fraction of the $[C_4mim][BF_4]$ at 303.15 K and 0.1 MPa. (See the Supporting Information.)

existing models reported for ionic liquids. Due to the high accuracy of the GCM presented and the versatility of this method, this simple model can be used to rapidly estimate new densities of several ILs. This information is of particular interest in the development a new ILs and also needed for the calculation of other properties such as surface tension and viscosity as well as property correlations such as the parachor.

Supporting Information Available:

Additional Supporting Information spreadsheets of IL density databases, effective molar volumes of 44 anions and 102 cations as a function of the temperature, and two examples of the methodology used in the calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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