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Prediction of Ionic Liquid Properties. II. Volumetric Properties as a Function of Temperature and Pressure

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The density of ionic liquids (ILs) as a function of pressure and temperature has been modeled using a group contribution model. This model extends the calculations previously reported (Jacquemin et al. *J. Chem. Eng. Data* **2008**) which used 4000 IL densities at 298.15 K and 600 IL densities as a function of temperature up to 423 K at 0.1 MPa to pressures up to 207 MPa by using described data in the literature and presented in this study. The densities of two different ionic liquids (butyltrimethylammonium bis(trifluoromethylsulfonyl)imide, $[N_{1114}][NTf_2]$, and 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide, $[C_4mPyrro][NTf_2]$) were measured as a function of temperature from (293 to 415) K and over an extended pressure range from (0.1 to 40) MPa using a vibrating-tube densimeter. The model is able to predict the ionic liquid densities of over 5080 experimental data points to within 0.36 %. In addition, this methodology allows the calculation of the mechanical coefficients using the calculated density as a function of temperature and pressure with an estimated uncertainty of ± 20 %.

Introduction

It is now generally accepted that ionic liquids (ILs) have to be considered when examining potential candidates for more environmentally friendly chemical processes.[1] The ability to tailor the physical and chemical properties of these liquids[2−5] has resulted in significant interest and a large number of studies for a wide range of applications. Despite the growing importance of ILs, only limited numbers of accurate values for many of their physical and chemical properties are available, and those reported concentrate on a small subset of the possible anion−cation combinations. The breadth of potential ionic liquids does not allow the collection of thermodynamic and thermophysical data for all systems, and therefore, it is necessary to develop predictive models to determine these values. Structure−property relationships are one of the simplest and effective ways by which useful predictive models may be developed, and this is one of the most promising methods to predict a range of properties for large families of materials, such as ionic liquids.

From an analysis of the density of 220 different ionic liquids, as a function of temperature and at pressures close to 0.1 MPa, we have reported a prediction method for their volumetric properties.[6] In contrast, much less volumetric data are available as a function of pressure with only 18 studies being reported which include volumetric data for 27 ionic liquids as a function of temperature and pressure.[7−24] Furthermore, more than half of the liquids studied are based on the 1-alkyl-3-methylimidazolium cation. On the basis of this published data, Gardas and Coutinho[25] have recently extended the Ye and Shreeve[26] group contribution model to predict the density as a function of the temperature and pressure of a range of ionic liquids with an uncertainty determined as 0.6 %. In this study, the calculation of ionic liquid density was determined from a prior knowledge of their mechanical coefficients limiting the general applicability of this methodology.

The lack of density data over a wide range of pressure is related to the experimental difficulties associated with obtaining accurate measurements. Most of the density data for ionic liquids as a function of temperature and pressure (≈ 90 %) have been obtained using the vibrating-tube technique that requires extensive calibration. These calibrations should be made with liquids of densities close to those of the ionic liquids to obtain data with sufficient accuracy. This constitutes a further difficulty in the case of the study of ionic liquids since their high densities prevent the use of standard liquids for the calibration of the vibrating-tube densimeter.

Furthermore, the possibility of calculating the density as a function of pressure and temperature gives access to estimations of the mechanical coefficients, namely, the isothermal compressibility and the thermal expansion coefficient, at pressures higher than atmospheric. The mechanical coefficients are relevant for essentially every technical application in which large temperature and pressure ranges are involved and provide fundamental information on the thermodynamics of liquids. For example, these values allow the calculation of the ionic liquid internal pressure.

Herein, we present an extension of the previously developed group contribution model[6] to calculate the molar volume and density of ionic liquids as a function of temperature and up to high pressures. The model used is based on the assumption that the molar volumes 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.[11,27,28] This relationship has been

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Table 1. Overview of Density Data Used to Establish the Group Contribution Model of Molar Volume (Density) of ILs as a Function of the Temperature and Pressure (See Supporting Information)

	M	temperature range	pressure range		
ionic liquid	g·mol^{-1}	K	MPa	data points	refs
[C$_2$mim][NTf$_2$]	391.31	283.15 to 414.96	0.10 to 40.00	308	6,16,19,29−43
[C$_3$mim][NTf$_2$]	405.34	298.15 to 333.15	0.10 to 59.59	166	12,30
[C$_4$mim][NTf$_2$]	419.36	273.15 to 414.96	0.10 to 56.64	421	6,10,19,29−31,35−38,40,42−51
[C$_5$mim][NTf$_2$]	433.39	298.15 to 333.15	0.10 to 59.59	167	12,30,43
[C$_6$mim][NTf$_2$]	447.42	298.15 to 423.15	0.10 to 65.02	428	6,10,17,23,30,38,40,42−44,52−55
[C$_7$mim][NTf$_2$]	461.45	293.15 to 393.15	0.10 to 30.00	97	16,30
[C$_8$mim][NTf$_2$]	475.47	283.15 to 393.15	0.10 to 30.00	134	6,16,30,38,40,42−44,47,52
[C$_4$mim][PF$_6$]	284.18	273.15 to 414.93	0.098 to 202.11	506	6,7,9,13,18,19,21,30,35,38,40,44,45,48,49,56−74
[C$_6$mim][PF$_6$]	312.23	273.15 to 393.15	0.10 to 20.00	143	14,15,30,46,51,57,62,63,68,74−77
[C$_8$mim][PF$_6$]	340.29	273.10 to 393.15	0.098 to 204.18	176	7,14,15,30,46,56,62,63,68,74,78
[C$_4$mmim][PF$_6$]	298.21	295.65 to 393.15	0.10 to 10.00	75	15,31
[C$_2$mim][BF$_4$]	197.97	285.00 to 393.15	0.10 to 30.00	135	16,39,40,63,67,79−84
[C$_4$mim][BF$_4$]	226.02	278.15 to 414.93	0.099 to 60.00	441	6,8,9,13,15,18,19,31,35,38,40,44−46,48,50,57,63,67,72,73,79−81,85−89
[C$_8$mim][BF$_4$]	282.13	273.10 to 393.15	0.099 to 206.94	162	7,15,45,56,63,78,89,90
[C$_2$mim][EtSO$_4$]	236.29	278.15 to 414.95	0.10 to 40.00	179	6,19,22,35,37,56,81,91−96
[C$_2$mim][OTf]	260.23	278.15 to 393.15	0.10 to 35.00	108	24,29,93,97,98
[C$_4$mim][OTf]	288.29	283.15 to 393.15	0.099 to 10.00	117	6,15,29,31,44,45,47,48,50,73
[C$_4$mim][OctSO$_4$]	348.50	278.15 to 423.15	0.10 to 60.00	124	20,99,100
[C$_4$mim][C(CN)$_3$]	229.28	293.15 to 393.15	0.10 to 30.00	96	16
[P$_{666\ 14}$][OAc]	542.91	298.15 to 334.11	0.21 to 65.01	144	11
[P$_{666\ 14}$][NTf$_2$]	764.01	293.15 to 363.15	0.10 to 65.01	134	6,11
[P$_{666\ 14}$]Cl	519.32	298.13 to 333.14	0.19 to 65.01	134	11
[C$_3$mPyrro][NTf$_2$]	408.39	293.15 to 393.15	0.10 to 35.00	91	24,41
[C$_4$mPyrro][NTf$_2$]	422.41	288.15 to 414.97	0.10 to 40.00	241	[a],24,34,40,45,52,101−104
[C$_3$mPy][NTf$_2$]	416.37	283.15 to 393.15	0.10 to 35.00	96	24,41
[C$_3$mPip][NTf$_2$]	422.41	293.15 to 393.15	0.10 to 35.00	91	24
[N$_{1114}$][NTf$_2$]	396.37	288.15 to 414.97	0.10 to 40.00	145	[a],34,35,73,102
[C$_4$Py][BF$_4$]	223.02	293.00 to 343.20	0.098 to 204.18	30	7,39,56
Data used				5089	

[a] This work.

shown by our group to predict the density of ionic liquids for temperatures up to 423 K with an uncertainty of 0.48 %.[6] In the present work, 5080 previously reported data points for the density of ionic liquids as a function of temperature at 0.1 MPa[7−104] and at higher pressures from (0.1 to 207) MPa[7−24] were combined with new measurements performed in our laboratory and have been used for the development of a group contribution model for the calculation of the density, molar volume, and mechanical coefficients of ionic liquids as a function of the temperature and pressure. The database used is summarized in Table 1 and is available in the Supporting Information.

Experimental measurements of the density as a function of pressure and temperature were performed to supplement the available data on the volumetric properties of ionic liquids. The principal focus of this work is to propose a group contribution method for the accurate prediction of ionic liquid molar volumes and densities as a function of temperature and over an extended range of pressures. In particular, the influence of the cation on the densities and mechanical coefficients of various ionic liquids is examined in detail and contrasted with that reported for the anion previously.[19]

Experimental

Materials. Butyltrimethylammonium bis(trifluoromethylsulfonyl)imide ([N$_{1114}$][NTf$_2$]) was supplied by the group of P. Wasserscheid (University of Erlangen-Nürnberg, Germany) (≥ 99 %). This IL was synthesized by reacting *N*,*N*-dimethylbutylamine and dimethyl sulfate to form butyltrimethylammonium methylsulfate. The bis(trifluoromethylsulfonyl)imide ionic liquid was then prepared by anion exchange via a metathesis reaction between the butyltrimethylammonium methylsulfate and the lithium bis(trifluoromethylsulfonyl)imide in water. 1-Butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide ([C$_4$mPyrro][NTf$_2$]) was supplied by the group of H. Olivier-Bourbigou (Institut Français du Pétrole, IFP, Solaize, France) (≥ 99 %). This IL was prepared via a methathesis reaction between [C$_4$mPyrro]Cl and lithium bis(trifluoromethylsulfonyl)imide. Prior to use, the halide and water contents of the ILs were determined to estimate their influence on the density measurements. The halide content of ionic liquids was determined using suppressed ion chromatography (IC),[105] and the water content was determined before and after measurements by volumetric Karl Fischer titration using a Mettler Toledo DL31 titrator. Lithium content was determined by inductively coupled plasma analysis (ICP). The structures, molar mass, halide, and water content after drying under a vacuum of the ionic liquids whose density was measured in this work are summarized in Table 2.

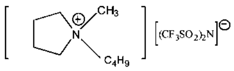
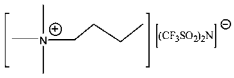
Method. An Anton Paar vibrating-tube densitometer, model DMA 512P, operating in a static mode and coupled to a pressure line, was used for the present density measurements. The experimental setup and procedure for the high-pressure measurements have been previously described.[19]

The densities were determined by measuring the oscillation period of the U-shaped tube. This measured period of vibration (τ) is related to the density (ρ) according to

$$\rho = A\tau^2 + B \qquad (1)$$

where A and B are parameters that are a function of temperature and pressure. The method described by Lagourette et al.[106] was used to calibrate the densimeter. Parameters A and B from eq 1 were then determined for all the temperatures and pressures studied, between (293 and 413) K and (0.1 and 40) MPa, respectively, using vacuum, air, nitrogen, triply distilled water,[107] and aqueous solutions of NaCl (nominal molalities of 1 mol·L^{-1} and 3 mol·L^{-1}).[108]

Table 2. Chemical Structures, Molar Masses (M_{IL}), Chloride Mass Fraction Content (w_{Cl^-}), 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	Chemical structures	M_{IL} /g·mol^{-1}	$10^3 \cdot w_w$	$10^3 \cdot x_w$	$10^6 \cdot w_{Cl^-}$	$10^6 \cdot w_{Li^+}$
[C_4mPyrro][NTf_2]		422.41	0.05	1.20	< 75	< 5
[N_{1114}][NTf_2]		396.38	0.07	1.50	-[a]	< 5

[a] Halide-free sample.

Table 3. Experimental Densities (ρ) of Selected ILs between (293 and 415) K at Atmospheric Pressure[a]

[C_4mPyrro][NTf_2]			[N_{1114}][NTf_2]		
T/K	ρ/g·cm^{-3}	[b]$100 \cdot \delta$	T/K	ρ/g·cm^{-3}	[b]$100 \cdot \delta$
293.49	1.3980	− 0.001	293.48	1.3963	− 0.006
302.66	1.3901	+ 0.000	302.84	1.3879	− 0.001
312.62	1.3815	− 0.001	312.82	1.3790	+ 0.000
322.35	1.3732	+ 0.001	322.33	1.3705	+ 0.010
332.63	1.3643	+ 0.002	332.75	1.3613	+ 0.005
342.54	1.3559	− 0.001	342.67	1.3525	+ 0.000
352.32	1.3475	+ 0.000	352.36	1.3439	+ 0.001
373.33	1.3295	+ 0.001	373.31	1.3255	− 0.006
391.30	1.3141	− 0.002	391.28	1.3097	− 0.011
414.93	1.2939	+ 0.001	414.93	1.2886	+ 0.009

[a] The reported deviations (δ) are relative to the fit of the data reported in Table 5. [b] $\delta = [(\rho_i^{\text{exptl}} - \rho_i^{\text{calcd}})/\rho_i^{\text{calcd}}]$.

Table 4. Experimental Densities (ρ) of Selected ILs between (293 and 415) K and between (1 and 40) MPa[a]

[C_4mPyrro][NTf_2]			[N_{1114}][NTf_2]		
T/K	ρ/g·cm^{-3}	[b]$100 \cdot \delta$	T/K	ρ/g·cm^{-3}	[b]$100 \cdot \delta$
$p = 1$ MPa					
293.51	1.3986	+ 0.001	293.48	1.3968	+ 0.004
322.33	1.3738	+ 0.000	322.34	1.3711	+ 0.002
352.35	1.3481	+ 0.001	352.36	1.3446	+ 0.007
373.32	1.3301	−0.003	373.33	1.3262	+ 0.012
391.26	1.3149	−0.002	391.27	1.3105	+ 0.020
414.94	1.2947	−0.001	414.95	1.2894	−0.005
$p = 5$ MPa					
293.51	1.4010	+ 0.001	293.49	1.3988	−0.004
322.32	1.3764	−0.000	322.29	1.3735	+ 0.003
352.33	1.3510	+ 0.004	352.30	1.3473	+ 0.005
373.31	1.3332	−0.004	373.28	1.3289	+ 0.000
391.30	1.3181	+ 0.003	391.31	1.3131	−0.005
414.93	1.2981	−0.004	414.94	1.2925	−0.013
$p = 10$ MPa					
293.50	1.4040	+ 0.001	293.51	1.4014	−0.003
322.31	1.3797	−0.002	322.32	1.3764	+ 0.003
352.32	1.3545	+ 0.000	352.29	1.3505	+ 0.005
373.33	1.3370	−0.000	373.30	1.3324	+ 0.002
391.29	1.3220	+ 0.000	391.26	1.3169	−0.002
414.93	1.3024	+ 0.001	414.94	1.2966	−0.008
$p = 20$ MPa					
293.50	1.4098	+ 0.001	293.51	1.4066	−0.001
322.31	1.3860	−0.002	322.31	1.3822	+ 0.004
352.31	1.3615	+ 0.000	352.27	1.3569	+ 0.003
373.34	1.3442	−0.003	373.30	1.3392	+ 0.004
391.32	1.3296	+ 0.001	391.28	1.3242	−0.001
414.93	1.3105	+ 0.004	414.94	1.3045	−0.001
$p = 30$ MPa					
293.50	1.4155	+ 0.000	293.51	1.4117	+ 0.000
322.32	1.3922	−0.001	322.33	1.3877	+ 0.001
352.33	1.3681	+ 0.000	352.34	1.3630	+ 0.002
373.31	1.3513	+ 0.000	373.31	1.3458	−0.001
391.29	1.3370	+ 0.004	391.25	1.3312	−0.001
414.93	1.3181	−0.005	414.89	1.3121	+ 0.003
$p = 40$ MPa					
293.50	1.4210	−0.001	293.50	1.4167	−0.002
322.31	1.3982	+ 0.002	322.32	1.3932	+ 0.000
352.31	1.3745	−0.002	352.32	1.3691	−0.002
373.34	1.3580	−0.001	373.35	1.3523	−0.003
391.32	1.3440	+ 0.001	391.31	1.3381	−0.003
414.93	1.3256	+ 0.001	414.92	1.3195	+ 0.005

[a] The reported deviations (δ) are relative to the fit of the data reported in Table 5. [b] $\delta = [(\rho_i^{\text{exptl}} - \rho_i^{\text{calcd}})/\rho_i^{\text{calcd}}]$.

During the measurements, the temperature was maintained constant to within 0.01 K by means of a recirculating bath equipped with a PID temperature controller (Julabo FP40-HP). The temperature was determined using a 100 Ω platinum resistance thermometer (repeatability, 0.02 K; uncertainty, 0.04 K) previously calibrated by comparison with a 100 Ω platinum resistance Hart Scientific model 1502A. The pressure was measured using a manometer (Druck, model PTX 610, (0 to 70) MPa, uncertainty 0.5 % full scale).

Measurements were performed in steps of approximately 10 K from (293 to 413) K and at six different pressures from (0.1 to 40) MPa. At least three independent density values were obtained for each temperature and pressure. No viscosity correction was applied to density measurements since this is only necessary for liquids with viscosity higher than 100 mPa·s.[89,109] For the case of the ILs studied herein, the viscosity correction would affect their densities by less than 0.1 %. The uncertainty of the density measurements is estimated to be 10^{-4} g·cm^{-3}.

Results and Discussion

Density Measurements. Density measurements of pure ionic liquids were initially performed over the temperature range from (293.15 to 415.15) K at 0.1 MPa and then as a function of pressure (up to 40 MPa). The experimental data obtained for [C_4mPyrro][NTf_2] and [N_{1114}][NTf_2] are summarized in Tables 3 and 4 as a function of the temperature at 0.1 MPa and the pressure up to 40 MPa, respectively.

Compared with 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide based ionic liquids, the two ionic liquids measured herein, [C_4mPyrro][NTf_2] and [N_{1114}][NTf_2], have a much lower density, as illustrated in Figure 1. In the present case, it is observed that a 125 K increase in temperature decreases the density by (7 to 8) % at 0.1 MPa, and by increasing the pressure up to 40 MPa, the density increases by (1 to 2) % at 293 K and by (2 to 3) % at 423 K. As previously reported for other ionic liquids,[19] over the temperature and pressure ranges studied, the effect of pressure on the volumetric properties is far less significant than the effect of the temperature.

A quadratic equation was used to fit the experimental densities as a function of temperature at $p_{\text{ref}} = 0.1$ MPa

$$\rho_{\mathrm{IL}}(T, p_{\mathrm{ref}}) = \sum_{i=0}^{2} (a_i \cdot (T)^i_{p_{\mathrm{ref}}}) \tag{2}$$

The fitted a_i parameters are presented in Table 5 together with the corresponding relative average absolute deviations (AAD), which is lower than 0.005 % for both [C_4mPyrro][NTf_2] and [N_{1114}][NTf_2].

The Tait equation with four adjustable parameters was combined with eq 2 to fit the experimental densities as a function of temperature and pressure

$$\rho_{\mathrm{IL}}(T, p, C, B) = \frac{\rho_{\mathrm{IL}}(T, p_{\mathrm{ref}})}{1 - C \cdot \ln\left(\dfrac{B(T) + p}{B(T) + p_{\mathrm{ref}}}\right)} \tag{3}$$

where $\rho_{\mathrm{IL}}(T,$ 0.1 MPa) is the reference density obtained using eq 2 and $p_{\mathrm{ref}} = 0.1$ MPa. C is an adjustable parameter, and $B(T)$ is a second-order polynomial expressed as

$$B(T) = \sum_{i=0}^{2} (B_i \cdot T^i) \tag{4}$$

The Tait parameters are presented in Table 5 together with the average absolute deviations (AADs) associated with the fits. These values can be considered as the uncertainty of our measurements over the extended pressure range. An AAD lower than 0.005 % in both cases was obtained for both [C_4mPyrro][NTf_2] and [N_{1114}][NTf_2].

Table 5. Tait Parameters a_0, a_1, a_2, C, B_0, B_1, and B_2 from Equations 2 and 3 Used to Fit the Experimental Densities as a Function of Pressure (up to 40 MPa) and Temperatures from (293 to 423) K and the Average Absolute Deviations of the Fit (AAD)

ionic liquid	a_0 g·cm^{-3}	$10^4 \cdot a_1$ g·cm^{-3}·K^{-1}	$10^8 \cdot a_2$ g·cm^{-3}·K^{-2}	^{a}AAD %
[C_4mPyrro][NTf_2]	1.6542	− 8.844	3.903	0.001
[N_{1114}][NTf_2]	1.6618	−9.184	4.645	0.005

ionic liquid	$10^2 \cdot C$	B_0 MPa	B_1 MPa·K^{-1}	$10^3 \cdot B_2$ MPa·K^{-2}	^{b}AAD %
[C_4mPyrro][NTf_2]	10.36	620.90	−1.765	1.543	0.003
[N_{1114}][NTf_2]	14.30	1117.4	−3.449	3.133	0.004

[a] Measurements as a function of temperature and at 0.1 MPa. [b] Measurements as a function of temperature between (1 and 40) MPa.

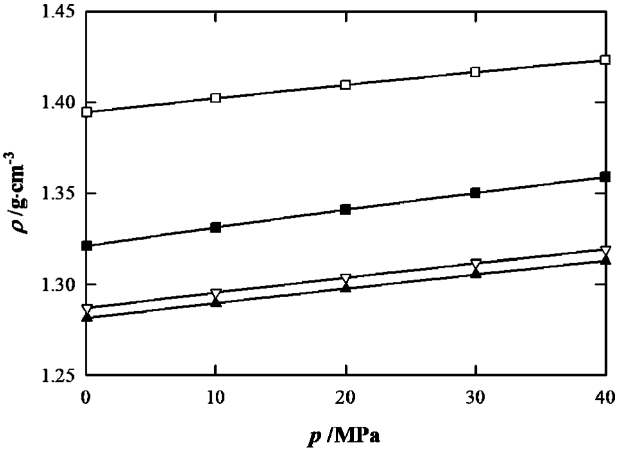


Figure 1. Comparison of experimental densities as a function of pressure at 423 K: ▽, [C_4mPyrro][NTf_2]; ▲, [N_{1114}][NTf_2]; ■, [C_4mim][NTf_2];[19] □, [C_2mim][NTf_2].[19] The lines correspond to the fit of the data by the Tait equation (eq 3).

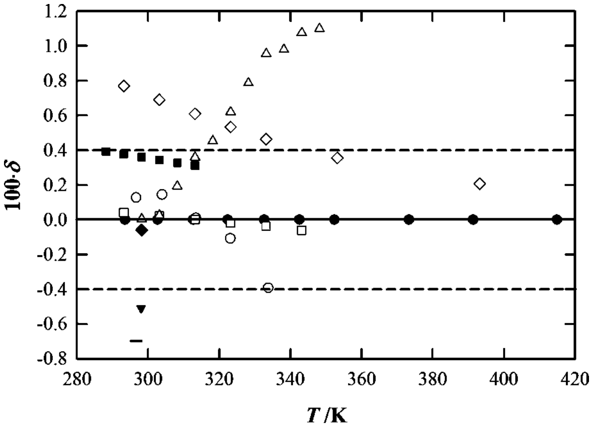


Figure 2. Relative deviations ($\delta = (\rho_{\mathrm{lit}} - \rho_{\mathrm{fit}})/\rho_{\mathrm{fit}}$) of the literature densities for [C_4mPyrro][NTf_2] from our fitted data: ◇, Gardas et al.;[24] ○, Anthony et al.;[101] ◆, Zhou et al.;[103] △, Kato et al.;[52] −, Ohlin et al.;[40] □, Hong et al.;[34] ▼, Dyson et al.;[45] ■, Tokuda et al.;[102] ●, this work. The dashed line represents the expected uncertainty of ionic liquid density according to ref 6.

The comparison between the present values for [N_{1114}][NTf_2] and [C_4mPyrro][NTf_2] and those previously measured by our group at atmospheric pressure and over a narrower temperature range from (293 to 343) K shows a deviation lower than 0.03 %.[34,35] Figure 2 illustrates the comparison of the data measured herein for [C_4mPyrro][NTf_2] with previously reported data as a function of temperature at 0.1 MPa. With the exception of the data reported by Kato and Gmehling[52] which deviates from the present values by up to 1.1 % at 348 K, the values determined here are in good agreement. Our data are ≈ 0.4 % lower than that of Tokuda et al.,[102] ≈ 0.6 % higher than data of Ohlin et al.,[40] ≈ 0.5 % lower than data of Gardas et al.,[24] and with an absolute average deviation lower than 0.15 % with the reported values of Anthony et al.[101] and Zhou et al.[103] For [N_{1114}][NTf_2], Tokuda et al.[73,102] have reported densities which deviate from the values of the present work by ≈ 0.4 % which is of the order expected due to the difference in concentration of impurities in the ionic liquid such as water or halide.[6]

The experimental densities of [C_4mPyrro][NTf_2] as a function of pressure may be compared with the data recently reported by Gardas et al.[24] Relatively good agreement is obtained between the two sets of data, with the densities reported herein being ≈ 0.65 % lower over the entire temperature and pressure ranges. For [N_{1114}][NTf_2], no data have been reported previously. In light of our previous studies on the volumetric properties of ILs as a function of the temperature and pressure, where comparison with a large number data sets could be made, the overall uncertainty associated with the data presented herein can be estimated as ± 0.4 %.[6]

Mechanical Coefficients. The experimental density values can be used to derive other thermodynamic properties, such as the isothermal compressibility (κ_T) and the isobaric thermal expansion coefficient (α_p). The calculation of these mechanical coefficients provides important information on the dependence of the volumetric properties on temperature and pressure. These mechanical coefficients could be calculated using eqs 5 to 6.

The isobaric thermal expansion coefficient, α_p, is related to the variation of the density with temperature and is defined as

$$\alpha_p = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \tag{5}$$

The isothermal compressibility, κ_T, is related to the variation of the density with pressure

$$\kappa_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T \qquad (6)$$

The accuracy of the mechanical coefficients is difficult to estimate precisely[9−12,19,22,23] because their values are dependent not only on the uncertainty associated with the experimental density data but also on the numerical errors associated with the fitting equations used. For example, the expression of the temperature dependence of the isobaric thermal expansion coefficient is strongly affected by the numerical fitting of the density as a function of the temperature for a given isobar.[19,22,23] This has also been reported by Gardas et al.[24] in interpreting the mechanical coefficients for [C_4mPyrro][NTf_2] (Figure 3). Therein, a decrease of the isobaric thermal expansion coefficient from (0.705 to 0.673)$\cdot 10^{-3}$ K^{-1} with temperature from (293 to 393) K was observed. Reprocessing the data using the calculations reported herein shows that this decrease does not depend on the fitting expressions used with their reported values for this IL. It is not clear why there is a discrepancy between the positive and negative variation of the isobaric thermal expansion coefficient with temperature for the [C_4mPyrro][NTf_2] ionic liquid reported herein and by Gardas et al.[24] It is possible that this difference may be linked to the presence of different impurities in the ionic liquid samples. It is notable that reported variation of the isobaric thermal expansion coefficient with the temperature for other ILs is consistent with the values for [C_4mPyrro][NTf_2] reported in this study (Figure 3 and Figure SI-1: SI, Supporting Information).

The mechanical coefficients from the recent report of Gardas et al.[24] confirmed than the reported values for the [C_4mPyrro][NTf_2] in this work can be expected with an uncertainty of ± 10 %. For this IL, they have reported a thermal expansion coefficient and an isothermal compressibility close to 0.515 GPa^{-1} (0.439 GPa^{-1} calculated in this work − 14 % of deviation) and 0.705$\cdot 10^{-3}$ K^{-1} (0.616$\cdot 10^{-3}$ K^{-1} calculated in this work − 12 % of deviation) at 293 K and at atmospheric pressure, respectively.[24] Furthermore, this uncertainty was considered for each mechanical coefficient based on this comparison and also from our previous report on the comparison of these thermodynamic properties with the literature, for other ILs.[19]

The mechanical coefficients calculated are presented in Table 6. The thermal expansion coefficients increase with increasing temperature varying from (0.64 to 0.68)$\cdot 10^{-3}$ K^{-1} and from (0.62 to 0.66)$\cdot 10^{-3}$ K^{-1} at 0.1 MPa for [N_{1114}][NTf_2] and [C_4mPyrro][NTf_2], respectively. These coefficients decrease with increasing pressure varying from (0.58 to 0.64)$\cdot 10^{-3}$ K^{-1} and from (0.56 to 0.62)$\cdot 10^{-3}$ K^{-1} at 298 K for [N_{1114}][NTf_2] and [C_4mPyrro][NTf_2], respectively. The isothermal compressibility increases with increasing temperature varying from (0.39 to 0.66) GPa^{-1} and from (0.45 to 0.69) GPa^{-1} at atmospheric pressure for [N_{1114}][NTf_2] and [C_4mPyrro][NTf_2], respectively. κ_T decreases with increasing pressure varying from (0.36 to 0.39) GPa^{-1} and from (0.39 to 0.45) GPa^{-1} at 298 K for [N_{1114}][NTf_2] and [C_4mPyrro][NTf_2], respectively. With the exception of the effect of temperature on the isothermal compressibility, the effect of temperature or the pressure on the mechanical coefficients is small.

Table 6. Isobaric thermal expansion coefficients (α_p) and isothermal compressibilities (κ_T) as a function of temperature and pressure calculated from the Tait equation between (298 and 423) K and (0.1 to 40) MPa.

	T/K					
p/MPa	298.15	373.15	423.15	298.15	373.15	423.15
	$10^3\cdot\alpha_p$ /K^{-1}					
	[N_{1114}][NTf_2]			[C_4mPyrro][NTf_2]		
0.1	0.641	0.666	0.684	0.618	0.643	0.661
10	0.625	0.645	0.662	0.602	0.624	0.642
20	0.609	0.625	0.640	0.588	0.607	0.624
30	0.594	0.605	0.621	0.574	0.591	0.608
40	0.580	0.587	0.602	0.561	0.576	0.594
	κ_T/GPa^{-1}					
	[N_{1114}][NTf_2]			[C_4mPyrro][NTf_2]		
0.1	0.389	0.536	0.653	0.447	0.585	0.689
10	0.380	0.519	0.628	0.430	0.557	0.651
20	0.372	0.504	0.606	0.415	0.531	0.616
30	0.364	0.489	0.585	0.401	0.508	0.586
40	0.356	0.476	0.566	0.387	0.487	0.558

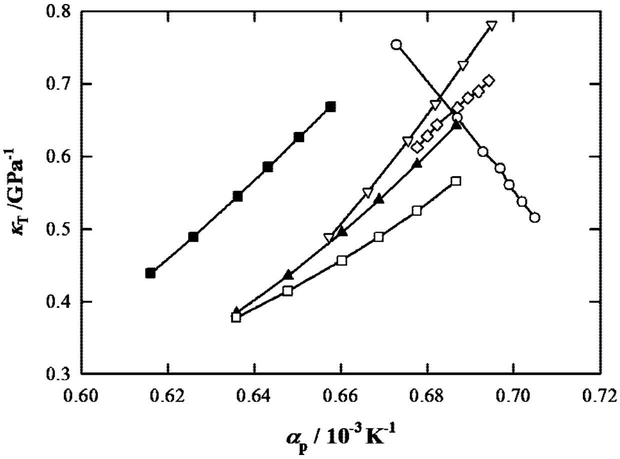


Figure 3. Isothermal compressibility, κ_T, as a function of the thermal expansion coefficient, α_P, for [NTf_2]$^-$ based ILs at atmospheric pressure between (273 and 423) K: ■, [C_4mPyrro][NTf_2]; ▲, [N_{1114}][NTf_2]; ○, [C_4mPyrro][NTf_2] from Gardas et al.;[24] ◇, [P_{66614}][NTf_2] at 0.2 MPa from Esperança et al.;[11] □, [C_2mim][NTf_2] from Jacquemin et al.;[19] ▽, [C_4mim][NTf_2] from Jacquemin et al.[19]

Figure 3 shows a comparison of the isothermal compressibility, κ_T, as a function of the thermal expansion coefficient, α_P, for a range of ionic liquids and molecular solvents at atmospheric pressure and from (273 to 423) K.[12,19,24] Although some variation is found with the cation for the [NTf_2]$^-$ based ionic liquids, this is small compared with the effect of the anion as reported in Figure SI-1 (see Supporting Information) and described in greater detail in our previous report.[19] In all cases, the ILs are characterized by smaller mechanical coefficients compared with molecular organic solvents (such as the methylimidazole) which indicates that the ionic interactions present in ILs lower considerably the mechanical coefficients.[7,19,22,24]

Development of Predictive Methods

Extension of the Empirical Method Based on "Ideal" Volumetric Behavior of ILs as a Function of Pressure. The development of a predictive model for the molar volumes of ILs as a function of temperature and pressure presents two major challenges. First, because of the large number of possible anion−cation combinations, it is not possible to determine a priori the volumetric properties of all ionic liquids. Second, the determination of the density as a function of pressure requires the availability of appropriate experimental techniques which require either specialized equipment or extensive calibration procedures. However, the knowledge of the volumetric properties of the ionic liquids is essential if these liquids are to be considered as media for reactions, solvents with which to perform extractions, or lubricants.

To date, only one predictive model has been described[25] which is able to provide values for the density of ionic liquids

Table 7. Parameters from Equation 11 Used to Predict the Effective Molar Volume of Anion Calculated in this Study as a Function of Temperature and Pressure

anion	M / $\mathrm{g{\cdot}mol^{-1}}$	D_0 / $\mathrm{cm^3{\cdot}mol^{-1}}$	$10^3{\cdot}D_1$ / $\mathrm{cm^3{\cdot}mol^{-1}{\cdot}K^{-1}}$	$10^6{\cdot}D_2$ / $\mathrm{cm^3{\cdot}mol^{-1}{\cdot}K^{-2}}$	H_0 / MPa	$10^2{\cdot}H_1$ / $\mathrm{MPa{\cdot}K^{-1}}$	$10^4{\cdot}H_2$ / $\mathrm{MPa{\cdot}K^{-2}}$	$10^2{\cdot}G$
$[BF_4]^-$	86.80	53.656	+ 24.04	+ 29.68	+ 255.2	+ 355.8	+ 25.41	−7.148
$[PF_6]^-$	144.96	73.710	+ 45.42	−58.03	+ 179.7	+ 258.3	−32.34	−3.944
Cl^-	35.45	27.003	+ 1.865	+ 5.873	+ 8.390	+ 1.364	+ 8.248	−2.396
$[NTf_2]^-$	280.15	157.60	+ 104.3	+ 50.52	+ 359.0	−327.0	+ 134.4	−12.68
$[OTf]^-$	149.07	87.472	+ 52.78	−15.82	+ 185.2	+ 5.250	+ 65.88	−10.23
$[OAc]^-$	59.04	49.177	+ 21.49	−27.75	+ 80.89	+ 57.25	+ 50.24	+ 9.140
$[C(CN)_3]^-$	90.07	84.586	+ 70.85	−227.3	+ 350.2	+ 395.4	−689.0	−9.436
$[EtSO_4]^-$	125.12	90.850	+ 19.89	+ 24.16	+ 588.7	+ 4.256	+ 3.105	−93.13
$[OctSO_4]^-$	209.28	191.40	+ 136.6	−316.2	+ 1126	+ 3.775	+ 3.373	−56.22

Table 8. Parameters from Equation 11 Used to Predict the Effective Molar Volume of Cation Calculated in this Study as a Function of Temperature and Pressure

cation	M / $\mathrm{g{\cdot}mol^{-1}}$	D_0 / $\mathrm{cm^3{\cdot}mol^{-1}}$	$10^3{\cdot}D_1$ / $\mathrm{cm^3{\cdot}mol^{-1}{\cdot}K^{-1}}$	$10^6{\cdot}D_2$ / $\mathrm{cm^3{\cdot}mol^{-1}{\cdot}K^{-2}}$	H_0 / MPa	$10^2{\cdot}H_1$ / $\mathrm{MPa{\cdot}K^{-1}}$	$10^4{\cdot}H_2$ / $\mathrm{MPa{\cdot}K^{-2}}$	$10^2{\cdot}G$
$[C_4mmim]^+$	153.25	146.55	+ 113.3	−128.2	+ 421.5	+ 232.3	+ 54.04	−76.95
$[C_4py]^+$	136.22	128.78	+ 78.05	+ 66.21	+ 450.8	+ 8.876	+ 56.30	−13.25
$[C_3m_{(3)}Py]^+$	136.21	129.64	+ 103.2	−8.740	+ 119.0	+ 15.89	−18.33	−9.484
$[C_3mPyrro]^+$	128.24	127.28	+ 96.13	−37.23	+ 152.2	+ 12.04	−2.953	−11.19
$[C_3mPip]^+$	142.26	141.53	+ 110.6	−60.44	+ 132.2	+ 10.22	−19.07	−9.236
$[C_4mPyrro]^+$	142.26	145.03	+ 99.96	−66.00	+ 729.4	+ 8.819	+ 54.70	−29.10
$[N_{1114}]^+$	116.23	126.64	+ 94.94	−60.06	+ 412.6	+ 8.374	+ 54.27	−16.26
$[P_{666\ 14}]^+$	483.86	560.51	+ 390.4	+ 118.4	+ 280.0	+ 8.318	+ 15.50	−20.85

Table 9. Parameters from Equations 10 and 11 Used to Predict the Effective Molar Volume of the Imidazolium Cation As a Function of Temperature and Pressure

	M / $\mathrm{g{\cdot}mol^{-1}}$	E_0 / $\mathrm{cm^3{\cdot}mol^{-1}}$	$10^2{\cdot}E_1$ / $\mathrm{cm^3{\cdot}mol^{-1}{\cdot}K^{-1}}$	$10^4{\cdot}E_2$ / $\mathrm{cm^3{\cdot}mol^{-1}{\cdot}K^{-2}}$	H_0 / MPa	H_1 / $\mathrm{MPa{\cdot}K^{-1}}$	$10^2{\cdot}H_2$ / $\mathrm{MPa{\cdot}K^{-2}}$	$10^2{\cdot}G$
$[C_0mim]^+$	83.11	66.509	+ 1.249	+ 5.529	+ 314.5	+ 2.558	−2.099	−4.628
	M / $\mathrm{g{\cdot}mol^{-1}}$	F_0 / $\mathrm{cm^3{\cdot}mol^{-1}}$	$10^2{\cdot}F_1$ / $\mathrm{cm^3{\cdot}mol^{-1}{\cdot}K^{-1}}$	$10^6{\cdot}F_2$ / $\mathrm{cm^3{\cdot}mol^{-1}{\cdot}K^{-2}}$	H_0 / MPa	$10^1{\cdot}H_1$ / $\mathrm{MPa{\cdot}K^{-1}}$	$10^3{\cdot}H_2$ / $\mathrm{MPa{\cdot}K^{-2}}$	$10^1{\cdot}G$
$-CH_2-$	14.03	16.967	+ 1.399	−1.946	+ 89.61	−5.108	+ 2.333	−1.503

as a function of temperature and pressure. However, this model is limited as it requires knowledge of the mechanical coefficients for the ionic liquid to be modeled. Rebelo and co-workers have observed and previously reported[11,27,28] that there is a linear variation of the molar volume as a function of the number of carbons in the alkyl chain for the 1,3-dialkylimidazolium cation and, irrespective of the anion, a constant variation of the molar volume per addition of two carbon atoms on this alkyl chain. From these observations, and assuming that the IL molar volume results from the addition of the cation and anion molar volumes, an empirical prediction model was proposed

$$V_{m_{IL}} = V^*_{\text{cation}} + V^*_{\text{anion}} \qquad (7)$$

$V_{m_{IL}}$ being the molar volume of the ionic liquid constituted by the cation with effective molar volume V^*_{cation} and the anion with effective molar volume V^*_{anion}.

On the basis of these assumptions, our group has proposed recently a group contribution method for predicting ionic liquid density as a function of temperature at 0.1 MPa.[6,19] This has been formulated by assuming that the variation of the density with temperature is proportional to the effective molar volume fraction of ions constituting the ionic liquid $[C_4mim][NTf_2]$.[6] Second-degree polynomials, as shown in eq 8, were found to satisfactorily fit the variation of the effective molar volumes with temperature

$$V^*_{\text{ion}}(\delta T) = \sum_{i=0}^{2} (D_i \cdot \delta T^i) \qquad (8)$$

where $\delta T = (T - 298.15\ \text{K})$ and D_i are the coefficients obtained by fitting the data at 0.1 MPa.[6] 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,[6] and a new relationship was then calculated and expressed as a function of δT using eqs 9 and 10

$$V^*_{[C_n\text{mim}]^+}(\delta T) = V^*_{[C_0\text{mim}]^+}(\delta T) + n \cdot a^* \qquad (9)$$

where a^* is the contribution to the molar volume of each extra $-CH_2-$ group on the alkyl chain and n is the number of $-CH_2-$ groups in the alkyl chain. Using eq 8 and the effective molar volume of $[C_n\text{mim}]^+$ cations calculated as a function of the temperature, the effective molar volume of the $[C_0\text{mim}]^+$ and the contribution of a $-CH_2-$ group in the alkyl chain as a function of temperature (parameters E_i and F_i) were then calculated. Second-degree polynomials were again found to be adequate for fitting the variation of these parameters with temperature

$$V^*_{[C_n\text{mim}]^+}(\delta T) = \left(\sum_{i=0}^{2} (E_i \cdot \delta T^i)\right) + n \cdot \left(\sum_{i=0}^{2} (F_i \cdot \delta T^i)\right) \qquad (10)$$

The parameters D_i, E_i, and F_i calculated previously[6] from a databank containing more than 2150 density data are used in the extension of the model as a function of pressure and are listed in Tables 7, 8, and 9.

Using these assumptions and this methodology, new parameters as a function of temperature and pressure have been calculated using more than 5080 available density data points and are presented in this work. The same procedure was used as reported previously for 0.1 MPa but extending the determination of the effective molar volumes of ions constituting the ionic liquid [C_4mim][NTf_2] as a function of the pressure. The parameters used in the predictive method were optimized using an iterative calculation to validate the assumptions and then the contribution of a $-CH_2-$ group in the alkyl chain of the imidazolium cation, for each temperature and pressure that was calculated from the difference between the effective molar volumes of the [C_2mim]$^+$ and the [C_4mim]$^+$ cations. The Tait equation was then used to calculate the contribution of each $-CH_2-$ group to the molar volume of 1-alkyl-3-methylimidazolium based ionic liquids. The effective molar volume of the [C_0mim]$^+$, as a function of temperature and pressure, was then determined using the effective molar volume of [C_4mim]$^+$ and the contribution of four $-CH_2-$ groups. To calculate new effective molar volumes for an anion, the values for [C_2mim]$^+$ and [C_4mim]$^+$ cations were preferentially used. For the case of ionic liquids based on other cation families, the effective molar volume of the cation was determined from the difference between the ionic liquid molar volume and the value for the [NTf_2]$^-$ anion. The comparison of the experimental and calculated molar volumes of alkyl$-$methylimidazolium based ionic liquids containing more than four carbons in the alkyl chain can be used to analyze the predictive capability of this model.

All the effective molar volumes were fitted using the equation

$$V^*_\alpha(\delta T, p, G, H) = \frac{V^*_\alpha(\delta T, p_{\mathrm{ref}})}{1 - G \cdot 1n\left(\dfrac{H(\delta T) + p}{H(\delta T) + p_{\mathrm{ref}}}\right)} \qquad (11)$$

where α stands for the cation or anion constituting an IL or for an extra $-CH_2-$ group in the alkyl chain length of an 1-alkyl-3-methylimidazolium based ionic liquid; $V^*_\alpha(\delta T, p_{\mathrm{ref}})$ is the reference effective molar volume obtained using the eq 8 or 9 and 11; and $p_{\mathrm{ref}} = 0.1$ MPa. G is an adjustable parameter, and $H(\delta T)$ is the second-order polynomial

$$H(\delta T) = \sum_{i=0}^{2} (H_i \cdot \delta T^i) \qquad (12)$$

The coefficients D_i, E_i, F_i, G_i, and H_i obtained by fitting the data for 9 anions and 15 cations are listed in Tables 7, 8, and 9.

Figure 4 shows the parity plot between predicted and experimental densities and molar volumes. The model described reproduces the ionic liquid molar volumes to within 0.36 % using 5080 experimental data points (1550 and 3530 data points at 0.1 MPa and for $p > 0.1$ MPa, respectively). By using a reduced data set of 1716 molar volumes, the expected uncertainty of the predicted values is 0.44 % (see Supporting Information).

To test the validity of the contribution of an extra $-CH_2-$ group in the alkyl chain for the density of nonimidazolium based ILs, the calculated density of the [C_3mPyrro][NTf_2] has been compared using two different approaches. In the first approach, the sum of the effective molar volumes of each ion constituting this IL was calculated. In the second approach, the following calculation was used

$$V_{\mathrm{m}[C_3\mathrm{mPyrro}][NTf_2]} = (V^*_{[C_4\mathrm{mPyrro}]^+} - V^*_{[-CH_2-]}) + V^*_{[NTf_2]^-} \qquad (13)$$

From this calculation, it was possible to determine that the uncertainty in the density associated with the contribution of an extra $-CH_2-$ group in the cation constitutes the ionic liquid. This uncertainty is evaluated as 0.40 % for the calculation of the molar volume (density) of [C_3mPyrro][NTf_2] at pressures up to 30 MPa (Figure 5). This result indicates the consistency of the methodology and points to the use of the second approach described to easily estimate the molar volume of other ILs. This calculation can be used, at first, to estimate the density for nonimidazolium-based ILs as a function of the temperature and pressure. However, the systematic error shown demonstrates that the contribution of an extra $-CH_2-$ group must be calculated from each family of cations, to acquire more accurate calculated densities values.

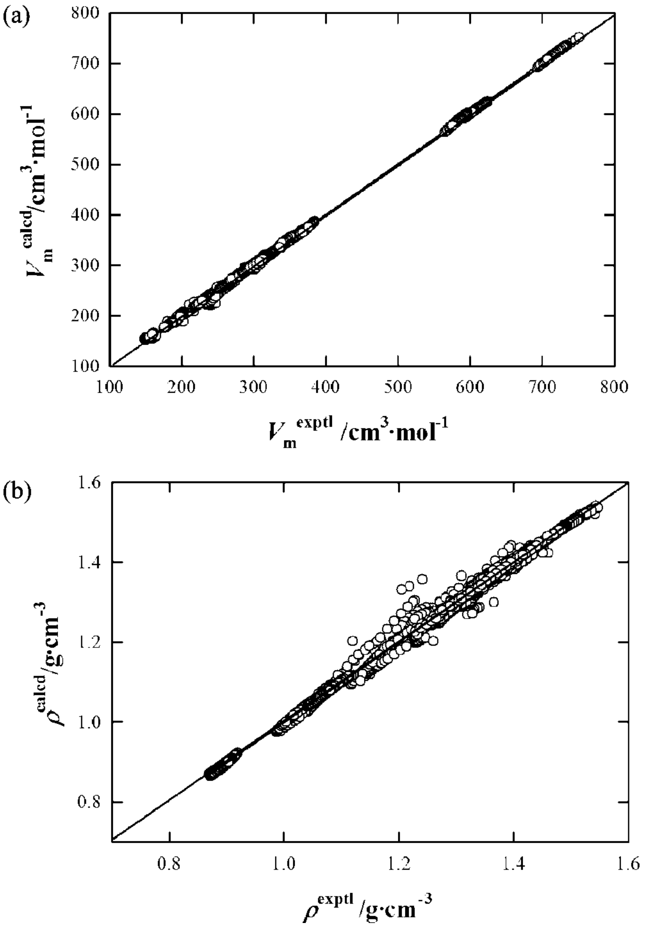


Figure 4. Experimental versus (a) predicted molar volumes and (b) predicted densities for 5080 ionic liquid data points (see Supporting Information) using the empirical method based on "ideal" volumetric behavior of ILs as a function of temperature between (273 and 423) K and pressures between (0.1 and 207) MPa. The predicted densities (molar volumes), Y, calculated from this methodology present an excellent agreement with the experimental densities (molar volumes), X, as demonstrated in Figure 5: $Y = (0.99962 \pm 0.00008) \cdot X$ (correlation coefficient: $R^2 = 0.99996$, in other words, the calculated difference between the experimental average density ($\rho_{\mathrm{exptl\ av.}} = 1.2910$ g·cm^{-3}) and predicted average density ($\rho_{\mathrm{calcd\ av.}} = 1.2905$ g·cm^{-3}) is close to $5 \cdot 10^{-4}$ g·cm^{-3}).

The estimation of the effective molar volume of the ions permits the evaluation of the effect of changing one of the ions on the volumetric properties of the ionic liquid. 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 at 0.1 MPa were calculated previously using this methodology.[6] In the present work, more than 135 IL densities (molar volumes) as a function of temperature up to 423 K and pressures up to 207 MPa (see Table 1) could be calculated. This methodology also allows the determination of the mechanical coefficients by using the calculated density as a function of temperature and pressure. An uncertainty of ± 20 % for each mechanical coefficient was estimated based on the comparison of these calculated thermodynamic properties using the present prediction

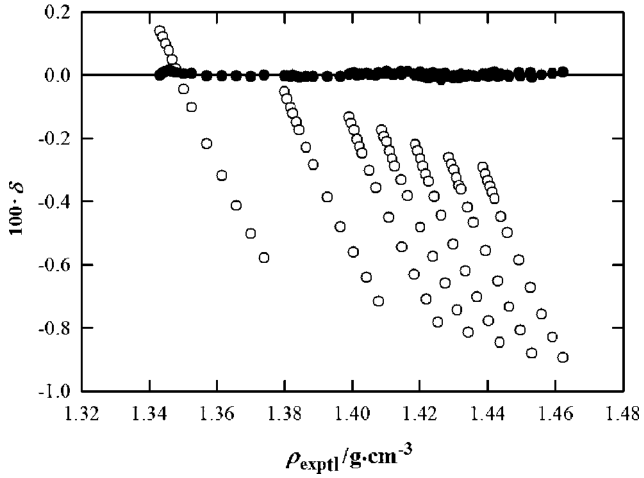


Figure 5. Relative deviations (δ) between the literature data and calculated density for $[C_3mPyrro][NTf_2]$ as a function of the reported densities (ρ_{exptl}/g·cm^{-3}) from Gardas et al.:[24] ●, by using the sum of the effective molar volumes of each ion constituting this IL (eq 7); ○, by using the difference obtained between the sum of effective molar volumes of each ion constituting the $[C_4mPyrro][NTf_2]$ and the contribution of a $-CH_2-$ group (eq 13) for temperatures between (293 and 393) K and pressures between (0.1 and 30) MPa.

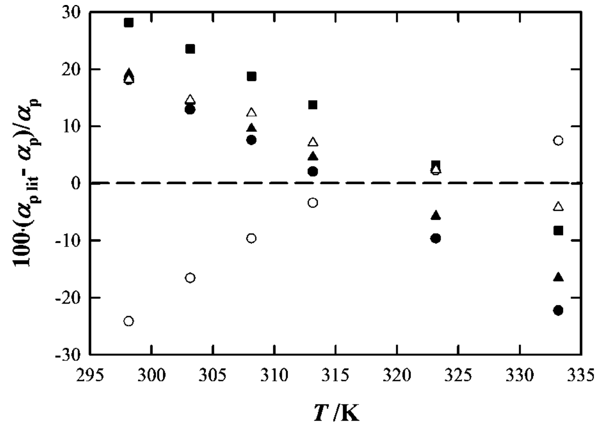


Figure 6. Percentage deviations as $100\cdot(\alpha_{\text{P lit}} - \alpha_{\text{P}})/\alpha_{\text{P}}$ of the literature thermal expansion coefficients from our calculated data for $[C_4mim][BF_4]$ at 10 MPa: ●, Rebelo et al.;[8] ○, Gomez de Azevedo et al.;[9] ▲, Tomida et al.;[13] ■, Gardas et al.;[15] △, Jacquemin et al.[19]

method and the experimental data reported herein or previously[7−24] (see Figures 6 and 7). The present prediction method constitutes an improvement to the previously reported group contribution method to calculate ionic liquid density as a function of temperature and pressure.[25] In the present case, it is not only possible to calculate the mechanical coefficients of single ILs, but based on the experimental observation of Rebelo et al.,[27] where the excess molar volumes of binary ILs mixtures were found to be independent of pressure, it is also possible to estimate the volumetric properties of binary and/or probably ternary IL mixtures. This significantly increases the impact of the prediction method described herein and shown previously at 0.1 MPa.[6]

Conclusions

The density of ionic liquids as a function of pressure and temperature has been modeled using a group contribution model between (298 and 423) K and between (0.1 and 207) MPa. Using over 5080 experimental data points, the density may be predicted to within 0.36 %. This methodology allows the determination of the mechanical coefficients using the calculated density over the temperature and pressure range studied with an estimated uncertainty of ± 20 %. Experimental data have also been reported for $[N_{1114}][NTf_2]$ and $[C_4mPyrro][NTf_2]$, and this information has been incorporated into the model. Good agreement is found with previously reported data with the exception of a positive variation of isothermal compressibility, α_P, as a function of the thermal expansion coefficient, κ_T, for *both* the ionic liquids studied. This is in agreement with many other ionic liquids previously reported but not for $[C_4mPyrro][NTf_2]$.

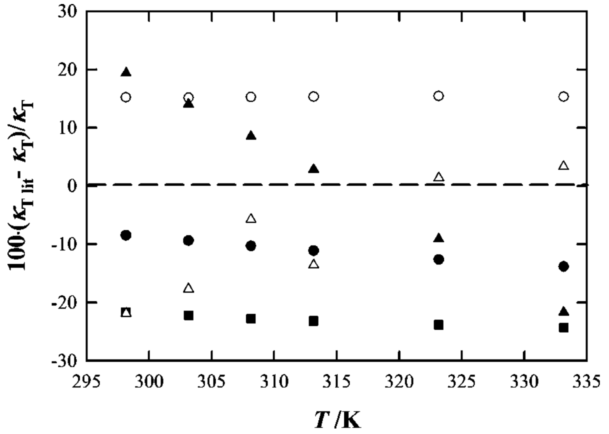


Figure 7. Percentage deviation as $100\cdot(\kappa_{\text{p lit}} - \kappa_{\text{p}})/\kappa_{\text{p}}$ of the reported isothermal compressibilities from calculated data for $[C_4mim][BF_4]$ at 10 MPa: ●, Rebelo et al.;[8] ○, Gomez de Azevedo et al.;[9] ▲, Tomida et al.;[13] ■, Gardas et al.;[15] △, Jacquemin et al.[19]

Supporting Information Available:

Additional Supporting Information spreadsheets of the IL density database, which gives some examples of calculation from effective molar volume of 9 anions and 15 cations as a function of the temperature and pressure presented in this manuscript. This material is available free of charge via the Internet at http://pubs.acs.org.

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