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High-Pressure Volumetric Properties of Imidazolium-Based Ionic Liquids: Effect of the Anion

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The densities of five imidazolium-based ionic liquids (ILs) (1-butyl-3-methylimidazolium tetrafluoroborate, $[C_1C_4Im][BF_4]$; 1-butyl-3-methylimidazolium hexafluorophosphate, $[C_1C_4Im][PF_6]$; 1-butyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide, $[C_1C_4Im][Tf_2N]$; 1-ethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide, $[C_1C_2Im][Tf_2N]$; 1-ethyl-3-methylimidazolium ethylsulfate, $[C_1C_2Im][EtSO_4]$) 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. Knowledge of the variation of the density with temperature and pressure allows access to the mechanical coefficients: thermal expansion coefficient and isothermal compressibility. The effects of the anion and of the length of the alkyl chain on the imidazolium ring on the volumetric properties were particularly examined. The mechanical coefficients were compared with those of common organic solvents, water and liquid NaCl. Finally, a prediction model, based on an "ideal" volumetric behavior of the ILs, is proposed to allow calculation of the molar volume of imidazolium-based ionic liquids as a function of temperature.

Introduction

Ionic liquids (ILs) are considered as potential substitutes to traditional organic solvents. They have negligible vapor pressure, low melting temperature, and good thermal stability, which make them liquid over a wide temperature range including ambient temperature. These unique properties make them very attractive, especially for applications in the field of green chemistry. Knowledge of their thermodynamic and thermophysical behavior is of particular value for technological use of this new class of substances. Given the considerable number of possible anion−cation combinations, it is impossible to collect all the thermodynamic and thermophysical data on these fluids. Thus the knowledge of the structure−property relationships is of particular interest for the development of predictive models. In this study, we have focused on the volumetric data which are lacking especially as a function of temperature and at pressures higher than atmospheric with a particular focus on the influence of changing the anion of the IL.

In the literature, the density of a variety of imidazolium-based ILs has been recently reported as a function of temperature at atmospheric pressure[1−17] and to a lesser extent over an extended pressure range.[18−24] The density decreases with temperature, and it only slightly increases with pressure. These effects can be quantified by the calculation of the mechanical coefficients. Thermal expansion coefficients, which represent the dependence of the volume (density) on temperature, are typically between $(4 \text{ and } 8)\cdot10^{-4}$ K^{-1} which is comparable with water and lower than that of organic solvents.[18,20,21,24] Isothermal compressibilities that correspond to the dependence of volume on pressure are typically between $(0.15 \text{ and } 0.70)\cdot10^{6}$ GPa^{-1} for the imidazolium-based ILs[18,20,21,24] and decrease with pressure. The density is mainly affected by the nature of the anion, decreasing with its increasing size[20,21,24] and to a lesser extent by the cation. Lower densities are observed for longer alkyl chains on the imidazolium cation,[18,21,24] and the addition of a third alkyl chain[2,21] on the ring contributes to a decrease in density.

As first observed by Seddon et al.,[25] the presence of impurities has a strong impact on the density of ILs. The two main impurity sources are water and halogenated compounds, both lowering the density. In particular, the presence of chloride has an important effect. Troncoso et al.[7] have observed that an increase in chloride content from (20 to 130) ppm decreases the density by 0.1 %. In that sense, the identification of the impurities in the samples is of particular importance.

In a previous work,[1] our group was interested in the densities and viscosities of a selection of six hydrophobic and hydrophilic ILs (five imidazolium and one ammonium based) as a function of temperature up to 343 K and at atmospheric pressure. The relationship property−ion structure was qualitatively examined, and we were particularly interested in the effect of the presence of a particular impurity, water, on these thermophysical properties. The densities of the water-saturated IL samples are lower than those of the dried samples. The observed differences are between (1 and 2) %. This study also highlighted the disparity in the experimental data presented in the literature that is mainly due to the differences in the sample purity.

The aim of the present work was the experimental determination of the density of ILs as a function of temperature on a more extended range than previously used, from (293 to 415) K, and as a function of pressure from (0.1 to 40) MPa. The densities were measured again at atmospheric pressure to obtain a consistent set of data. The knowledge of the volumetric properties as a function of temperature and pressure allows access to the mechanical coefficients. We have selected five ILs: three containing the cation 1-butyl-3-methylimidazolium, $C_1C_4Im^+$, combined with either the anion tetrafluoroborate,

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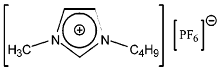
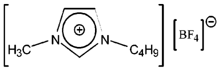
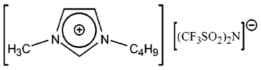
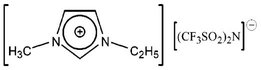
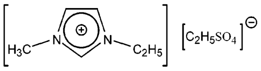
Table 1. Chemical Structure, Molar Mass (M_{IL}), Water Content in Mass Fraction w_w, and Mole Fraction x_w and Halide Mass Fraction w_{halide} of the Selected ILs[a]

IL	Chemical structures	M_{IL} /g.mol^{-1}	$w_w \times 10^3$	$x_w \times 10^3$	$w_{halide} \times 10^6$
$[C_1C_4Im][PF_6]$		284.18	0.19	3.00	< 50[1]
$[C_1C_4Im][BF_4]$		226.03	0.70	8.60	< 50[1]
$[C_1C_4Im][Tf_2N]$		419.37	0.05	1.20	< 50[1]
$[C_1C_2Im][Tf_2N]$		391.31	0.05	1.10	< 50[2]
$[C_1C_2Im][EtSO_4]$		236.29	0.10	1.30	-

[a] 1, Cl^-; 2, Br^-. Measured using ion chromatography.

BF_4^-, hexafluorophosphate, PF_6^-, or bis{(trifluoromethyl)-sulfonyl}imide, Tf_2N^-, and two ILs containing the cation 1-ethyl-3-methylimidazolium, $C_1C_2Im^+$, combined with the anion Tf_2N^- or ethyl sulfate $EtSO_4^-$. These salts were chosen to investigate the effect of changing the anion and modifying the length of the alkyl chain on the imidazolium ring on the density and the volumetric properties. To the best of our knowledge, the densities of $[C_1C_2Im][Tf_2N]$[2,5,12,13,26,31] and of $[C_1C_2Im][EtSO_4]$[13,14,31,34] have only been measured at atmospheric pressure.

Experimental

Materials. The 1-butyl-3-methylimidazolium tetrafluoroborate $[C_1C_4Im][BF_4]$ (CAS 174501-65-6) and 1-butyl-3-methylimidazolium hexafluorophosphate $[C_1C_4Im][PF_6]$ (CAS 174501-64-5) samples were purchased from Solvionic with a minimum stated mole fraction purity of 0.98 and 0.999, respectively. The chloride contents of these samples, determined by ion chromatography (IC),[27] are less than 50 ppm. The three other imidazolium-based ILs (1-ethyl-3-methylimidazolium ethylsulfate $[C_1C_2Im][EtSO_4]$ (CAS 342573-75-5), 1-ethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide $[C_1C_2Im][Tf_2N]$ (CAS 174899-82-2), and 1-butyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide $[C_1C_4Im][Tf_2N]$ (CAS 174899-83-3) were supplied by the group of Wasserscheid (University of Erlangen-Nürnberg, Germany) with a minimum stated purity of 0.99 in mole fraction. The $[C_1C_2Im][Tf_2N]$ and $[C_1C_4Im][Tf_2N]$ samples contain less than $50 \cdot 10^{-6}$ (mass fraction) of bromide and chloride, respectively, determined by ion chromatography (IC).

After treating the ILs for 15 h at 323 K under a vacuum, the samples were considered as dried and were conditioned under a nitrogen atmosphere. To avoid any contact of the sample with atmosphere, a Schlenk-type tube and a syringe equipped with a luer lock valve were used to load the samples into the densimeter. A coulometric Karl Fisher titration (Mettler Toledo DL31) on water was performed before and after each series of measurements, and it was found that there was no variation of the water quantity in the samples. The structures, molar masses, and quantities of water after having treated the samples under a vacuum are presented for the ILs studied in Table 1.

Measurements. The experimental apparatus used to measure the densities, a U-shape vibrating-tube densimeter (Anton Paar, model DMA 512) operating in a static mode, was used at atmospheric pressure and has been previously described.[1] For this study, it was modified to work at pressures up to 40 MPa. The experimental apparatus is schematically represented in Figure 1. The IL was first degassed and dried under a vacuum by connecting the Schlenk-type tube containing the sample to C1, valve V3 being closed. The Schlenk-type tube was then transferred to connection C2. The whole installation being under a vacuum (V1 closed, V2 and V3 opened), the valve V1 was opened to introduce the sample in the U-tube. Then valves V1 and V3 were closed, and the desired working pressure was obtained using the high-pressure generator leading to a reduction of the total volume.

The temperature was maintained constant to 0.01 K in the densimeter by means of a recirculating bath equipped with a PID temperature controller (Julabo FP40-HP). For measuring temperature, a 100 Ω platinum resistance thermometer (uncertainty 0.02 K, accuracy 0.04 K) was used. Its calibration was performed against 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). It was possible to study different pressures and temperatures without introducing the sample again by simply moving the high-pressure generator or changing the liquid thermostat setpoint.

The measured period of vibration τ of a U tube is related to the density ρ according to $\rho = A\tau^2 + B$, where A and B are parameters that are a function of temperature and pressure. The method described by Lagourette et al.[28] was used to calibrate the densimeter. The A and B parameters were determined at all the studied temperatures and pressures, between (293 and 413) K and (0.1 and 40) MPa, respectively, using a vacuum, air, nitrogen, three-times distilled water,[42] and aqueous solutions of NaCl (molalities of (1 and 3) M).[43]

Measurements were performed with a step of 10 K from (293 to 413) K and at six different pressures from atmospheric to 40 MPa. At least three independent values were obtained at each temperature and pressure. No viscosity correction was applied to density measurements. According to the manufacturer, it is necessary only for liquids with viscosity higher than 100 mPas. It is the case of $[C_1C_4Im][PF_6]$ for which this correction affects the density by less than 0.1 %. That is the reason why this was not considered in this work. The uncertainty of the density measurement is 10^{-4} g·cm^{-3}.

Results and Discussion

Densities at Atmospheric Pressure. The first part of this work consisted of the measurement of the densities at atmospheric

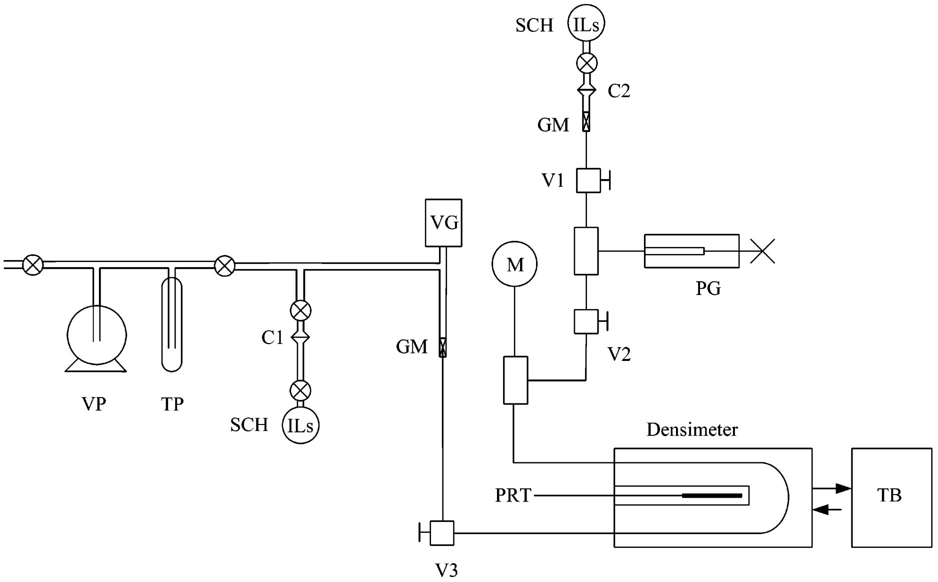


Figure 1. Vibrating-tube densimeter: VP, vacuum pump; TP, cold trap; VG, vacuum gauge; M, precision manometer; PG, pressure generator; TB, thermostated bath; PRT, thermometer; GM, glass-metal connexion; V1, V2, V3, valves; C1, C2, vacuum o'ring connections; SCH, Schlenk-type tube.

Table 2. Experimental Values of Densities ρ between (293 and 415) K at Atmospheric Pressure

$[C_1C_4Im][PF_6]$		$[C_1C_4Im][BF_4]$		$[C_1C_4Im][Tf_2N]$		$[C_1C_2Im][Tf_2N]$		$[C_1C_2Im][EtSO_4]$	
T/K	ρ/g·cm^{-3}	T/K	ρ/g·cm^{-3}	T/K	ρ/g·cm^{-3}	T/K	ρ/g·cm^{-3}	T/K	ρ/g·cm^{-3}
293.49	1.3698	292.94	1.2048	293.49	1.4422	293.49	1.5223	292.49	1.2421
302.73	1.3620	302.80	1.1975	303.15	1.4330	302.68	1.5132	302.61	1.2367
312.86	1.3535	312.79	1.1902	312.84	1.4239	312.64	1.5032	312.47	1.2307
322.28	1.3455	322.83	1.1829	322.31	1.4149	322.30	1.4932	322.3	1.2244
332.73	1.3370	332.53	1.1758	332.78	1.4051	332.58	1.4832	332.74	1.2184
342.50	1.3287	342.72	1.1686	342.98	1.3955	342.49	1.4736	342.42	1.2126
352.29	1.3209	352.32	1.1617	352.33	1.3866	352.32	1.4636	352.32	1.2063
373.33	1.3039	373.32	1.1469	373.32	1.3671	373.32	1.4432	373.36	1.1941
391.30	1.2891	391.29	1.1345	391.28	1.3504	391.29	1.4256	391.39	1.1832
414.93	1.2697	414.92	1.1165	414.92	1.3285	414.92	1.4024	414.95	1.1691

pressure. The experimental densities for the five ILs studied here are presented in Table 2 as a function of temperature from (293 to 415) K. As previously observed, they are related to the molar masses of the ions. The ILs containing the anion Tf_2N^-, having the higher molar masses, present the highest densities followed by the ILs containing PF_6^-, $EtSO_4^-$, and then BF_4^-. The comparison between $[C_1C_2Im][Tf_2N]$ and $[C_1C_4Im][Tf_2N]$ indicates that the density decreases when increasing the alkyl chain length on the imidazolium ring.

As expected, the density decreases with temperature. A 125 K increase of the temperature decreases the density by (6 to 9) %. A quadratic equation was used to fit the experimental densities as a function of temperature

$$\rho(T, 0.1\ \mathrm{MPa}) = A_0 + A_1T + A_2T^2 \qquad (1)$$

The A_i parameters are presented in Table 3 together with the corresponding relative average absolute deviations (AADs), generally lower than 0.01 %. This value can be regarded as the uncertainty of our measurement. The maximum AAD, 0.014 %, was obtained for $[C_1C_4Im][BF_4]$.

Table 3. Parameters A_i of Equation 1 Used to Smooth the Experimental Densities at 0.1 MPa as a Function of Temperature along with the Percent Average Absolute Deviations of the Fit (AAD)

IL	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}	AAD %
$[C_1C_4Im][PF_6]$	1.6312	−9.392	16.48	0.008
$[C_1C_4Im][BF_4]$	1.4189	−7.403	3.007	0.014
$[C_1C_4Im][Tf_2N]$	1.7315	−10.21	11.97	0.002
$[C_1C_2Im][Tf_2N]$	1.8313	−10.99	15.83	0.011
$[C_1C_2Im][EtSO_4]$	1.4297	−6.651	8.966	0.011

Table 4. Maximum Deviations δ_{max} between the Experimental Densities of the Present Work and of the Literature between (293 and 423) K at (0.1, 10, and 40) MPa

IL	δ_{max}/%		
	p = 0.1 MPa	p = 10 MPa	p = 40 MPa
$[C_1C_4Im][PF_6]$	± 0.5[4,20,24]	± 0.2[19,20,24]	± 0.2[20,24]
$[C_1C_4Im][BF_4]$	± 0.5[2,4,20,22,34]	± 0.4[19−22]	± 0.3[20]
$[C_1C_4Im][Tf_2N]$	± 0.2[2,5,13,18,33]	± 0.1[18]	± 0.1[18]
$[C_1C_2Im][Tf_2N]$	± 0.3[2,5,12,13,26,31]	−	−
$[C_1C_2Im][EtSO_4]$	± 0.3[13,14,31,32]	−	−

In our previous study,[1] the volumetric properties of these ILs were measured at atmospheric pressure but over a narrower temperature range (from (293 to 343) K). The maximum deviation between the densities of the present work and of the previous study was 0.03 %. The present density results obtained at atmospheric pressure can be compared to the data presented in the literature. In Table 4, we compare our experimental densities with the literature data. Because in most cases several sources are available, the deviations calculated in this table can be regarded as a measure of the accuracy of our measurement. The maximum values (0.5 %) were obtained for $[C_1C_4Im][PF_6]$ and $[C_1C_4Im][BF_4]$.

Densities Over an Extended Pressure Range. The second part of this study consisted of the measurement of the densities at high pressures, up to 40 MPa, for the five ILs studied here. The data are presented in Table 5 as a function of pressure (up

Table 5. Experimental Densities ρ of the Five Selected ILs between (293 and 415) K up to 40 MPa

$[C_1C_4Im][PF_6]$		$[C_1C_4Im][BF_4]$		$[C_1C_4Im][Tf_2N]$		$[C_1C_2Im][Tf_2N]$		$[C_1C_2Im][EtSO_4]$	
T/K	ρ/g·cm^{-3}	T/K	ρ/g·cm^{-3}	T/K	ρ/g·cm^{-3}	T/K	ρ/g·cm^{-3}	T/K	ρ/g·cm^{-3}
				$p = 1$ MPa					
293.48	1.3699	293.50	1.2047	293.49	1.4428	293.50	1.5229	293.47	1.2429
322.31	1.3462	322.31	1.1836	322.31	1.4156	322.32	1.4940	322.31	1.2256
352.31	1.3216	352.33	1.1621	352.33	1.3875	352.34	1.4644	352.33	1.2076
373.33	1.3044	373.34	1.1473	373.32	1.3680	373.31	1.4439	373.36	1.1950
391.32	1.2895	391.27	1.1350	391.27	1.3513	391.25	1.4263	391.39	1.1842
414.94	1.2702	414.93	1.1171	414.92	1.3295	414.93	1.4031	414.95	1.17020
				$p = 5$ MPa					
293.51	1.3717	293.51	1.2065	293.50	1.4456	293.50	1.5250	293.47	1.2465
322.33	1.3482	322.33	1.1854	322.32	1.4187	322.31	1.4965	322.31	1.2295
352.32	1.3237	352.32	1.1641	352.31	1.3909	352.32	1.4670	352.33	1.2118
373.30	1.3066	373.31	1.1494	373.31	1.3716	373.30	1.4465	373.36	1.1994
391.30	1.2920	391.31	1.1371	391.3	1.3551	391.29	1.42900	391.39	1.1888
414.93	1.2726	414.92	1.1194	414.92	1.3336	414.92	1.4060	414.95	1.1749
				$p = 10$ MPa					
293.50	1.3740	293.49	1.2085	293.49	1.4490	293.49	1.5278	293.46	1.2509
322.30	1.3506	322.30	1.1877	322.30	1.4225	322.30	1.4995	322.32	1.2342
352.31	1.3263	352.31	1.1665	352.31	1.3951	352.31	1.4702	352.33	1.2169
373.31	1.3094	373.32	1.1520	373.32	1.3760	373.32	1.4499	373.36	1.2048
391.27	1.2947	391.29	1.1397	391.28	1.3598	391.28	1.4326	391.39	1.1946
414.91	1.2756	414.93	1.1221	414.92	1.3386	414.92	1.4098	414.94	1.1808
				$p = 20$ MPa					
293.49	1.3783	293.50	1.2126	293.50	1.4557	293.49	1.5333	293.46	1.2593
322.30	1.3552	322.31	1.1920	322.31	1.4298	322.30	1.5053	322.31	1.2433
352.31	1.3312	352.32	1.1711	352.32	1.4030	352.30	1.4765	352.34	1.2267
373.34	1.3143	373.31	1.1568	373.31	1.3845	373.33	1.4565	373.37	1.2150
391.31	1.3000	391.29	1.1448	391.28	1.3688	391.31	1.4394	391.41	1.2051
414.92	1.2810	414.92	1.1274	414.91	1.3481	414.92	1.4172	414.94	1.1921
				$p = 30$ MPa					
293.51	1.3822	293.49	1.2165	293.49	1.4621	293.49	1.5386	293.47	1.2675
322.33	1.3593	322.31	1.1962	322.31	1.4368	322.31	1.5109	322.33	1.2521
352.34	1.3356	352.32	1.1757	352.32	1.4107	352.32	1.4825	352.34	1.2360
373.32	1.3190	373.33	1.1616	373.30	1.3927	373.30	1.4628	373.36	1.2250
391.28	1.3047	391.29	1.1497	391.28	1.3773	391.28	1.4460	391.39	1.2154
414.93	1.2859	414.93	1.1325	414.92	1.3572	414.92	1.4242	414.94	1.2029
				$p = 40$ MPa					
293.50	1.3859	293.49	1.2204	293.49	1.4684	293.49	1.5436	293.48	1.2754
322.31	1.3633	322.30	1.2004	322.30	1.4436	322.30	1.5163	322.31	1.2606
352.30	1.3398	352.33	1.18001	352.32	1.4180	352.30	1.4882	352.34	1.2452
373.33	1.3233	373.33	1.1661	373.33	1.4004	373.33	1.4687	373.36	1.2344
391.31	1.3091	391.29	1.1544	391.28	1.3854	391.31	1.4523	391.39	1.2252
414.92	1.2905	414.92	1.1374	414.91	1.3658	414.92	1.4309	414.95	1.2132

to 40 MPa) and temperature (from (293 to 415) K). Figure 2 illustrates the variation of the density as a function of pressure at 423 K. The densities increase with an increase in pressure to 40 MPa from (1 to 3) % at 293 K and from (2 to 4) % at 423 K. In the temperature and pressure ranges studied, the effect of changing the pressure is far less important than the effect of the temperature on the volumetric properties. $[C_1C_2Im][EtSO_4]$ is more affected by the pressure changes and less affected by the temperature changes.

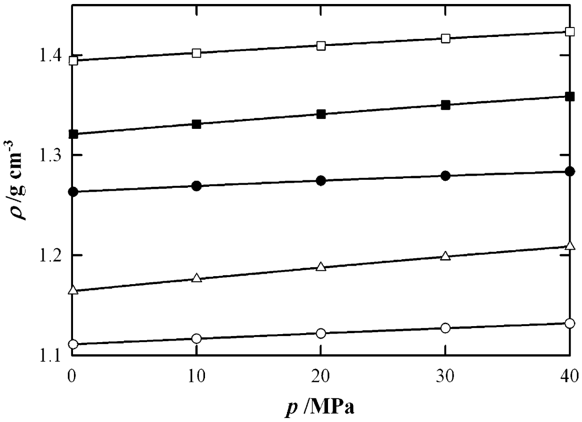


Figure 2. Experimental densities as a function of pressure at 423 K: ●, $[C_1C_4Im][PF_6]$; ○, $[C_1C_4Im][BF_4]$; ■, $[C_1C_4Im][Tf_2N]$; □, $[C_1C_2Im][Tf_2N]$; Δ, $[C_1C_2Im][EtSO_4]$. The lines correspond to the fit of the data by the Tait equation (eq 2).

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

$$\rho(T, p, C, B) = \frac{\rho(T, 0.1\ \mathrm{MPa})}{1 - C \ln\left(\dfrac{B(T) + p}{B(T) + p_{\mathrm{ref}}}\right)} \qquad (2)$$

where $\rho(T, 0.1\ \mathrm{MPa})$ is the reference density obtained using eq 1 and $p_{\mathrm{ref}} = 0.1$ MPa. C is an adjustable parameter, and $B(T)$ is a second-order polynomial expressed as

$$B(T) = \sum_{i=0}^{2} B_i T^i \qquad (3)$$

The Tait parameters are presented in Table 6 together with the average absolute deviations (AADs) associated to the fits. These values can be considered as the uncertainty of our measurements over the extended pressure range. A maximum AAD of 0.02 % was obtained for $[C_1C_4Im][BF_4]$.

The molar volumes, $V_m = M/\rho$, reflecting the size of the ions can be obtained from the densities calculated via the Tait equation. It varies from (188 to 203) cm^3·mol^{-1} at atmospheric pressure and from (186 to 200) cm^3·mol^{-1} at 40 MPa. As expected, it increases with temperature and decreases with pressure.

For three of the ILs studied, the experimental densities as a function of pressure can be compared with those presented in the literature. In Table 4 are presented the maximum deviations

Table 6. Tait Parameters C, B_0, B_1, and B_2 of Equation 2 Used to Smooth the Experimental Densities as a Function of Pressure (to 40 MPa) and Temperature (from (293 to 423) K) along with the Percent Average Absolute Deviations of the Fit (AADs)

IL	$10^2 \cdot C$	B_0 MPa	B_1 MPa·K^{-1}	$10^3 \cdot B_2$ MPa·K^{-2}	AAD %
[C_1C_4Im][PF_6]	3.680	424.83	−1.648	1.935	0.009
[C_1C_4Im][BF_4]	8.284	698.85	−2.279	2.375	0.022
[C_1C_4Im][Tf_2N]	9.981	589.12	−1.788	1.625	0.002
[C_1C_2Im][Tf_2N]	8.849	579.62	−1.546	1.284	0.006
[C_1C_2Im][$EtSO_4$]	12.89	489.17	−1.483	1.445	0.008

between our data and those of the literature. They can be regarded as a measure of the accuracy of our measurement. In the case of [C_1C_4Im][BF_4], a maximum value of 0.4 % was obtained at 10 MPa. For this IL, our experimental densities are systematically lower than those presented in the literature which is coherent with a higher water content in our sample. When increasing temperature, except in the case of Gardas et al.,[21] the deviations between our data and those of the literature increase. The experimental densities of [C_1C_4Im][Tf_2N] as a function of pressure can only be compared with the work of Gomez de Azevedo et al.[18] Excellent agreement is obtained between the two sets of data (maximum deviation of 0.09 % at 40 MPa and 330 K). Excellent agreement is also obtained for the density of [C_1C_4Im][PF_6] with the work of Tomida et al.,[19] over the whole pressure range considered (maximum deviation of 0.2 %). Our data are also coherent with the set of data proposed by Gomez de Azevedo et al.[20] with larger deviations at higher pressures. The values of Gu and Brennecke[24] deviate from ours at lower pressure.

Mechanical Coefficients. The calculation of the mechanical coefficients leads to useful information on the dependence of the volumetric properties on temperature and pressure. The coefficient of thermal expansion, α_P, is related to the variation of the density with temperature.

$$\alpha_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P \tag{4}$$

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

$$\kappa_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T \tag{5}$$

It has to be stated that the differences in the values of the mechanical coefficients from the literature are due not only to differences in density values but also to the fitting equations used. The mechanical coefficients calculated from the fitted densities at the two extreme temperatures and pressures are presented in Table 7. The uncertainty on these coefficients, calculated by a propagation error method, is ± 5 %. The thermal expansion coefficients increase with temperature varying from (0.41 to 0.66)·10^{-3} K^{-1} at 298 K and from (0.43 to 0.70)·10^{-3} K^{-1} at 423 K, increasing with temperature. The isothermal compressibilities decrease with pressure varying from (0.35 to 1.07) GPa at atmospheric pressure and from (0.26 to 0.83) GPa at 40 MPa. The effect of changing the temperature or the pressure has more impact on the values of the isothermal compressibility than on the thermal expansion coefficient. In the temperature and pressure ranges studied, the two mechanical coefficients are of the same order of magnitude for all the ILs except for [C_1C_2Im][$EtSO_4$] for which lower thermal expansion coefficients and higher isothermal compressibilities were calculated compared to the other samples.

Table 7. Densities and Mechanical Coefficients as a Function of Temperature and Pressure Calculated from the Tait Equation between (293 and 423) K up to 40 MPa

IL	0.1 MPa 298.15 K	0.1 MPa 423.15 K	40 MPa 298.15 K	40 MPa 423.15 K
	ρ/g·cm^{-3}			
[C_1C_4Im][PF_6]	1.3658	1.2633	1.3821	1.2836
[C_1C_4Im][BF_4]	1.2008	1.1110	1.2169	1.1319
[C_1C_4Im][Tf_2N]	1.4378	1.3210	1.4643	1.3589
[C_1C_2Im][Tf_2N]	1.5177	1.3945	1.5392	1.4233
[C_1C_2Im][$EtSO_4$]	1.2394	1.1643	1.2729	1.2088
	$10^3 \cdot \alpha_p$/K^{-1}			
[C_1C_4Im][PF_6]	0.616	0.633	0.568	0.631
[C_1C_4Im][BF_4]	0.602	0.643	0.555	0.615
[C_1C_4Im][Tf_2N]	0.660	0.696	0.591	0.612
[C_1C_2Im][Tf_2N]	0.662	0.692	0.618	0.638
[C_1C_2Im][$EtSO_4$]	0.493	0.506	0.407	0.435
	κ_T/GPa			
[C_1C_4Im][PF_6]	0.348	0.496	0.256	0.328
[C_1C_4Im][BF_4]	0.360	0.519	0.311	0.423
[C_1C_4Im][Tf_2N]	0.498	0.808	0.423	0.628
[C_1C_2Im][Tf_2N]	0.380	0.569	0.329	0.462
[C_1C_2Im][$EtSO_4$]	0.733	1.068	0.614	0.833

For [C_1C_4Im][BF_4], [C_1C_4Im][PF_6], and [C_1C_4Im][Tf_2N], it is possible to compare the mechanical coefficients calculated from the present experimental densities with those of the literature. The deviations are presented in Figures 3 and 4. The data of Gardas et al.[21] on [C_1C_4Im][BF_4] are 15 % higher than ours, but all the other thermal expansion coefficients lie within ± 10 % of our values. We will consider it as the accuracy for the thermal expansion coefficient for these three ILs. Larger differences are observed for the isothermal compressibilities. For [C_1C_4Im][PF_6], Gu and Brennecke[24] and Gomez de Azevedo et al.[20] present deviations of more than 20 % from our set of data. These differences can be explained by the presence of different quantities of water in the samples (our sample contains more water than those used by Gomez de Azevedo et al.[20]). Finally, an accuracy of ± 10 % for the isothermal compressibility was also considered.

To study the variation of the mechanical coefficients with the structure of the cation and of the anion, it can be of interest to plot the variation of the isothermal compressibility κ_T as a function of the thermal expansion coefficient α_P. This is presented in Figure 5 at atmospheric pressure from (273 to 423) K. In this figure, our experimental data are compared with data presented in the literature. As appears in this graph, the behavior

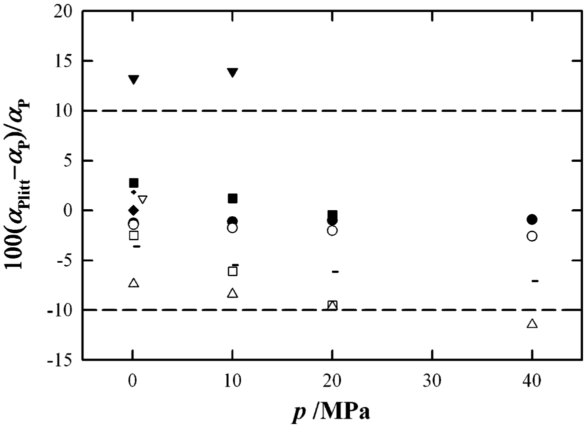


Figure 3. Percentage deviations $100(\alpha_{P\text{lit}} - \alpha_P)/\alpha_P$ of the literature thermal expansion coefficients from our data for [C_1C_4Im][BF_4]: ●, Gomez de Azevedo et al.;[20] ■, Tomida et al.;[19] ▼, Gardas et al.[21] For [C_1C_4Im][PF_6]: ○, Gomez de Azevedo et al.;[20] □, Tomida et al.;[19] Δ, Gu and Brennecke.[24] For [C_1C_4Im][Tf_2N]: -, Gomez de Azevedo et al.[18]

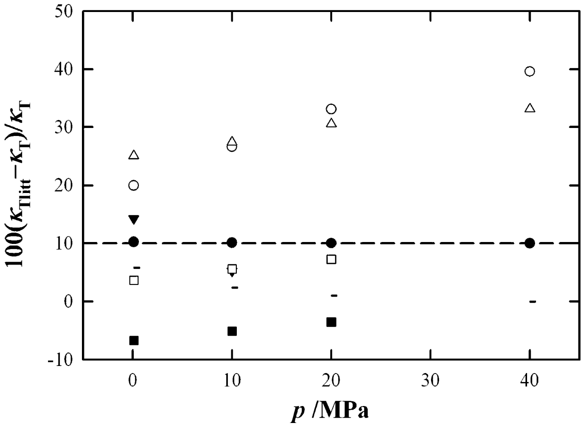


Figure 4. Percentage deviations $100(\kappa_{T\mathrm{lit}} - \kappa_T)/\kappa_T$ of the literature isothermal compressibilities from our data for [C_1C_4Im][BF_4]: ●, Gomez de Azevedo et al.;[20] ■, Tomida et al.;[19] ▼, Gardas et al.[21] For [C_1C_4Im]-[PF_6]: ○, Gomez de Azevedo et al.;[20] □, Tomida et al.;[19] Δ, Gu and Brennecke.[21] For [C_1C_4Im][Tf_2N]: -, Gomez de Azevedo et al.[18]

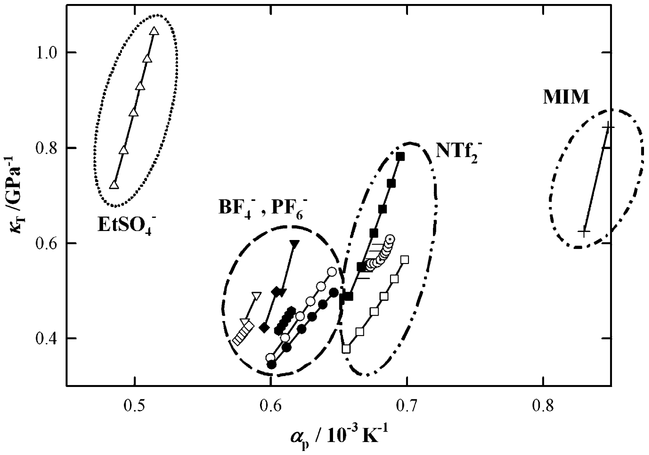


Figure 5. Isothermal compressibilities, κ_T, as a function of the thermal expansion coefficients, α_P, for imidazolium-based ILs at atmospheric pressure and in the range between (273 and 423) K: ●, [C_1C_4Im][PF_6]; ○, [C_1C_4Im][BF_4]; ■, [C_1C_4Im][Tf_2N]; □, [C_1C_2Im][Tf_2N]; Δ, [C_1C_2Im]-[$EtSO_4$]; ▽, [C_1C_8Im][PF_6] from Gu and Brennecke;[24] ◇, [C_1C_4Im][BF_4] from Gomez de Azevedo et al.;[20] ◆, [C_1C_4Im][PF_6] from Gu and Brennecke;[24] ▼, [C_1C_8Im][BF_4] from Gu and Brennecke;[24] ⬢, [C_1C_4Im]-[PF_6] from Gomez de Azevedo et al.;[20] −, [C_1C_4Im][Tf_2N] from Gomez de Azevedo et al.;[18] ⊙, [C_1C_6Im][Tf_2N] from Gomez de Azevedo et al.;[18] +, methylimidazole (MIM) from Gu and Brennecke.[24]

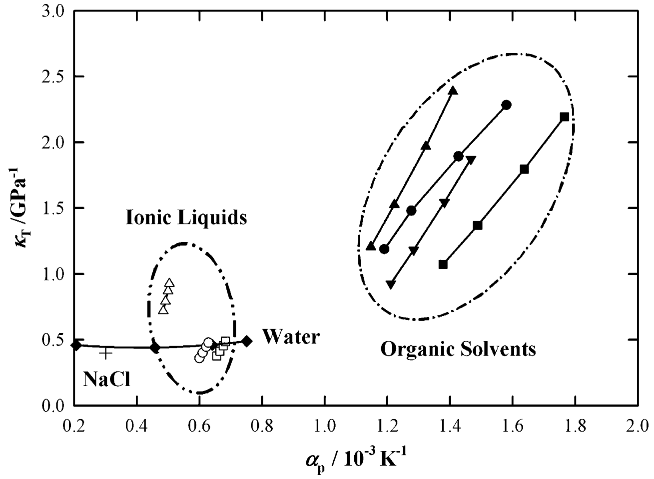


Figure 6. Isothermal compressibilities, κ_T, as a function of the thermal expansion coefficients, α_P, for imidazolium-based ILs, usual solvents, and NaCl at atmospheric pressure and in the range between (298 and 373) K (1273 K for NaCl): ○, [C_1C_4Im][BF_4]; □, [C_1C_2Im][Tf_2N]; Δ, [C_1C_2Im]-[$EtSO_4$]; ◆, water from Harvey et al.;[35] ▲, octane from Cibulka and Hnedkovsky;[36] ●, methanol from Cibulka and Zikova;[37] ▼, benzene from Cibulka and Takagi;[38] ■, acetonitrile from Cibulka and Takagi;[39] +, NaCl.[40,41]

of the mechanical coefficients is more affected by the anion than by the cation. Three distinct domains can be observed: ILs containing the anion Tf_2N^- exhibit the highest thermal expansion coefficients, followed by a second group of ILs composed of the anions BF_4^- and PF_6^-, and a third group, corresponding to the asymmetric anion $EtSO_4^-$ presents higher isothermal compressibilities and lower thermal expansion coefficients. The methylimidazole precursor of the imidazolium-based ILs is characterized by higher mechanical coefficients which indicates that the presence of charges in the IL lowers considerably the mechanical coefficients.

It is also of interest to compare the mechanical coefficients of ILs with those of liquid NaCl, water, and polar and nonpolar and cyclic and noncyclic organic solvents. The variation of κ_T as a function of α_P is presented for these species and for some imidazolium-based ILs in Figure 6 at atmospheric pressure and for temperatures between (298 and 373) K (except for NaCl at 1273 K, in the liquid state). It clearly appears that ILs exhibit a different behavior from organic solvents that present higher mechanical coefficients. ILs have isothermal compressibilities similar to those of liquid NaCl and water and thermal expansion coefficients higher than those of NaCl.

Predictive Model. The development of a prediction model for the molar volumes of ILs is of particular interest given the huge number of possible anion−cation combinations. The densities of a series of imidazolium-based ILs were measured by Rebelo et al.[29] They have observed, for different anions, a linear variation of the molar volume as a function of the number of carbons in the alkyl chain of the imidazolium cation and a constant variation of the molar volume per addition of two carbon atoms on this alkyl chain, irrespective of the anion. From these observations and assuming an "ideal" volumetric behavior of the IL (the volumes of the cation and anion are additive to give the volume of the IL), they have developed a model[12,29,30] that considers the molar volume of a given IL as the addition of the effective molar volume of the anion and of the cation

$$V_{\mathrm{m}_{\mathrm{IL}}} = V^*_{\mathrm{m}_{\mathrm{cation}}} + V^*_{\mathrm{m}_{\mathrm{anion}}} \tag{6}$$

and the molar volume of an imidazolium cation as the sum of the contribution of the methylimidazolium ring V_{C0C1Im} and of the alkyl chain.

$$V^*_{\mathrm{m}_{\mathrm{cation}}} = V^*_{\mathrm{mC0C1}_{\mathrm{Im}}} + na^* \tag{7}$$

where a^* is the contribution to the molar volume of two CH_2 groups on the alkyl chain and n is the number of C_2H_4 groups on the alkyl chain. To start, the effective molar volume of the anion PF_6^- was calculated using the P−F bond length and the Van der Waals radius of the fluorine ion, and the model was developed at 298.15 K. In the present work, we have extended this model, initially developed by Rebelo et al.,[29] as a function of temperature. The difference between the molar volumes of [C_1C_2Im][Tf_2N] and [C_1C_4Im][Tf_2N] allows the calculation of the contribution of two CH_2 groups to the molar volume as a function of temperature (parameters E_i). Assuming that the variation of the density with temperature is the same for the anion and the cation and using the experimental density of [C_1C_4Im][Tf_2N], we can then calculate the variation of the molar volume of the anion and of the cation as a function of temperature (parameters D_i and F_i). Quadratic equations were

Table 8. Parameters of Equation 8 Used to Predict the Molar Volume of the Imidazolium Cation as a Function of Temperature from (293 to 423) K

	D_0	$10^2 \cdot D_1$	$10^6 \cdot D_2$
	$\mathrm{cm^3 \cdot mol^{-1}}$	$\mathrm{cm^3 \cdot mol^{-1} \cdot K^{-1}}$	$\mathrm{cm^3 \cdot mol^{-1} \cdot K^{-2}}$
$C_0C_1Im^+$	64.677	5.4671	2.8571
	E_0	$10^2 \cdot E_1$	$10^6 \cdot E_2$
	$\mathrm{cm^3 \cdot mol^{-1}}$	$\mathrm{cm^3 \cdot mol^{-1} \cdot K^{-1}}$	$\mathrm{cm^3 \cdot mol^{-1} \cdot K^{-2}}$
$C_{2n}C_1Im^+$	34.451	2.0429	28.571

Table 9. Parameters of Equation 9 Used to Predict the Molar Volume of the Anion as a Function of Temperature from (293 to 423) K

	F_0	$10^2 \cdot F_1$	$10^6 \cdot F_2$
	$\mathrm{cm^3 \cdot mol^{-1}}$	$\mathrm{cm^3 \cdot mol^{-1} \cdot K^{-1}}$	$\mathrm{cm^3 \cdot mol^{-1} \cdot K^{-2}}$
PF_6^-	74.520	3.0986	8.5714
BF_4^-	53.415	1.9171	−5.7143
Tf_2N^-	158.71	9.5529	60.000
$EtSO_4^-$	91.468	2.0200	−5.7143

found satisfactory for fitting the variation of the molar volumes with temperature (eqs 8 and 9).

$$V^*_{\mathrm{m}_{\mathrm{C2nC1Im+}}}(T - 298.15) = \left(\sum_{i=0}^{2} (D_i(T - 298.15)^i)\right) + n\left(\sum_{i=0}^{2} E_i(T - 298.15)^i\right) \quad (8)$$

$$V^*_{\mathrm{m}_{\mathrm{anion}}}(T - 298.15) = \left(\sum_{i=0}^{2} (F_i(T - 298.15)^i)\right) \quad (9)$$

The D_i, E_i, and F_i parameters, calculated from the experimental data of this work for the four anions studied, are presented in Tables 8 and 9. The comparison of density data (250 experimental points) from the literature with those calculated using this extended model indicates an average absolute deviation of 0.24 % for imidazolium-based ILs with an alkyl chain containing between 1 and 14 carbon atoms.

Conclusion

This paper presents original density data on five imidazolium-based ILs as a function of temperature and over an extended pressure range (from atmospheric to 40 MPa). As previously observed, this property is more affected by the anion and is related to the molar masses of the ions, the density increasing with the molar mass. It also decreases when increasing the length of the alkyl chain on the imidazolium ring. For the ILs studied, a decrease with temperature and an increase with pressure of the densities were observed. A Tait equation with four adjustable parameters was used to fit the experimental data as a function of temperature and pressure, and the mechanical coefficients (thermal expansion coefficient and isothermal compressibility) were calculated. They are lower than those of usual organic solvents. ILs have similar isothermal compressibilities to those of liquid NaCl and water and thermal expansion coefficients slightly higher than those of NaCl. Finally, a prediction model, based on an ideal volumetric behavior of these components, was developed to calculate the molar volume of imidazolium-based ILs as a function of temperature. An AAD of 0.24 % between the literature densities and those calculated using this extended model was obtained. We are now extending the prediction model to ILs containing a cation other than imidazolium using the experimental data obtained in our laboratory completed by all the experimental densities presented in the literature. The extension of the model to the density of ILs as a function of pressure is also under study.

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