

Volume Expansivities and Isothermal Compressibilities of Imidazolium and Pyridinium-Based Ionic Liquids

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From ambient- and high-pressure density measurements, we report the volume expansivities and isothermal compressibilities of four room-temperature ionic liquids and 1-methylimidazole at temperatures between 298.2 and 343.2 K and pressures to 206.9 MPa. The compounds studied are 1-butyl-3-methylimidazolium hexafluorophosphate ($[\text{C}_4\text{mim}][\text{PF}_6]$), 1-octyl-3-methylimidazolium hexafluorophosphate ($[\text{C}_8\text{mim}][\text{PF}_6]$), 1-octyl-3-methylimidazolium tetrafluoroborate ($[\text{C}_8\text{mim}][\text{BF}_4]$), and *N*-butylpyridinium tetrafluoroborate ($[\text{NBuPy}][\text{BF}_4]$). The density is affected by the natures of the anion, cation, and substituents on the cation, with lower densities observed for longer alkyl chains. Density decreases fairly linearly with increasing temperature but at a rate less than that for molecular organic compounds. In addition, the high-pressure measurements reveal that ionic liquids are significantly less compressible than organic solvents, with isothermal compressibility values similar to that of water. The high-pressure density data can be adequately described by the Tait equation.

Introduction

Room-temperature ionic liquids (organic salts that are liquid at conditions around room temperature) are being explored as potential environmentally benign solvents.^{1–3} A major reason for this interest in ionic liquids (ILs) is their negligible vapor pressure,^{2,4} which decreases the risk of worker exposure and the loss of solvent to the atmosphere. Numerous types of reactions have been performed successfully in these solvents.⁵

Accurate volumetric properties of any solvent are very important for thermodynamic calculations and process design. Moreover, volume expansivities and isothermal compressibilities can provide information on fluid structure and molecular interactions. However, the data on volumetric properties of ionic liquids are rather limited. A number of important studies on ambient-pressure densities of chloroaluminate ionic liquids and their mixtures with organic solvents such as benzene have been published.^{6–10} However, chloroaluminate ILs are not stable when exposed to water vapor in the atmosphere. As a result, considerable recent attention has focused on water-stable ionic liquids, for which very few quantitative data have been available until quite recently, which greatly limits their applications and further development. Published data are available for 1-ethyl-3-methylimidazolium tetrafluoroborate ($[\text{C}_2\text{mim}][\text{BF}_4]$),¹¹ 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{C}_4\text{mim}][\text{BF}_4]$), and 1-butyl-3-methylimidazolium hexafluorophosphate ($[\text{C}_4\text{mim}][\text{PF}_6]$),¹² as well as for a series of 1,3-dialkyl imidazolium salts at 22 °C.¹³ In addition, ambient-pressure density data as a function of temperature have recently been reported by Seddon and co-workers¹⁴ for $[\text{C}_n\text{mim}][\text{BF}_4]$, $[\text{C}_n\text{mim}][\text{PF}_6]$, $[\text{C}_n\text{mim}][\text{NO}_3]$, and $[\text{C}_n\text{mim}][\text{Cl}]$, where *n* is the number of carbons on the 1-*n*-alkyl chain of the 1-*n*-alkyl-3-methylimidazolium cation. These data provide a wonderful complement to the data presented here. However, we know of no high-pressure density data (and, therefore, no isothermal compressibilities) for any ionic liquids.

Thus, we report here measurements of the density of four air- and water-stable ILs and 1-methylimidazole at various temperatures between 298.2 and 343.2 K and pressures to 206.9 MPa. The volume expansivities and isothermal compressibilities are calculated and compared with normal organic solvents. Finally, the Tait equation is used to correlate the high-pressure density data. The results show that the two-parameter Tait equation works extremely well for both the ILs and 1-methylimidazole, although it should be noted that the two parameters are purely empirical.

Experimental Section

Experimental Apparatus. A standard pycnometer in a water bath was used to measure the isobaric density of the ILs at ambient pressure, (0.99 ± 0.01) bar, and in the temperature range from 298.2 to 343.2 K. Its calibrated volume was (5.07 ± 0.03) mL, and the temperature of the water bath was controlled to within ±0.1 K, as measured by a glass thermometer.

An ultrahigh-pressure density apparatus, which has been described in more detail elsewhere,¹⁵ was used to measure the densities at 298.2 and 323.2 K and pressures to 206.9 MPa. The ultrahigh-pressure density apparatus consists of a dead-weight gauge (Aschcroft Portable Gauge Tester, Manning, Maxwell & Moore, Inc.), a pressure magnifier, and a high-pressure chamber containing the pressurizing fluid penta-erithritol. A calibrated glass cell, with a volume of approximately 6.9 mL, is filled with the sample and fully immersed in the liquid in the high-pressure chamber. The neck of the cell is marked and can be read to ±0.05 mL. It is fitted with a Nichrome ring below a plunger cap. When pressurized, the plunger forces the ring down, where it remains after depressurization. Thus, the volume of the liquid at high pressure can be measured to ±0.05 mL. This system was used to measure the volume variation of ionic liquid samples at different pressures. A variac autotransformer (General Radio Company) was used to increase and maintain the temperature to within ±0.1 °C, which was read by a thermometer immersed in the oil

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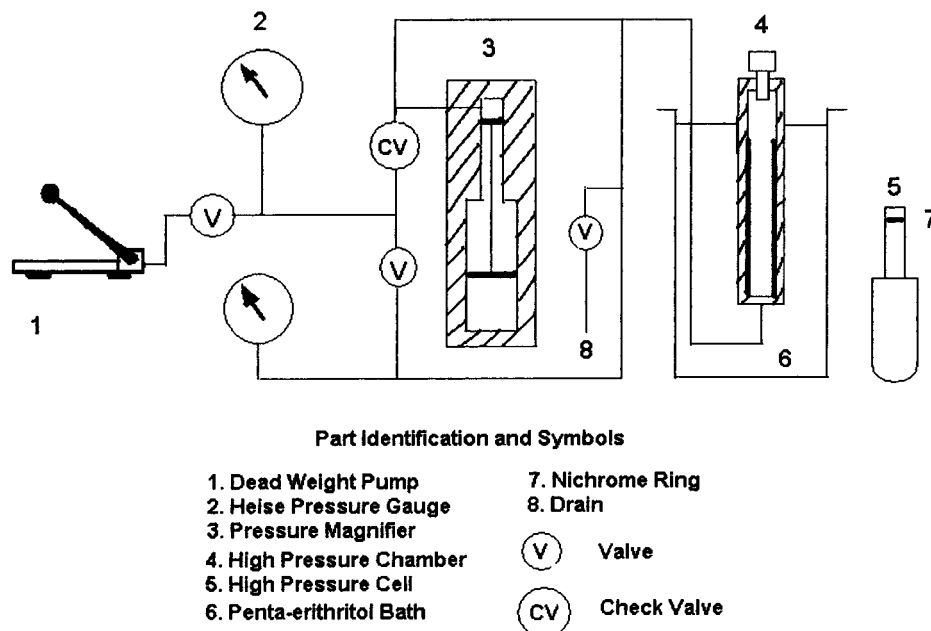


Figure 1. Schematic of ultrahigh-pressure density measurement apparatus.

bath surrounding the high-pressure chamber to within ± 0.1 °C. This apparatus has been used previously to measure the density of a variety of liquids at elevated pressures.¹⁵ A schematic of the ultrahigh-pressure unit is shown in Figure 1.

Experimental Procedure. For ambient-pressure density measurements, the pycnometer was filled with the sample and immersed in the water bath. After thermal equilibration, any excess liquid was wiped from the pycnometer neck, and the sample was weighed with a Mettler AE160 electronic balance. Densities were determined directly from the pycnometer volume and the mass of the sample. Aside from the uncertainty in the volume and the mass, another common source of error is evaporation of the sample. However, this is not a problem for ionic liquids because they are nonvolatile. In addition, the vapor pressure of 1-methylimidazole is quite small, only 0.525 Pa at 30.65 °C,¹⁶ so this does not introduce any additional error for this sample. Propagation of the errors involved in the measurements (the volume of the pycnometer and the mass of the samples) resulted in maximum uncertainties in the measured densities of ± 0.0080 g/cm³. Our measurements of the density of toluene match literature data¹⁷ to within 0.18% (i.e., better than ± 0.002 g/cm³).

All ambient-pressure measurements were made open to the atmosphere. However, we do not expect large amounts of air or water to have been dissolved in the samples because of the relatively short contact times and the narrow-necked configuration of the pycnometer, which would minimize mass transfer. The samples were dried prior to use, as described below. The pressure ranged from 98.9 to 100 kPa over the course of these experiments. Thus, ambient-pressure measurements were at (0.099 ± 0.001) MPa.

Isothermal density data at elevated pressure were measured with the ultrahigh-pressure density apparatus by filling the cell with the sample to the neck, placing the Nichrome ring at the liquid interface, and resting the plunger on top of the ring, taking care to remove any gas bubbles. Then, the cell was placed inside the high-pressure chamber and pressurized to the desired values using the piston screw associated with the dead-weight gauge. The cell was removed from the chamber, and the position of

the Nichrome ring gave the total volume of the sample at the highest pressure achieved during that run. The initial volume and ambient density fixed the mass of sample in the cell, which, along with each position of the Nichrome ring, was all that was necessary to calculate the density at each elevated pressure. Comparison of measurements of the density of toluene with published values at 50 °C and pressures to 200 MPa¹⁷ reveals differences $[(\rho_{\text{exp}} - \rho_{\text{lit}})/\rho_{\text{lit}} \times 100]$ ranging from 0.05% at the highest pressure to 1.3% at the lowest pressure, where the change in cell volume upon pressurization is smallest. Propagation of errors encountered in the experiment (initial cell volume, ambient sample density, and final cell volume) results in a maximum uncertainty of the IL densities at elevated pressures of ± 0.014 g/cm³, which is consistent with the observed uncertainty in the toluene measurements cited above. We anticipate that the values at higher pressures are actually quite a bit more accurate than this.

Materials. Toluene (CAS 108-88-3), certified ACS, $\geq 99.5\%$ purity, was obtained from Fisher Scientific. 1-Methylimidazole, 99% purity, was purchased from Aldrich. 1-Butyl-3-methylimidazolium hexafluorophosphate ($[\text{C}_4\text{mim}][\text{PF}_6]$) was purchased from SACHEM. The following three ionic liquids were generously given to us by Professor K. R. Seddon's research group at The Queen's University of Belfast: 1-octyl-3-methylimidazolium hexafluorophosphate ($[\text{C}_8\text{mim}][\text{PF}_6]$), 1-octyl-3-methylimidazolium tetrafluoroborate ($[\text{C}_8\text{mim}][\text{BF}_4]$), and *N*-butylpyridinium tetrafluoroborate ($[\text{NBuPy}][\text{BF}_4]$).

Because trace amounts of water in ILs can have a dramatic effect on transport properties and phase behavior,^{18,19} all of the ILs were dried and degassed under vacuum at ambient temperature for 2–3 days before use. Karl-Fisher analysis of the samples subjected to this treatment indicated that the water content was reduced to between 0.15 and 0.67 mass %. Our best estimates of the water content of the samples used here are: $[\text{C}_4\text{mim}][\text{PF}_6]$, 0.15 mass %; $[\text{C}_8\text{mim}][\text{PF}_6]$, 0.24 mass %; $[\text{C}_8\text{mim}][\text{BF}_4]$, 0.46 mass %; and $[\text{NBuPy}][\text{BF}_4]$, 0.67 mass %. Another impurity that can affect physical properties is residual chloride content.¹⁸ SACHEM reported the residual chloride content of the $[\text{C}_4\text{mim}][\text{PF}_6]$ as less than 3 ppm (0.0003 mass %). However, the chloride contents of several

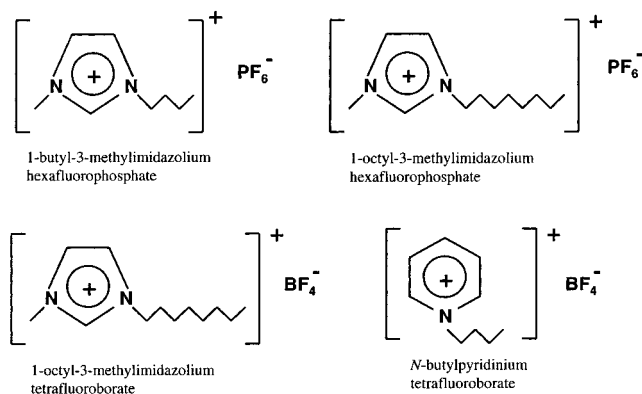


Figure 2. Schematic of chemical structures of ionic liquids studied.

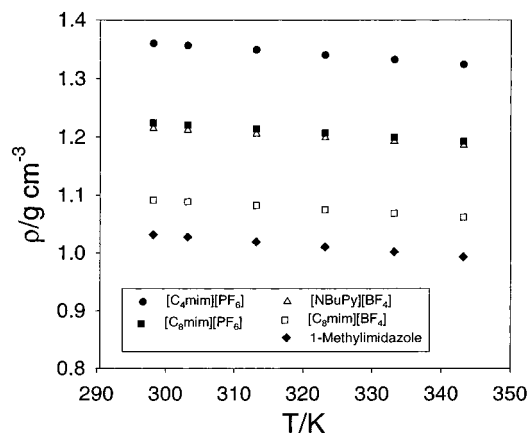


Figure 3. Densities of (●) $[C_4mim][PF_6]$, (■) $[C_8mim][PF_6]$, (□) $[C_8mim][BF_4]$, (△) $[NBuPy][BF_4]$, and (◆) 1-methylimidazole at 0.099 MPa and temperatures between 298.2 and 343.2 K.

of the samples from Seddon and co-workers were significantly higher. Using a spectrofluorometric method,^{20,21} we estimate that the $[C_8mim][PF_6]$ and $[C_8mim][BF_4]$ samples contained 0.14 mass % (1400 ppm) and 0.095 mass % (950 ppm) chloride, respectively. The uncertainty in this technique at these concentrations is approximately ± 100 ppm. The chloride in the $[NBuPy][BF_4]$ sample is below the detection limit of the fluorescence technique, which would normally be around 10 ppm. However, with the added solvent required to make a sample large enough for analysis, we estimate the detection limit to be about 75 ppm (0.0075 mass %) for this sample. 1-Methylimidazole and toluene were used without further purification. The chemical structures of the ionic liquids are shown in Figure 2.

Results and Discussion

Here, we report the densities and molar volumes of $[C_4mim][PF_6]$, $[C_8mim][PF_6]$, $[C_8mim][BF_4]$, $[NBuPy][BF_4]$, and 1-methylimidazole at temperatures between 298.2 and 343.2 K and pressures to 206.9 MPa. 1-Methylimidazole is a neutral compound used in the preparation of the imidazolium salts. From these data, we calculate the corresponding volume expansivities and isothermal compressibilities. To understand the physical behavior of ILs, comparisons are made with normal solvents such as toluene and water.

Volume Expansivity. The densities of the four ILs and 1-methylimidazole at ambient pressure are shown in Figure 3 as a function of temperature. These values, along with the corresponding molar volumes, volume ratios, and

volume expansivities, are shown in Table 1 for the ILs, 1-methylimidazole, and toluene. In the temperature range studied, the molar volumes of the ionic liquids, as well as those of 1-methylimidazole and toluene, increase linearly with temperature.

The ionic liquids having the bulky octyl chain on the imidazolium cation ($[C_8mim][PF_6]$ and $[C_8mim][BF_4]$) have the largest molar volumes. The larger size of the PF_6^- anion compared to the BF_4^- anion is reflected in the larger molar volume of $[C_8mim][PF_6]$ compared to $[C_8mim][BF_4]$. The diameters of these two anions are given as 4.51 Å for BF_4^- and 5.06 Å for PF_6^- by McEwen and co-workers (1999).²² Not unexpectedly, the molar volumes of all of the ionic liquids are greater than that of 1-methylimidazole.

The values of the densities as a function of temperature reported here can be compared with literature values for $[C_4mim][PF_6]$, $[C_8mim][PF_6]$, and $[C_8mim][BF_4]$. Our values for $[C_4mim][PF_6]$ are somewhat lower than those reported by Suarez et al.,¹² who did not report the level of impurities in the samples used. However, our values for both $[C_4mim][PF_6]$ and $[C_8mim][PF_6]$ agree to within our experimental uncertainty with those measured by Seddon and co-workers.¹⁴ This excellent agreement is not surprising, even though the residual water content and chloride impurity in the $[C_8mim][PF_6]$ sample are significantly higher than in the sample used by Seddon and co-workers. Specifically, they report a water content of 35 ppm (0.0035 mass %) and chloride below the detection limit of their technique.¹⁸ Although they do not clearly indicate the detection limit, values as low as 0.001 mass % (10 ppm) are reported for some samples.¹⁴ The $[C_8mim][PF_6]$ sample used here contained approximately 1400 ppm (0.14 mass %) chloride and 2400 ppm (0.24 mass %) water. Seddon and co-workers reported the effect of chloride and water impurities on the density of a similar compound, $[C_4mim][BF_4]$.¹⁸ For that compound, they found that relatively large amounts of impurities were required to cause significant changes in the density. In particular, estimates from their graphs¹⁸ indicate that impurities of the level reported here (1400 ppm chloride and 2400 ppm water) would each cause less than a 0.001 g/cm³ change in the density, which is within the experimental uncertainty of the density measurements. Conversely, our values for the density of $[C_8mim][BF_4]$ are about 1.2% lower than those reported by Seddon et al.¹⁴ We estimate that our sample contained approximately 4600 ppm (0.46 mass %) water and 950 ppm chloride, compared to 80 ppm water and no detectable chloride reported by Seddon et al.¹⁴ Although the water content of the $[C_8mim][BF_4]$ sample used for these studies was relatively high, this fact still cannot fully explain the discrepancy between these data and those reported by Seddon and co-workers,¹⁴ in terms of the effect of water concentration on the density of $[C_4mim][BF_4]$.¹⁸ Nonetheless, the discrepancy is not particularly large and might well be within the combined uncertainties in the measurements by the two research groups.

The ionic liquids do not expand appreciably from 298.2 to 343.2 K. This small expansion with temperature is best quantified by the volume expansivity, which is defined as

$$\alpha_p \equiv (\partial \ln V / \partial T)_p \equiv -(1/\rho)(\partial \rho / \partial T)_p \quad (1)$$

Because the molar volumes and densities of the ionic liquids are linear functions of temperature, the volume expansivities were easily obtained from linear fits of the density data. The volume expansivities for each sample at (0.099 \pm 0.001) MPa are listed in Table 1, where one can see that the volume expansivities of all of the ILs are in

Table 1. Density (ρ), Molar Volume (V_m), Volume Expansivity (α_p), and Ratio of Molar Volume to the Value at 298.2 K (V_m/V_{m0}) at (0.099 \pm 0.001) MPa

T/K	$\rho/(g\ cm^{-3})$	$V_m/(cm^3\ mol^{-1})$	$10^4\ \alpha_p/K^{-1}$	V_m/V_{m0}
		[C ₄ mim][PF ₆]		
298.2 \pm 0.1	1.3603 \pm 0.0080	208.91 \pm 1.24	6.1126 \pm 0.0352	1
303.2 \pm 0.1	1.3564 \pm 0.0080	209.51 \pm 1.24	6.0952 \pm 0.0354	1.0029
313.2 \pm 0.1	1.3489 \pm 0.0080	210.69 \pm 1.25	6.0611 \pm 0.0356	1.0086
323.2 \pm 0.1	1.3400 \pm 0.0079	212.09 \pm 1.26	6.0211 \pm 0.0359	1.0152
333.2 \pm 0.1	1.3324 \pm 0.0079	213.29 \pm 1.26	5.9872 \pm 0.0361	1.0210
343.2 \pm 0.1	1.3239 \pm 0.0078	214.66 \pm 1.27	5.9490 \pm 0.0362	1.0275
		[C ₈ mim][PF ₆]		
298.2 \pm 0.1	1.2245 \pm 0.0072	277.91 \pm 1.64	5.9515 \pm 0.0352	1
303.2 \pm 0.1	1.2207 \pm 0.0072	278.76 \pm 1.65	5.9333 \pm 0.0351	1.0030
313.2 \pm 0.1	1.2141 \pm 0.0072	280.28 \pm 1.66	5.9012 \pm 0.0349	1.0085
323.2 \pm 0.1	1.2069 \pm 0.0071	281.94 \pm 1.67	5.8664 \pm 0.0347	1.0145
333.2 \pm 0.1	1.1999 \pm 0.0071	283.60 \pm 1.68	5.8322 \pm 0.0345	1.0205
343.2 \pm 0.1	1.1922 \pm 0.0071	285.42 \pm 1.69	5.7950 \pm 0.0343	1.0270
		[C ₈ mim][BF ₄]		
298.2 \pm 0.1	1.0912 \pm 0.0065	258.55 \pm 1.53	6.2464 \pm 0.0370	1
303.2 \pm 0.1	1.0887 \pm 0.0064	259.14 \pm 1.53	6.2320 \pm 0.0369	1.0023
313.2 \pm 0.1	1.0823 \pm 0.0064	260.67 \pm 1.54	6.1956 \pm 0.0367	1.0082
323.2 \pm 0.1	1.0747 \pm 0.0064	262.52 \pm 1.55	6.1520 \pm 0.0364	1.0153
333.2 \pm 0.1	1.0685 \pm 0.0063	264.05 \pm 1.56	6.1163 \pm 0.0362	1.0213
343.2 \pm 0.1	1.0618 \pm 0.0063	265.71 \pm 1.57	6.0782 \pm 0.0360	1.0277
		[NBuPy][BF ₄]		
298.2 \pm 0.1	1.2144 \pm 0.0072	183.65 \pm 1.09	5.4287 \pm 0.0321	1
303.2 \pm 0.1	1.2118 \pm 0.0072	184.04 \pm 1.09	5.4172 \pm 0.0321	1.0022
313.2 \pm 0.1	1.2053 \pm 0.0071	185.03 \pm 1.10	5.3883 \pm 0.0319	1.0075
323.2 \pm 0.1	1.1988 \pm 0.0071	186.04 \pm 1.10	5.3591 \pm 0.0317	1.0130
333.2 \pm 0.1	1.1922 \pm 0.0071	187.06 \pm 1.11	5.3298 \pm 0.0315	1.0186
343.2 \pm 0.1	1.1856 \pm 0.0070	188.11 \pm 1.11	5.3002 \pm 0.0314	1.0243
		1-Methylimidazole		
298.2 \pm 0.1	1.0316 \pm 0.0061	79.60 \pm 0.47	8.6310 \pm 0.0511	1
303.2 \pm 0.1	1.0274 \pm 0.0061	79.92 \pm 0.47	8.5964 \pm 0.0509	1.0041
313.2 \pm 0.1	1.0193 \pm 0.0060	80.55 \pm 0.48	8.5287 \pm 0.0505	1.0120
323.2 \pm 0.1	1.0101 \pm 0.0060	81.29 \pm 0.48	8.4515 \pm 0.0500	1.0213
333.2 \pm 0.1	1.0019 \pm 0.0059	81.96 \pm 0.49	8.3823 \pm 0.0496	1.0297
343.2 \pm 0.1	0.9931 \pm 0.0059	82.68 \pm 0.49	8.3087 \pm 0.0492	1.0388
		Toluene		
298.2 \pm 0.1	0.8626 \pm 0.0051	106.81 \pm 0.63	11.2909 \pm 0.0668	1
303.2 \pm 0.1	0.8582 \pm 0.0051	107.36 \pm 0.64	11.2329 \pm 0.0665	1.0051
313.2 \pm 0.1	0.8492 \pm 0.0050	108.50 \pm 0.64	11.1149 \pm 0.0658	1.0158
323.2 \pm 0.1	0.8399 \pm 0.0050	109.71 \pm 0.65	10.9928 \pm 0.0651	1.0271
333.2 \pm 0.1	0.8307 \pm 0.0049	110.92 \pm 0.66	10.8727 \pm 0.0644	1.0384
343.2 \pm 0.1	0.8165 \pm 0.0048	112.85 \pm 0.67	10.6868 \pm 0.0633	1.0565

the range of $5\text{--}6 \times 10^{-4}\ K^{-1}$. This is significantly lower than the α_p values for most molecular organic liquids. For instance, as shown in Table 1, the α_p values for 1-methylimidazole and toluene are in the range of $8\text{--}11 \times 10^{-4}\ K^{-1}$. Rather, the volume expansivities of the ILs are similar to those of water, which range from $2.57 \times 10^{-4}\ K^{-1}$ at 298.2 K to $5.84 \times 10^{-4}\ K^{-1}$ at 343.2 K.²³ In addition, the α_p values for high-temperature molten salts are quite low. For instance, the volume expansivities for NaCl and KCl at 1100 K are 3.094×10^{-4} and $3.632 \times 10^{-4}\ K^{-1}$, respectively.^{24,25}

Isothermal Compressibility. The densities of the four ionic liquids and 1-methylimidazole at 298.2 K and pressures to 206.9 MPa are shown in Figure 4. These values and the corresponding values of molar volume, isothermal compressibility, and volume ratio for 298.2 and 323.2 K are listed in Table 2. In addition, measurements for toluene at 323.2 K are given in Table 2. Clearly, the densities increase with increasing pressure for all of the compounds studied. We know of no other measurements of the densities of ILs as a function of pressure, so we cannot compare these data with any literature values. However, because the ambient-pressure density values were consistent with the limited available literature results, we have significant confidence in these data.

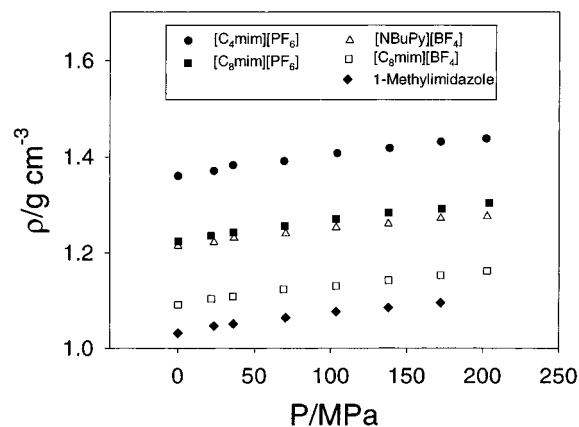


Figure 4. Densities of (●) [C₄mim][PF₆], (■) [C₈mim][PF₆], (□) [C₈mim][BF₄], (△) [NBuPy][BF₄], and (◆) 1-methylimidazole at 298.2 K and pressures to 206.9 MPa.

The Tait equation is an excellent model for high-pressure density correlation.^{26–29} It has the form

$$\frac{\rho - \rho^0}{\rho} = C \ln \left(\frac{B + p}{B + p^0} \right) \quad (2)$$

where ρ^0 is the reference density at a reference pressure,

Table 2. Experimental Density (ρ), Molar Volume (V_m), Isothermal Compressibility (β_T), Ratio of Molar Volume to the Molar Volume at (0.099 \pm 0.001) MPa (V_m/V_{m0}), and Percent Deviation between Experimental and Tait Equation Densities [$(\rho_{\text{exp}} - \rho_{\text{tait}}/\rho_{\text{exp}}) \times 100$]

P/MPa	$\rho/(\text{g cm}^{-3})$	$V_m/(\text{cm}^3 \text{ mol}^{-1})$	$10^6 \beta_T/\text{bar}^{-1}$	V_m/V_{m0}	$(\rho_{\text{exp}} - \rho_{\text{tait}}/\rho_{\text{exp}}) \times 100$
[C ₄ mim][PF ₆] at (298.2 \pm 0.1) K					
0.099 \pm 0.001	1.3603 \pm 0.0080	208.92 \pm 1.24	42.3 \pm 0.4	1	
23.54 \pm 0.69	1.3712 \pm 0.0131	207.26 \pm 1.98	37.0 \pm 0.4	0.9928	0.13
35.95 \pm 0.69	1.3833 \pm 0.0132	205.45 \pm 1.97	34.9 \pm 0.3	0.9841	0.30
69.39 \pm 0.69	1.3914 \pm 0.0133	204.24 \pm 1.95	29.8 \pm 0.3	0.9783	0.19
104.21 \pm 0.69	1.4081 \pm 0.0135	201.83 \pm 1.93	26.1 \pm 0.3	0.9667	0.03
138.68 \pm 0.69	1.4187 \pm 0.0136	200.31 \pm 1.92	23.2 \pm 0.2	0.9595	0.07
172.47 \pm 0.69	1.4317 \pm 0.0137	198.50 \pm 1.90	21.0 \pm 0.2	0.9508	0.10
202.11 \pm 0.69	1.4382 \pm 0.0138	197.60 \pm 1.89	19.3 \pm 0.2	0.9465	0.04
[C ₄ mim][PF ₆] at (323.2 \pm 0.1) K					
0.099 \pm 0.001	1.3400 \pm 0.0079	212.08 \pm 1.26	49.8 \pm 0.5	1	
69.05 \pm 0.69	1.3753 \pm 0.0133	206.65 \pm 1.99	32.3 \pm 0.3	0.9741	0.14
102.83 \pm 0.69	1.3938 \pm 0.0135	203.90 \pm 1.97	27.7 \pm 0.3	0.9612	0.19
137.99 \pm 0.69	1.4021 \pm 0.0135	202.68 \pm 1.96	24.0 \pm 0.2	0.9555	0.12
171.09 \pm 0.69	1.4171 \pm 0.0137	200.55 \pm 1.94	21.5 \pm 0.2	0.9454	0.19
200.74 \pm 0.69	1.4214 \pm 0.0137	199.94 \pm 1.93	19.6 \pm 0.2	0.9425	0.11
[C ₆ mim][PF ₆] at (298.2 \pm 0.1) K					
0.099 \pm 0.001	1.2245 \pm 0.0072	277.90 \pm 1.64	43.6 \pm 0.5	1	
21.47 \pm 0.69	1.2358 \pm 0.0131	275.35 \pm 2.92	39.6 \pm 0.4	0.9913	0.03
36.30 \pm 0.69	1.2431 \pm 0.0132	273.74 \pm 2.91	37.3 \pm 0.4	0.9855	0.05
69.73 \pm 0.69	1.2560 \pm 0.0133	270.93 \pm 2.88	32.9 \pm 0.4	0.9754	0.09
103.52 \pm 0.69	1.2710 \pm 0.0135	267.72 \pm 2.84	29.5 \pm 0.3	0.9639	0.05
137.99 \pm 0.69	1.2845 \pm 0.0136	264.91 \pm 2.81	26.7 \pm 0.3	0.9538	0.14
173.16 \pm 0.69	1.2924 \pm 0.0137	263.31 \pm 2.80	24.3 \pm 0.3	0.9480	0.14
204.18 \pm 0.69	1.3043 \pm 0.0138	260.90 \pm 2.77	22.6 \pm 0.2	0.9393	0.05
[C ₈ mim][PF ₆] at (323.2 \pm 0.1) K					
0.099 \pm 0.001	1.2069 \pm 0.0071	281.95 \pm 1.67	49.1 \pm 0.5	1	
69.05 \pm 0.69	1.2422 \pm 0.0133	273.94 \pm 2.93	37.1 \pm 0.4	0.9713	0.05
103.52 \pm 0.69	1.2589 \pm 0.0135	270.30 \pm 2.89	33.2 \pm 0.4	0.9584	0.08
137.99 \pm 0.69	1.2723 \pm 0.0136	267.47 \pm 2.86	30.0 \pm 0.3	0.9484	0.05
172.47 \pm 0.69	1.2820 \pm 0.0137	265.44 \pm 2.84	27.4 \pm 0.3	0.9412	0.18
202.81 \pm 0.69	1.2958 \pm 0.0139	262.61 \pm 2.81	25.5 \pm 0.3	0.9311	0.09
[C ₈ mim][BF ₄] at (298.2 \pm 0.1) K					
0.099 \pm 0.001	1.0912 \pm 0.0065	258.55 \pm 1.53	49.8 \pm 0.6	1	
21.82 \pm 0.69	1.1040 \pm 0.0132	255.54 \pm 3.06	42.8 \pm 0.5	0.9884	0.16
35.95 \pm 0.69	1.1089 \pm 0.0133	254.42 \pm 3.05	39.2 \pm 0.5	0.9840	0.03
69.05 \pm 0.69	1.1238 \pm 0.0135	251.04 \pm 3.01	32.9 \pm 0.4	0.9710	0.18
103.52 \pm 0.69	1.1306 \pm 0.0135	249.54 \pm 2.99	28.1 \pm 0.3	0.9652	0.26
137.99 \pm 0.69	1.1426 \pm 0.0137	246.91 \pm 2.96	24.6 \pm 0.3	0.9550	0.12
172.47 \pm 0.69	1.1531 \pm 0.0138	244.66 \pm 2.93	21.9 \pm 0.3	0.9463	0.00
202.81 \pm 0.69	1.1621 \pm 0.0139	242.79 \pm 2.91	20.1 \pm 0.2	0.9390	0.14
[C ₈ mim][BF ₄] at (323.2 \pm 0.1) K					
0.099 \pm 0.001	1.0747 \pm 0.0064	262.52 \pm 1.55	60.0 \pm 0.7	1	
35.61 \pm 0.69	1.0938 \pm 0.0131	257.94 \pm 3.08	43.9 \pm 0.5	0.9829	0.05
69.39 \pm 0.69	1.1099 \pm 0.0133	254.19 \pm 3.04	35.1 \pm 0.4	0.9686	0.09
103.52 \pm 0.69	1.1215 \pm 0.0134	251.56 \pm 3.01	29.3 \pm 0.3	0.9586	0.03
137.99 \pm 0.69	1.1299 \pm 0.0135	249.69 \pm 2.99	25.0 \pm 0.3	0.9514	0.15
172.47 \pm 0.69	1.1419 \pm 0.0137	247.06 \pm 2.95	22.0 \pm 0.2	0.9414	0.10
206.94 \pm 0.69	1.1489 \pm 0.0137	245.57 \pm 2.94	19.6 \pm 0.2	0.9357	0.00
[NBuPy][BF ₄] at (298.2 \pm 0.1) K					
0.099 \pm 0.001	1.2144 \pm 0.0072	183.65 \pm 1.09	37.8 \pm 0.4	1	
23.54 \pm 0.69	1.2224 \pm 0.0131	182.44 \pm 1.96	33.2 \pm 0.4	0.9928	0.17
36.64 \pm 0.69	1.2314 \pm 0.0132	181.11 \pm 1.94	31.2 \pm 0.3	0.9855	0.14
70.43 \pm 0.69	1.2405 \pm 0.0133	179.78 \pm 1.93	26.9 \pm 0.3	0.9783	0.10
103.52 \pm 0.69	1.2535 \pm 0.0135	177.92 \pm 1.91	23.7 \pm 0.3	0.9682	0.11
137.99 \pm 0.69	1.2610 \pm 0.0135	176.86 \pm 1.90	21.1 \pm 0.2	0.9624	0.07
172.47 \pm 0.69	1.2725 \pm 0.0137	175.26 \pm 1.88	19.1 \pm 0.2	0.9537	0.15
202.81 \pm 0.69	1.2764 \pm 0.0137	174.73 \pm 1.88	17.6 \pm 0.2	0.9508	0.10
[NBuPy][BF ₄] at (323.2 \pm 0.1) K					
0.099 \pm 0.001	1.1988 \pm 0.0071	186.04 \pm 1.10	40.6 \pm 0.4	1	
71.46 \pm 0.69	1.2286 \pm 0.0132	181.53 \pm 1.95	28.2 \pm 0.3	0.9757	0.06
103.52 \pm 0.69	1.2377 \pm 0.0133	180.20 \pm 1.94	24.8 \pm 0.3	0.9685	0.05
137.99 \pm 0.69	1.2487 \pm 0.0134	178.60 \pm 1.92	22.0 \pm 0.2	0.9599	0.03
172.47 \pm 0.69	1.2562 \pm 0.0135	177.53 \pm 1.91	19.8 \pm 0.2	0.9542	0.09
204.18 \pm 0.69	1.2657 \pm 0.0136	176.20 \pm 1.89	18.1 \pm 0.2	0.9471	0.07
1-Methylimidazole at (298.2 \pm 0.1) K					
0.099 \pm 0.001	1.0316 \pm 0.0061	79.59 \pm 0.47	62.5 \pm 0.8	1	
23.54 \pm 0.69	1.0466 \pm 0.0133	78.45 \pm 1.00	49.4 \pm 0.6	0.9855	0.14
36.30 \pm 0.69	1.0513 \pm 0.0133	78.11 \pm 0.99	44.3 \pm 0.6	0.9811	0.00
70.42 \pm 0.69	1.0639 \pm 0.0135	77.18 \pm 0.98	34.8 \pm 0.4	0.9695	0.15
103.52 \pm 0.69	1.0768 \pm 0.0137	76.25 \pm 0.97	29.0 \pm 0.4	0.9578	0.00
137.99 \pm 0.69	1.0850 \pm 0.0138	75.68 \pm 0.96	24.7 \pm 0.3	0.9506	0.16
172.47 \pm 0.69	1.0951 \pm 0.0139	74.98 \pm 0.95	21.5 \pm 0.3	0.9419	0.02

Table 2 (Continued)

P/MPa	$\rho/(\text{g cm}^{-3})$	$V_m/(\text{cm}^3 \text{mol}^{-1})$	$10^6 \beta_T/\text{bar}^{-1}$	V_m/V_{m0}	$(\rho_{\text{exp}} - \rho_{\text{tail}} /\rho_{\text{exp}}) \times 100$
1-Methylimidazole at $(323.2 \pm 0.1) \text{ K}$					
0.099 ± 0.001	1.0101 ± 0.0060	81.29 ± 0.48	84.3 ± 1.0	1	
35.61 ± 0.69	1.0385 ± 0.0132	79.06 ± 1.00	56.8 ± 0.7	0.9730	0.34
69.39 ± 0.69	1.0508 ± 0.0133	78.14 ± 0.99	43.3 ± 0.6	0.9616	0.15
104.56 ± 0.69	1.0650 ± 0.0135	77.10 ± 0.98	34.9 ± 0.5	0.9488	0.18
138.68 ± 0.69	1.0779 ± 0.0137	76.17 ± 0.97	29.5 ± 0.4	0.9374	0.07
172.47 ± 0.69	1.0895 ± 0.0138	75.36 ± 0.95	25.6 ± 0.3	0.9275	0.08
203.49 ± 0.69	1.0979 ± 0.0139	74.79 ± 0.95	22.9 ± 0.3	0.9203	0.10
Toluene at $(323.2 \pm 0.1) \text{ K}$					
0.099 ± 0.001	0.8399 ± 0.0050	109.70 ± 0.65	157.4 ± 2.3	1	
35.61 ± 0.69	0.8774 ± 0.0135	105.01 ± 1.61	88.2 ± 1.4	0.9570	0.26
69.74 ± 0.69	0.8949 ± 0.0137	102.97 ± 1.58	62.2 ± 1.0	0.9384	0.28
103.52 ± 0.69	0.9158 ± 0.0141	100.61 ± 1.54	48.8 ± 0.8	0.9169	0.17
129.72 ± 0.69	0.9230 ± 0.0142	99.82 ± 1.53	41.6 ± 0.6	0.9097	0.22
170.40 ± 0.69	0.9393 ± 0.0144	98.09 ± 1.51	34.2 ± 0.5	0.8940	0.01
201.43 ± 0.69	0.9500 ± 0.0146	96.99 ± 1.49	30.2 ± 0.5	0.8840	0.13

Table 3. Correlation Coefficients for Tait Equation and Average and Maximum Relative Deviations from Experimental Data

liquid	C	B/MPa	$(\rho_{\text{exp}} - \rho_{\text{tail}} /\rho_{\text{exp}})_{\text{avg}} \times 100$	$(\rho_{\text{exp}} - \rho_{\text{tail}} /\rho_{\text{exp}})_{\text{max}} \times 100$
$T = 298.2 \text{ K}$				
[C ₄ mim][PF ₆]	0.1829	1.8925	0.12	0.30
[C ₈ mim][PF ₆]	0.2376	2.3451	0.08	0.14
[C ₈ mim][BF ₄]	0.1751	1.5506	0.13	0.26
[NBuPy][BF ₄]	0.1657	1.9086	0.12	0.17
1-methylimidazole	0.1348	0.9436	0.08	0.16
$T = 323.2 \text{ K}$				
[C ₄ mim][PF ₆]	0.1630	1.4333	0.15	0.19
[C ₈ mim][PF ₆]	0.2866	2.5574	0.09	0.18
[C ₈ mim][BF ₄]	0.1508	1.1041	0.07	0.15
[NBuPy][BF ₄]	0.1706	1.8452	0.06	0.09
1-methylimidazole	0.1652	0.8766	0.15	0.34
toluene	0.1986	0.5717	0.18	0.28

p^0 , which we choose to be 0.099 MPa. B and C are constants at a given temperature.

The best-fit Tait equation coefficients for the four ionic liquids and 1-methylimidazole are listed in Table 3 for 298.2 and 323.2 K. The objective function was minimization of the relative error between the experimental and calculated data. The Tait equation gives an excellent correlation of the high-pressure densities of ionic liquids, as indicated by the small differences between the experimental and calculated values shown in Table 3. The average deviations are very small, ranging from 0.06 to 0.15%, and the maximum deviation is actually for 1-methylimidazole, 0.34% at 323.2 K. For the ILs, the maximum deviation is 0.30% for [C₄mim][PF₆] at 298.2 K.

It should be noted that the parameter C could be either taken as constant for a given compound, independent of temperature, or generalized to a constant fitted for all compounds.^{27,29} Conversely, parameter B is always considered to be a function of temperature. However, parameter C for ionic liquids varies with temperature and cannot be set to a constant value.

The effect of pressure on density is best described by the isothermal compressibility, which is defined as

$$\beta_T = -(1/V)(\partial V/\partial P)_T = (1/\rho)(\partial \rho/\partial P)_T \quad (3)$$

The isothermal compressibility can be calculated from the model used to fit the density data, which is the Tait equation in this case. The isothermal compressibilities of the four ionic liquids and 1-methylimidazole determined in this way are listed in Table 2 and shown for 298.2 K in Figure 5.

Because ionic liquids consist purely of ions, it is expected that ionic liquids should be less compressible than organic

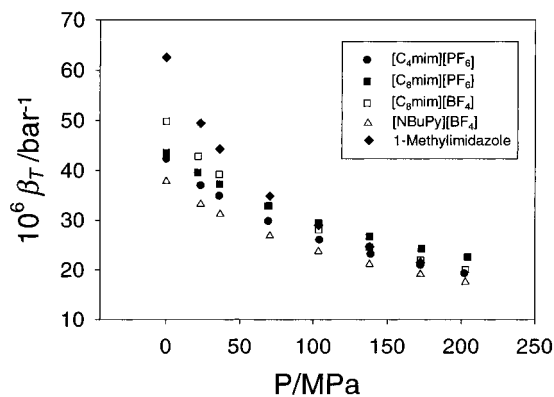


Figure 5. Isothermal compressibilities of (●) [C₄mim][PF₆], (■) [C₈mim][PF₆], (□) [C₈mim][BF₄], (△) [NBuPy][BF₄], and (◆) 1-methylimidazole at 298.2 K and pressures to 206.9 MPa.

solvents because of the strong Coulombic interactions between the ions. The results (Figure 5) show that all of the ionic liquids are less compressible than 1-methylimidazole. The β_T values for ILs are similar to those of water³⁰ and high-temperature molten salts. For instance, the isothermal compressibilities of molten NaCl at 800, 900, and 1000 °C are 28.1×10^{-6} , 33.8×10^{-6} , and $40.0 \times 10^{-6} \text{ bar}^{-1}$, respectively, at a low pressure of just 1.3 Pa.^{24,25} The values for KCl at the same three temperatures are 38.4×10^{-6} , 45.7×10^{-6} , and $54.7 \times 10^{-6} \text{ bar}^{-1}$, respectively.^{24,25} Although the liquidus temperature ranges are drastically different, both ILs and high-temperature molten salts become more compressible at higher temperatures.

A comparison of the β_T values in Figure 5 and the molar volume data in Table 1 reveals that the ionic liquids having greater molar volumes are generally more compressible (excluding 1-methylimidazole, which is a molecular organic

compound with a β_T of $62.5 \times 10^{-6} \text{ bar}^{-1}$ at ambient conditions). For example, $[\text{C}_8\text{mim}][\text{BF}_4]$, $[\text{C}_8\text{mim}][\text{PF}_6]$, and $[\text{C}_4\text{mim}][\text{PF}_6]$ have relative large compressibilities and molar volumes, whereas $[\text{NBUpy}][\text{BF}_4]$ is the most incompressible IL and has the smallest molar volume. However, the correlation between the molar volume and the compressibility is not complete because, for instance, $[\text{C}_8\text{mim}][\text{BF}_4]$ is more compressible than $[\text{C}_8\text{mim}][\text{PF}_6]$ even though the molar volume of $[\text{C}_8\text{mim}][\text{BF}_4]$ is smaller than that of $[\text{C}_8\text{mim}][\text{PF}_6]$. This might indicate a greater free volume in $[\text{C}_8\text{mim}][\text{BF}_4]$ because of the smaller size of the BF_4 anion.

All of the ILs (and 1-methylimidazole) become less compressible with increasing pressure. In fact, at a pressure of 200 MPa, the β_T 's of all four ionic liquids and 1-methylimidazole approaches a value of about $20 \times 10^{-6} \text{ bar}^{-1}$. This undoubtedly corresponds to the approach to a close-packed volume.

Summary

Ambient- and high-pressure density measurements at temperatures between 298.2 and 343.2 K and pressures to 206.9 MPa reveal that ionic liquids exhibit less expansion and are less compressible than molecular organic solvents. The compounds measured were 1-butyl-3-methylimidazolium hexafluorophosphate ($[\text{C}_4\text{mim}][\text{PF}_6]$), 1-octyl-3-methylimidazolium hexafluorophosphate ($[\text{C}_8\text{mim}][\text{PF}_6]$), 1-octyl-3-methylimidazolium tetrafluoroborate ($[\text{C}_8\text{mim}][\text{BF}_4]$), and *N*-butylpyridinium tetrafluoroborate ($[\text{NBUpy}][\text{BF}_4]$). The isothermal compressibility values of ILs are similar to those of water and high-temperature molten salts. ILs with longer alkyl chains are more compressible. The high-pressure density data can be adequately described by the Tait equation.

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