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Temperature and Pressure Dependence of the Viscosity of the Ionic Liquid 1-Butyl-3-methylimidazolium Tetrafluoroborate: Viscosity and Density Relationships in Ionic Liquids

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The viscosity of the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF_4) has been measured between (0 and 80) °C with a falling-body viscometer. High-pressure measurements were made at (10, 25, 50, and 75) °C to a maximum pressure of 300 MPa. The expanded uncertainty is estimated at ± 2 %. Modified Litovitz and Vogel−Fulcher−Tammann (VFT) equations are used to represent the temperature and pressure dependence. The Angell equation relating the strength parameter D, the VFT parameter T_0, and the glass temperature T_g is again confirmed. Comparing D for the salts [BMIM]PF_6, [HMIM]PF_6, [OMIM]PF_6, [BMIM]BF_4, [OMIM]BF_4, and [BMIM][Tf_2N], we find $D([\mathrm{BMIM}]^+) < D([\mathrm{HMIM}]^+) < D([\mathrm{OMIM}]^+)$ where the anion is common and $D([\mathrm{Tf_2N}]^-) < D(\mathrm{BF_4}^-) < D(\mathrm{PF_6}^-)$ where the cation is common. Densities and thermal expansivities between (0 and 90) °C at atmospheric pressure with overall uncertainty estimated at ± 0.000 05 $g\cdot cm^{-3}$ and ± $0.02\cdot10^{-3}$ K^{-1} are also reported. The densities are compared with our previously published values for [BMIM]PF_6, [HMIM]PF_6, [OMIM]PF_6, [OMIM]BF_4, and [BMIM][Tf_2N].

Introduction

This work is the sixth in a series on the transport properties of ionic liquids at high pressure. Three have reported high-pressure viscosities, for 1-butyl-3-methylimidazolium, 1-hexyl-3-methylimidazolium, and 1-methyl-3-octylimidazolium hexafluorophosphates ([BMIM]PF_6,[1] [HMIM]PF_6,[2] and [OMIM]PF_6[3]), 1-methyl-3-octylimidazolium tetrafluoroborate ([OMIM]BF_4),[3] and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][Tf_2N]).[2] The fourth reported high-pressure ionic self-diffusion coefficients and conductivities for [BMIM]PF_6.[4] The fifth dealt with high-pressure conductivities for [OMIM]PF_6 and [OMIM]BF_4.[5] The viscosity studies showed how the falling-body method could be used successfully for these highly viscous fluids and how the Litovitz and Vogel−Fulcher−Tammann (VFT) equations for the temperature representation of the viscosity could be extended to high pressures. The diffusion and conductivity study allowed the first determination of ionic velocity cross correlation functions for molten salts at high pressures and the correlation of the pressure dependences of the transport properties using the Nernst−Einstein equation and the fractional form of the Stokes−Einstein equation. Here, we extend high-pressure viscosity measurements to 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF_4) for comparison with [OMIM]BF_4. We also report density measurements for [BMIM]BF_4 and compare trends in density, molar volume, and thermal expansivity for the six ionic liquids that we have now studied.

Experimental Section

Two samples of [BMIM]BF_4 (CAS Registry No.: 174501-65-6), BB1 and BB2, were prepared. Initially we carried out only atmospheric pressure viscosity and density measurements on BB1. Some time later, *pVT* data became available in the literature, so sample BB2 was prepared for the high-pressure measurements.

The general preparation and purification of the samples was similar to the procedures used for [BMIM]PF_6,[6] but with changes necessary to accommodate the “hydrophilic” nature of [BMIM]BF_4 and its high solubility in water. A measured quantity of 40 % HBF_4 aqueous solution (Wako Pure Chemical Industries) was gently dropped into dichloromethane containing an equimolar amount of [BMIM]Cl, the mixture being cooled in an ice bath. The denser dichloromethane phase was washed with water and $NaHCO_3$-saturated aqueous solutions repeatedly until the chloride contents of aqueous solutions in contact with the samples were less than the detection limit of $AgNO_3$ testing. During the washing procedure, a large proportion of the [BMIM]BF_4 was lost to the aqueous phase, such that the approximate yield was less than 30 %, much smaller than for “hydrophobic” analogues such as [BMIM]PF_6 and [BMIM]Tf_2N. After again washing with water, the dichloromethane was removed by rotary evaporation. The ionic liquid remaining was further treated with activated charcoal and neutral alumina. The colorless [BMIM]BF_4 was dried under vacuum for 30 h, sealed into a glass ampule, transported to Australia, and then opened and transferred to the high-pressure cell inside a dry glovebox just prior to use.

The water contents of the samples were (77 and 68)$\cdot10^{-6}$ mass fraction, respectively, as determined by Karl Fischer titration, and the chloride contents of aqueous solutions in contact with the samples were less than the detection limit of

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$AgNO_3$ testing. An energy dispersive X-ray fluorescence spectrometer (Shimadzu EDX800HS) became available to us after the second set of viscosity measurements was completed. Analysis for chloride in sample BB2 was carried out by comparison with standard KCl(aq) solutions using a Rh anode with an Al filter. A linear response was found in the range (0 to 0.0227) $mol\cdot L^{-1}$. The chloride concentration was (0.0032 ± 0.0003) $mol\cdot L^{-1}$, equivalent to mass fraction $(92 \pm 9)\cdot 10^{-6}$. The molar mass of $[BMIM]BF_4$ was taken as 226.021 $g\cdot mol^{-1}$.

We have determined the densities at atmospheric pressure using an Anton-Paar DMA5000 vibrating tube densimeter, with an expanded uncertainty of 0.000 05 $g\cdot cm^{-3}$. The built-in viscosity correction for this instrument has been confirmed for samples with known densities and with viscosities as high as 16 Pa·s.[2]

The experimental methods for the viscosity measurements have been given previously.[1−3] In this case, only one sinker was employed, with a nominal diameter of 6.0 mm for which the calibration extends to 2875 mPa·s.[1−3] A combination of the uncertainties in replicate measurements (± 1 %), the calibration (± 1 %), and the calibrant viscosities (the uncertainty for the most viscous, Cannon N1000, is ± 0.38 % for the temperatures employed) in quadrature yields an expanded uncertainty of ± 2 %.

Falling-body viscosity measurements require a value for the density for the buoyancy factor $(1 - \rho/\rho_s)$ in the primary working equation

$$\eta(p,T) = \frac{t(1 - \rho/\rho_s)}{A[(1 + 2\alpha(T - T_{ref})][1 - 2\beta(p - p_{ref})/3]} \qquad (1)$$

where ρ/ρ_s is the ratio of the density ρ for the fluid at the temperature T and pressure p of the measurement to that of the sinker, ρ_s. The other quantities in eq 1 are the calibration constant, A, the fall time, t, and α and β, the coefficients of expansion and compressibility of the sinker and viscometer tube material (316 stainless steel) at (T_{ref}, p_{ref}). ρ_s is 7.285 $g\cdot cm^{-3}$ at 25 °C and 0.1 MPa, so for a fluid such as $[BMIM]BF_4$ with a density of 1.2014 $g\cdot cm^{-3}$ under the same conditions, the density need only be known to better than 0.5 % to give 0.1 % accuracy in the buoyancy factor.

Gomez de Azevedo et al.[7] have reported *pVT* data from (25 to 60) °C to pressures of 59 MPa. Following the procedures of our earlier studies, we have calculated bulk secant moduli K from these and estimated the densities at higher pressures from a fit of $K(T, p)$. K is defined in terms of the pressure and molar volume (V)

$$K = V_0(p - p_0)/(V_0 - V) \qquad (2)$$

where V_0 is the molar volume at a given temperature obtained from our own atmospheric pressure (p_0) densities. K was expressed by the Hayward-type equation

$$K = (\alpha_{00} + \alpha_{10}/T) + (\alpha_{01} + \alpha_{11}/T)p \qquad (3)$$

and the fitted set of α_{ij} coefficients is $\alpha_{00} = 1723.6$ MPa, $\alpha_{10} = 2.6457\cdot 10^5$ MPa·K, $\alpha_{01} = -11.347$, and $\alpha_{11} = 4880.3$ K. The uncertainty in the densities estimated from this method should be less than 0.2 %.

The viscosity tables presented below give sufficient detail for the viscosities to be recalculated when more extensive *pVT* data become available.

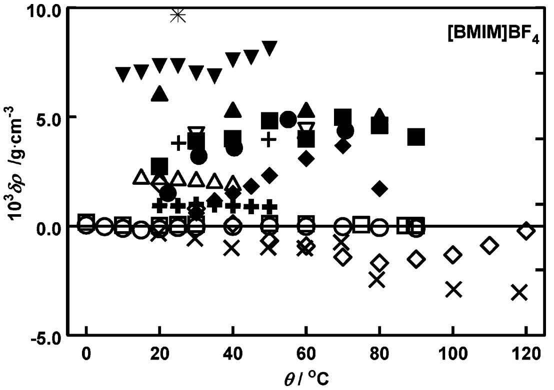

Figure 1. Residuals (experimental − calculated values) for the fit of the experimental atmospheric pressure and literature densities for $[BMIM]BF_4$ to eq 4 as a function of temperature, θ. Open symbols and bold plus sign, *, ×, and + refer to vibrating tube densimeters. Closed symbols refer to pycnometric and other gravimetric techniques. Water mass fractions, w, where known, are given below. Symbols: ○, this work, sample BB1 ($10^6w = 77$); □, this work, sample BB2 ($10^6w = 68$); +, ref 7 ($10^6w < 70$); *, ref 9; △, ref 11 ($10^6w < 40$); ▽, ref 12 ($10^6w < 70$) (obscured behind ref 8 values); ×, ref 13 ($10^6w < 100$); ◇, ref 17 ($10^6w = 485$); bold plus sign, ref 18 ($10^6w = 2614$); ■, ref 8 ($10^6w = 307$); ●, ref 10 ($10^6w = 1900$); ▲, ref 14 ($10^6w = 130$); ▼, ref 16; ◆, ref 15 ($10^6w = 200$).

Table 1. Density ρ of $[BMIM]BF_4$ from θ = (0 to 90) °C

θ/°C	ρ/g·cm^{-3}	θ/°C	ρ/g·cm^{-3}
Sample BB1		Sample BB2	
0.00	1.21950	0.00	1.21964
5.00	1.21579	10.00	1.21222
10.00	1.21207	20.00	1.20498
15.00	1.20838	25.00	1.20143
20.00	1.20483	30.00	1.19788
25.00	1.20129	50.00	1.18379
30.00	1.19775	60.00	1.17681
40.00	1.19068	75.00	1.16645
50.00	1.18367	87.00	1.15827
60.00	1.17670	89.61	1.15651
70.00	1.16979	90.01	1.15622
80.00	1.16292		
90.00	1.15611		

Results and Discussion

Density. The density results at atmospheric pressure for two samples are presented in Table 1 and can be represented by the polynomial

$$\rho/g\cdot cm^{-3} = 1.21947 - 7.32279\cdot 10^{-4}\,(\theta/°C) + 3.28140\cdot 10^{-7}\,(\theta/°C)^2 \qquad (4)$$

where θ is the Celsius temperature, with a standard uncertainty of fit of ± 0.000 08 $g\cdot cm^{-3}$. The results from the second sample are slightly higher than those from the first, the average difference being 0.000 12 $g\cdot cm^{-3}$. There have been a large number of measurements made of the density of $[BMIM]BF_4$.[7−18] Figure 1 shows deviations of the literature data from eq 4. While the scatter within a given data set tends to be small, the densities obtained from pycnometric and other gravimetric measurements[8,10,14−16] are generally higher than those from this work and from some of the vibrating tube densimeter studies.[13,17,18] On the other hand, there are higher values among the other vibrating tube densimeter measurements.[7,9,11,12] The exceptions do not correlate with water content (given in the caption to Figure 1). It is possible that the higher values are due to other impurities such as halides (though their presence was determined to be small[13,14,17] or negligible[7,8,11,12] in a number of cases), but again there is no obvious correlation. The differences observed seem more likely to be due to differences in sample handling and technique or to

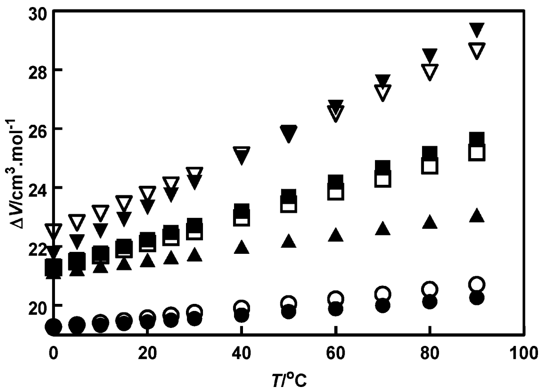

Figure 2. Differences in molar volumes for pairs of salts with common ions as a function of temperature. Some sets have been offset to fit them within the scale of the graph. Symbols: ○, {V([BMIM]PF_6) − V([BMIM]BF_4)}; ●, {V([OMIM]PF_6) − V([OMIM]BF_4)}; □, {V([OMIM]PF_6) − V([BMIM]PF_6) − 45 cm^3·mol^{-1}}; ■, {V([OMIM]BF_4) − V([BMIM]BF_4) − 45 cm^3·mol^{-1}}; ▲, {V([HMIM]PF_6) − V([BMIM]PF_6) − 12 cm^3·mol^{-1}}; ▼, {V([BMIM]Tf_2N) − V([BMIM]BF_4) − 80 cm^3·mol^{-1}}; ▽, {V([BMIM]Tf_2N) − V([BMIM] PF_6) − 60 cm^3·mol^{-1}}.

Table 2. Summary of Thermal Expansivity, α, and Results for Ionic Liquids

salt	10^3·α/K^{-1} this work	10^3·α/K^{-1} literature
[BMIM]BF_4	0.59 ± 0.02	0.58,[7] 0.64,[17] 0.59[18]
[OMIM]BF_4	0.62 ± 0.02	0.67,[17] 0.62,[18] 0.62[19]
[BMIM]PF_6	0.61 ± 0.02	0.61,[7] 0.61[19]
[HMIM]PF_6	0.62 ± 0.02	0.68,[17] 0.61[18]
[OMIM]PF_6	0.62 ± 0.02	0.67,[17] 0.60[19]
[BMIM]Tf_2N	0.67 ± 0.01	0.66[20]

errors in relating the temperature of the measurements to a common scale or in calibration. We also note that only two other sets of vibrating tube measurements explicitly incorporated a viscosity correction:[17,18] Gomes de Azevedo et al.[7] also noted the desirability for this correction for viscous liquids but were unable to apply it to their particular instrument.

A more stringent test where data are available over a temperature range is to examine the expansivity, $\alpha \equiv -(1/\rho)(d\rho/dT)$. In all the cases we have examined, smoothed values of $d\alpha/dT$ are slightly negative and largest in magnitude for the [BMIM]$^+$ salts. However, the variation in α over the range (0 to 90) °C is within the experimental uncertainty of ± $0.02 \cdot 10^{-3}$ K^{-1} (derived from the uncertainties in the fitted coefficients in eq 4), so one would need to determine densities over an even greater temperature range, or with higher precision, to be certain of the sign of $d\alpha/dT$. Table 2 summarizes our mean thermal expansivities for the six ionic liquids we have studied thus far.[1−3] For [BMIM]BF_4, the value for α is (0.59 ± 0.02)·10^{-3} K^{-1}: this compares favorably with values from the literature, {(0.58 ± 0.01),[7] (0.64 ± 0.04),[17] and (0.59 ± 0.01)}·10^{-3} K^{-1}.[18]

Finally, Figure 2 shows differences in molar volumes for salts with common anions. These prove to be very similar for the anions BF_4^- and PF_6^- but increase with increasing temperature. The same effect is seen for $\Delta V(PF_6^- - BF_4^-)$ with common cations. For PF_6^- salts, ΔV([OMIM]$^+$ − [BMIM]$^+$) is exactly twice ΔV([HMIM]$^+$ − [BMIM]$^+$) over the temperature range (0 to 90) °C, e.g., (67.31 and 33.62) cm^3·mol^{-1}, respectively, at 25 °C, the increment for two (CH_2) groups being very close to that found for [Tf_2N]$^-$ salts, (34.4 ± 0.5) cm^3·mol^{-1}.[20] For the [BMIM]$^+$ salts, the difference ΔV([Tf_2N]$^-$ − [BF_4]$^-$) is 1.23 times ΔV([Tf_2N]$^-$ − [PF_6]$^-$) over the whole temperature range.

Viscosity. Tables 3 and 4 list the viscosity results for samples BB1 (atmospheric pressure) and BB2 [(0.1 to 300) MPa], respectively. As in our earlier studies,[1−3] data obtained at atmospheric pressure were fitted to the two-coefficient Litovitz equation

$$\eta = A \exp(B/RT^3) \tag{5}$$

and the more flexible three-coefficient Vogel−Fulcher−Tammann (VFT) equation

$$\eta = A' \exp(B'/(T - T_0)) \tag{6}$$

with coefficients being given in Table 5.

There is a slight difference between the viscosities of samples BB1 and BB2, which is largest (6 %) at low temperature. BB2 is the more viscous. While the overall expanded uncertainty of our results is ± 2 %, the precision for a given set is ± 1 %, and the sinker and calibration are the same in both cases. So the difference is greater than the experimental error. There was also a small difference in the densities, BB1 being the less dense. At this stage, there is no *experimental* reason to discard either set, but the data for BB2 are probably to be preferred as they are more consistent with correlations with conductivity and diffusion coefficient results that will be published separately. The deviations of our results and the literature data[8,11,13−15,21−24] from eqs 5 and 6 given in Figure 3 are relative to the results for this sample. There is a large scatter in the literature results, with values both larger and smaller than ours, and it is apparent that [BMIM]BF_4, like [BMIM]PF_6,[1] is a much more difficult system with which to work than [BMIM][Tf_2N].[2]

Table 3. Viscosity η of [BMIM]BF_4 (Sample BB1) from θ = (0 to 75) °C and p = 0.1 MPa

θ / °C	t / s	V / cm^3·mol^{-1}	ρ / g·cm^{-3}	η / mPa·s	Re[a]	θ / °C	t / s	V / cm^3·mol^{-1}	ρ / g·cm^{-3}	η / mPa·s	Re[a]
0.00	1516.4	185.34	1.2195	510.8	0.011	25.00	306.3	188.19	1.2010	103.4	0.26
0.00	1516.8	185.34	1.2195	511.0	0.011	30.00	238.7	188.77	1.1974	80.6	0.43
5.00	1047.5	185.91	1.2158	353.0	0.023	30.00	238.9	188.77	1.1974	80.7	0.43
5.00	1047.3	185.91	1.2158	352.9	0.023	40.00	151.7	189.91	1.1902	51.3	1.1
10.00	743.5	186.48	1.2121	250.7	0.045	40.00	151.7	189.91	1.1902	51.3	1.1
10.00	743.4	186.48	1.2121	250.6	0.045	50.00	102.3	190.95	1.1837	34.6	2.3
15.00	540.7	187.05	1.2084	182.4	0.085	50.00	102.3	190.95	1.1837	34.6	2.3
15.00	540.7	187.05	1.2084	182.4	0.085	60.00	72.4	192.08	1.1767	24.5	4.6
20.00	401.7	187.60	1.2048	135.6	0.15	60.00	72.4	192.08	1.1767	24.5	4.6
20.00	402.1	187.60	1.2048	135.7	0.15	70.00	53.3	193.22	1.1698	18.1	8.4
25.00	307.7	188.19	1.2010	103.9	0.26	70.00	53.4	193.22	1.1698	18.1	8.4
25.00	307.2	188.19	1.2010	103.7	0.26	80.00	40.9	194.36	1.1629	13.9	14.2
25.00	306.5	188.19	1.2010	103.5	0.26	80.00	40.6	194.36	1.1629	13.8	14.4

[a] Reynolds number for annular flow: $Re = 2r_1^2\rho v/((r_2 - r_1)\eta)$ where v is the terminal velocity of the sinker and r_1 and r_2 are the radii of the sinker and tube, respectively.

Table 4. Viscosity η of [BMIM]BF_4 (Sample BB2) from θ = (0 to 75) °C and p = (0.1 to 300) MPa

θ	t	p	V	ρ	η		θ	t	p	V	ρ	η	
°C	s	MPa	$cm^3 \cdot mol^{-1}$	$g \cdot cm^{-3}$	mPa·s	Re[a]	°C	s	MPa	$cm^3 \cdot mol^{-1}$	$g \cdot cm^{-3}$	mPa·s	Re[a]
0.00	1611.8	0.1	185.318	1.21964	543.0	0.01	50.00	106.4	0.1	190.930	1.18379	36.0	2.14
0.00	1611.4	0.1	185.318	1.21964	542.8	0.01	50.00	116.4	10.5	187.261	1.20699	39.2	1.83
10.00	782.2	0.1	186.452	1.21222	263.7	0.04	50.00	132.0	25.4	186.082	1.21463	44.4	1.43
10.00	782.4	0.1	186.452	1.21222	263.8	0.04	50.00	164.6	50.5	184.266	1.22660	55.3	0.93
10.00	789.8	0.8	186.404	1.21253	266.3	0.04	50.00	202.6	75.6	182.623	1.23764	67.9	0.62
10.00	897.2	11.0	185.671	1.21732	302.2	0.03	50.00	248.1	100.6	181.135	1.24781	83.0	0.42
10.00	1067.2	24.9	184.721	1.22358	359.1	0.02	50.00	302.9	125.5	179.778	1.25723	101.2	0.28
10.00	1443.1	49.6	183.157	1.23403	484.8	0.01	50.00	368.1	150.4	178.539	1.26595	122.8	0.19
10.00	1955.4	75.3	181.678	1.24407	655.9	0.01	50.00	446.4	175.5	177.393	1.27413	148.7	0.13
10.00	2612.4	100.6	180.344	1.25328	875.0	0.00	50.00	539.4	200.3	176.342	1.28172	179.5	0.09
20.00	421.1	0.1	187.573	1.20498	142.1	0.14	50.00	650.4	225.3	175.365	1.28886	216.2	0.06
20.00	421.0	0.1	187.573	1.20498	142.0	0.14	50.00	783.0	250.1	174.464	1.29552	260.0	0.04
25.00	320.1	0.1	188.127	1.20143	108.0	0.24	60.00	74.5	0.1	192.062	1.17681	25.2	4.34
25.00	320.0	0.1	188.127	1.20143	108.0	0.24	60.00	75.3	0.1	192.062	1.17681	25.5	4.25
25.00	321.4	0.1	188.127	1.20143	108.5	0.24	70.00	54.3	0.1	193.202	1.16987	18.4	8.10
25.00	322.1	0.1	188.127	1.20143	108.7	0.24	70.00	53.3	0.1	193.202	1.16987	18.0	8.43
25.00	321.8	0.5	188.098	1.20161	108.6	0.24	75.00	47.81	0.1	193.768	1.16645	16.2	10.43
25.00	423.4	25.9	186.216	1.21376	142.6	0.14	75.00	46.83	0.1	193.768	1.16645	15.9	10.87
25.00	550.3	50.8	184.549	1.22472	185.0	0.08	75.00	51.48	11.7	192.695	1.17295	17.4	9.05
25.00	714.2	75.9	183.022	1.23494	239.8	0.05	75.00	57.47	25.2	191.507	1.18023	19.4	7.32
25.00	919.6	101.1	181.627	1.24442	308.3	0.03	75.00	69.16	50.7	189.466	1.19294	23.3	5.12
25.00	1176.9	126.2	180.352	1.25322	393.9	0.02	75.00	82.60	75.6	187.664	1.20440	27.8	3.63
25.00	1495.2	150.6	179.210	1.26121	499.9	0.01	75.00	98.12	100.6	186.031	1.21497	33.0	2.60
25.00	1497.6	150.7	179.208	1.26123	500.6	0.01	75.00	115.7	125.6	184.549	1.22472	38.8	1.89
25.00	1901.0	175.4	178.140	1.26878	634.7	0.01	75.00	136.1	150.6	183.194	1.23378	45.6	1.38
25.00	2423.8	200.9	177.122	1.27607	808.3	0.00	75.00	159.6	175.6	181.952	1.24220	53.4	1.01
30.00	250.5	0.1	188.684	1.19788	84.6	0.39	75.00	186.4	200.6	180.810	1.25004	62.3	0.74
30.00	250.5	0.1	188.684	1.19788	84.6	0.39	75.00	217.4	225.5	179.761	1.25734	72.6	0.55
40.00	158.3	0.1	189.810	1.19078	53.5	0.97	75.00	253.5	250.4	178.791	1.26417	84.6	0.41
40.00	158.6	0.1	189.810	1.19078	53.6	0.97	75.00	295.2	275.3	177.886	1.27059	98.4	0.30
50.00	105.4	0.1	190.930	1.18379	35.6	2.18	75.00	342.4	300.0	177.053	1.27657	114.0	0.23

[a] Reynolds number for annular flow: $\mathrm{Re} = 2r_1^2\rho v/((r_2 - r_1)\eta)$ where v is the terminal velocity of the sinker and r_1 and r_2 are the radii of the sinker and tube, respectively.

Table 5. Coefficients of Best Fit for Equations 5 and 6

	Coefficients and Standard Uncertainties	
	BB1	BB2
	Litovitz, eq 5	
$\ln(A/\mathrm{mPa \cdot s})$	−0.5004 ± 0.0148	−0.5211 ± 0.0148
$B \cdot 10^{-6}/\mathrm{K}^3$	136.69 ± 0.40	138.37 ± 0.42
standard uncertainty of fit/%	1.0	1.5
	VFT, eq 6	
$\ln(A'/\mathrm{mPa \cdot s})$	−2.2254 ± 0.0028	−2.4263 ± 0.061
B'/K	907.31 ± 7.89	963.64 ± 17.41
T_0/K	166.00 ± 0.59	162.68 ± 1.27
D[a]	5.46	5.92
standard uncertainty of fit/%	0.4	0.7

[a] Angell strength parameter (B'/T_0).

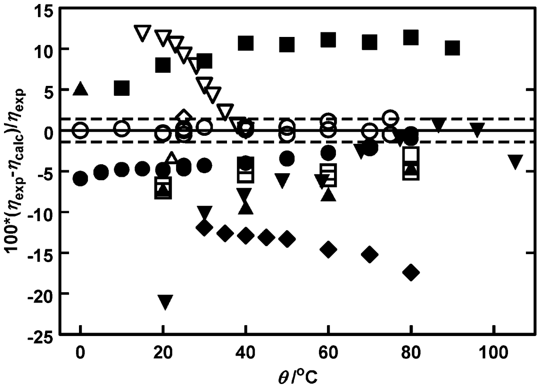

Figure 3. Residuals (experimental − calculated values) for the fit of the experimental atmospheric pressure and literature viscosities for [BMIM]BF_4 to eq 6 (VFT) as a function of temperature, θ. The dashed lines represent the expanded uncertainty of fit (k = 2) or 95 % confidence limits for sample BB2. Symbols (with literature uncertainties in parentheses, where given): ○, this work, sample BB2; ●, this work, sample BB1; ■, ref 8 (± 1 %); ◇, ref 9 (± 0.3 %); ▲, ref 11; ▼, ref 13 (± 1 %); □, ref 14 (both rolling ball [± 2.1 %] and capillary); ◆, ref 15; △, ref 23 (± 1 %); ▽, ref 24 (± 1.2 %). The value of Kim et al.[21] is far too viscous, with a deviation of 158 %.

As for other ionic liquids,[1−3] we have used modified Litovitz (ML) and VFT (MVFT1 and MVFT2) equations to fit the high-pressure measurements

$$\eta = \exp(a + bp + (c + dp + ep^2)/T^3) \tag{7}$$

$$\eta = \exp(a' + b'p + (c' + d'p + e'p^2)/(T - T_0)) \tag{8}$$

$$\eta = \exp(a'' + b''p + DT_0(p)/(T - T_0))$$

$$T_0(p) = x + yp + zp^2 \tag{9}$$

The Angell strength parameter D ($\equiv B'/T_0$ in eq 6) is large for "strong" liquids where the viscosity approaches an Arrhenius (Andrade) temperature dependence and is small for "fragile" liquids. The MVFT1 form has a pressure-dependent strength parameter D [$=(c' + d'p + e'p^2)/T_0$], whereas the MVFT2 form has a pressure-dependent T_0. The coefficients for these fits (for sample BB2) are given in Table 6. Figure 4 shows residuals for MVFT1 together with the moderate pressure results of Tomida et al.[14] The difference between the two sets of results is more than the sum of their uncertainties. In contrast, the results of Tomida et al. for [BMIM]PF_6,[14] [HMIM]PF_6, and [OMIM]PF_6[25] agree well with those of our earlier work,[1,2] with a mean difference of approximately +2 %.

The D value determined from the atmospheric pressure values is 5.46 for BB1 and 5.92 for BB2, so [BMIM]BF_4 is more fragile than [OMIM]BF_4, where D = 8.25.[3] We have again tested the

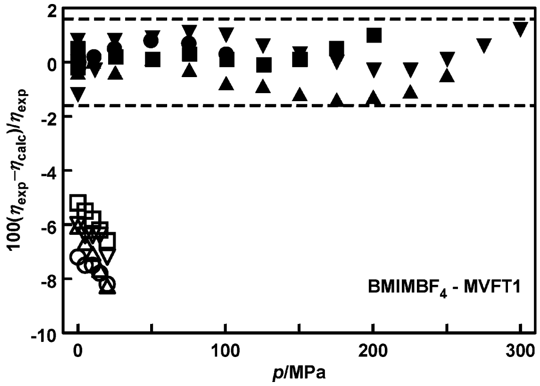

Figure 4. Residuals (experimental − calculated values) for the fit of the experimental and literature high-pressure viscosities to eq 8 (MVFT1) as a function of pressure, *p*. The dashed lines represent the expanded uncertainty of fit ($k = 2$) or 95 % confidence limits for the fit. Symbols: this work, ●, 10 °C; ■, 25 °C; ▲, 50 °C; ▼, 75 °C; ref 14 (uncertainty, ± 2.1 %), ○, 20 °C; □, 40 °C; △, 60 °C; ▽, 80 °C.

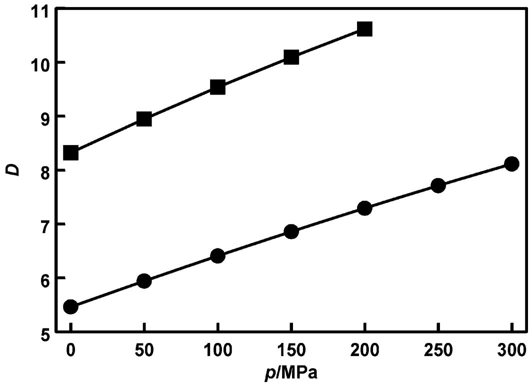

Figure 5. Pressure dependence of the Angell strength parameter *D*, obtained from the parameters of eq 8. Symbols: ●, [BMIM]BF$_4$; ■, [OMIM]BF$_4$, from ref 3.

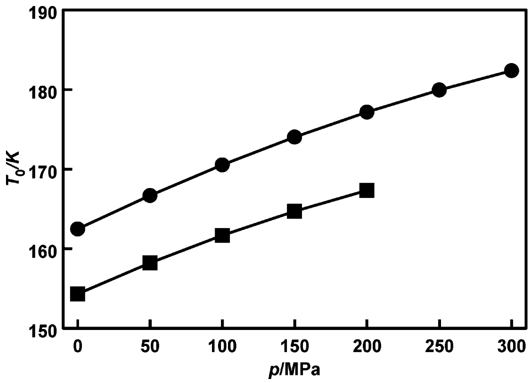

Figure 6. Pressure dependence of the VFT parameter T_0, obtained from the parameters of eq 9. Symbols: same as for Figure 5.

Table 6. Coefficients of Best Fit for Equations 7, 8, and 9

Coefficients and Standard Uncertainties	
ML, eq 7	
a	-0.5142 ± 0.011
$b \cdot 10^3$/MPa^{-1}	1.785 ± 0.12
$c \cdot 10^{-6}$/K^3	138.166 ± 0.30
$d \cdot 10^{-6}$/(K$^3 \cdot$MPa^{-1})	0.23854 ± 0.0033
e/(K$^3 \cdot$MPa^{-2})	-124.4 ± 11
standard uncertainty of fit/%	1.4
MVFT1, eq 8	
a'	-2.2403 ± 0.046
$b' \cdot 10^3$/MPa^{-1}	-1.6207 ± 0.098
c'/K	910.5 ± 13
d'/(K$\cdot$MPa^{-1})	1.62761 ± 0.018
$e' \cdot 10^5$/(K$\cdot$MPa^{-2})	-51.65 ± 3.0
T_0/K	166.642 ± 0.94
standard uncertainty of fit/%	0.8
MVFT2, eq 9	
a''	-2.4299 ± 0.042
$b'' \cdot 10^3$/MPa^{-1}	2.0472 ± 0.059
D	5.942 ± 0.11
x/K	162.486 ± 0.87
$y \cdot 10^2$/(K$\cdot$MPa^{-1})	8.7659 ± 0.063
$z \cdot 10^5$/(K$\cdot$MPa^{-2})	-7.101 ± 0.17
standard uncertainty of fit/%	0.7

Table 7. Test of the Angell Relationship between *D*, T_0, and T_g

	BB1	BB2
Parameters from VFT, eq 6		
T_0/K	166.00	162.68
D	5.466	5.923
T_g/K	190[a]	190
T_g/T_0	1.15	1.17
T_g/T_0 from eq 10	1.14	1.15
Parameters from MVFT2, eq 9		
$T_0(=x)$/K	−	162.49
D	−	5.942
T_g/T_0	−	1.17
T_g/T_0 from eq 10	−	1.15

[a] Mean of values given in ref 10 (188 K), ref 11 (190 K), and ref 27 (192 K): the value of 202 K given in ref 28 appears to be too high.

Table 8. Angell Strength Parameters, *D*, for 1-Methyl-3-alkylimidazolium Salts

salt	ref	T_0/K	D
[BMIM]PF$_6$	1	161.8	6.96
[HMIM]PF$_6$	3	161.8	7.81
[OMIM]PF$_6$	2	158.0	8.91
[BMIM]BF$_4$	this work	162.7	5.92
[OMIM]BF$_4$	2	155.5	8.25
[BMIM][Tf$_2$N]	3	164.7	4.65

Angell relation between *D*, T_0, and the glass temperature T_g, based on the scaling of the (coexistence line) viscosities of a wide range of liquids in the range $0 < (T_g/T_0) < 1$, with the assumption of a common single viscosity value (η_g) at T_g.[26] Thus

$$T_g/T_0 = 1 + D/(2.303 \log(\eta_g/\eta_0)) \tag{10}$$

η_0 is A' of the VFT equation (eq 6). Angell found $\log(\eta_g/\eta_0)$ empirically to be about 17. Both BB1 and BB2 samples conform to eq 10 (see Table 7), as the difference in *D* is compensated by that in T_0, so we are unable to use this test to determine a preference for one set over the other: this probably reflects the flexibility of the VFT equation in fitting transport properties. Nevertheless, eq 10 is useful for selecting between experimental values of T_g when these are discordant, as is sometimes the case. Finally, Table 8 lists strength parameters for the six ionic liquids we have now examined. For the PF$_6^-$ salts, the order is D([BMIM]$^+$) < D([HMIM]$^+$) < D([OMIM]$^+$), and for the BF$_4^-$ salts, D([BMIM]$^+$) < D([OMIM]$^+$). For the [BMIM]$^+$ salts, it is D([Tf$_2$N]$^-$) < D(BF$_4^-$) < D(PF$_6^-$), and for the [OMIM]$^+$ salts, D(BF$_4^-$) < D(PF$_6^-$). Interestingly, the salts become more fragile as the cation volume becomes smaller, but *D* does not correlate with anion volume. For comparison with [OMIM]BF$_4$,[3] Figures 5 and 6 show the pressure dependence of *D* (from MVFT1) and T_0 (from MVFT2), respectively.

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