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Temperature and Pressure Dependence of the Viscosity of the Ionic Liquid 1-Butyl-3-methylimidazolium Hexafluorophosphate

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New measurements have been made for the viscosity of the room-temperature ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF_6) between (0 and 80) °C with a falling-body viscometer. High-pressure measurements were made at (25, 35, 50, 60, and 70) °C. The overall uncertainty is estimated at ± (2 to 3) %. Atmospheric pressure densities obtained with a vibrating tube densimeter are also reported for temperatures between (0 and 90) °C with an overall uncertainty estimated at ± 0.00005 $g\cdot cm^{-3}$. The viscosity behavior is qualitatively different from that of molecular liquids, with isotherms being best fitted as functions of the applied pressure rather than as functions of the molar volume. Modified Litovitz and Vogel−Fulcher−Tammann equations have been used to incorporate both the temperature and pressure dependence. Interestingly, the T_0 parameter of the VFT equation appears to be independent of pressure within the state point range of the data, but the Angell strength parameter increases with increasing pressure.

Introduction

This work forms the first paper in a series on the transport properties of room temperature ionic liquids at high pressure. Here we report high-pressure viscosities for 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]-PF6). This substance was chosen as it is a typical example of the imidazolium group of ionic liquids and for the practical reason that the *pVT* data required for high-pressure viscosity measurements are available. It is an example of a moderately “fragile” liquid,[1] and a number of its thermodynamic and transport properties have been determined[2−6] and its liquid structure investigated.[7] There have been very few studies of the viscosity of a molten salt at high pressure.[8−10] Only one of these deals with salts (nitrates) showing typical liquid behavior with the viscosity increasing with applied pressure;[8] the others refer to networked liquids that show anomalous behavior (e.g., $ZnCl_2$, where the viscosity shows a water-like minimum,[10] and certain silicates, where the viscosity decreases with increasing pressure[9]). The ease with which ionic liquids such as [BMIM]PF_6 can be investigated at high pressure may lead in time to a better understanding of the behavior of the transport properties of molten salts generally.

We have determined viscosities (η) between (0 and 80) °C at atmospheric pressure, and at (25 and 50) °C, the isotherms for which high-pressure densities are available,[11] at pressures up to approximately 200 MPa. High-pressure data are also reported for (35, 60, and 75) °C using an equation of state based on the literature *pVT* data. Atmospheric pressure densities obtained with a vibrating tube densimeter are also reported for temperatures between (0 and 90) °C.

Experimental Section

The sample of [BMIM]PF_6 was prepared in the Sendai laboratory as previously described[6] as a modified version of that published by Carda-Broch et al.[3] The colorless liquid obtained was dried under vacuum at 70 °C for 30 h to remove any excess water and sealed in a borosilicate glass vial for shipment to the Canberra laboratory. It was confirmed that any residual chloride was less than the detection limit of elemental titration analyses. The (partial) elemental analysis found, in mass fractions, was ($w_C = 0.3397$, $w_H = 0.0525$, $w_N = 0.0980$); that calculated was ($w_C = 0.3381$, $w_H = 0.0532$, $w_N = 0.0986$). The molar mass was taken to be 284.1791 g/mol.

The high-pressure viscometer and its operation have been described previously.[12,13] Platinum resistance thermometers calibrated between (−65 and 100) °C on ITS-90 to a tolerance of ± 8 mK were employed. The viscometer oil-bath temperature was controlled to within ± 0.01 K. The primary pressure gauge (400 MPa Heise CM) was calibrated against a deadweight tester, and pressures have an overall uncertainty of ± 0.2 MPa.

The dry viscometer tube was filled with [BMIM]PF_6 inside a glovebox with an atmosphere dried with either phosphorus pentoxide or concentrated sulfuric acid. A check was made for water content by ^1H NMR at 400 MHz following the manipulations of the sample: no trace of water was found.

The working equation for the falling-body viscometer is[12,14−15]

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

where t is the fall time; ρ is the density of the fluid; ρ_s is

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Table 1. Viscometer Calibration Data

sinker diameter/mm	calibrants[a]	viscosity range/(mPa·s)	Reynolds number range	10^{-3} A/Pa^{-1}
5.90_5	N100, S60, (20−50) °C	30−157	0.12−3.4	1.476 ± 0.017
6.00_0	N100, S200, (20−50) °C	51−585	0.0067−0.84	2.454 ± 0.012
6.09_5	N100, 37.78 °C	95	2.4	4.623
6.29_0	N100 (37.78−50) °C; list in ref 13, 25 °C	0.51−201.8	0.013−1650	28.72 ± 0.07

[a] Lot numbers: N100-03501, S60-04101, and S200-04201.

that of the sinker; α is the coefficient of thermal expansion ($1.6 \cdot 10^{-5}$ K^{-1}); β is the bulk compressibility ($2 \cdot 10^{-6}$ Pa^{-1}) of the sinker and tube material, in this case 316 stainless steel; and A is the calibration constant. The viscometer tube diameter is 6.52 mm. The sinker densities were corrected for changes in T and p from the reference state point, $T_{\mathrm{ref}} = 298.15$ K and $p_{\mathrm{ref}} = 0.1$ MPa using the relation:[16]

$$\rho_s = \frac{\rho_s(T_{\mathrm{ref}}, p_{\mathrm{ref}})}{[1 + 3\alpha(T - T_{\mathrm{ref}})][1 - \beta(p - p_{\mathrm{ref}})]} \tag{2}$$

The measured viscosities for [BMIM]PF$_6$ extended from (25 to 2700) mPa·s and were therefore much larger than have been determined previously with this instrument. A number of sinkers with different clearances were required to keep fall times to reasonable values. This also avoided very low Reynolds numbers where the sinker (a hollow cylinder containing a ferrite core and having a hemispherical face), which is unguided, may not be self-centering and therefore fall eccentrically. The effect of eccentric fall is to reduce the flow time,[17] as also happens with turbulent flow, so measurements are best made within upper and lower Reynold's number limits where the calibration factor A is constant. According to Harlow,[18] the distance travelled by a sinker to reach terminal velocity, s, depends on the sixth power of the clearance, $c = r_2 - r_1$, where r_2 is the radius of the viscometer tube and r_1 is that of the sinker:

$$s \propto \frac{c^6}{\eta^2 r_1^{\,2}} \tag{3}$$

The calibration of the 6.3 mm diameter sinker we have used until now[13,19] ($A = 28.71 \cdot 10^3$ Pa^{-1} ± 0.2 %) was extended by an order of magnitude to $Re = 0.029$ by further calibration with the Cannon certified viscosity standard N100.

For high pressures and lower temperatures, other sinkers were employed {(5.9, 6.0, and 6.1) mm}; these were calibrated with Cannon certified viscosity standards N100, S60, and S200 (Table 1). Irving and Barlow[20] have noted that unguided sinkers with a diameter less than about 93 % of the tube diameter may fall erratically. We did observe this for the 5.9 mm sinker with the most viscous calibrant, S200, at (20 and 25) °C, although curiously not for [BMIM]PF$_6$ at similar Reynolds numbers. Scott,[21] cited by Cappi,[17] has shown that for a right cylinder the calibration constant varies with the clearance, *c,* as

$$A^{-1} = \frac{c^3 g}{6 L r_1 F}$$

$$F = 1 + \frac{3c}{2r_1} + \frac{7c^2}{5r_1^{\,2}} + ... \tag{4}$$

where g is the local acceleration due to gravity and L is the distance between the inductance sensor coils. To a first approximation, the sinkers used here should behave in a similar fashion. For the smallest clearance sinker, $2r_1 = 6.3$ mm, the second term in F is 0.023; for the largest, with $2r_1 = 5.9$ mm, it is 0.069, giving a difference of 4.4 % in its effect on A. Figure 1 shows A^{-1} plotted against c^3/r_1: the plot is linear within experimental error (greater in the abscissas), suggesting that the higher terms in F are smaller than are given by eq 4 and may be neglected for the type of sinker used here. The overall uncertainty in the viscosity, based on replicate measurements (± 1 %) and the uncertainty in the calibration {Cannon standards: ± 0.3 %, reproducibility ± (1 to 2) %}, is estimated at ± (2 to 3) %.

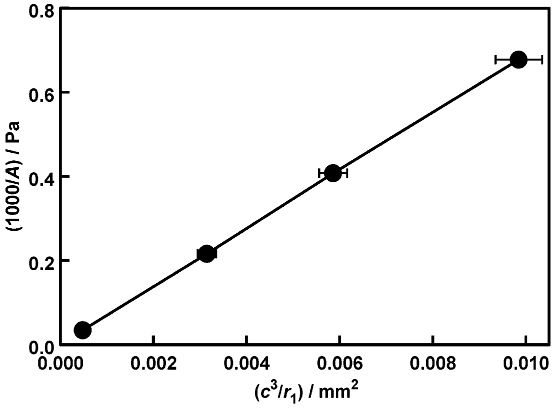

Figure 1. Plot of the reciprocal viscometer calibration constant for different sinkers against the quantity (c^3/r_1). Linear best fit: ($1000/A^{-1}$)/Pa = (68.98 ± 0.21){(c^3/r_1)/mm^2}.

Calculation of the viscosity from fall times requires knowledge of the density as a function of T and p. The only pVT data available to us were those of Gu and Brennecke,[11] which are for (25 and 50) °C. These measurements were made by an unusual piezometer variant,[22] where high pressure applied to the sample forces a marker ring at the boundary of the ionic liquid and the pressurizing fluid into a fixed position. This position can be read relative to calibration marks to determine the volume of the liquid. Gu and Brennecke[11] used the Tait equation to represent their results, but the parameters reported are incorrect: for example, their values for toluene at 323.2 K ($B = 0.5717$ MPa, $C = 0.1986$, for the ln form of the Tait equation) are quite different from those in the literature ($B = 80$ MPa, $C = 0.0916$)[23] with which they make comparison. Consequently, we have refitted the densities for [BMIM]PF$_6$ using a nonlinear least squares procedure: this method yields Tait parameters for toluene and bromobenzene in satisfactory agreement with the those in the literature.[23,24] We obtain the following values for [BMIM]PF$_6$: $T = 298.15$ K, $B = 152.5_6$ (1.893) MPa, $C = 0.06499$ (0.1829), standard uncertainty of the fit to the density = 0.4 %; $T = 323.15$ K, $B = 117.15$ (1.433) MPa, $C = 0.05845$ (0.1630), standard uncertainty = 0.2 %. The values in parentheses are those given by Gu and Brennecke.[11]

Table 2. Density ρ of [BMIM]PF$_6$ from θ = (0 to 90) °C

θ/°C	ρ/g·cm^{-3}	θ/°C	ρ/g·cm^{-3}
0	1.388 85	40	1.354 95
5	1.384 55	40	1.354 96
10	1.380 27	50	1.346 75
15	1.375 99	60	1.338 58
20	1.371 72	70	1.330 45
25	1.367 45	80	1.322 38
30	1.363 19	90	1.314 36

As we needed to extrapolate these pVT data to higher temperatures, they were used to calculate the linear secant modulus

$$\kappa = V_0(p - p_0)/(V_0 - V) \tag{5}$$

as a function of temperature and pressure. κ was fitted to[25]

$$\kappa = (\alpha_{00} + \alpha_{10}/T) + (\alpha_{01} + \alpha_{11}/T)p \tag{6}$$

where V_0 is the molar volume at the saturation pressure p_0 for a given temperature. The coefficients α_{ii} were −608.022 MPa, 864032 MPa·K, 3.37099, and 1125.40 K, respectively: the standard deviation in V was 0.3 cm^3/mol or 0.14 %. High-pressure densities needed for the viscosity measurements were calculated using our atmospheric pressure densities and eqs 5 and 6. The accuracy of the densities used in this way for temperatures other than (25 and 50) °C is difficult to estimate. In previous work (for example, toluene[13] and hexane[25]), terms up to fourth or fifth order in p have been required for wide temperature ranges (over 100 K), giving a precision of ± 0.1−0.2 %. As the limited pVT data available for [BMIM]PF$_6$ justify only the linear form of eq 6, the overall uncertainty is probably of the order of ± 0.5 %. Clearly it would be useful to have more extensive pVT studies for ionic liquids.

Densities at atmospheric pressure were determined with an Anton-Paar DMA5000 vibrating tube densimeter, calibrated with dry air and degassed, deionized water (resistivity 18 MΩ·cm) at (20, 40, and 60) °C. The manufacturer's specification for temperature reproducibility is ± 1 mK. The sample is injected from a hot (≈70 °C), dried glass syringe, filled within the dry atmosphere of the glovebox referred to above. The densimeter automatically provides a viscosity correction based on higher moments of the fundamental vibration frequency.[26] This was checked using the high-viscosity Cannon standard S200 (T = 283.15 K, ρ = 0.8851 g·cm^{-3}, η = 584.8 mPa·s): the uncorrected and viscosity corrected densities were 0.885 55 g·cm^{-3} and 0.885 14 g·cm^{-3}, a significant difference of 0.05 %. The overall reproducibility for the density is estimated at ± 0.000 05 g·cm^{-3} (see below): Fitzgerald's analysis[26] gives ± 0.000 015 g·cm^{-3} as the best attainable uncertainty for the DMA5000.

Results and Discussion

The density results at atmospheric pressure are presented in Table 2 and can be represented by the polynomial

$$\rho/(\text{g}\cdot\text{cm}^{-3}) = 1.388\,827 - 8.625\,522\cdot10^{-4}\,(\theta/°\text{C}) + 3.984\,010\cdot10^{-7}\,(\theta/°\text{C})^2 \tag{7}$$

with an uncertainty of ± 0.000 05 g·cm^{-3}. Figure 2 shows deviations of literature density data[2,4,11,27−29] from eq 7: vibrating tube results are shown with open symbols and pycnometric, dilatometer or density bottle results are shown with filled symbols. Error bars are given where the experimental precision is larger than the size of the symbols; in the case of the data of Gu and Brennecke[11] the lesser of their two error estimates is shown, as being more consistent with the scatter in the data. Generally speaking all the data sets show the same temperature dependence, with the exception of that of Dzyuba and Bartsch,[28] which suggests problems with their thermometry. There is good agreement between our results and those of Seddon et al.[2] and of Kabo et al.[29] although the small negative offset of the latter set is greater than the combined estimated experimental uncertainties. The negative offset of the Gu and Brennecke[11] results is consistent with the reported mass fraction of water in their sample, 0.15 % or mole fraction 0.023. On the basis of our results, an ideal solution of this composition would have a density of 1.3599 g·cm^{-3} at 25 °C, and their value is 1.3603 g·cm^{-3}. The sample used by Tokuda et al.[4] was carefully purified and dried, but the densimeter used has a low precision (± 0.001 g·cm^{-3}). The dilatometric data of Suarez et al.[27] are systematically higher than our results.

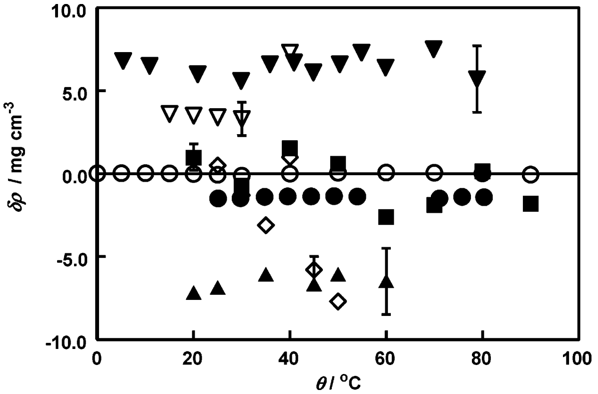

Figure 2. Residuals (experimental − calculated values) for the fit of the experimental atmospheric pressure and literature densities for [BMIM]PF$_6$ to eq 7 as a function of temperature, θ. Symbols: ○, this work; ■, ref 2; ▲, ref 11; ▼, ref 27; ◇, ref 28; ●, ref 29; ▽, ref 4.

The viscosities are presented in Table 3. The data were obtained in two groups, several months apart. The sample was dried under vacuum prior to both sets of measurements. There is good agreement between the results for the 5.9 mm and 6.3 mm sinkers, but the later values, obtained with the 6.0 mm sinker, are slightly higher, and the pressure dependence (discussed below) is slightly greater. The cause is unclear but is unlikely to be due to calibration errors.

As there seem to be no high-pressure data in the literature, comparison with the results of other workers[2,30−34] is confined to atmospheric pressure. The viscosity temperature dependence is non-Arrhenius; instead the data may be fitted to a simple empirical equation first employed by Litovitz:[35]

$$\eta = A\,\exp(B/RT^3) \tag{8}$$

Figure 3a shows deviations of our first group of measurements from this equation with A = (0.6630 ± 0.0086) mPa·s and B/R = (159.66 ± 0.39)·10^6 K^3: the standard deviation of the fit was ± 1.4 %. There is fair to good agreement between the data sets for the three sinkers employed: the results from the 6.0 mm sinker, obtained some months after the others, tend to be higher. The three-parameter Vogel−Fulcher−Tammann equation

$$\eta = A'\,\exp(B'/(T - T_0)) \tag{9}$$

is commonly used for ionic liquids. The Angell strength

Table 3. Viscosity η of [BMIM]PF_6 from θ = (0 to 80) °C and p = (0.1 to 250) MPa

θ/°C	t/s	p/MPa	V/$cm^3 \cdot mol^{-1}$	ρ/$g \cdot cm^{-3}$	η/mPa·s	Re^a	θ/°C	t/s	p/MPa	V/$cm^3 \cdot mol^{-1}$	ρ/$g \cdot cm^{-3}$	η/mPa·s	Re^a
5.9 mm Sinker													
0.00	3128	0.1	204.61	1.3889	1717	0.002	50.00	133.5	0.1	211.01	1.3468	73.6	0.79
5.00	2037	0.1	205.25	1.3846	1119	0.004	50.00	134.3	0.1	211.01	1.3468	74.1	0.79
10.00	1374	0.1	205.89	1.3803	755	0.008	50.00	135.7	1.3	210.89	1.3475	74.9	0.77
15.00	947.8	0.1	206.53	1.3760	521	0.016	50.00	139.5	3.1	210.71	1.3487	76.9	0.73
20.00	671.7	0.1	207.17	1.3717	369	0.032	50.00	141.8	5.6	210.46	1.3503	78.2	0.71
25.00	495.3	0.1	207.82	1.3674	273	0.059	50.00	150.0	10.7	209.96	1.3535	82.7	0.63
25.00	492.0	0.1	207.82	1.3674	271	0.060	50.00	179.8	25.8	208.60	1.3623	98.9	0.44
25.00	598.1	12.1	206.77	1.3744	329	0.041	50.00	232.8	50.8	206.58	1.3757	127.8	0.27
25.00	712.2	24.7	205.75	1.3812	391	0.029	50.00	316.7	75.8	204.83	1.3874	173.5	0.15
25.00	710.3	25.7	205.67	1.3817	390	0.029	50.00	409.6	100.7	203.31	1.3978	224	0.088
25.00	996.7	50.6	203.86	1.3940	546	0.015	50.00	514.5	125.5	201.96	1.4071	281	0.057
25.00	1391	75.8	202.26	1.4050	761	0.008	50.00	679.3	150.4	200.77	1.4155	371	0.033
25.00	1918	100.3	200.89	1.4146	1047	0.004	50.00	883.1	175.2	199.70	1.4231	481	0.019
25.00	2627	125.1	199.66	1.4233	1432	0.002	50.00	1131	200.0	198.73	1.4299	616	0.012
25.00	2679	125.6	199.64	1.4235	1461	0.002	50.00	1442	224.6	197.87	1.4362	784	0.007
25.00	3663	150.3	198.54	1.4313	1995	0.001	50.00	1832	249.3	197.08	1.4420	995	0.005
25.00	4953	174.1	197.59	1.4382	2694	0.001	60.00	88.7	0.1	212.30	1.3386	49.0	1.8
30.00	366.7	0.1	208.47	1.3632	202	0.11	60.00	89.1	0.1	212.30	1.3386	49.2	1.8
40.00	217.0	0.1	209.73	1.3550	120	0.30							
6.0 mm Sinker													
35.00	478.0	0.1	209.09	1.3591	158.4	0.13	70.00	118.0	10.6	212.47	1.3375	39.2	2.0
35.00	482.0	0.9	209.02	1.3596	159.7	0.13	70.00	137.5	25.7	210.98	1.3470	45.6	1.5
35.00	540.8	9.6	208.21	1.3649	179.1	0.10	70.00	175.2	50.6	208.80	1.3610	58.0	0.93
35.00	668.5	25.8	206.83	1.3740	221	0.067	70.00	223.4	75.6	206.92	1.3734	73.7	0.58
35.00	914.3	50.3	204.97	1.3864	302	0.036	70.00	281.8	100.6	205.28	1.3844	92.9	0.37
35.00	1252	75.6	203.30	1.3978	412	0.020	70.00	353.1	125.4	203.85	1.3941	116.2	0.24
35.00	1695	100.3	201.86	1.4078	557	0.011	70.00	403.3	140.2	203.07	1.3994	132.6	0.18
35.00	2285	125.2	200.58	1.4168	750	0.006	70.00	439.5	149.9	202.59	1.4027	144.4	0.15
35.00	2737	140.6	199.86	1.4219	898	0.004	70.00	536.7	172.9	201.53	1.4101	176.1	0.10
35.00	3098	151.0	199.40	1.4252	1016	0.003	80.00	76.7	0.1	214.90	1.3224	25.5	4.7
70.00	105.5	0.1	213.60	1.3304	35.1	2.5	80.00	76.7	0.1	214.90	1.3224	25.5	4.7
70.00	111.9	5.5	213.00	1.3341	37.2	2.2							
6.3 mm Sinker													
40.00	4234	0.1	209.73	1.3550	120.0	0.05	60.00	3031	51.1	207.65	1.3685	85.6	0.10
50.00	2641	0.1	211.01	1.3468	74.9	0.12	60.00	3897	75.7	205.87	1.3804	109.8	0.06
60.00	1755	0.1	212.29	1.3386	49.9	0.28	60.00	4548	91.1	204.87	1.3871	128.0	0.04
60.00	1742	0.1	212.29	1.3386	49.5	0.28	60.00	4955	100.1	204.32	1.3909	139.4	0.04
60.00	1742	0.1	212.29	1.3386	49.5	0.28	70.00	1219	0.1	213.59	1.3305	34.7	0.57
60.00	1967	10.7	211.21	1.3455	55.8	0.22	70.00	1217	0.1	213.59	1.3305	34.6	0.57
60.00	2332	26.2	209.74	1.3549	66.0	0.16							

[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.[14]

Table 4. Coefficients of Best Fit for Equations 10 and 11

modified Litovitz eq			modified VFT eq		
coefficient		standard uncertainty	coefficient		standard uncertainty
a	−0.406 1	0.014	a'	−2.654	0.13
$b \times 10^3/MPa^{-1}$	2.354	0.21	$b' \times 10^3/MPa^{-1}$	−2.323	0.32
$c \times 10^{-6}/K^3$	159.49	0.43	c'/K	1121	37
d x $10^{-6}/(K^3 \cdot MPa^{-1})$	0.3167	0.0068	$d'/(K \cdot MPa^{-1})$	2.269	0.067
$e/(K^3 \cdot MPa^{-2})$	−191.3	17	$e' \times 10^5/(K \cdot MPa^{-2})$	−94.45	8.3
			T_0/K	162.2	2.4
standard uncertainty of fit		1.8 %	standard uncertainty of fit		1.8 %

parameter D ($\equiv B'/T_0$) is large for "strong" liquids where the viscosity approaches an Arrhenius (Andrade) temperature dependence and is small for "fragile" liquids.[1,36] The VFT equation gives a slightly better fit than the Litovitz, 1.2 %, with $A' = (0.06923 \pm 0.0080)$ mPa·s, $B' = (1127 \pm 32)$ K, and $T_0 = (161.8 \pm 2.0)$ K. The glass temperature is 197.15 K,[5] giving a ratio to T_0 of 1.22 and a D value of 7.0, typical values for a moderately fragile liquid.[36] Our parameters are somewhat different from those of Tokuda et al.,[4] who report $A' = (0.36 \pm 0.5)$ mPa·s, $B' = (639 \pm 25)$ K, and $T_0 = (201 \pm 2)$ K for 10 < θ/°C < 80.

Figure 3b shows the deviations of literature data from the Litovitz equation. While there is considerable scatter and most results lie lower than ours, there is general agreement for the temperature dependence for the majority of data sets: the exception is the rolling-ball data set of Okoturo and VanderNoot.[34] Our results are in good agreement with those of Seddon et al.[2] below 30 °C, but their values are generally higher above this temperature.

The temperature and density dependence of the transport properties of liquids are usually best represented as functions of the molar volume. For some molecular liquids, $\sqrt{T}/\eta$ isotherms form a family of curves that may be collapsed onto a common curve by suitable shifts along the molar volume axis.[13,37] This is not the case for [BMIM]PF_6. For other molecular liquids, the Dymond reduced fluidity {which is often used to relate simulation results for model fluids (e.g., hard spheres and Lennard−Jones) to those for real fluids} can be used in place of $\sqrt{T}/\eta$,[38,39] but again the isotherms for [BMIM]PF_6 do not form a family collapsible

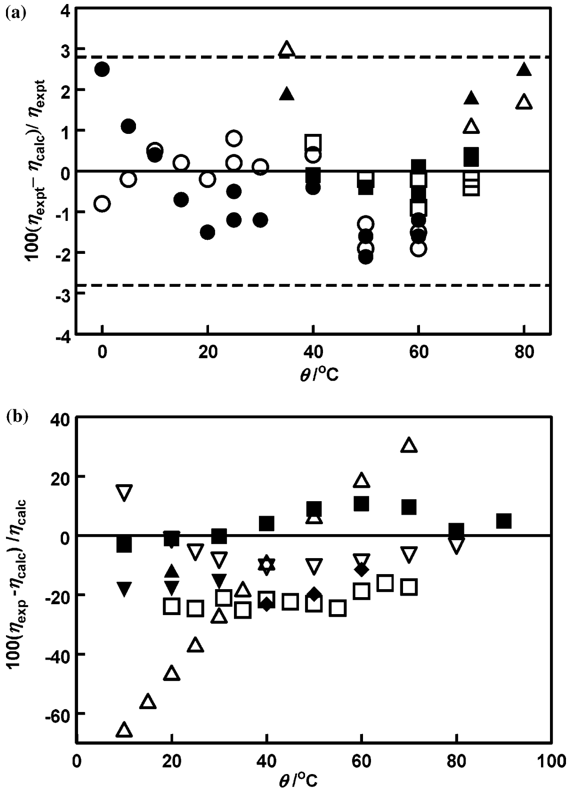

Figure 3. (a) Residuals (experimental − calculated values) for the fit of the experimental viscosities for [BMIM]PF_6 at atmospheric pressure to eq 8 (Litovitz, closed symbols) and eq 9 (VFT, open symbols) as a function of temperature, θ. Sinkers: ●, ○, 5.9 mm; ▲, △, 6.0 mm; ■, □, 6.3 mm. The dashed lines represent the expanded uncertainty of fit or 95 % confidence limits for the Litovitz equation. (b) Residuals (experimental − calculated values) for the fit of the literature viscosities for [BMIM]PF_6 at atmospheric pressure to eq 8 as a function of temperature, θ. Symbols: ■, ref 2; ▲, ref 30; □, ref 31; ▼, ref 32; ◆, ref 33; △, ref 34, ▽, ref 4.

onto a common curve. Despite its large molecular cation, [BMIM]PF_6 behaves differently than molecular liquids.

Examination of the data showed that individual isotherms approximate exponential functions of the pressure, although a better fit is obtained by including a p^2 term in the exponent. In our experience, this is certainly not the case for molecular fluids. Isobars can be fitted to both the Litovitz and VTF equations: the preexponential term decreases with increasing pressure in both cases, whereas the coefficient of the temperature term increases. Interestingly, T_0 in the VTF equation is found to be independent of pressure. These findings have been used to construct modified Litovitz and VTF equations to fit the data set as a whole:

$$\eta = \exp\{a + bp + (c + dp + ep^2)/T^3\} \tag{10}$$

$$\eta = \exp\{a' + b'p + (c' + d'p + e'p^2)/(T - T_0)\} \tag{11}$$

The quality of the fits for the two equations is very similar: coefficients are given in Table 4, and a residual plot for the Litovitz equation is shown as Figure 4. The modified VFT equation yields a pressure-dependent strength parameter, $D = (c' + d'p + e'p^2)/T_0$, that increases with increasing pressure, from 6.9 at atmospheric pressure to 8.9 at 150 MPa (with $T_0 = 162.3$ K).

Figure 5 shows the apparent "activation" volumes, $V^{\ddagger}$, derived from the modified VFT equation parameters, as a function of temperature and pressure. $V^{\ddagger}$ decreases with increasing temperature at constant pressure. Palmer et al.[40] have reported a similar result for the self-diffusion coefficient of [BMIM]$^+$ in liquid [BMIM]PF_6 at pressures to 300 MPa from fits to a simple exponential in the pressure but report lower values of $V^{\ddagger}$ (approximately 15 to 19 $cm^3 \cdot mol^{-1}$). Our own self-diffusion data, to be reported elsewhere, fit the diffusion analogues of eqs 10 and 11 with $V^{\ddagger}$ values about 5 $cm^3 \cdot mol^{-1}$ lower than those for the viscosity. Despite these differences it is clear that the pressure and density dependence of the viscosity and diffusion coefficients of this molten salt are qualitatively different from that observed for molecular liquids. Unfortunately, the literature data for the viscosity of molten salts under pressure are either not extensive enough for comparison, as in the case of alkali metal nitrates,[8] which are limited to pressures below 40 MPa, or are for network-forming liquids that show anomalous pressure dependence.[9,10] It will be interesting to see whether the behavior observed for [BMIM]PF_6 holds true more generally for other molten salts and what is the effect of ion association.

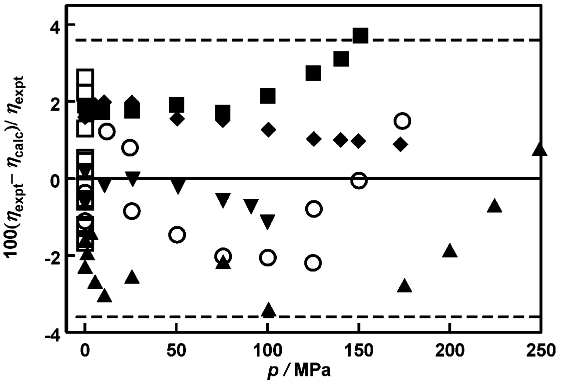

Figure 4. Residuals (experimental − calculated values) for the fit of the experimental viscosities for [BMIM]PF_6 to eq 10 (modified Litovitz) as a function of pressure, p. Symbols: □, 0.1 MPa, (0−80) °C; ○, 25 °C; ■, 35 °C; ▲, 50 °C; ▼, 60 °C; ◆, 70 °C. The dashed lines represent the expanded uncertainty of fit or 95 % confidence limits.

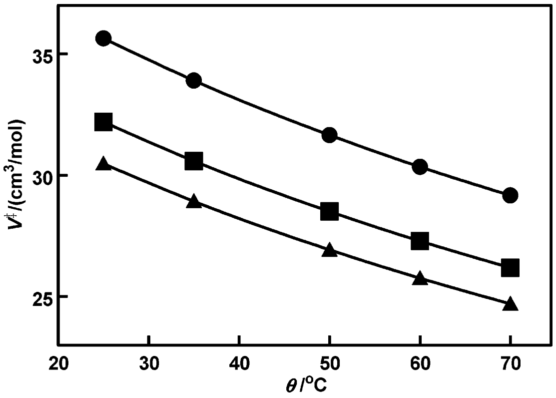

Figure 5. "Activation" volume $V^{\ddagger}$ (derived from fit to the VFT equation) as a function of θ. Symbols: ●, 0.1 MPa; ■, 100 MPa; ▲, 150 MPa.

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Literature Cited

(1) Xu, W.; Cooper, E. I.; Angell, C. A. Ionic liquids: ion mobilities, glass temperatures, and fragilities. *J. Phys. Chem. B* **2003**, *107*, 6170−6178.

(2) Seddon, K. R.; Stark, A.; Torres, M.-J. Viscosity and density of 1-alkyl-3-methylimidazolium ionic liquids. In *Clean Solvents: Alternative Media for Chemical Reactions and Processing*; Abraham, M. A., Moens, L., Eds.; ACS Symposium Series 819; American Chemical Society: Washington, DC, 2002; pp 34−49.

(3) Carda-Broch, S.; Berthod, A.; Armstrong, D. W. Solvent properties of the 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid. *Anal. Bioanal. Chem*. **2003**, *375*, 191−199.

(4) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. Physicochemical properties and structures of room-temperature ionic liquids. 1. Variation of anionic species. *J. Phys. Chem. B* **2004**, *108*, 16593−16600.

(5) Fredlake, C. P.; Crosthwaite, J. M.; Hert, D. G.; Aki, S. N. V. K.; Brennecke, J. F. Thermophysical properties of imidazolium-based ionic liquids. *J. Chem. Eng. Data* **2004**, *49*, 954−964.

(6) Umecky, T.; Kanakubo, M.; Ikushima, Y. Self-diffusion coefficients of 1-butyl-3-methylimidazolium hexafluorophosphate with pulsed-field gradient spin−echo NMR technique. *Fluid Phase Equilib.* **2005***, 228−229*, 329−333.

(7) Antony, J. H.; Mertens, D.; Breitenstein, T.; Dölle, A.; Wasserscheid, P.; Carper, W. R. Molecular structure, reorientational dynamics, and intermolecular interactions in the neat ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate. *Pure Appl. Chem.* **2004**, *76*, 255−261.

(8) Copeland, J. L.; Christie, J. R. On the constant volume viscous properties of molten alkali nitrates. *J. Chem. Phys.* **1971**, *55*, 4925−4932.

(9) Kushiro, I. Changes in viscosity and structure of melt of NaAlSi$_2$O$_6$ [jadeite] composition at high pressures. *J. Geophys. Res.* **1976**, *81*, 6347−6350.

(10) Cleaver, B.; Koronaios, P. Effect of pressure on the viscosity of liquid ZnCl$_2$. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 1601−1604.

(11) Gu, Z.; Brennecke, J. F. Volume expansivities and isothermal compressibilities of imidazolium and pyridinium-based ionic liquids. *J. Chem. Eng. Data* **2002**, *47*, 339−345.

(12) Malhotra, R.; Price, W. E.; Woolf, L. A.; Easteal, A. J. Thermodynamic and transport properties of 1,2-dichloroethane. *Int. J. Thermophys*. **1990**, *11*, 835−861.

(13) Harris, K. R. Temperature and density dependence of the viscosity of toluene. *J. Chem. Eng. Data* **2000**, *45*, 893−897.

(14) Isdale, J. D.; Spence, C. M. A. Self-Centering Falling Body Viscometer for High Pressures. National Engineering Laboratory Report 592: Department of Industry: UK, 1975.

(15) Isdale, J. D.; Easteal, A. J.; Woolf, L. A. Shear viscosity of methanol and methanol + water mixtures under pressure. *Int. J. Thermophys*. **1985**, *6*, 439−450.

(16) Dymond, J. H.; Young, K. J.; Isdale, J. D. Transport properties of nonelectrolyte liquid mixtures. II. Viscosity coefficients for *n*-hexane + *n*-hexadecane system at temperatures from 25 to 100 °C at pressures up to the freezing pressure or 500 MPa. *Int. J. Thermophys*. **1980**, *1*, 345−373.

(17) Cappi, J. B. The Viscosity of Water at High Pressure. Thesis, Imperial College of Science and Technology, University of London, 1964; p 62.

(18) Harlow, A. Further Investigations into the Effect of High Pressure on the Viscosity of Liquids. Thesis, Imperial College of Science and Technology, University of London, 1967; p 91.

(19) Harris, K. R.; Woolf, L. A. Temperature and volume dependence of the viscosity of water and heavy water at low temperatures. *J. Chem. Eng. Data* **2004**, *49*, 1064−1069.

(20) Irving, J. B.; Barlow, A. J. An automatic high-pressure viscometer. *J. Phys. E: Sci. Instrum.* **1971**, *4*, 232−236.

(21) Scott, R. The Viscosity of Argon. Thesis, Imperial College of Science and Technology, University of London, 1959.

(22) Rossen, W. R.; Kohn, J. P. Behaviour of microemulsions under compression. *Soc. Pet. Eng. J.* **1984**, *24*, 536−544.

(23) Dymond, J. H.; Malhotra, R.; Isdale, J. D.; Glen, N. F. (p, ρ, T) of *n*-heptane, toluene and oct-1-ene in the range 298 to 373 K and 0.1 to 400 MPa and representation by the Tait equation. *J. Chem. Thermodym*. **1988**, *20*, 603−614.

(24) Easteal, A. J.; Woolf, L. A. *p, V, T* and derived thermodynamic data for bromobenzene at temperatures from 278 to 323 K and pressures up to 280 MPa. *Int. J. Thermophys.* **1988**, *8*, 557−565.

(25) Harris, K. R. Temperature and density dependence of the self-diffusion coefficient of *n*-hexane from 223 to 333 K and up to 400 MPa. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 2265−2275.

(26) Fitzgerald, D. *Technical Assessment of the Anton Paar DMA5000 Density Meter*; H. and D. Fitzgerald Ltd: St Asaph, U.K., 2000; http://www.density.co.uk/review_of_5000.pdf.

(27) Suarez, P. A. Z.; Einloft, S.; Dullius, J. E. L.; de Souza, R. F.; Dupont, J. Synthesis and physical−chemical properties of ionic liquids based on the 1-*n*-butyl-3-methylimidazolium cation. *J. Chim. Phys.* **1998**, *95*, 1626−1639.

(28) Dzyuba, S. V.; Bartsch, R. A. Influence of structural variations in 1-alkyl(aralkyl)-3-methylimidazolium hexafluorophosphates and bis(trifluromethylsulfonyl)imides on physical properties of the ionic liquids. *ChemPhysChem* **2002**, *3*, 161−166.

(29) Kabo, G. J.; Blokhin, A. V.; Paulechka, Y. U.; Kabo, A. G.; Shymanovich, M. P.; Magee, J. W. Thermodynamic properties of 1-butyl-3-methylimidazolium hexafluorophosphate in the condensed state. *J. Chem. Eng. Data* **2004**, *49*, 453−461.

(30) Gordon, C. M.; McLean, A. J. Photoelectron transfer from excited-state ruthenium(II) tris(bipyridyl) to methylviologen in an ionic liquid. *Chem. Commun.* **2000**, *100*, 1395−1396.

(31) Baker, S. N.; Baker, G. A.; Kane, M. A.; Bright, F. V. The cybotactic region surrounding fluorescent probes dissolved in 1-butyl-3-methylimidazolium hexafluorophosphate: effects of temperature and added carbon dioxide. *J. Phys. Chem. B* **2001**, *105*, 9663−9668.

(32) Branco, L. C.; Rosa, J. N.; Moura Ramos, J. J.; Alfonso, C. A. M. Preparation and characterization of new room-temperature ionic liquids. *Chem. Eur. J.* **2002**, *8*, 3671−3677.

(33) Liu, Z.; Wu, W.; Han, B.; Dong, Z.; Zhao, G.; Wang, J.; Jiang, T.; Yang, G. Study on the phase behaviours, viscosities, and thermodynamic properties of CO$_2$/[C$_4$mim][PF$_6$]/methanol system at elevated pressures. *Chem. Eur. J.* **2003**, *9*, 3897−3903.

(34) Okoturo, O. O.; VanderNoot, T. J. Temperature dependence of viscosity for room-temperature ionic liquids. *J. Electroanal. Chem.* **2004**, *568*, 167−181.

(35) Litovitz, T. A. Temperature dependence of the viscosity of associated liquids. *J. Chem. Phys.* **1952**, *20*, 1088−1089, 1980.

(36) Angell, C. A. Formation of glasses from liquids and biopolymers. *Science* **1995**, *267*, 1924−1935.

(37) Harris, K. R.; Newitt, P. J.; Woolf, L. A. Temperature and density dependence of the viscosity of cyclopentane. *J. Chem. Eng. Data* **2004**, *49*, 138−142.

(38) Dymond, J. H. The interpretation of transport coefficients on the basis of the van der Waals model. I. Dense fluids. *Physica A* **1974**, *75*, 100−114.

(39) Harris, K. R. Correlation of dense fluid self-diffusion and shear viscosity coefficients. *High Temp.—High Pressures* **1993**, *25*, 359−366.

(40) Palmer, G.; Richter, J.; Zeidler, M. D. An NMR spin−echo study of diffusion in a room-temperature molten salt. *Z. Naturforsch.* **2004**, *59A*, 59−63.

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