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Viscosity of [bmim][PF$_6$] and [bmim][BF$_4$] at High Pressure[1]

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The viscosities of 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF$_6$]) and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF$_4$]) were measured by using a rolling-ball viscometer. The experimental temperatures were from 293.15 to 353.15 K, and the pressures were from 0.1 to 20.0 MPa.

KEY WORDS: [bmim][BF$_4$]; [bmim][PF$_6$]; high pressure; ionic liquids; rolling-ball viscometer; viscosity.

1. INTRODUCTION

Ionic liquids draw much attention as green solvents [1–3] since they have almost no vapor pressure and can be used repeatedly after extracting reaction products.

The viscosity of ionic liquids is one of the most important properties since they have high viscosity compared to conventional organic solvents [4]. There are, however, a few studies about the viscosity of ionic liquids. In this study, we measured the viscosity of two ionic liquids, [bmim][PF$_6$] and [bmim][BF$_4$], since these ionic liquids are widely used as solvents or catalysts for many reactions such as Diels-Alder and Heck reactions. The viscosities of these ionic liquids at normal pressure were reported by several researchers [5–14], but the literature values generally show large discrepancies because of different measurement methods and/or the purity of

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liquid samples. Furthermore, there are few studies about the viscosity of ionic liquids at high pressure.

The viscosities and densities of [bmim][PF_6] and [bmim][BF_4] were measured at temperatures from 293.15 to 353.15 K and at pressures from 0.1 to 20.0 MPa. The experimental values were compared with literature values at 0.1 MPa. These results were correlated with the Vogel–Tamman–Fulcher (VTF) equation and a Tait-form equations.

2. EXPERIMENTAL

The liquid samples of [bmim][PF_6] and [bmim][BF_4] were prepared in our laboratory following the procedures reported by other authors [15–17]. The product purity was confirmed by CHN elementary analysis (Table I). The ionic liquids were degassed and dried under vacuum for 24 h at a temperature of approximately 333.15 K before measuring the viscosity. The water content of each ionic liquid was determined using coulometric Karl–Fischer titration (Mitsubishi Chemical, Co., CA-02) after the viscosity measurements were completed. Chloride measurements were conducted using a chloride-selective electrode (Thermo Electron, Co.). The results are listed in Table I.

The viscosities were measured by using a rolling-ball viscometer. The viscometer constructed in this study is illustrated in Fig. 1. The glass tube was approximately 10 cm in length with an internal diameter of 7.15 mm (± 0.01 mm), and the diameter of the stainless steel ball was 7.00 mm (± 0.01 mm). The upper part of the glass tube is open in order to produce equal pressure inside and outside of the glass tube. The pressure was regulated with movement of a piston in a lower position of the viscometer

Table I. Purity of Synthesized Ionic Liquids

	[bmim][PF_6]		[bmim][BF_4]	
	Calculated	Found	Calculated	Found
Element	(mass%)		(mass%)	
C	33.81	33.53	42.53	41.31
H	5.32	5.18	6.64	6.45
N	9.86	9.86	12.39	12.22
Water (ppm)	130 ± 43		336 ± 100	
[Cl^-] (ppm)	–[a]		421 ± 1	

[a] detection limit <18 ppm.

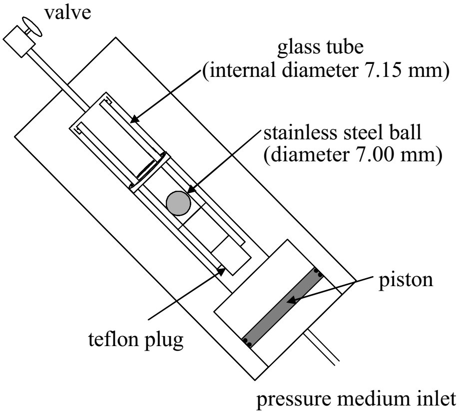

Fig. 1. Rolling-ball viscometer.

with the use of a pressure medium. The temperature of the thermostat was measured with a quartz thermometer. The pressure was measured with a Bourdon tube pressure gauge that is calibrated periodically against a deadweight gauge. The densities of the sample fluid were obtained by using a glass piezometer that was used in a previous study [18].

The viscosity, η, was calculated from the fall time of the ball, t, using the following equation:

$$\eta = K(\rho_s - \rho)t \tag{1}$$

where K is the viscometer constant, and ρ_s and ρ are the densities of the stainless steel ball and sample fluid, respectively. Since the viscometer constant depends on both the temperature and pressure, it should be determined at each temperature and pressure. Based on the Hubbard and Brown [19] and Lewis [20] equations, Izuchi and Nishibata [21] proposed the following equation:

$$\begin{aligned}(K/l)/(K_0/l_0) = 1 &+ \left\{\beta_b + \left(\frac{r}{1+r} - \frac{5}{2}\frac{r}{1-r}\right)(\beta_b - \beta_t)\right\}(T - T_0) \\ &- \left\{\kappa_b + \left(\frac{r}{1+r} - \frac{5}{2}\frac{r}{1-r}\right)(\kappa_b - \kappa_t)\right\}P\end{aligned} \tag{2}$$

where β_b and β_t are the thermal expansion coefficients of the ball and tube materials; κ_b and κ_t are the linear compressibilities of those materials; l is the distance for measuring the fall time of the ball; $r(=d_0/D_0)$ is the diameter ratio of the ball to the tube at the reference condition (293.15 K, 0.1 MPa); T and T_0 are the temperatures of the viscometer at the measuring and reference conditions, respectively; and P is the pressure. The viscometer constant K_0 at 293.15 K and 0.1 MPa was determined by using a standard liquid for calibration of the viscometer, that is, by using JS100 from the National Metrology Institute of Japan. The experimental uncertainties in temperature and pressure are estimated to be within ±10 mK and ±0.1 MPa, respectively. The uncertainty of the reported viscosity data is estimated to be ±2.1%.

In order to demonstrate the reliability of the experimental procedures for the rolling-ball viscometer used here, viscosities at 0.1 MPa were also measured using a capillary viscometer described in detail in a previous paper [22] with measurements on the same ionic liquids.

3. RESULTS

The experimental viscosity data of [bmim][PF$_6$] and [bmim][BF$_4$] are given in Tables II and III together with values for the density under the same conditions, which are interpolated from the experimental density values. The density has an estimated uncertainty of ±0.2%. No literature viscosity values have been found for [bmim][PF$_6$] and [bmim][BF$_4$] except at 0.1 MPa. Therefore, the experimental values were compared with literature

Table II. Viscosity and Density of [bmim][PF$_6$]

T(K)	P(MPa)	ρ(kg m^{-3})	η(mPa s)
293.15	0.1	1370	382
	5.0	1372	409
	10.0	1374	442
	15.0	1377	468
	20.0	1379	504
313.15	0.1	1354	119
	5.0	1357	126
	10.0	1359	133
	15.0	1362	140
	20.0	1364	151
333.15	0.1	1337	52.5
	5.0	1340	55.3
	10.0	1343	58.2
	15.0	1346	61.0
	20.0	1349	63.2
353.15	0.1	1321	25.7
	5.0	1324	26.9
	10.0	1327	28.1
	15.0	1330	29.3
	20.0	1332	30.5

Table III. Viscosity and Density of [bmim][BF_4]

T(K)	P(MPa)	ρ(kg m^{-3})	η(mPa s)
293.15	0.1	1211	132
	5.0	1213	139
	10.0	1215	147
	15.0	1217	155
	20.0	1219	163
313.15	0.1	1196	50.5
	5.0	1198	52.7
	10.0	1200	55.1
	15.0	1202	57.5
	20.0	1204	60.0
333.15	0.1	1182	23.7
	5.0	1185	24.5
	10.0	1187	25.4
	15.0	1190	26.3
	20.0	1192	27.2
353.15	0.1	1168	13.2
	5.0	1171	13.6
	10.0	1173	14.1
	15.0	1176	14.6
	20.0	1179	15.0

Table IV. Comparison of Present Viscosities of [bmim][PF_6] at 0.1 MPa with Previous Results

Author	This work	This work	Seddon et al. [5]	Liu et al. [6]
Method	Rolling ball (mPa s)	Capillary (mPa s)	Cone and plate (mPa s)	Falling ball (mPa s)
293.15 K	382	391	371	–
313.15 K	119	123	125	92.3
333.15 K	52.5	51.3	55.1	44.1
353.15 K	25.7	25.8	25.3	–

values [5, 6] only at 0.1 MPa (Tables IV and V). As can be seen from Table IV, the results of this work for [bmim][PF_6] were in good agreement with the literature values of Seddon et al. [5]. But the viscosities reported by Liu et al. [6] were lower than our experimental values. Widegren et al. [23] studied the effect of dissolved water on the viscosities of ionic liquids at 293.15 K. It was found that the addition of 100 ppm water decreased the viscosity about 1%. The viscosity of [bmim][PF_6] at 293.15 K with 30 ppm

Table V. Comparisons of Present Viscosities of [bmim][BF_4] at 0.1 MPa with Previous Results

Author	This work	This work	Seddon et al. [5]
Method	Rolling ball (mPa s)	Capillary (mPa s)	Cone and plate (mPa s)
293.15 K	132	133	154
313.15 K	50.5	51.1	59.1
333.15 K	23.7	23.9	28.0
353.15 K	13.2	13.5	15.5

water was 394 mPas. Our experimental value is expected to be about 1% lower than the value of Widegren et al. Therefore, it was in good agreement with their value. The sample of Liu et al. contains 1000 ppm water. This is the main reason for discrepancies between our experimental values and their results.

Table V shows comparisons of experimental viscosity values of [bmim] [BF_4] with literature values [5]. In spite of the different experimental methods, values obtained by the rolling-ball and capillary viscometers were in good agreement. But when compared with the literature values of Seddon et al. [5], deviations were larger than 15%. The chloride content of our sample is higher than that of Seddon et al., while the water content is almost the same. Hence, our values are expected to be higher than their values. But, in practice, our values were lower than their results. Although the different measurement methods may be the cause of the discrepancies between our values and their results, we cannot make any definitive conclusions.

The viscosities at 0.1 MPa were correlated with the VTF empirical equation [24, 25]:

$$\eta = \eta' \exp[B/(T - T_0)] \tag{3}$$

where η', B, and T_0 are adjustable parameters, which are calculated using experimental data and a least-squares method. The VTF equation parameters are listed in Table VI. The VTF equation was used to correlate the experimental data of [bmim][PF_6] and [bmim][BF_4] and showed maximum deviations of 3.7% and 1.1%, respectively.

The experimental viscosity data at high pressures were fitted with a Tait-form equation in terms of viscosity [26];

$$\ln\left(\eta_p/\eta_0\right) = E \ln\left[(D + P) \,/\, (D + 0.1)\right] \tag{4}$$

Table VI. VTF Equation Parameters

	$\eta'(10^{-1}$ mPa s)	$B(10^2$ K)	$T_0(10^2$ K)
[bmim][PF$_6$]	1.06	10.0	1.71
[bmim][BF$_4$]	0.933	9.37	1.64

Table VII. Tait-form Equation Parameters

	D	E
[bmim][PF$_6$]	1.914T/K—374.8	2.7
[bmim][BF$_4$]	1.612T/K—326.0	1.6

where η_p and η_0 are the viscosities at a pressure P and at 0.1 MPa, respectively. E and D are adjustable parameters. Table VII shows the values of the parameters determined from the present data. The E values are constant. The D values are given as linear functions of temperature. If the value calculated with the VTF equation is substituted for η_0, the viscosity at an arbitrary temperature and pressure could be interpolated. The results are shown in Figs. 2 and 3. This equation correlated the experimental values of [bmim][PF$_6$] and [bmim][BF$_4$] with maximum deviations of 4.2% and 1.4%, respectively.

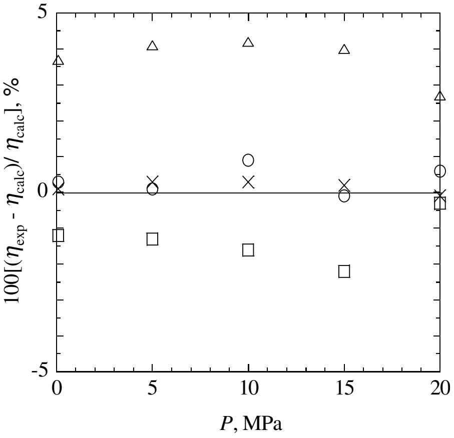

Fig. 2. Deviations of the experimental values of the viscosity of [bmim][PF$_6$] from Eq. (4): (○) 293.15 K, (□) 313.15 K, (△) 333.15 K, (×) 353.15 K.

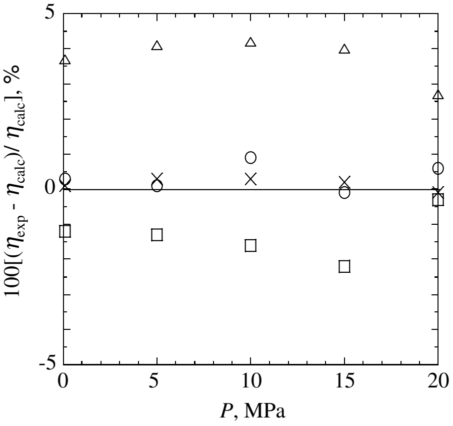

Fig. 3. Deviations of the experimental values of the viscosity of [bmim][BF_4] from Eq. (4): (○) 293.15 K, (□) 313.15 K, (△) 333.15 K, (×) 353.15 K.

4. CONCLUSION

The viscosities of [bmim][PF_6] and [bmim][BF_4] were measured at temperatures from 293.15 to 353.15 K and at pressures from 0.1 to 20 MPa with an uncertainty of ±2.1%. The VTF and Tait-form equations were use to correlate the experimental data of [bmim][PF_6] and [bmim][BF_4] within 4.2% and 1.4%, respectively.

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