Viscosity of 1-Hexyl-3-methylimidazolium Hexafluorophosphate and 1-Octyl-3-methylimidazolium Hexafluorophosphate at High Pressure

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The viscosities of 1-hexyl-3-methylimidazolium hexafluorophosphate ([hmim][PF_6]) and 1-octyl-3-methylimidazolium hexafluorophosphate ([omim][PF_6]) were measured with a rolling ball viscometer. The experimental temperatures were from (293.15 to 353.15) K and pressures were up to 20.0 MPa. The experimental values were correlated with a Vogel−Tamman−Fulcher (VTF) equation and a Tait-form equation.

Introduction

Ionic liquids (ILs) are called “designer solvent” since various thermophysical properties and functions can be created by the choice of cation and anion. In order to design ionic liquids with the thermophysical properties according to the purpose, much knowledge is required. Viscosity is one of the most important thermophysical properties since ILs have generally high viscosity compared to conventional organic solvents.[1] Several researchers reported the viscosities of different class of ILs at normal pressure.[2−10] Also, there are only a few reports about the viscosity of ILs at high pressure.[11−13] Liu et al.[11] measured viscosities of the mixtures of CO_2 and 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) at vapor−liquid equilibrium (VLE) conditions with a falling ball viscometer. Their viscosity values of [bmim][PF_6] at 0.1 MPa, however, deviate more than 20 % from those of Seddon et al.[3] Harris et al.[12,13] measured viscosities of [bmim][PF_6], 1-octyl-3-methylimidazolium hexafluorophosphate ([omim][PF_6]), and 1-octyl-3-methylimidazolium tetrafluoroborate ([omim][BF_4]) at high pressures with a falling body viscometer. However, there are hardly sufficient experimental viscosity data for ionic liquids. In order to develop correlation methods and a reliable database of viscosity of ionic liquids appreciable over a wide range of temperature and pressure, it is necessary to accumulate experimental data of thermophysical properties of various ionic liquids.

In our continuing work on the experimental determination of viscosity for the system containing ILs, we reported the viscosities of [bmim][PF_6] and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) in our previous paper.[14] In this paper, we report the viscosities of 1-hexyl-3-methylimidazolium hexafluorophosphate ([hmim][PF_6]) and [omim][PF_6]. The viscosities and densities of [hmim][PF_6] and [omim][PF_6] were measured at temperatures from (293.15 to 353.15) K and pressures up to 20.0 MPa. These results were correlated with the Vogel−Tamman−Fulcher (VTF) equation and a Tait-form equation.

Experimental Section

Materials. [hmim][PF_6] and [omim][PF_6] were prepared following the procedures reported by other authors.[15,16] The purities of products were confirmed by CHN elementary analysis (Table 1). They were degassed and dried under vacuum for 24 h at a temperature of approximately 343.15 K before measurement. After measurement, a water content of the ionic liquid sample was determined with a coulometric Karl Fischer titration apparatus (Mitsubishi Chemical, Co., CA-02). Measurements of chloride concentrations were conducted using a chloride-selective electrode (Thermo Electron, Co.). The results are listed in Table 1.

Table 1. Purities of Synthesized Ionic Liquids

	100 ω			
	[hmim][PF_6]		[omim][PF_6]	
element	calculated	found	calculated	found
C	38.46	38.25	42.35	42.20
H	6.13	5.99	6.81	6.63
N	8.97	8.96	8.23	8.21
10^6 $\omega(H_2O)$	40		94	
10^6 $\omega(Cl^-)$	*a*		*a*	

[a] Detection limit $< 18 \times 10^{-6}$.

Measurements. The viscosities were measured with a rolling ball viscometer, which has been described in detail elsewhere.[14] The glass tube was approximately 10 cm in length with an internal diameter of 7.30 mm (± 0.01 mm), and the diameter of the stainless steel ball was 7.00 mm (± 0.01 mm). An angle of glass tube is estimated to be about 29.7°, 16.3°, or 9.9°, calculating with the Hubbard-Brown equation.[17] The sample that was degassed and dried under vacuum for 24 h at about 343.15 K was introduced into the viscometer under atmosphere. The densities of sample fluid were obtained by using a glass piezometer, which was used in our previous study.[18] The densities have an estimated uncertainty of ± 0.2 %. The experimental uncertainties in temperature and pressure are estimated within ± 10 mK and ± 0.1 MPa, respectively. The uncertainty of the reported viscosity values is estimated to be ± 1.6 %.

In order to elucidate a consistency of the experimental procedure of the rolling ball viscometer, the viscosities of [hmim][PF_6] and [omim][PF_6] at 0.1 MPa were also measured with a capillary viscometer described previously.[19] The uncertainty of the viscosities was 1.6 %.

Results and Discussion

The experimental viscosity values of [hmim][PF_6] and [omim][PF_6] are given in Tables 2 and 3 together with values of the

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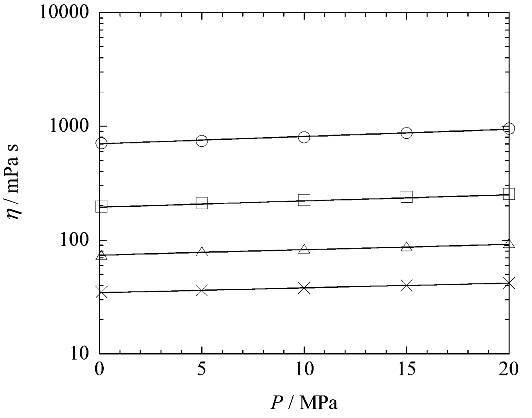

Figure 1. Pressure dependence of the viscosity for [hmim][PF_6]: ○, 293.15 K; □, 313.15 K; △, 333.15 K; ×, 353.15 K; —, correlations.

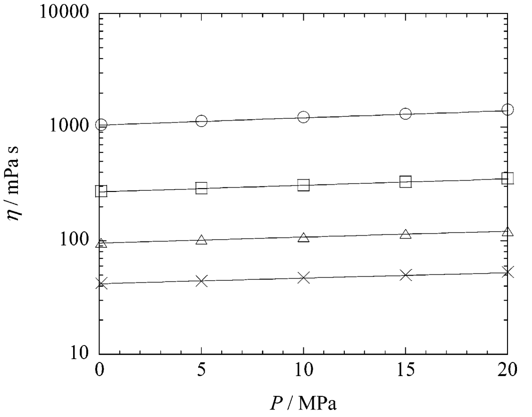

Figure 2. Pressure dependence of the viscosity for [omim][PF_6]: ○, 293.15 K; □, 313.15 K; △, 333.15 K; ×, 353.15 K; —, correlations.

Table 2. Experimental Results of the Viscosities η and Densities ρ of [hmim][PF_6]

T	P	ρ	η	T	P	ρ	η
K	MPa	kg·m^{-3}	mPa·s	K	MPa	kg·m^{-3}	mPa·s
293.15	0.1	1295	707	333.15	0.1	1264	73.8
	5.0	1298	753		5.0	1267	79.4
	10.0	1301	799		10.0	1270	83.8
	15.0	1304	869		15.0	1273	87.6
	20.0	1307	953		20.0	1275	93.7
313.15	0.1	1279	197	353.15	0.1	1248	34.7
	5.0	1282	210		5.0	1251	36.0
	10.0	1285	224		10.0	1254	37.9
	15.0	1288	239		15.0	1257	39.8
	20.0	1291	253		20.0	1260	41.9

Table 3. Experimental Results of the Viscosities η and Densities ρ of [omim][PF_6]

T	P	ρ	η	T	P	ρ	η
K	MPa	kg·m^{-3}	mPa·s	K	MPa	kg·m^{-3}	mPa·s
293.15	0.1	1238	1052	333.15	0.1	1209	95.7
	5.0	1242	1128		5.0	1213	102
	10.0	1245	1218		10.0	1216	107
	15.0	1248	1305		15.0	1219	115
	20.0	1251	1427		20.0	1221	121
313.15	0.1	1223	273	353.15	0.1	1194	42.2
	5.0	1226	290		5.0	1196	44.3
	10.0	1229	308		10.0	1199	47.2
	15.0	1232	329		15.0	1202	49.9
	20.0	1235	354		20.0	1205	53.0

Table 4. Comparison of the Present Viscosity Values of [hmim][PF_6] at 0.1 MPa with Literature Ones

author method	this work rolling ball	this work capillary	Seddon et al.[3] cone and plate
T/K		η/mPa·s	
293.15	707	711	690
313.15	197	199	209
333.15	73.8	74.8	80.3
353.15	34.7	35.2	37.6

Table 5. Comparison of the Present Viscosity Values of [omim][PF_6] at 0.1 MPa with Literature Ones

author method	this work rolling ball	this work capillary	Seddon et al.[3] cone and plate	Harris et al.[13,a] falling body
T/K		η/mPa·s		
293.15	1052	1070	866	1059
313.15	273	279	252	277
333.15	95.7	99.5	94.5	97.9
353.15	42.2	44.1	42.8	42.9

[a] Correlation values.

Table 6. Comparison of the Present Viscosity η (mPa·s) for [omim][PF_6] with Literature Results at 298.15 K

author	η/mPa·s	method	ref
this work	714[a]	rolling ball	
Huddleston et al.	682	rotational	2
Seddon et al.	610[b]	cone and plate	3
McLean et al.	691[c]	cone and plate	6
Fortunato et al.	599[b]	rotating coaxial	8
Harris et al.	731[b]	falling body	13

[a] Correlation value from eq 1. [b] Correlation value. [c] At 298 K.

density under the same conditions and shown graphically in Figures 1 and 2. The experimental values at 0.1 MPa were compared with literature values (Tables 4 and 5). The experimental values obtained with the rolling ball viscometer were in good agreement with those obtained with the capillary viscometer. Compared with the literature values of Seddon et al.[3] for [hmim][PF_6] and [omim][PF_6], there were more than 9 % and 18 % deviations, respectively. It is well-known that the effect of dissolved water on the viscosities of ionic liquids is large. The addition of 100 ppm water decreases the viscosity of [bmim][PF_6] about 1 %. Although there are no literature researched the effect of dissolved water on the viscosities of [hmim][PF_6] and [omim][PF_6], it may be about the same effect of dissolved water on viscosities of [bmim][PF_6]. The sample of Seddon et al. contains 28 ppm ([hmim][PF_6]) and 35 ppm ([omim][PF_6]) water, respectively. The water in the sample of Seddon et al. is lower than ours, but the viscosity values of Seddon et al. are lower than our values at the high viscosity region. This result means the difference of water content in the sample is not main reason for discrepancies between our experimental values and their values. Therefore, we think this difference may be caused by experimental methods.

Table 6 shows the comparison of our results for [omim][PF_6] at 0.1 MPa and 298.15 K with the literature data. The results of Huddleston et al.,[2] McLean et al.,[6] and Harris et al.[13] agree with our values within ± 5 %, while the results of Seddon et al.[3] and Fortunato et al.[8] are much lower than ours.

As there are no viscosity data at high pressure for [hmim][PF_6], the deviation of correlation values of Harris et al.[13] and our experimental values for [omim][PF_6] are shown in Figure 3. It was found that the present viscosity values deviate from the correlation values of Harris et al.[13] with an average deviation of 1.6 % and maximum deviation of 3.0 %.

The viscosities at 0.1 MPa were correlated with the VTF equation expressed as follows:[20−22]

$$\eta = \eta' \exp[B/(T - T_0)] \tag{1}$$

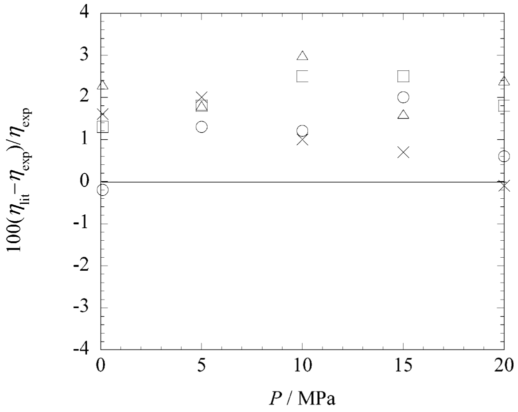

Figure 3. Deviation of experimental data from correlation of Harris et al.[13] for [omim][PF_6]: ○, 293.15 K; □, 313.15 K; △, 333.15 K; ×, 353.15 K.

Table 7. VTF Equation Parameters

	η'	B	T_0	standard uncertainty of fit
	10^{-2} mPa·s	10^3 K	10^2 K	%
[hmim][PF_6]	6.77	1.148	1.69	0.6
[omim][PF_6]	3.55	1.359	1.61	1.1

Table 8. Tait-Form Equation Parameters

	D		standard uncertainty of fit
	MPa	E	%
[hmim][PF_6]	$1.730T/\text{K} - 312.0$	3.0	1.0
[omim][PF_6]	$1.100T/\text{K} - 127.7$	3.0	0.9

where η', B, and T_0 are adjustable parameters. The values of these parameters were determined by using the present experimental results with a least-squares method and are listed in Table 7. The VTF equation correlated the experimental values of [hmim][PF_6] and [omim][PF_6] with maximum deviation of 1.2 % and 1.6 %, respectively.

The experimental viscosity values at high pressure were fitted to a Tait-form equation in terms of viscosity:[23]

$$\ln(\eta_p/\eta_0) = E \ln[(D + P)/(D + 0.1)] \tag{2}$$

where η_p and η_0 are the viscosities at P and 0.1 MPa, respectively. E and D are adjustable parameters. Table 8 shows the values of the parameters determined by using the present experimental results. The E values were a constant. The D values were given by a linear function of the temperature shown in Table 8. If the value calculated with the VTF equation is substituted for η_0 in eq 2, the viscosity at arbitrary temperature and pressure can be interpolated. The results are shown in Figures 1 and 2. Solid lines represent the values calculated from eqs 1 and 2. These equations can correlate the experimental viscosities of [hmim][PF_6] and [omim][PF_6] with maximum deviation of 2.2 % and 2.6 %, respectively.

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