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Viscosity of 1-Butyl-3-methylimidazolium Hexafluorophosphate + CO_2 Mixture

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The viscosities of 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) + CO_2 mixtures 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 CO_2 mole fractions of the mixtures were in the range up to 0.440. The McAllister four-body model has been used to correlate the viscosity data.

Introduction

As alternatives to conventional organic solvents, ionic liquids (ILs) present a wide range of properties for applications as new solvents and catalysts in many areas of organic synthesis and in separation chemistry. As for product separation and catalyst recycling, it is essential to separate the product without degrading the ionic liquids. Supercritical CO_2 has recently been shown to be a potential alternative solvent for extraction of organics from ILs because CO_2 has a remarkably high solubility in ILs.[1,2] It has been demonstrated that the combination of ILs and supercritical CO_2 offers a highly attractive approach for the development of environmentally benign and economically viable homogeneously and/or heterogeneously catalyzed processes.[3−5] To develop these processes based on the ILs + CO_2 systems, several groups have studied the thermophysical properties of the ILs + CO_2 systems. Although over the past few years a number of studies have been done on phase behavior and solubility for the ILs + CO_2 systems, only few attempts have so far been made to measure transport properties such as viscosity and thermal conductivity. Viscosity is one of the most important thermophysical properties to design chemical processes using ILs as solvent, because it affects practical issues such as stirring and pumping.[6] The viscosities of pure ILs have been measured by several researchers. However, only Liu et al. have measured the viscosities of the 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) + CO_2 mixtures along the saturated liquid line.[7]

As a continuous study of viscosity measurements of ILs and asymmetric mixtures consisting of viscous liquids and gases, we have measured viscosities of [bmim][PF_6], 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]), squalane + CO_2, and squalane + butane systems in our previous studies.[8−11] As pointed out in ref 8, our viscosity values of [bmim][PF_6] deviate from those of Liu et al.[7] The purpose of this study is to measure the viscosity of [bmim][PF_6] + CO_2 over a wide range of temperatures and pressures.

Viscosities and densities were measured with a rolling ball viscometer and glass piezometer, respectively. The experimental temperature ranges were from (293.15 to 353.15) K, and pressures were up to 20.0 MPa. The CO_2 mole fraction of the mixtures was in the range up to 0.440.

Table 1. Purities of Synthesized [bmim][PF_6]

	[bmim][PF_6]	
	100 *w*	
element	calculated	found
C	33.81	33.46
H	5.32	5.16
N	9.86	9.84
10^6 w (H_2O)	152 ± 70	
10^6 w (Cl^-)	−[a]	

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

Table 2. Comparison of the Present Viscosity for [bmim][PF_6] with Literature Results at 293.15 K and 0.1 MPa

author	η/mPa·s	method	ref
this work	395	capillary	
our previous work	391	capillary	8
Widegren et al.	394	capillary	15
Harris et al.	369	falling body	16

Experimental Section

Materials. [bmim][PF_6] was prepared following the procedures reported in a previous paper.[12,13] The purity was confirmed by CHN elementary analysis. The water content of ionic liquid was determined by using a coulometric Karl−Fischer titration (Mitsubishi Chemical, Co., CA-02). The results are listed in Table 1. The sample of [bmim][PF_6] was degassed and dried under a vacuum for 24 h at a temperature of approximately 343.15 K before measurement. CO_2 which had a stated purity of 99.99 % was purchased from Showa Tansan Co., Ltd. (Japan) and used without further purifications.

Measurements. The viscosities of the mixture were measured with a rolling ball viscometer, as described in the previous report.[8−10] The mixture was prepared as follows. [bmim][PF_6] was introduced into the viscometer. After evacuation of air in the viscometer from the valve, CO_2 was introduced into the viscometer. The amount of CO_2 charged in the viscometer was determined by weighing the viscometer with the use of an electrical balance with an uncertainty of 0.01 g before and after loading CO_2. The viscosity of [bmim][PF_6] at 293.15 K and 0.1 MPa was also measured with a capillary viscometer described previously.[14]

The density of sample fluid was obtained with a piezometer described in a previous study.[8−11] Weighed [bmim][PF_6] was

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Table 3. Experimental Values of Viscosities and Densities for the [bmim][PF$_6$] (2) + CO$_2$ (1) Mixture

T/K	x_1	P/MPa	η/mPa·s	ρ/Kg·m^{-3}	T/K	x_1	P/MPa	η/mPa·s	ρ/Kg·m^{-3}	T/K	x_1	P/MPa	η/mPa·s	ρ/Kg·m^{-3}
293.15	0[a]	10.0	442	1374		0.123	10.0	84.8	1342		0.332	10.0	20.5	1268
		15.0	468	1377			15.0	90.1	1351			15.0	21.1	1308
		20.0	504	1379			20.0	92.4	1356			20.0	21.7	1319
	0.056	10.0	372	1371		0.229	10.0	54.1	1329		0.440	10.0	16.1	1223
		15.0	397	1374			15.0	55.8	1344			15.0	16.5	1286
		20.0	424	1377			20.0	61.2	1350			20.0	17.0	1304
	0.123	10.0	277	1368		0.332	10.0	36.9	1313	353.15	0[a]	10.0	28.1	1327
		15.0	287	1371			15.0	39.9	1337			15.0	29.3	1330
		20.0	310	1375			20.0	41.6	1342			20.0	30.5	1332
	0.229	10.0	135	1361		0.440	10.0	24.7	1288		0.056	10.0	25.2	1306
		15.0	144	1365			15.0	24.8	1323			15.0	26.4	1319
		20.0	150	1368			20.0	26.8	1330			20.0	28.0	1325
	0.332	10.0	89.2	1354	333.15	0[a]	10.0	58.2	1343		0.123	10.0	21.6	1286
		15.0	91.9	1358			15.0	61.0	1346			15.0	22.6	1310
		20.0	100	1362			20.0	63.2	1349			20.0	23.4	1319
	0.440	10.0	43.9	1346		0.056	10.0	49.3	1327		0.229	10.0	15.8	1260
		15.0	45.9	1351			15.0	51.9	1338			15.0	16.5	1299
		20.0	46.8	1355			20.0	54.5	1343			20.0	16.9	1310
313.15	0[a]	10.0	133	1359		0.123	10.0	40.6	1313		0.332	10.0	12.3	1226
		15.0	140	1362			15.0	42.8	1330			15.0	12.7	1284
		20.0	151	1364			20.0	44.2	1338			20.0	12.8	1298
	0.056	10.0	119	1350		0.229	10.0	27.2	1293		0.440	10.0	10.7	1162
		15.0	125	1356			15.0	28.3	1321			15.0	10.8	1255
		20.0	132	1360			20.0	29.1	1329			20.0	10.9	1278

[a] Previous reported values.[8]

charged in the glass cell, and the valve was attached with the glass cell. After degassing, CO$_2$ was introduced into the glass cell from the valve by immersing the glass cell in the methanol which was cooled at about 243 K. The amount of CO$_2$ charged in the cell was determined by weighing the cell with the use of an electrical balance with an uncertainty of 0.0001 g before and after loading CO$_2$. The temperature of the thermostat was measured with a quartz thermometer. The pressure was measured with a bourdon tube pressure gauge. The experimental uncertainties in temperature, pressure, and mole fraction are estimated within ± 10 mK, ± 0.1 MPa, and 0.001, respectively. The uncertainty of the reported viscosity data is estimated to be ± 3.0 %.

Results and Discussion

Table 2 shows the comparison of our results for [bmim][PF$_6$] used in this study at 0.1 MPa and 293.15 K with the literature data. The results of our previous work[8] and Widegren et al.[15] agree with our values within ± 1 %, whereas Harris et al.[16] is somewhat lower than ours.

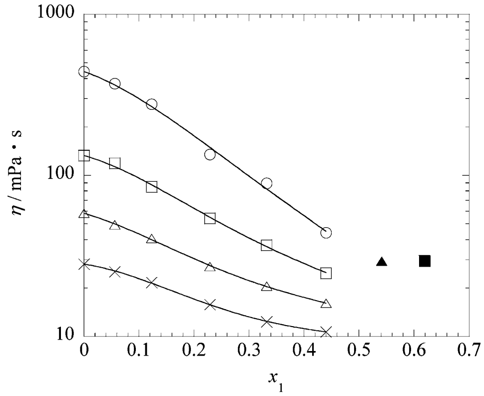

Figure 1. Comparison of the viscosity data for the [bmim][PF$_6$] (2) + CO$_2$ (1) mixture at 10.0 MPa with correlation from the McAllister four-body model: ○, 293.15 K; □, 313.15 K; △, 333.15 K; ×, 353.15 K; Liu et al.,[7] ■, 313.15 K (9.9 MPa); ▲, 333.15 K (9.9 MPa); −, eq 1.

Table 4. Parameters of the McAllister Equation

T/K	P/MPa	$\ln \nu_{1112}$	$\ln \nu_{1122}$	$\ln \nu_{2221}$	$\ln \nu_1$	$\ln \nu_2$
293.15	10.0	−9.8545	−11.735	−8.6846	−16.168	−8.0419
	15.0	−9.7664	−11.745	−8.6309	−16.095	−7.9869
	20.0	−10.363	−11.386	−8.6410	−16.040	−7.9143
313.15	10.0	−8.7314	−12.609	−9.7103	−16.394	−9.2319
	15.0	−9.5874	−12.206	−9.7394	−16.261	−9.1828
	20.0	−9.8974	−11.826	−9.8193	−16.189	−9.1087
333.15	10.0	−8.5873	−12.850	−10.509	−16.316	−10.047
	15.0	−8.6395	−12.945	−10.452	−16.390	−10.002
	20.0	−8.4830	−13.046	−10.394	−16.306	−9.9686
353.15	10.0	−8.1633	−13.554	−10.904	−16.128	−10.763
	15.0	−8.6569	−13.469	−10.897	−16.394	−10.723
	20.0	−8.3788	−13.727	−10.806	−16.375	−10.684

The experimental viscosity data of the [bmim][PF$_6$] + CO$_2$ mixtures are given in Table 3 together with values for density under the same conditions, which are interpolated from the experimental values. The density values have an estimated uncertainty of ± 0.2 %. The viscosity values of [bmim][PF$_6$] + CO$_2$ at 10.0 MPa are shown in Figure 1. In Figure 1, the viscosity values reported by Liu et al. are also plotted. As pointed out in ref 8, their viscosity values of [bmim][PF$_6$] at 0.1 MPa were lower than our experimental values. However, their viscosity values of the [bmim][PF$_6$] + CO$_2$ mixture at saturated lines (9.9 MPa) were larger than our correlation values at 10.0 MPa.

We correlated the experimental values with McAllister four-body model.[17] For the binary mixture, this semitheoretical equation is written as

$$\ln \nu = x_1^4 \ln \nu_1 + 4x_1^3 x_2 \ln \nu_{1112} + 6x_1^2 x_2^2 \ln \nu_{1122} + 4x_1 x_2^3 \ln \nu_{2221} + x_2^4 \ln \nu_2 - \ln\left[x_1 + x_2\frac{M_2}{M_1}\right] + 4x_1^3 x_2 \ln\left[\frac{3 + M_2/M_1}{4}\right] + 6x_1^2 x_2^2 \ln\left[\frac{1 + M_2/M_1}{2}\right] + 4x_1 x_2^3 \ln\left[\frac{1 + 3M_2/M_1}{4}\right] + x_2^4 \ln\left[\frac{M_2}{M_1}\right] \quad (1)$$

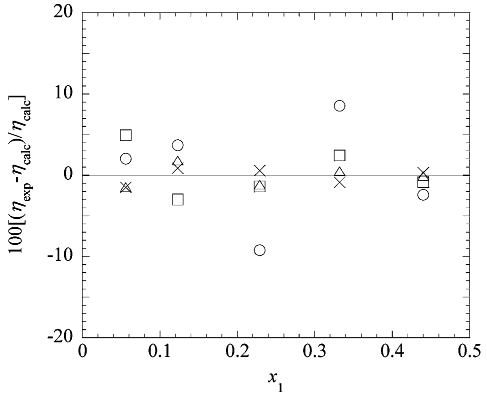

Figure 2. Deviation of the experimental values of the viscosity of the [bmim][PF_6] (2) + CO_2 (1) mixture at 10.0 MPa from McAllister four-body model: ○, 293.15 K; □, 313.15 K; △, 333.15 K; ×, 353.15 K.

where ν is the kinematic viscosity of the mixture and ν_i is the kinematic viscosity of the pure component at the same condition as that of the mixture. x_i is the mole fraction, and M_i is the molecular mass. The subscripts 1 and 2 represent CO_2 and [bmim][PF_6], respectively. The viscosities and densities of pure CO_2 applied literature data.[18,19] ν_{1112}, ν_{1122}, and ν_{2221} are adjustable parameters and are calculated by using experimental data with the least-squares method. The obtained parameters are listed in Table 4. The correlated results at 10.0 MPa and deviations are shown in Figures 1 and 2. The McAllister four-body model correlated the experimental data with an AAD of 2.4 % and a maximum deviation of −11 %.

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