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Thermal Conductivities of Imidazolium-Based Ionic Liquid + CO_2 Mixtures

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Abstract Experimental results for the thermal conductivities of imidazolium-based ionic liquid + CO_2 mixtures are reported. The thermal conductivities were measured with a transient short-hot-wire method. The experimental temperatures were from 294 K to 334 K, and pressures were 10.0 MPa and 20.0 MPa. The CO_2 mole fractions of the mixtures covered a range up to 0.42. It was found that the thermal conductivities of ionic liquids have a very small CO_2 mole fraction dependence.

Keywords 1-Butyl-3-methylimidazolium hexafluorophosphate · 1-Butyl-3-methylimidazolium tetrafluoroborate · CO_2 · 1-Methylimidazole · Thermal conductivity · Transient short-hot-wire method

1 Introduction

Ionic liquids (ILs) have recently drawn much attention as green solvents for synthetic chemistry. Since ILs have many advantages over traditional organic solvents, researchers have been investigating their properties to develop new environmentally friendly chemical processes. For product separation and catalyst recycling, it is essential to separate the product without the degrading ILs. Supercritical CO_2 was recently shown to be a potential alternative solvent for extraction of organics from ILs, since CO_2 has remarkably high solubility in ILs. It has been demonstrated that the

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combination of ILs and supercritical CO_2 offers a highly attractive approach for the development of the environmentally benign and economically viable homogeneous and heterogeneous catalyst processes. Thermal conductivity is one of the most important physical properties to design chemical processes. Thermal conductivities of ILs were measured by several researchers [1–4]. However, there are no literature data for IL + CO_2 mixtures.

In this article, the thermal conductivities of imidazolium-based ionic liquid + CO_2 mixtures were measured with the transient short-hot-wire method. The experimental temperature range was 294 K to 334 K; pressure range was up to 20.0 MPa; and CO_2 mole fraction range was up to about 0.42.

2 Experimental

The liquid samples of 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) were prepared following procedures reported previously [2,3]. The product purity was confirmed by CHN elementary analysis. The ionic liquids were degassed and dried under vacuum at 343 K for 24 h before measuring the thermal conductivity. The water content in the ionic liquids was checked by a Karl-Fisher titration. Measurement of chloride concentration was conducted using a chloride selectivity electrode (Thermo Electron, Co.). The results are listed in Table 1. CO_2 which had a stated purity of 99.99 % was purchased from Showa Tansan Co., Ltd. (Japan) and used without further purification. The 1-methylimidazole which had a stated purity of 99 % was purchased from Aldrich Chemical Co.

The thermal conductivities of the mixtures were measured with the transient short-hot-wire method, which has been described in detail elsewhere [2,3]. The transient short-hot-wire cell used in this study is shown in Fig. 1. Both ends of a platinum wire having a diameter of about 50 μm and a length of about 13 mm were welded to a platinum lead terminal. This lead terminal was supported by a circular Teflon plate having a diameter of 24 mm and a thickness of 5 mm. Platinum lead wires for electric current heating and voltage measurement were welded to a platinum lead terminal. The maximum volume of the stainless-steel pressure-resistant cell was approximately 65 cm^3. In this cell, the pressure was regulated by moving a piston at the lower end of the short-hot-wire cell using a pressure medium. The mixture was prepared as follows. First, a liquid sample was introduced into the cell. Then, after evacuation of air in the

Table 1 Purity of synthesized [bmim][PF_6] and [bmim][BF_4]

Element	[bmim][PF_6] (mass%)		[bmim][BF_4] (mass%)	
	Calculated	Found	Calculated	Found
C	33.81	33.46	42.53	41.31
H	5.32	5.16	6.64	6.45
N	9.86	9.84	12.39	12.22
Water (ppm)	130 ± 41		151 ± 63	
[Cl^-] (ppm)	–[a]		421	

[a] Detection limit <18 ppm

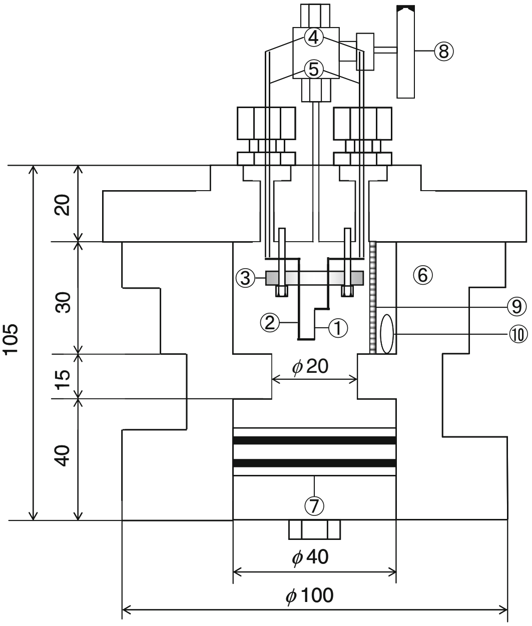


Fig. 1 Transient short-hot-wire cell (dimensions in mm): ① Platinum wire (50 µm ϕ), ② Platinum lead terminal (1.5 mm ϕ), ③ Teflon disk, ④ Platinum lead wire for voltage measurement (0.5 mm ϕ), ⑤ Platinum lead wire for heating electric current (0.5 mm ϕ), ⑥ Pressure vessel, ⑦ Piston, ⑧ Valve, ⑨ Mesh, ⑩ Magnetic bar

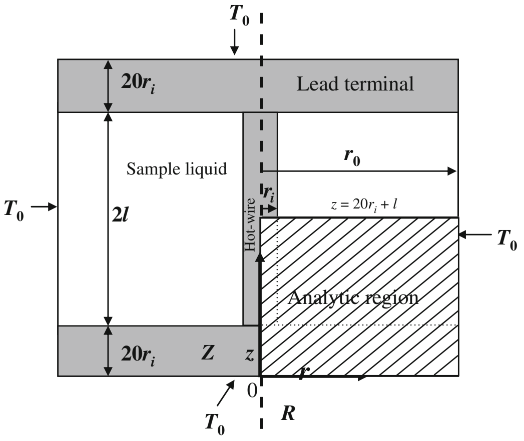
cell, CO_2 was introduced into the cell from a valve. The amount of CO_2 charged in the cell was determined by weighing the cell with the use of an electrical balance. In order to obtain homogeneous conditions, the mixture was stirred with a magnetic bar at ambient temperature and 10.0 MPa for 1 day.

The temperature of the thermostat was regulated within ±20 mK. The pressure was measured using a Bourdon-tube pressure gauge that was periodically calibrated against a dead-weight gauge. The experimental uncertainty in the pressure is estimated to be 0.1 MPa.

The measurement system is similar to that of Fujii et al. [5]. The data acquisition procedure was as follows. First, a small current of approximately 3 mA was supplied to the main circuit, and the voltages of the standard resistance and probe were measured. The current was determined from the voltage of the standard resistance. The resistance of the probe was then calculated using the values of the current and the voltage of the probe. The initial temperature of the sample was determined by using the relation between the resistance of the probe and temperature. The switch was then turned on to the dummy circuit, and a heating current (80 mA to 200 mA) was supplied. After the current was stable, the switch was again closed to the main circuit in order to begin heating the hot wire, and the voltages of the standard resistance and probe were measured. From the measurements using the probe, the measured temperature rise ΔT of the wire is given approximately by the following equation:

$$\Delta T = a \ln t + b \tag{1}$$

Fig. 2 Physical model



The values of *a* and *b* were determined by least squares from a plot of ln *t* versus ΔT. When the probe was heated, the wire temperature increased but the lead terminal temperature remained at the initial temperature. The correction in the probe temperature rise is similar to that of Fujii et al. [5]. The temperature of the probe increased from 1 K to 3 K after 1 s.

A numerical analysis was performed based on the model proposed by Fujii et al. In this model, the following three assumptions were adopted: (1) the rate of heat generation per unit volume and time is uniform and constant; (2) the temperature of the lead wires is maintained at its initial temperature during the heating process; and (3) the temperature distribution in the vessel is symmetric. In this study, we applied assumptions (1) and (3), but abandoned assumption (2) and attempted to simulate the heat conduction from the hot wire to the lead wire. Hence, we include the lead wire in the physical model, as shown in Fig. 2. The sample liquid was poured into a cylindrical vessel of radius r_0, with a short hot wire at each end. The hatched region in Fig. 2 is taken as the solution domain.

The two-dimensional heat-conduction equations for the hot wire, liquid layer, and lead wire are expressed as follows:

$$\frac{\partial \theta_s}{\partial Fo} = \frac{1}{C}\left(\frac{\partial^2 \theta_s}{\partial R^2} + \frac{1}{R}\frac{\partial \theta_s}{\partial R} + \frac{\partial^2 \theta_s}{\partial Z^2}\right) + \frac{D}{C} \tag{2}$$

$$\frac{\partial \theta_f}{\partial Fo} = \frac{\partial^2 \theta_f}{\partial R^2} + \frac{1}{R}\frac{\partial \theta_f}{\partial R} + \frac{\partial^2 \theta_f}{\partial Z^2} \tag{3}$$

$$\frac{\partial \theta_l}{\partial Fo} = \frac{1}{C}\left(\frac{\partial^2 \theta_l}{\partial R^2} + \frac{1}{R}\frac{\partial \theta_l}{\partial R} + \frac{\partial^2 \theta_l}{\partial Z^2}\right) \tag{4}$$

where θ, R, and Z are the dimensionless temperature and radial and longitudinal coordinates, respectively, and subscripts s, f, and l refer to the hot wire, liquid layer, and lead wire, respectively. θ, R, Z, and the Fourier number *Fo* are defined as follows:

$$\theta = \lambda \frac{T - T_0}{q_v r_i^2}, \quad Fo = \frac{\alpha t}{r_i^2}, \quad R = \frac{r}{r_i}, \quad Z = \frac{z}{r_i} \tag{5}$$

C and D are the ratio of the thermal diffusivity α and thermal conductivity λ, respectively, to that of the wire; they are defined as

$$C = \frac{\alpha}{\alpha_\mathrm{s}}, \quad D = \frac{\lambda}{\lambda_\mathrm{s}} \tag{6}$$

The values of thermal conductivity and thermal diffusivity that were calculated by an analytical solution of the one-dimensional heat equation were used as the initial values for the numerical analysis.

Equations 2–4 were solved numerically by a finite difference method with an implicit subsequent substitution scheme. A nonuniform grid arrangement was used, and the node numbers were 201 and 51 in the R and Z directions, respectively. From numerical analysis, a relationship between a dimensionless temperature of the wire and the Fourier number was obtained. The numerical results were approximated by using the following equation:

$$\theta_v = A \ln Fo + B \tag{7}$$

Equation 7 is dimensionalized, and by comparing the corresponding coefficients of Eqs. 1 and 7, the thermal conductivity of a liquid is expressed by

$$\lambda = q_v r_i^2 \frac{A}{a} = \frac{VI}{2\pi l} \frac{A}{a} \tag{8}$$

where V and I are the voltage and current supplied to the wire, respectively, and $2l$ is the length of the hot wire. The characteristics of the platinum wire were examined by using pure water and toluene as standard liquids of known thermal conductivity and thermal diffusivity. The uncertainty of the present thermal-conductivity data is estimated to be within 3.0 %.

3 Results and Discussion

It is well known that a small amount of impurity affects the viscosity of ionic liquids [6]. Valkenburg et al. [1] measured the thermal conductivities of 1,2-diethyl-3-propylimidazolium bis(trifluorosulfonyl)imide whose water content was 500 ppm and 2,000 ppm. The difference in the thermal conductivity was 0.8 %. The effect of water content on the thermal conductivity is relatively small. The effect of chloride impurity on the thermal conductivity has never been researched. We measured the thermal conductivity of [bmim][BF_4] for which the chloride concentration is 4580 ppm and compared with the sample for which the chloride concentration is 421 ppm. The difference in the thermal conductivity was 1.2 %. The effects of water and chloride on the thermal conductivity are smaller than those on the viscosity.

Table 2 Experimental results for thermal conductivity of [bmim][PF_6]+CO_2 mixture

T (K)	P (MPa)	x_{CO_2}	λ $(\mathrm{W \cdot m^{-1} \cdot K^{-1}})$	T (K)	P (MPa)	x_{CO_2}	λ $(\mathrm{W \cdot m^{-1} \cdot K^{-1}})$
294.4	10.0	0[a]	0.146	314.5	20.0	0[a]	0.147
		0.108	0.148			0.108	0.151
		0.220	0.149			0.220	0.152
		0.328	0.150			0.328	0.153
		0.420	0.148			0.420	0.148
	20.0	0[a]	0.148	334.2	10.0	0[a]	0.145
		0.108	0.150			0.108	0.148
		0.220	0.151			0.220	0.150
		0.328	0.152			0.328	0.150
		0.420	0.149			0.420	0.148
314.5	10.0	0[a]	0.146		20.0	0[a]	0.147
		0.108	0.149			0.108	0.151
		0.220	0.149			0.220	0.152
		0.328	0.152			0.328	0.151
		0.420	0.148			0.420	0.149

[a] Previously reported values [3]

Table 3 Experimental results for thermal conductivity of [bmim][BF_4]+CO_2 mixture

T (K)	P (MPa)	x_{CO_2}	λ $(\mathrm{W \cdot m^{-1} \cdot K^{-1}})$	T (K)	P (MPa)	x_{CO_2}	λ $(\mathrm{W \cdot m^{-1} \cdot K^{-1}})$
294.2	10.0	0[a]	0.171	314.3	20.0	0[a]	0.173
		0.169	0.173			0.169	0.175
		0.308	0.170			0.308	0.170
		0.422	0.171			0.422	0.170
	20.0	0[a]	0.173	334.3	10.0	0[a]	0.171
		0.169	0.174			0.169	0.173
		0.308	0.172			0.308	0.169
		0.422	0.171			0.422	0.169
314.3	10.0	0[a]	0.171		20.0	0[a]	0.173
		0.169	0.173			0.169	0.175
		0.308	0.169			0.308	0.170
		0.422	0.170			0.422	0.169

[a] Previously reported values [2]

Since ILs are highly electrically conducting liquids, one should consider the effect of current leakage. As described in our previous article [3], the effect of leakage current was negligible at these experimental conditions.

The thermal conductivities of [bmim][PF_6] + CO_2 and [bmim][BF_4] + CO_2 mixtures are shown in Tables 2 and 3. For comparison, the thermal conductivities of the 1-methylimidazole + CO_2 mixture were measured at 294.2 K. The experimental results are shown in Table 4. The thermal conductivities of [bmim][PF_6] + CO_2, [bmim][BF_4] + CO_2, and 1-methylimidazole + CO_2 at 294 K, 20.0 MPa are shown in Fig. 3. The thermal conductivity of CO_2 is taken from the literature [7]. As shown in Fig. 3, the thermal conductivities of 1-methylimidazole, which is a molecular liquid, decreased with increasing CO_2 mole fraction. However, the thermal conductivities of [bmim][PF_6] and [bmim][BF_4], which are ILs, remained almost constant with an increase in the CO_2 mole fraction. Although there are few literature data for the thermal conductivity

Table 4 Experimental results for the thermal conductivity of 1-methylimidazole + CO_2 mixture

T (K)	P (MPa)	x_{CO_2}	λ ($W \cdot m^{-1} \cdot K^{-1}$)
294.2	10.0	0	0.194
		0.157	0.187
		0.261	0.184
		0.337	0.180
		0.430	0.176
	20.0	0	0.196
		0.157	0.190
		0.261	0.187
		0.337	0.184
		0.430	0.180

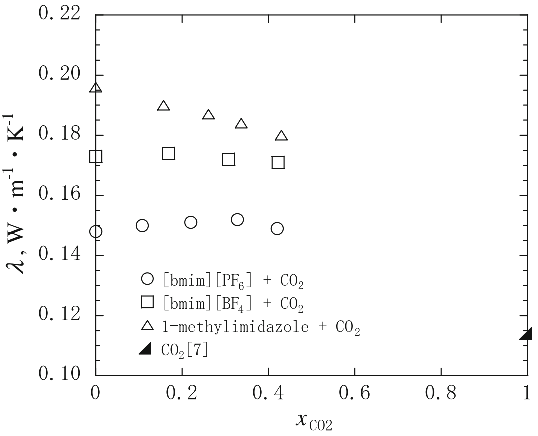


Fig. 3 CO_2 mole fraction dependence of thermal conductivity of [bmim][PF_6] + CO_2, [bmim][BF_4] + CO_2, and 1-methylimidazole + CO_2 mixtures at 294 K, 20.0 MPa

of mixtures such as CO_2 dissolved in a liquid, the CO_2 mole fraction dependence of the thermal conductivities of the ILs + CO_2 is different from that of molecular liquids + CO_2.

4 Conclusions

The thermal conductivities of [bmim][PF_6] + CO_2 and [bmim][BF_4] + CO_2 mixtures were measured in the temperature range from 294 K to 334 K and at pressures up to 20.0 MPa. It was found that the thermal conductivities of ILs have very small CO_2 mole fraction dependence.

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