

Physical and Electrochemical Properties of 1-Butyl-3-methylimidazolium Bromide, 1-Butyl-3-methylimidazolium Iodide, and 1-Butyl-3-methylimidazolium Tetrafluoroborate

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Abstract—The density, viscosity, refractive index, heat capacity, heat of dilution, ionic conductivity, and electrochemical stability of 1-butyl-3-methylimidazolium bromide ([bmim][Br]), 1-butyl-3-methylimidazolium iodide ([bmim][I]), and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) were measured at room temperature or over a temperature range of 293.2 to 323.2 K. The density and refractive index values of [bmim][I] appeared to be the highest among three ionic liquids (ILs). However, the experimental viscosity values of [bmim][Br] were higher than those of [bmim][BF₄], while the heat capacities and heats of dilution of [bmim][BF₄] were higher than those of [bmim][Br]. The cyclic voltammogram of [bmim][Br] and [bmim][BF₄] indicated electrochemical windows in the stability range from 2.7 V of [bmim][Br] to 4.7 V of [bmim][BF₄].

Key words: Physical Property, Electrochemical Property, 1-Butyl-3-methylimidazolium Bromide, 1-Butyl-3-methylimidazolium Tetrafluoroborate, and 1-Butyl-3-methylimidazolium Iodide

INTRODUCTION

Ionic Liquids (ILs) are generally salts based on a substituted heterocyclic cation and an inorganic anion such as [AlCl₄]⁻, [BF₄]⁻, or [PF₆]⁻ existing as a liquid state at room temperature condition. These ILs can be synthesized in an endless number of ways according to the proper combination of ions. Accordingly, their physical and thermal properties strongly depend on the species of cation and anion as well as the length of the alkyl groups on the cation [Marsh et al., 2002]. ILs based on imidazolium cation are especially favorable for various industrial applications. Their solvating properties, low melting points, air and water stabilities, high conductivities, and wide window of electrochemical stability make these materials excellent candidates for catalysis, capacitors, batteries, liquid-liquid extractions and absorption heat pumps [Ngo et al., 2000; Huddleston et al., 1998].

To design any process involving ILs on an industrial scale, their physical properties and electrochemical characteristics must be primarily provided before any further steps are taken. Therefore, experimental measurements and molecular simulations for physical properties of ILs play key parts in their application to many processes [Hanke et al., 2002]. In this work several physical and electrochemical properties of 1-butyl-3-methylimidazolium bromide ([bmim][Br]), 1-butyl-3-methylimidazolium iodide ([bmim][I]), and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) such as the density, reflective index, viscosity, heat capacity, heat of dilution, ionic conductivity, and electrochemical stability were investigated at room temperature or over a temperature range of 293.2 to 323.2 K.

EXPERIMENTAL SECTION

1. Materials

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The 1-methylimidazole (99%), 1-chlorobutane (99.5%), 1-bromobutane (99%), 1-iodobutane (99%), 1,1,1-trichloroethane (99.5%), ethyl acetate, and sodium tetrafluoroborate (98%) were supplied by Aldrich. Dichloromethane and acetonitrile were supplied by KAUO and MERCK, respectively. All materials were used without any further purification.

2. Synthesis of Ionic Liquids

[bmim][BF₄], [bmim][Br], and [bmim][I] were prepared according to literature procedures [Welton, 1999; Wasserscheid and Welton, 2002; Bonhôte et al., 1996].

2-1. [bmim][BF₄]

A 1,000 mL three-neck round-bottom flask fitted with a water condenser and a gas inlet and provided with a Teflon-coated magnetic bar was charged with 1-methylimidazole (246.3 g, 3 mol) under N₂. Butyl chloride (390 mL) was added into the reaction vessel with continuous magnetic stirring. The reaction mixture was heated until two phases were formed. The top phase, containing the unreacted starting material, was decanted and ethyl acetate (300 mL) was added to the vessel. The ethyl acetate was decanted, followed by the addition of fresh ethyl acetate. This step was repeated twice. The product is slightly yellow and may be crystalline at room temperature, depending on the amount of water present in that phase. The product was recrystallized from dry acetonitrile and dried under vacuum at 343.2 K for 12 h to yield pure crystalline [bmim][Cl]. A solution of [bmim][Cl] (93 g, 0.531 mol) in acetone (500 cm³) at room temperature was added to sodium tetrafluoroborate (58.3 g, 0.531 mol). After 24 h stirring, the resulting NaCl precipitate was then filtered through a plug of celite and the volatiles were removed by rotary evaporation to a yellowish, clear liquid. The product was dried for three more days under high vacuum at 0.03 mmHg. The chemical shift for ¹H NMR spectrum (ppm, D₂O) appears as follows: δ 8.71[s, 1H, H(2)], 7.49[s, 1H, H(4)], 7.44[s, 1H, H(5)], 4.21[t, 2H, NCH₂], 3.91[s, 3H, NCH₃], 1.87[m, 2H, NCH₂CH₂], 1.35[m, 2H, NCH₂CH₂CH₂] and 0.94[t, 3H, CH₃].

2-2. [bmim][Br]

A 1,000 mL three-neck round-bottom flask fitted with a water condenser and a gas inlet and provided with a Teflon coated magnetic bar was prepared. 305.64 g (390 mL, 2.85 mol) freshly distilled bromobutane was added dropwise over 1 h to a solution 225.43 mL (232.2 g, 2.83 mol) of 1-methylimidazole in 200 mL of 1,1,1-trichloroethane at ambient temperature. The mixture was heated under reflux for 2 h and decanted from hot solution in a separatory funnel, washed twice with 300 mL of trichloroethane at 323.2 K, dried under reduced pressure at 313.2 K for 3 days. The ¹H NMR spectrum (ppm, D₂O) contains peaks: δ 8.91[s, 1H, H(2)], 7.64[s, 1H, H(4)], 7.59[s, 1H, H(5)], 4.32[t, 2H, NCH₂], 4.02[s, 3H, NCH₃], 1.95[m, 2H, NCH₂CH₂], 1.42[m, 2H, NCH₂CH₂CH₂], 1.00[t, 3H, CH₃].

2-3. [bmim][I]

1-Methylimidazole (50 cm³, 0.627 mol) was dissolved in 500 cm³ of THF, and 55 cm³ (0.668 mol) of iodobutane was added to the solution in a 1 L round bottomed three-necked flask. The mixture was refluxed with vigorous stirring at 323.2 K for 20 h. This brown color liquid was isolated and washed with 300 ml of THF. The salt was dried in Rotary-evaporator and under vacuum for 24 h. The ¹H NMR spectrum (ppm, D₂O) contains peaks: δ 8.75[s, 1H, H(2)], 7.51[s, 1H, H(4)], 7.46[s, 1H, H(5)], 4.21[t, 2H, NCH₂], 3.92[s, 3H, NCH₃], 1.86[m, 2H, NCH₂CH₂], 1.34[m, 2H, NCH₂CH₂CH₂], 0.96 [t, 3H, CH₃].

3. Apparatus and Procedure

3-1. Density

Two pycnometers were used for the density measurement. The equipment and procedure used for the density measurement were similar to our previous investigation [Kim and Lee, 2002]. The densities of the ILs were calculated from the measured volume and mass values. To determine the volume of the pycnometers at various temperatures (298.2 to 323.2 K, at interval of 5 K), calibration was carried out using triple-distilled water. The volumes of each pycnometer were reproducible within 0.2%. The pycnometers were put in an air bath to control temperature and measured by a thermometer within ± 0.05 K.

3-2. Viscosity

The viscosities of ILs were measured with three appropriate Ubbelohde viscometers. The equipment and procedure used for the viscosity measurement were the same as for our previous investigation [Kim and Lee, 2002a]. A suitable viscometer was selected considering the viscosity values. The efflux time of the liquid solution through the capillary was measured manually with a stopwatch.

3-3. Refractive Index

A precision Abbe refractometer 3T (Atago Co.) was used for the measurement of refractive index. The whole experimental apparatus consisted of the main measurement unit, thermosensor for temperature measurement, and bath circulator. The external bath circulator could control the temperature of the sample droplet within 0.1 K. Every measurement was performed three times with a reproducibility of $\pm 10^{-4}$.

3-4. Heat Capacity

A differential scanning calorimeter (TA Instruments DSC Q100) was used for the measurements of heat capacity. The calorimeter was calibrated by measuring the heat capacities of a standard sample, synthetic sapphire, at different temperatures. A test experiment

was done with a lithium bromide+1,3-propanediol+water mixture, and the resulting relative error was within 1.5% [Kim et al., 1997]. A sample of 5 mg was placed in a stainless steel sample container, which was then placed in the calorimeter. Another empty container of the same size was put in the calorimeter as a reference. The experimental reproducibility was within $\pm 2\%$ and the uncertainty of measurement was 1% accuracy.

3-5. Heat of Dilution

The heats of dilution for each IL were measured by using an Iso-peribol Solution Calorimeter (CSC4300) from Calorimetric Science Corporation. The calorimeter consisted of a constant temperature bath, Dewar vessel with a volume of about 25 cm³, calibration heater including a 100 Ω resistor, thermistor, and stirring rod made of glass. The measurement of the heat of dilution was carried out through two phases of operation. Prior to the measurement, an absorbent solution about 25 cm³ of the desired concentration was introduced into the Dewar vessel. A small amount of water (about 0.01 g) whose weight was accurately measured was placed in the small cylindrical container. The top and bottom of the cylindrical container were blocked by fragile cover glass in order to make the inner space of the cylindrical container isolated from the outer space.

The calibration procedures were as follows. The thermistor, calibration heater, and stirring rod were immersed after the vessel was clamped on the calorimeter. The stirrer and heater were turned on for heating. The heat was supplied until the solution temperature reached slightly below the desired temperature. With heating for 300 seconds, the actual calibration started through 200 seconds of holding without heating, 400 seconds of heating, and 200 seconds of holding. The amount of heat supplied during the calibration was calculated through measuring the current and voltage values with built-in digital voltmeter. All procedures were controlled by a connected computer and the measured temperature difference was used to determine the calibration constant in the following equation:

$$Q = (mC_p + \varepsilon)\Delta T \quad (1)$$

where Q is the total amount of heat added, m the mass of the sample solution, C_p the heat capacity of the sample in kJ·kg⁻¹·K⁻¹, ε the heat capacity (kJ·K⁻¹) of the apparatus, and ΔT the temperature difference measured by calorimeter. From the above equation, the heat equivalent E, mC_p+ ε , can be determined. The actual measurement of the heat of dilution is similar to the calibration procedure. In this case, the mixing of the solution with water by breaking the cover glass caused the temperature difference. Since we know the heat equivalent, E, from the calibration procedure, the evolved heat can be calculated from the following equation:

$$H_d = \Delta TE / m_{\text{water}} \quad (2)$$

where the H_d is the heat of dilution in kJ/kg, m the weight of water charged in kg. The temperature resolution of the calorimeter was 2 mK, the temperature noise level ± 30 mK, and the bath temperature stability ± 0.0005 K [Kim and Lee, 2002b, c].

3-6. Conductivity

IL electrolytes were placed between the two stainless steel (SS) electrodes. The ionic conductivities of the each IL were measured by complex impedance analysis with a Solartron 1260A frequency response analyzer coupled to an IBM computer over a frequency range of 100 Hz-1 MHz. An a.c. perturbation of 10 mV was applied

to the cell. The real and imaginary parts of the complex impedance were plotted, and the ionic conductivity could be calculated from the bulk resistance (Rb) found in a complex impedance diagram.

3-7. Electrochemical Stability

Electrochemical stability was analyzed by using a Solartron 1287A potentiostat/galvanostat coupled to an IBM computer at room temperature. A glassy carbon working electrode of 3 mm diameter was

used with a platinum wire as the counter electrode and a silver wire as the reference electrode.

RESULTS AND DISCUSSION

1. Density, Viscosity, Refractive Index, and Heat Capacity

Densities and refractive indices of the [bmim][Br], [bmim][BF₄], and [bmim][I], and Viscosities and heat capacities of the [bmim][Br] and [bmim][BF₄] were measured at 298.2 K or in a temperature range from 298.2 to 323.2 K. The experimental results are presented in Tables 1, 2, 3, and 4, and Figs. 1, 2, and 3. The density val-

Table 1. Measured densities of [bmim][Br], [bmim][I], and [bmim][BF₄]

T/K	d/g·cm ⁻³		
	[bmim][BF ₄]	[bmim][Br]	[bmim][I]
298.2	1.20	1.30	1.46
303.2	1.20	1.30	1.45
308.2	1.19	1.29	1.45
313.2	1.19	1.29	1.44
318.2	1.19	1.29	1.44
323.2	1.18	1.28	1.44

Table 2. Measured viscosities of [bmim][Br], [bmim][I], and [bmim][BF₄]

T/K	η /mPa·s	
	[bmim][BF ₄]	[bmim][Br]
298.2	279.86	1486.49

Table 3. Measured refractive indices of [bmim][Br], [bmim][I], and [bmim][BF₄]

T/K	n		
	[bmim][BF ₄]	[bmim][Br]	[bmim][I]
298.2	1.4227	1.5450	1.5695
303.2	1.4214	1.5446	1.5680
308.2	1.4200	1.5420	1.5670
313.2	1.4192	1.5410	1.5662
318.2	1.4188	1.5398	1.5639
323.2	1.4172	1.5369	1.5608

Table 4. Measured heat capacities of each [bmim][Br] and [bmim][BF₄]

[bmim][Br]		[bmim][BF ₄]	
T/K	$C_p/J\cdot g^{-1}\cdot K^{-1}$	T/K	$C_p/J\cdot g^{-1}\cdot K^{-1}$
298.2	1.35	298.2	1.72
301.2	1.39	300.2	1.73
303.2	1.41	303.2	1.75
305.2	1.44	306.2	1.77
308.2	1.47	308.2	1.78
310.2	1.49	311.2	1.79
313.2	1.52	313.2	1.80
315.2	1.54	318.2	1.83
318.2	1.58	321.2	1.84
320.2	1.60	323.2	1.85
323.2	1.64		

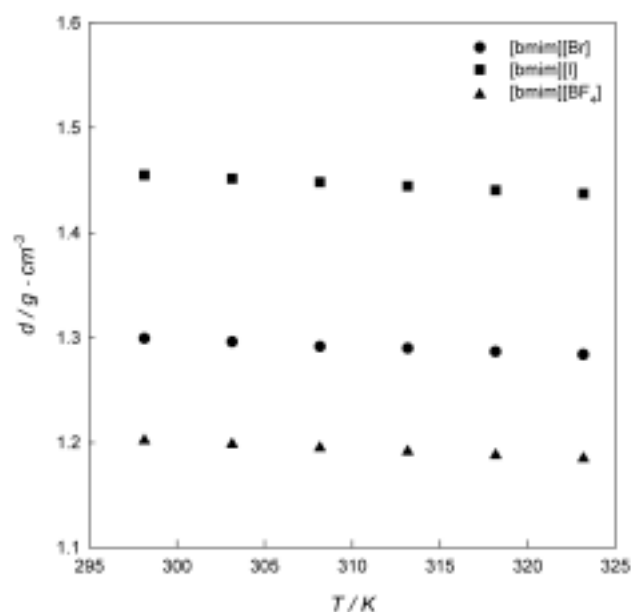


Fig. 1. Densities of [bmim][Br] (●), [bmim][I] (■), and [bmim][BF₄] (▲).

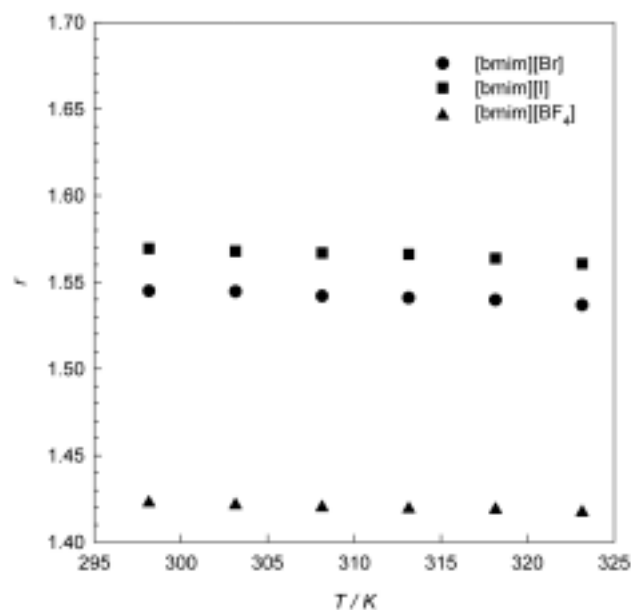


Fig. 2. Refractive Indices of [bmim][Br] (●), [bmim][I] (■), and [bmim][BF₄] (▲).

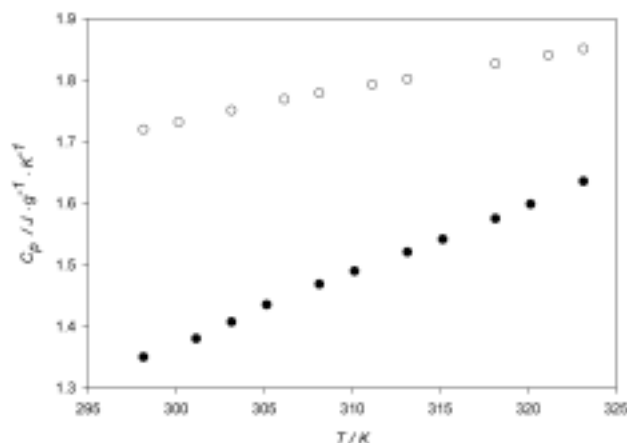


Fig. 3. Heat capacities of the [bmim][Br] (●) and [bmim][BF₄] (○).

ues decrease, but the heat capacities increase with increasing temperature. The temperature effect on refractive index appears to be almost negligible. Density and refractive index values of [bmim][I] are the highest among three ILs. In the case of viscosity measurement the experimental value of [bmim][Br] was higher than that of [bmim][BF₄], while the heat capacities and heats of dilution of [bmim][BF₄] were higher than that of [bmim][Br].

2. Heat of Dilution

The experimental apparatus and procedure were verified in our previous work [Kim and Lee, 2002b]. Heat of dilution of [bmim][BF₄] and [bmim][Br] were measured at 313.2 K. The experimen-

Table 5. Measured heat of dilution of [bmim][Br] and [bmim][BF₄] at 313.2 K

[bmim][BF ₄]	[bmim][Br]
69.5 kJ·kg ⁻¹	28.7 kJ·kg ⁻¹

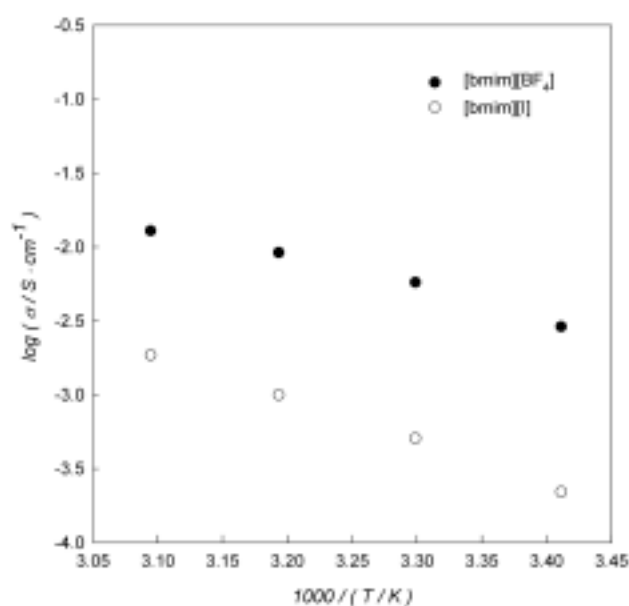


Fig. 4. Ionic conductivities of [bmim][BF₄] (●) and [bmim][I] (○).

Table 6. Measured electrochemical stabilities of [bmim][Br] and [bmim][BF₄]

Electrochemical windows/V	
[bmim][BF ₄]	[bmim][Br]
-2.1~2.6	-1.5~1.2

tal results of the heat of dilution of [bmim][BF₄] and [bmim][Br] are presented in Table 5. The heat of dilution of [bmim][BF₄] is higher than that of [bmim][Br].

3. Conductivity and Electrochemical Stability

Ionic conductivities of [bmim][I] and [bmim][BF₄] were measured in the temperature range from 293.2 to 323.2 K. Conductivity data for three ILs are presented in Fig. 4 as a function of temperature. The conductivities of the pure [bmim][BF₄] lie within 10⁻³ S cm⁻¹.

A cyclic voltammogram of [bmim][Br] and [bmim][BF₄] was measured and presented in Table 6. The ILs have wide electrochemical windows in the stability range from 2.7 V for [bmim][Br] to 4.7 V for [bmim][BF₄].

CONCLUSION

The physical and electrochemical properties of [bmim][Br], [bmim][I], and [bmim][BF₄] were investigated at various temperature conditions. The ILs suggested in this work provide a wide liquid range without vapor pressure. The viscosity values of [bmim][Br] were higher than those of [bmim][BF₄], while the heat capacities and heats of dilution of [bmim][BF₄] were higher than those of [bmim][Br]. The conductivities of [bmim][BF₄] lay within 10⁻³ S cm⁻¹ in the temperature range from 298.2 to 323.2 K and the electrochemical windows of [bmim][Br] and [bmim][BF₄] lay in the stability range from 2.7 V for [bmim][Br] to 4.7 V for [bmim][BF₄]. The obtained properties of three ILs are changed according to the species of anion and indicate that they can be potential candidates as electrolytes and solvents.

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NOMENCLATURE

- d : density
- h : viscosity
- r : refractive index
- C_p : heat capacity [kJ·kg⁻¹·K⁻¹]
- ε : heat capacity of the apparatus kJ·K⁻¹
- H_d : heat of dilution
- Q : heat [kJ]
- δ : chemical shift in NMR
- T : temperature [K]
- σ : conductivity

IL : ionic liquid

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