

Surface tension and viscosity of 1-butyl-3-methylimidazolium iodide and 1-butyl-3-methylimidazolium tetrafluoroborate, and solubility of lithium bromide+1-butyl-3-methylimidazolium bromide in water

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Abstract—The surface tension and viscosity of 1-butyl-3-methylimidazolium iodide ([bmim][I]) and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) were measured over a temperature range of 298.15 to 323.15 K. It was found that both the viscosity and surface tension decrease with increasing temperature and that the surface tension and viscosity values of [bmim][I] were higher than those of [bmim][BF₄]. Additionally, the solubility of lithium bromide (2)+1-butyl-3-methylimidazolium bromide ([bmim][Br]) (3) in water (1) was measured at three different mass ratios (w₂/w₃=4 and 7, w₃=0) by using a visual polythermal method. The solubility of the suggested systems was better than that of lithium bromide in water.

Key words: Surface Tension, Viscosity, Solubility, Ionic Liquid, Imidazolium Salt

INTRODUCTION

As a neoteric solvent, ionic liquids (ILs) have attracted increasing interest over the recent years because they have proven to be excellent alternatives to conventional organic solvents. Potentially, ILs can be used in various industrial applications, such as in liquid-liquid extractions, reaction media, catalysts, and electrolytes [Marsh et al., 2002; Kim et al., 2004a]. Typical ILs are salts that are based on a substituted heterocyclic cation and an inorganic anion such as a halide, [AlCl₄], [BF₄], or [TFSI]. Accordingly, an IL can be synthesized in an enormous number of ways depending on the proper combination of ions. There is a limited amount of reliable data related to the physical and chemical properties of ILs because even a small amount of impurity, including that caused by water and halide anions, critically affects the properties of an IL. To rectify this gap in knowledge, our highest research priority should be in performing a severe synthesis of ILs and an exact analysis of their purity.

In our recent publication, we suggested some ILs that have potential as working fluids for use in an absorption heat pump [Kim et al., 2004b, c]. A working fluid actually consists of two fluids: one acts as a refrigerant and the other acts as an absorbent. For the refrigerant, a fluid with strong volatility is used, whereas the fluid for the absorbent is characterized by a much smaller volatility, though it still has a strong affinity to the refrigerant. A system consisting of water (H₂O)+Lithium bromide (LiBr) is a conventional working fluid. However, the H₂O+LiBr system is hampered by an operational limit caused by salt crystallization [Kim et al., 1996, 2001;

Park et al., 1997]. To suppress the crystallization of the working fluid solutions, organic compounds such as ethanolamine and 1,3-propanediol were added, and the systems were found to have adequately wide operation ranges without salt crystallization. However, because of the volatility of the additives, the absorption heat pump performed poorly. Therefore, we suggest a new working fluid that consists of H₂O+LiBr+IL because the addition of the IL can effectively suppress crystallization without the vaporization in an absorption cycle as its vapor pressure is not detectable.

In this work, 1-butyl-3-methylimidazolium bromide ([bmim][Br]) and 1-butyl-3-methylimidazolium chloride ([bmim][Cl]), 1-butyl-3-methylimidazolium iodide ([bmim][I]), and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) were synthesized and the purity of each IL was checked. The solubility of LiBr (2)+IL (3) in H₂O (1) at three different mass ratios (w₂/w₃=4 and 7, w₃=0) was measured by using a visual polythermal method, and we compared them to the conventional H₂O+LiBr system. Furthermore, the surface tension and viscosity of [bmim][I] and [bmim][BF₄] were measured. The measured physical properties of the suggested systems are essential in order to design an absorption heat pump.

EXPERIMENTAL SECTION

1. Synthesis of ILs

[bmim][Br], [bmim][Cl], [bmim][I], and [bmim][BF₄] were prepared according to our previous reports [Kim et al., 2004b, c, d]. The ¹H NMR and FAB Mass spectra were recorded on a Bruker DMX 600 MHz NMR spectrometer and FAB mass JMS-HX110A, respectively. The presence of residual Cl⁻ was examined by the ionic chromatography (System: Bio-LC DX-300 (Dionex, Sunnyvale,

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CA, USA), Detector: Suppressed Conductivity (PED2), Column: ICsep AN300 with ICsep ANSC guard). Water contents were determined by 756 Karl Fisher coulometer.

1-1. [bmim][Br]

In a 1,000 mL three-necked round-bottomed flask equipped with a reflux condenser, dropping funnel, and magnetic stirrer, under vigorous stirring, 305.64 g (390 mL, 2.85 mol) of freshly distilled bromobutane was added dropwise under vigorous stirring over a period of 1 h to a 225.43 mL (232.2 g, 2.83 mol) solution of 1-methylimidazole in 200 mL of 1,1,1-trichloroethane at ambient temperature. The mixture was then heated under reflux for 2 h and was decanted from the hot solution in a separatory funnel, washed twice with 300 mL of trichloroethane at 50 °C, and dried under reduced pressure at 40 °C 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]. FAB MS: m/z=139. The water content was 1300 parts per million.

1-2. [bmim][Cl]

A 1,000 mL three-necked round-bottom flask fitted with a water condenser and a gas inlet and provided with a Teflon-coated magnetic bar was charged under N₂ with 1-methylimidazole (246.3 g, 3 mol). Butyl chloride (390 mL) was added into the reaction vessel under continuous magnetic stirring in batches of 1,000 mL. The reaction mixture was heated under nitrogen N₂ at 80 °C for 72 h with stirring until two phases formed. The top phase, containing the unreacted starting material, was decanted and ethyl acetate (300 ml) was added through mixing. The ethyl acetate was first decanted and then fresh ethyl acetate was added; this step was repeated twice. After the third decanting of ethyl acetate, any remaining ethyl acetate was removed by heating the bottom phase to 60 °C and stirring while on a vacuum line. The product was found to be slightly yellow and became 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 70 °C for 12 h to yield pure crystalline [bmim][Cl]. The ¹H NMR spectrum (ppm, D₂O) contains peaks: δ 8.7 [s, 1H, H(2)], 7.5 [s, 1H, H(4)], 7.4 [s, 1H, H(5)], 4.2 [t, 2H, NCH₂], 3.9 [s, 3H, NCH₃], 1.8 [m, 2H, NCH₂CH₂], 1.3 [m, 2H, NCH₂CH₂CH₂], 0.9 [t, 3H, CH₃]. FAB MS: m/z=139.

1-3. [bmim][I]

1-Methylimidazole (50 cm³, 0.63 mol) was dissolved in 500 cm³ of THF, and 55 cm³ (0.67 mol) of iodobutane was added to the solution in a 1 L round-bottomed three-necked flask. The mixture was refluxed for 20 h with vigorous stirring under nitrogen pressure. Initially, the mixture formed two liquid phases. After the reaction period was completed and the mixture had been cooled to room temperature, the two layers were isolated from each other. The brown liquid was isolated and washed with 300 ml of THF. The salt was dried in a rotary-evaporator and was placed under a 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]. FAB MS: m/z=139. The water content was 220 parts per million.

1-4. [bmim][BF₄]

A solution of [bmim][Cl] (93 g, 0.53 mol) in acetone (500 cm³) at room temperature was added to sodium tetrafluoroborate (58.3 g,

0.53 mol). After stirring for 24 h, the resulting NaCl precipitate was then filtered through a plug of celite and the volatiles were removed by rotary evaporation, leaving a yellowish, opaque liquid. The product was dried for 3 more days under a high vacuum at 0.03 mmHg. The chemical shift for the ¹H NMR spectrum (ppm, D₂O) is 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], 0.94 [t, 3H, CH₃]. FAB MS: m/z=139. The water and chloride contents were 200 and 13 parts per million, respectively.

2. Apparatus and Procedure

2-1. Viscosity

Appropriately, the viscosities of the imidazolium salts were measured with two appropriate Ubbelohde viscometers. First, in consideration of the viscosity values, a suitable viscometer was selected. Then, the viscometer was put into a bath in which the temperature was controlled with a bath circulator within ±0.05 K. The equilibrium time was about 15 min. The efflux time of the liquid solution through the capillary was measured manually with a stopwatch. The dynamic viscosity values were calculated from the following Eq. (1)

$$\eta = tK\rho \quad (1)$$

where η is the dynamic viscosity, K the instrument constant, t the efflux time, and ρ the density of the sample.

2-2. Surface Tension

The surface tension of each IL was measured by the Plate (Wilhelmy) method using a Dynamic Contact Angle analyzer (DCA) manufactured by Cahn Instruments [Kim and Lee, 2002a]. The plate was made of perfectly clear glass measuring 24×30 mm² and with uniform surface quality, precisely squared edges, perfect flatness, and exact dimensions. The operation and analysis of the procedure were automatically controlled by an external computer that was connected to the DCA. To control the temperature of the sample within ±0.05 K, a bath circulator was used. The accuracy of the instrument is ±0.01 mN/m.

2-3. Solubility

Solubilities were measured by a visual polythermal method. A schematic diagram of the apparatus is shown in Fig. 1. The apparatus consisted of a glass vessel with an internal volume of 50 cm³, a thermistor thermometer capable of measuring up to 0.01 K, a constant temperature bath, a circulator for both cooling and heating, and two stirrers. Each sample solution of a desired water concen-

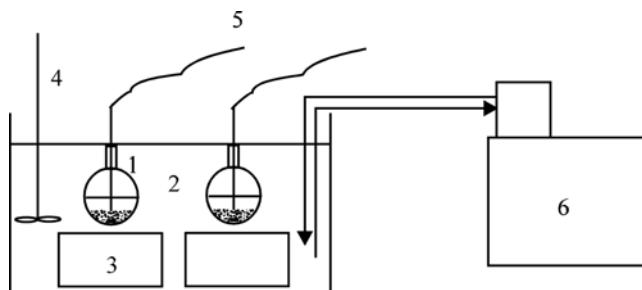


Fig. 1. Experimental apparatus for measuring solubility.

1. Sample vessel	5. Thermometer
2. Constant temperature bath	6. Circulator for heating
3,4. Stirrer	and cooling

tration at a given mixing ratio was accurately prepared by weighing each component with a precise balance. Approximately 30 cm³ of the sample solution was placed in the vessel and stirred well. The solution was first incrementally heated above the crystallization temperature to dissolve all the crystals. The constant temperature bath and the circulator enabled the solution temperature to be lowered and then raised at a very slow rate, less than 0.1 K min⁻¹. After a series of dissolving and nucleation procedures, the temperature at which the last crystal disappeared was taken as the crystallization temperature for a given solution in this polythermal run.

RESULTS AND DISCUSSION

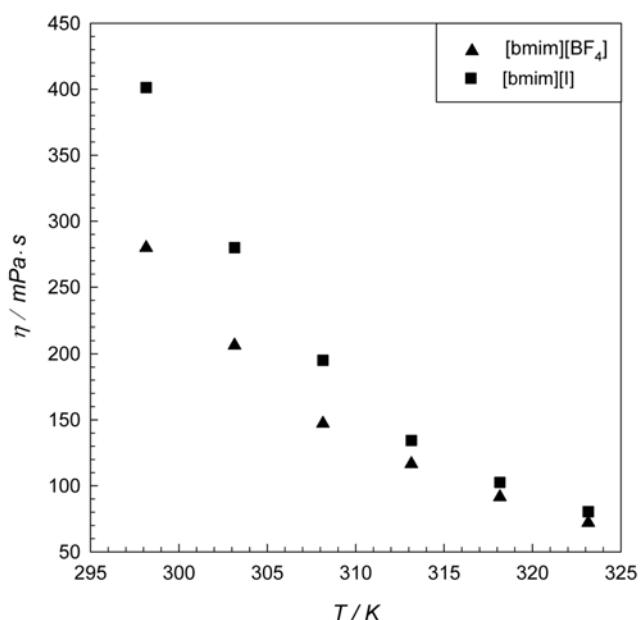


Fig. 2. Viscosities of [bmim][I] (■) and [bmim][BF₄] (▲).

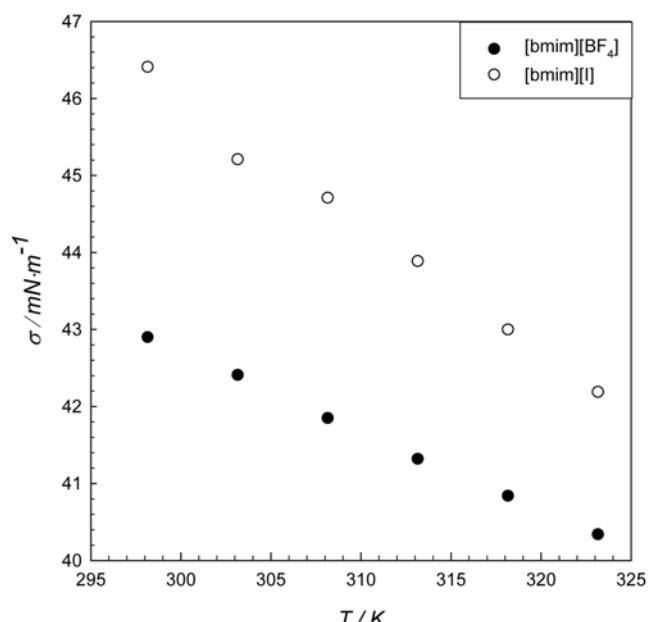


Fig. 3. Surface tensions of [bmim][I] (○) and [bmim][BF₄] (●).

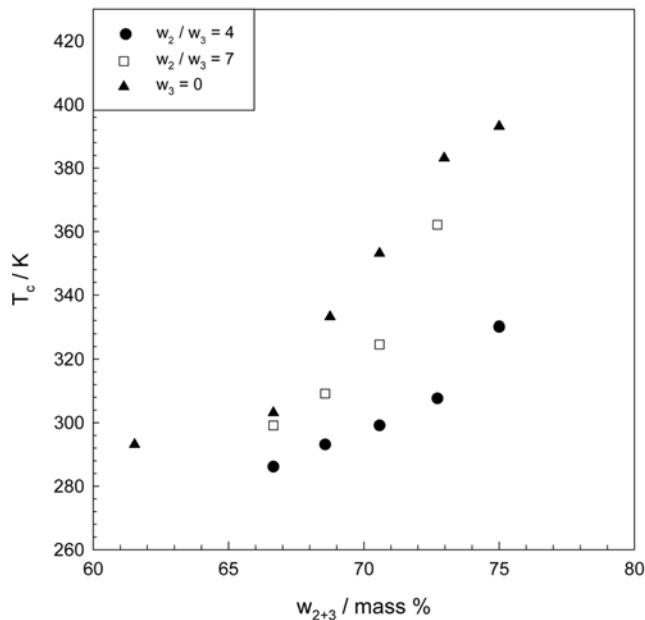


Fig. 4. Solubilities of the H_2O (1)+LiBr (2)+[bmim][Br] (3) System: $w_2/w_3=4$ (●); $w_2/w_3=7$ (□); $w_3=0$ (▲).

The viscosities and surface tensions of [bmim][I] and [bmim][BF₄] were measured over a temperature range of 298.15 to 323.15 K. The experimental results for the viscosities of [bmim][I] and [bmim][BF₄] are plotted in Figs. 2 and 3. The viscosity and surface tension values were found to decrease with increasing temperature in both samples, but the measured values of [bmim][I] were higher than those of [bmim][BF₄].

The solubility of the LiBr (2)+[bmim][Br] (3) in H₂O (1) was measured at three different mass ratios, $w_2/w_3=4$ and 7, and $w_3=0$. The saturated solubilities at crystallization temperatures were measured in the 61.5 to 75.0 mass% range of LiBr+IL concentration. The experimental results are presented in Fig. 4. In Fig. 4, the solubility curves show a shift to the right, indicating enhanced solubility when the amount of [bmim][Br] increases. There is little solubility effect at $w_2/w_3=7$. For the specified temperature and concentration ranges of this study, the maximum solubility was found to be about 75 mass% of LiBr+[bmim][Br] at 330.15 K with a mass ratio of $w_2/w_3=4$. It should be noted that adding [bmim][Br] as an anticrystallization additive into the H₂O+LiBr solution resulted in increased salt solubility and reduced crystallization temperature. Until now, the use of organic compounds such as ethylene glycol and 1,3-propanediol has caused operational difficulties because a rectifier is needed to ensure the purity of the regenerated refrigerant since a noticeable amount of the organic additives can exist with refrigerants in the vapor phase in the generator. In contrast, an absorption cycle that includes ILs as anticrystallization additives does not require the use of a rectifier because most ILs do not have a detectable vapor pressure. The solubility result presented in Fig. 4 assists in extending the operation range of the absorption chiller.

CONCLUSION

We synthesized [bmim][Br], [bmim][Cl], [bmim][I], and [bmim][BF₄] and analyzed the purity of each. The viscosities and surface

tensions of [bmim][I] and [bmim][BF₄] were investigated under various temperature conditions, and the solubility of the LiBr+[bmim][Br] in H₂O was measured. The viscosity and surface tension values of [bmim][I] were higher than those of [bmim][BF₄]. The solubility data indicate that [bmim][Br] extends the solubility area for the absorption process. Therefore, the IL can be a potential an additive as an alternative to the conventional organic compounds. However, further tests of other thermodynamic and transport properties are required before this mixture can be used as a working fluid.

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