J. Chem. Eng. Data **2007,** *52,* 377−380

Physical Properties of 1-Butyl-3-methylimidazolium Methyl Sulfate as a Function of Temperature

Ana B. Pereiro,[†] Pedro Verdía,[‡] Emilia Tojo,[‡] and Ana Rodríguez*,[†]

Chemical Engineering Department and Organic Chemistry Department, Vigo University, 36210, Vigo, Spain

Density, speed of sound, refractive index, dynamic viscosity, and surface tension measurements of 1-butyl-3-methylimidazolium methyl sulfate have been made as a function of temperature. The synthesis of the ionic liquid is given. The low viscosity of the ionic liquid suggests its use as a solvent in the extraction process for the separation of azeotropic mixtures. The thermal expansion coefficient of the ionic liquid was calculated from the density, and the results are discussed. An analysis of the influence of the alkyl chain length of the cation on the density was performed by comparison with recently published values.

Introduction

Ionic liquids (ILs) are a special class of molten salts that are liquid below 373.15 K and have an appreciable liquid range.[1] This is the most common definition of the ILs, and taking into account the recent attention that they have received due to their unusual properties, more data related to these compounds and their mixtures with organic solvents are published each year. These studies have demonstrated that some of their unique properties should be considered in a different way. For example, negligible vapor pressures were a characteristic of the ILs; however, it appears that many ILs can be distilled at low pressure without decomposition.[2] Although the exploration of ILs is in its infancy, it is necessary to characterize the pure ILs by their physicochemical properties including their transport properties as such information allows us to determine their use in industrial processes.

The most commonly studied ILs contain an imidazolium cation with varying heteroatom functionality. In this paper, we have considered the 1-butyl-3-methylimidazolium cation and the methyl sulfate $[CH_3SO_4]^-$ anion. Densities, speeds of sound, refractive indices, dynamic viscosities, and surface tensions were measured. The density and the speed of sound were determined at the temperature range from (278.15 to 343.15) K, the refractive index from (283.15 to 343.15) K, the dynamic viscosity from (293.15 to 343.15) K, and the surface tension from (283.15 to 313.15) K. Finally, the thermal expansion coefficient was calculated from the density as a function of the temperature. The Eötvos[3] empirical equation was applied, and the results are discussed.

An exhaustive literature survey reveals that a considerable amount of data on the density of ILs are available in the literature; however, for the 1-butyl-3-methylimidazolium methyl sulfate $[BMIM][CH_3SO_4]$ these data are scarce or even absent. In this work, a comparison on the density[4,5] of the IL was made, but no published work on the other physical properties of the alkylimidazolium methyl sulfate was found.

Experimental Section

Chemicals. The reagents used for the synthesis of the IL were of Lichrosolv quality. Before using, the reagents were degassed ultrasonically, dried over freshly activated molecular sieves (types 3 and 4 Å, supplied by Aldrich) for several weeks, and kept in an inert argon atmosphere as soon as the bottles were opened. The chemicals were supplied by Aldrich for 1-butylimidazole (98.0 % mass fraction), by Fluka for dimethyl sulfate (99.0 % mass fraction), and by Merck for toluene (99.9 % mass fraction) and ethyl acetate (99.5 % mass fraction). Chromatographic (GLC) tests of the solvents showed purities that fulfilled purchaser specifications.

Synthesis of 1-Butyl-3-methylimidazolium Methylsulfate. NMR spectra were measured on a Bruker ARX 400 with chemical shifts given in parts per million and coupling constants (*J*) in hertz. Positive FAB mass spectra were recorded on a FISONS VG Autospec spectrometer, using 3-nitrobenzyl alcohol as the matrix.

1-Butyl-3-methylimidazolium methyl sulfate was prepared according to a slightly modified literature procedure.[6] The $[BMIM][CH_3SO_4]$ structure is shown in Figure 1.

Dimethyl sulfate was added dropwise to a solution of equal molar amounts of 1-butylimidazole in toluene (150 mL per 0.42 mol of starting 1-butylimidazole), cooled in an ice-bath under nitrogen at a rate to maintain the reaction temperature below 313.15 K (highly exothermic reaction). The reaction mixture was stirred at room temperature for (1 to 4) h depending on the amount of starting materials (the progress of the reaction was monitored by thin layer chromatography using silica gel 60 GF-254 aluminum sheets and dichloromethane + 10 % methanol as eluent). The upper organic phase of the resulting mixture was decanted, and the lower ionic liquid phase was washed with ethyl acetate (4 × 70 mL per 0.4 mol of starting 1-butylimidazole). After the last washing, the remaining ethyl acetate was removed by heating under reduced pressure. The IL obtained was dried by heating at (343.15 to 353.15) K and stirring under high vacuum (2×10^{-1} Pa) for 48 h. The IL was kept in bottles under an inert gas. In order to reduce the water content to negligible values (lower than 0.03 mass %), vacuum (2×10^{-1} Pa) and moderate temperature (343.15 K) were applied to the IL for several days always immediately prior to their use. Yield: 75 %. ^1H NMR (400 MHz, $CDCl_3$, ppm, δ): 9.18 [s,

---

* Corresponding author. Tel.: +34 986812312. Fax: +34 986812382. E-mail: aroguez@uvigo.es.

[†] Chemical Engineering Department.

[‡] Organic Chemistry Department.

10.1021/je060313v CCC: $37.00

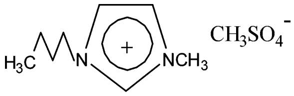

Figure 1. Schematic structure of [BMIM][CH_3SO_4].

1H, H(2)], 7.48 [s, 1H, H(5)], 7.43 [s, 1H, H(4)], 4.12 [t, $J = 7.3$ Hz, 2H, NCH_2], 3.88 [s, 3H, OCH_3], 3.57 [s, 3H, NCH_3], 1.74 [m, 2H, NCH_2CH_2], 1.23 [m, 2H, $N(CH_2)_2CH_2$], 0.81 [t, $J = 7.4$ Hz, 3H, $N(CH_2)_3CH_3$]. Positive FABMS (FISONS VG AUTOSPEC mass spectrometer): *m*/*z* 391 [$(BMIM)_2(CH_3SO_4) + 2]^+$ (8 %), 390 [$(BMIM)_2(CH_3SO_4) + 1]^+$ (22 %), 389 [$(BMIM)_2(CH_3SO_4)]^+$ (100 %).

The IL was kept in bottles under an inert gas. To reduce the water content to negligible values (mass fraction lower than 300 ppm, determined using a 756 Karl Fisher coulometer), vacuum (2×10^{-1} Pa) and moderate temperature (343.15 K) were applied to the IL for several days, always immediately prior to their use.

Experimental Procedure. The samples were prepared by filling glass vials with the IL. Vials are closed with screw caps to ensure a secure seal and to prevent humidity. The sample is taken from the vial with a syringe through a silicone septum and immediately is put into the apparatus.

The density and speed of sound of the IL were measured with an Anton Paar DSA-5000 digital vibrating-tube densimeter. The uncertainty in the measurement is $\pm 2 \times 10^{-5}$ g·cm^{-3} for the density and $\pm$ 0.5 m·s^{-1} for the speed of sound. The apparatus was calibrated with Millipore quality water and ambient air according to instructions. The calibration was checked with pure liquids with known density and speed of sound.

The refractive indices were determined using an automatic refractometer ABBEMAT-WR Dr. Kernchen. The uncertainty in the measurement is $\pm 4 \times 10^{-5}$. The apparatus was calibrated by measuring the refractive index of Millipore quality water and tetrachloroethylene (supplied by the company) before each series of measurements according to manual instructions. The calibration was checked with pure liquids with known refractive index.

Kinematic viscosities were determined experimentally using an automatic viscometer Lauda PVS1 with two Ubbelhode capillary microviscometers with a diameter of 1.26×10^{-3} m. Gravity fall is the principle of measurement on which this viscometer is based. The capillary is maintained in a D20KP LAUDA thermostat with a resolution of $\pm$ 0.01 K. The capillaries were calibrated, and they were credited by the supplier company. The calibration was checked with pure liquids with known dynamic viscosity. The uncertainty of the capillary diameter is $\pm$ 0.005 mm. The maximum deviation between experimental and calculated measurements is 3 %. The equipment has a control unit PVS1 (processor viscosity system) that is a PC-controlled instrument for the precise measurement of liquid viscosity using standardized glass capillaries with an uncertainty of $\pm$ 0.01 s.

The kinematic viscosity was determined from the following relationship:

$$\nu = k(t - y) \tag{1}$$

where y is the Hagenbach correction, t is the flow time, and k is the Ubbelhode capillary microviscometer constant, being y and k supplied by the company.

The surface tension of the IL was measured with the Lauda TVT2 tensiometer by the hanging drop method. The measuring tank was thermostatized in a Polyscience temperature controller with a temperature stability of $\pm$ 0.005 K, which is regulated in a D20KP LAUDA thermostat. The uncertainty in the temperature is $\pm$ 0.01 K. The equipment has both a control and a mechanic unit that are connected to a PC-controlled instrument for the precise measurement of liquid with an uncertainty of $\pm$ 0.1 mN·m^{-1}. The radiuses of the needles were calibrated, and they were credited by the supplier company. The calibration was checked with pure liquids with known surface tension.

Table 1. Density ρ, Speed of Sound u, Refractive Index n_D, Dynamic Viscosity η, and Surface Tension σ of [BMIM][CH_3SO_4] as a Function of Temperature

T/K	ρ/g·cm^{-3}	u/m·s^{-1}	n_D	η/mPa·s	σ/mN·m^{-1}
278.15	1.22584	1708.3			
283.15	1.22244	1695.8	1.48351		45.9
288.15	1.21903	1683.4	1.48213		45.0
293.15	1.21562	1670.9	1.48076	288.99	44.1
298.15	1.21222	1658.4	1.47942	213.19	43.3
303.15	1.20881	1646.0	1.47805	160.93	42.8
308.15	1.20541	1633.5	1.47671	123.73	42.3
313.15	1.20204	1621.1	1.47536	96.83	41.8
318.15	1.19866	1608.6	1.47400	77.08	
323.15	1.19534	1596.1	1.47266	62.22	
328.15	1.19202	1583.7	1.47132		
333.15	1.18873	1571.2	1.47000	42.24	
338.15	1.18545	1558.8	1.46864		
343.15	1.18219	1546.3	1.46725	29.99	

Results and Discussion

The following properties of [BMIM][CH_3SO_4] as a function of temperature have been measured: the density and the speed of sound from (278.15 to 343.15) K, the refractive index from (283.15 to 343.15) K, the dynamic viscosity from (293.15 to 343.15) K, and the surface tension from (288.15 to 313.15) K. The experimental values are listed in Table 1.

Physical Properties. The density ρ, speed of sound u, refractive index n_D, dynamic viscosity η, and surface tension σ values were fitted by the method of least-squares using the following equations:

$$z = A_0 + A_1 T + A_2 T^2 \tag{2}$$

$$\log \eta = A_0/T - A_1 \tag{3}$$

where z is ρ, u, n_D, or σ; T is the absolute temperature; and A_0, A_1, and A_2 are adjustable parameters. The correlation parameters are given in Table 2 together with the standard deviations (SD). These deviations were calculated by applying the following expression:

$$\mathrm{SD} = \left(\frac{\sum_{i}^{n_{\mathrm{DAT}}} (z_{\mathrm{exp}} - z_{\mathrm{adjust}})^2}{n_{\mathrm{DAT}}} \right)^{1/2} \tag{4}$$

where property values and the number of experimental and adjustable data are represented by z and n_{DAT}, respectively. The variation of the physical properties are plotted graphically as a function of the T in Figure 2.

Thermodynamic Properties. Density data were used to derive other thermodynamic properties such as the thermal expansion coefficient. This coefficient is directly related to temperature derivative of the density through the equation:

$$\alpha = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P \tag{5}$$

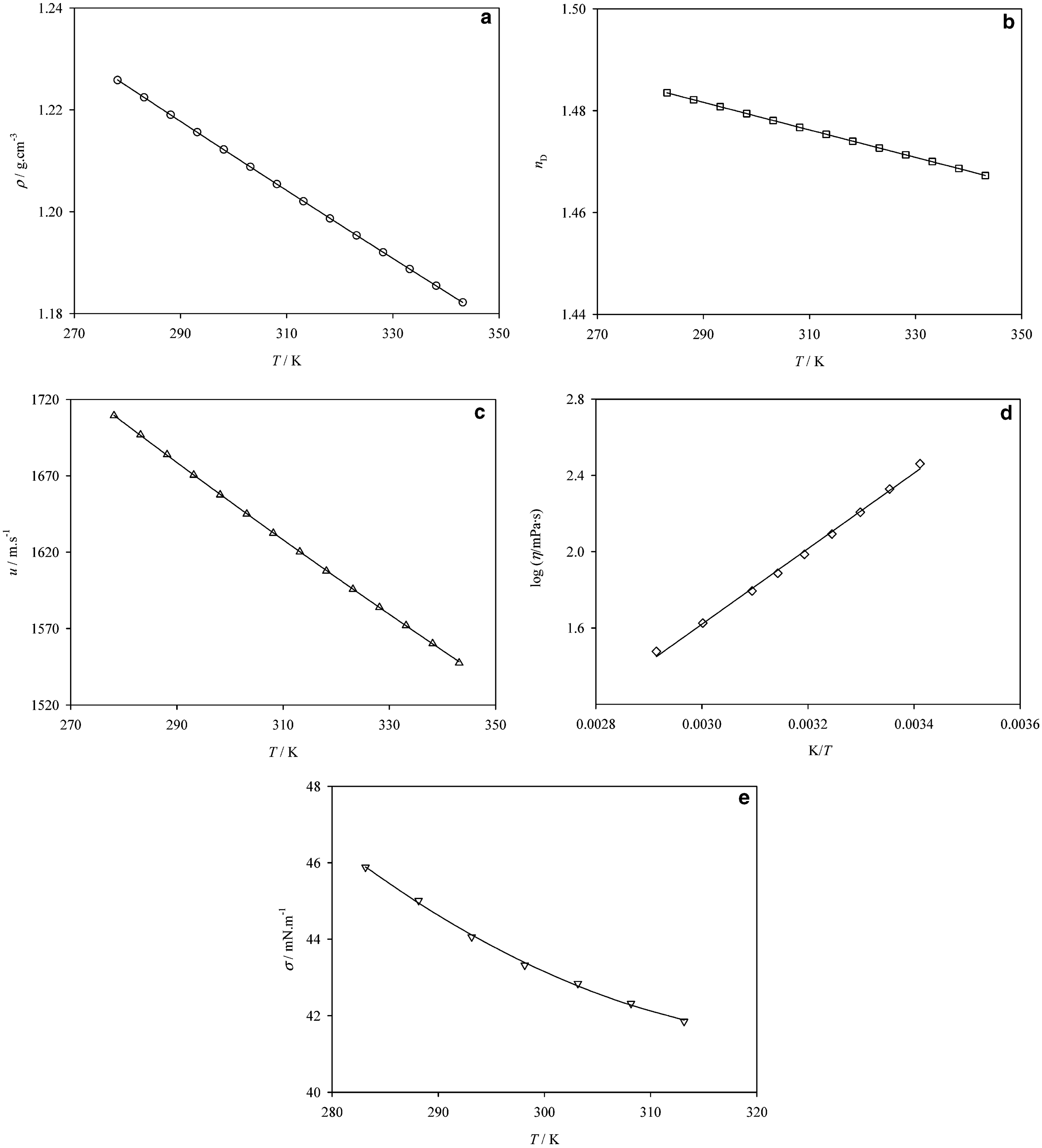

Figure 2. Physical properties at several temperatures: (a) ○, density ρ; (b) □, refractive index n_D; (c) △, speed of sound u; (d) ◇, logarithmic dynamic viscosity, $\log(\eta)$; and (e) ▽, surface tension σ against T and fitted curves for [BMIM][CH_3SO_4].

Table 2. Fitting Parameters of Equations 2 and 3 and Standard Deviations (eq 4) To Correlate the Physical Properties of [BMIM][CH_3SO_4] as a Function of Temperature

physical properties	A_0	A_1	A_2	SD
ρ/g·cm^{-3}	1.43968/g·cm^{-3}	-8.5×10^{-4}/g·cm^{-3}·K^{-1}	2.8×10^{-7}/g·cm^{-3}·K^{-2}	0.00003/g·cm^{-3}
u/m·s^{-1}	2621.6/m·s^{-1}	-3.93/m·s^{-1}	2.3×10^{-3}/m·s^{-1}·K^{-2}	0.2/m·s^{-1}
n_D	1.56283	-2.9×10^{-4}	2.9×10^{-8}/K^{-2}	0.00001
log η/(mPa·s)	1980.1/mPa·s·K	4.3205/mPa·s		0.02/mPa·s
σ/mN·s^{-1}	280.87/mN·s^{-1}	-1.46/mN·s^{-1}·K	2.2×10^{-3}/mN·s^{-1}·K^{-2}	0.04/mN·s^{-1}

where α is the thermal expansion coefficient and ρ is the density of the IL, respectively. The numerical procedure allows us to obtain $\alpha = 4 \times 10^{-4}$ K^{-1} at 298.15 K.

The surface tension of the IL has been measured as a function of temperature. The experimental data decrease with increase in temperature. In Figure 3, these values were compared with

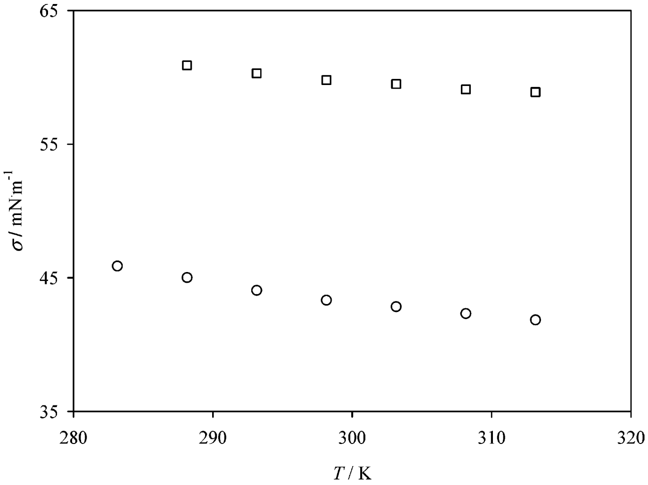

Figure 3. Comparison values of surface tension σ (○) of [BMIM][CH_3SO_4] with (□) [MMIM][CH_3SO_4].

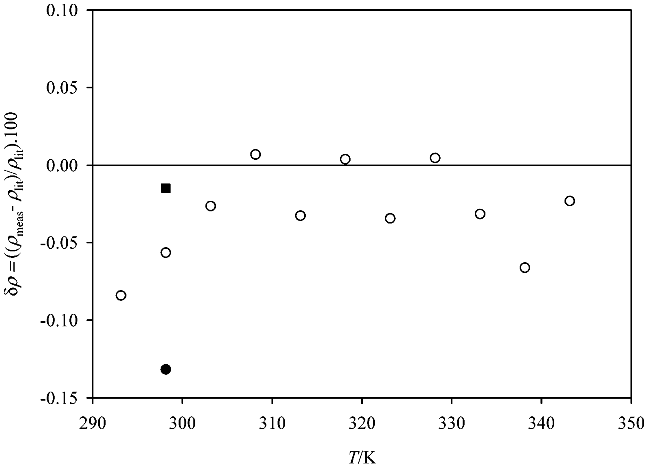

Figure 4. Percentage deviations of density ρ as a function of the temperature of [BMIM][CH_3SO_4]: ■, Domanska et al.;[4] and of [MMIM][CH_3SO_4]: ●, Domanska et al.;[4] ○, Kato and Ghmeling.[5]

those obtained with [MMIM][CH_3SO_4]. Based on these data, it appears that the surface tension increases when the length of the alkyl chain in the imidazolium cation decreases.

The relationship between surface tension and temperature of a pure component can be represented properly using the Eötvos empirical equation:

$$\sigma\cdot V_{\text{molec}}^{2/3} = k(T_c - T) \qquad (6)$$

where V_{molec} is the molecular volume of the liquid, T_c is the critical temperature, and k is an empirical constant related to the polarity of the pure component. The molecular volume of [BMIM][CH_3SO_4] was calculated from the experimental density using the following equation:

$$V_{\text{molec}}/\text{nm}^3 = \frac{M}{N\cdot\rho} \qquad (7)$$

where M is the molar mass (250.32 g·mol^{-1}), N is the Avogadro number, V_{molec} is the molecular volume, and ρ is the density that in this case is a function of temperature.

Using a linear regression for the surface tension and experimental values for the density as a function of the temperature, the Eötvos equation for [BMIM][CH_3SO_4] is found to be $\sigma\cdot V^{2/3} = 4\cdot10^{20} - 0.6\cdot10^{-24}\cdot T$. The k value can represent the polarity of the IL which in this case is 0.6×10^{-24} J·K^{-1}.

A comparison with the literature data in terms of percentage deviations of the density of the [BMIM][CH_3SO_4] and [MMIM][CH_3SO_4] (published in a previous paper[7]) is made in Figure 4. The obtained results allow us to assume that relative error in density measurements does not exceed ± 0.1 and 0.15 % in the temperature range for [MMIM][CH_3SO_4] from those published by Domanska et al.[4] and Kato and Ghmeling,[5] respectively. The relative error for [BMIM][CH_3SO_4] does not exceed ± 0.01 % from the published by Domanska et al.[4] In this case, the density decreases with the temperature and alkyl chain on the cation as it was documented[8] for imidazolium-based cations.

Conclusions

The density, refractive index, speed of sound, dynamic viscosity, and surface tension data for the [BMIM][CH_3SO_4] were measured as a function of the temperature at atmospheric pressure. A comparison of the density between our synthesized IL and others with different origin agree with the reported value at 298.15 K. This result confirms the good purity of the IL synthesized in our laboratory. Related to densities, it normally depends on the molar mass of the ILs, which should be denser in [BMIM][CH_3SO_4] than in [MMIM][CH_3SO_4] due to the length of the alkyl chain; however, this is not valid for strongly asymmetric cations. In this case, the density decreases with the length of the alkyl chain on the imidazolium cation.

Since the densities of the ILs are polynomial functions of temperature, the thermal expansion coefficient is easily obtained from the fitting density polynomial equation. This value is significantly lower than those for most organic liquids. For instance, the toluene α is 11×10^{-4} but is higher than for fused molten salts; for example, $\alpha = 3.632 \times 10^{-4}$ for KCl. The presence of the [BMIM] cation seems to yield a lower volume expansity or thermal expansion than for the conventional organic compounds.

Literature Cited

(1) Holbrey, J. D.; Rogers, R. D. *Ionic Liquids in Synthesis*; VCH-Wiley: Weinheim, 2002.

(2) Earle, M. J.; Esperança, J. M. S. S.; Gilea, M. A.; Canongia Lopes, J. N.; Rebelo, L. P. N.; Magee, J. W.; Seddon, K. R.; Widegren, J. A. The distillation and volatility of ionic liquids. *Nature* **2006**, *439*, 831−834.

(3) Adamson, A. W. *Physical Chemistry of Surfaces*, 3rd ed.; Wiley: New York, 1976 (translation by Gu, T. R. Science Press, Beijing, 1986).

(4) Domanska, U.; Pobudkowska, A.; Wisniewska, A. Solubility and excess molar properties of 1,3-dimethylimidazolium methylsulfate, or 1-butyl-3-methylimidazolium methylsulfate, or 1-butyl-3-methylimidazolium octylsulfate ionic liquids with *n*-alkanes and alcohols: analysis in terms of the PFP and FBT models. *J. Solution Chem.* **2006**, *35*, 311−334.

(5) Kato, R.; Gmehling, J. Activity coefficients at infinite dilution of various solutes in the ionic liquids [MMIM][CH_3SO_4], [MMIM][$CH_3OC_2H_4SO_4$], [MMIM][$(CH_3)_2PO_4$], [$C_5H_5NC_2H_5$][$(CF_3SO_2)_2N$] and [C_5H_5NH][$C_2H_5OC_2H_4OSO_3$]. *Fluid Phase Equilib.* **2004**, *226*, 37−44.

(6) Holbrey, J. D.; Reichert, W. M.; Swatloski, R. P.; Broker, G. A.; Pitner, W. R.; Seddon, K. R.; Rogers, R. Efficient, halide free synthesis of new, low cost ionic liquids: 1,3-dialkylimidazolium salts containing methyl- and ethyl-sulfate anions. *Green Chem.* **2002**, *4*, 407−413.

(7) Pereiro, A. B.; Santamarta, F.; Tojo, E.; Rodríguez, A.; Tojo, J. Temperature dependence of physical properties of ionic liquid 1,3-dimethylimidazolium methyl sulfate. *J. Chem. Eng. Data* **2006**, *51*, 952−954.

(8) Gu, Z.; Brennecke, J. Volume expansivities and isothermal compressibilities of imidazolium and pyridinium-based ionic liquids. *J. Chem. Eng. Data* **2002**, *47*, 339−345.

Received for review July 7, 2006. Accepted December 18, 2006. We thank the Ministerio de Educación y Ciencia (Spain) for the financial support through Project CTQ 2004-00454.

JE060313V