Temperature Dependence of Physical Properties of Ionic Liquid 1,3-Dimethylimidazolium Methyl Sulfate

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This paper reports on the synthesis of the ionic liquid 1,3-dimethylimidazolium methyl sulfate [MMIM][MeSO$_4$]. Experimental densities, speed of sounds, and refractive indices were determined from (283.15 to 343.15) K. Dynamic viscosities were measured from (293.15 to 343.15) K. Surface tensions were measured from (288.15 to 313.15) K. The coefficient of thermal expansion and molecular volume of [MMIM][MeSO$_4$] were calculated from experimental values of density.

Introduction

Room-temperature ionic liquids (RTILs) are organic salts that melt below 373.15 K and have an appreciable liquid range.[1] The most commonly studied ionic liquids (ILs) contain ammonium, phosphonium, pyridinium, or imidazolium cations, with varying heteroatom functionality. In this paper, we have considered the use of imidazolium cation and methyl sulfate $[CH_3SO_4]^-$ as anion.

Recently, RTILs have received more attention because of their unusual properties. Thus, they have great potential as “green” solvents for industrial processes,[2] possibly replacing currently used organic solvents due to their unique properties such as negligible vapor pressures, broad liquid temperature range, and high specific solvent abilities. Despite the importance of RTILs and their interest, accurate values for many of their fundamental physical−chemical properties are either scarce or even absent, but a few authors[3−5] have studied the structural organization of ILs and the dependence of their physical−chemical properties with different parameters of some ILs.

Densities, refractive indices, dynamic viscosities, and other physical properties are very useful industrially. An exhaustive literature survey reveals no published work on the physical properties of the ionic liquid 1,3-dimethylimidazolium methyl sulfate [MMIM][MeSO$_4$]. With the aim of characterizing the pure component, experimental densities, speed of sounds, refractive indices, dynamic viscosities, and surface tensions at a temperature range of (283.15 to 343.15) K of the [MMIM][MeSO$_4$] have been determined. From the experimental density, the coefficient of thermal expansion and the molecular volume have been calculated.

In this paper, the IL is characterized as liquid in this interval due to the solid−liquid transition[6] being broad, between −18 °C (super-cooling temperature for crystallization in the cooling cycle) and 43 °C (melting point in heating cycle).

Experimental Section

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

Synthesis of 1,3-Dimethylimidazolium Methyl Sulfate. 1,3-Dimethylimidazolium methyl sulfate was prepared according to a slightly modified literature procedure.[6] Figure 1 shows the [MMIM][MeSO$_4$] structure.

Dimethyl sulfate was added dropwise to a solution of equal molar amounts of 1-methylimidazol in toluene (150 mL/0.42 mol of starting 1-methylimidazol) and cooled in an ice bath under nitrogen at a rate to maintain the reaction temperature below 313.15 K, due to the reaction being highly exothermic. 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 aluminum sheets silica gel 60 GF-254, dichloromethane + 10 % methanol as eluent). The upper organic phase of the resulting mixture was decanted, and the lower IL phase was washed with ethyl acetate (4 × 70 mL per 0.4 mol of starting 1-methylimidazol). After the last washing, the remaining ethyl acetate was removed by heating under reduced pressure. The ionic liquid obtained was dried by heating to (343.15 to 353.15) K and stirring under high vacuum (2×10^{-1} Pa) for 48 h. ^{1}H NMR (400 MHz, D$_2$O, ppm): δ 8.69 [s, 1 H, H-2], 7.48 [d, $J = 1.4$ Hz, 2 H, H-4,5], 3.95 [6 H, NCH$_3$], 3.79 [s, 3 H, OCH$_3$]. The ionic liquid was kept in bottles with inert gas. To reduce the water content to negligible values (mass fraction lower than 0.03 %, 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 density and speed of sound of the pure liquid were measured with an Anton Paar DSA-5000 digital vibrating-tube densimeter. The repeatability and the uncertainty in experimental measurements have been found to be lower than ($\pm 2 \times 10^{-6}$ and $\pm 10^{-5}$) g·cm^{-3} for the

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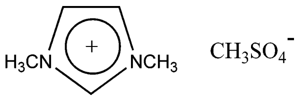

Figure 1. Schematic structure of [MMIM][MeSO$_4$].

density and (± 0.01 and ± 0.1) m·s^{-1} for the speed of sound. The apparatus was calibrated by measuring the density of Millipore quality water and ambient air according to manual instruction. The calibration was checked with pure liquids with known density and speed sound.

The refractive indices were determined by the automatic refractometer ABBEMAT-WR Dr. Kernchen with a resolution of ± 10^{-6} and an uncertainty in the experimental measurements of ± 4·10^{-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 instruction. 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 (7·10^{-4} and 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 ± 0.01 K. The capillaries were calibrated and were credited by the supplier company. The calibration was checked with pure liquids with known dynamic viscosity. The uncertainty of the capillary diameter is ± 0.005 mm. The uncertainty in the experimental measurements has been found to be ± 0.01 mPa·s. 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 ± 0.01 s.

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

Results and Discussion

The physical properties of [MMIM][MeSO$_4$] were measured experimentally from (283.15 to 343.15) K for the density, speed of sound, and refractive index from (293.15 to 343.15) K for the dynamic viscosity and from (288.15 to 313.15) K for the surface tension. The values are listed in Table 1.

The frequency of an Anton Paar densimeter is affected by the viscosity of the sample,[7] at high viscosity a correction has to be applied to the density. Our samples have low viscosities, and this correction must not be applied.

Table 1. Density ρ, Speed of Sound u, Refractive Index n_D, Dynamic Viscosity η, and Surface Tension σ of [MMIM][MeSO$_4$] at Several Temperatures

T/K	ρ/g·cm^{-3}	u/m·s^{-1}	n_D	η/mPa·s	σ/mN·m^{-1}
283.15	1.33824	1851	1.48659		
288.15	1.33454	1838	1.48525		60.9
293.15	1.33088	1826	1.48392	92.76	60.3
298.15	1.32725	1813	1.48270	72.91	59.8
303.15	1.32365	1801	1.48129	58.35	59.5
308.15	1.32009	1789	1.47999		59.1
313.15	1.31657	1777	1.47867	39.21	58.9
318.15	1.31305	1765	1.47726		
323.15	1.30955	1753	1.47593	27.78	
328.15	1.30606	1742	1.47421		
333.15	1.30259	1730	1.47294	21.01	
338.15	1.29914	1719	1.47154		
343.15	1.29570	1708	1.47027	16.01	

Table 2. Fitting Parameters of Equations 2 and 3 and Standard Deviations (eq 4) To Correlate the Physical Properties of [MMIM][MeSO$_4$]

physical properties	A_0	A_1	SD
ρ/g·cm^{-3}	1.538397	−0.000708	0.00014
ln(ρ/g·cm^{-3})	0.443489	−0.000538	0.00010
u/m·s^{-1}	2522.9	−2.3794	0.8
n_D	1.564301	−0.000274	0.00012
log(η/mPa·s)	1532.2	3.2799	0.02
σ/mN·m^{-1}	83.385	−0.0787	0.1

Density, Speed of Sound, Refractive Index, Dynamic Viscosity, Surface Tension, and Miscibility. 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:

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

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

where z is ρ, u, n_D, or σ; T is the absolute temperature; and A_0 and A_1 are adjustable parameters. The correlation coefficient of the linear regression is 0.9999 for the density, 0.9997 for the speed of sound, 0.9995 for the refractive index, 0.9968 for the dynamic viscosity, and 0.9728 for the surface tension. The correlation parameters are listed 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. Figures 2 to 5 show the physical properties against T.

Thermodynamic Properties. The values of density were fitted by the method of the least-squares using the following empirical equation:

$$\ln \rho = A_0 + A_1 T \tag{5}$$

where T is the absolute temperature and A_0 and A_1 are fitting parameters. Figure 2 shows the experimental and adjustable values of ln ρ against T. The correlation coefficient of the linear regression is 0.9999.

The coefficient of thermal expansion of [MMIM][MeSO$_4$] is defined by the following equation:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{\mathrm{P}} = -\left(\frac{\partial \ln \rho}{\partial T}\right)_{\mathrm{P}} \tag{6}$$

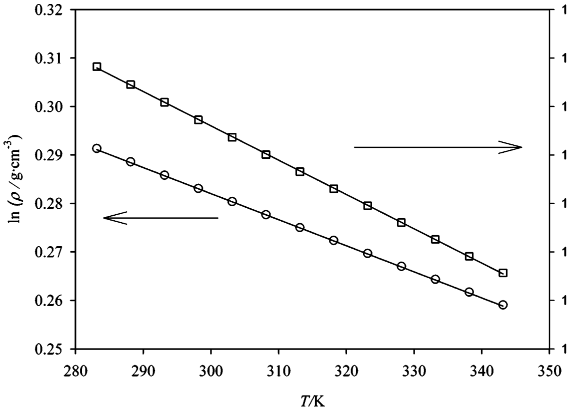

Figure 2. Plot of experimental values of ln ρ (○) and ρ (□) against T and fitted curves for [MMIM][MeSO$_4$].

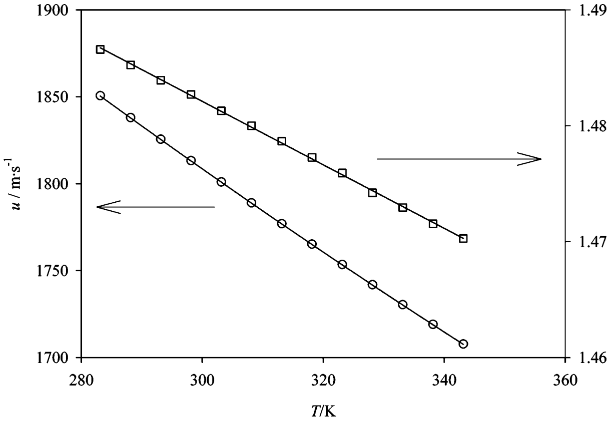

Figure 3. Plot of experimental values of speed of sound u (○) and n_D (□) against T and fitted curves for [MMIM][MeSO$_4$].

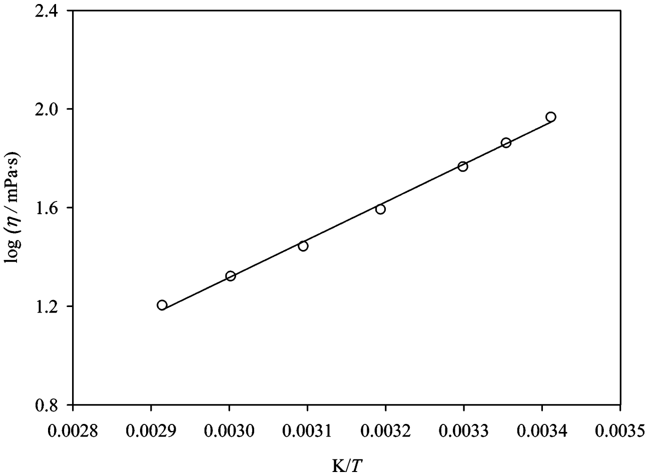

Figure 4. Plot of experimental values of log η (○) against 1/T and fitted curve for [MMIM][MeSO$_4$].

where α is the coefficient of thermal expansion, V is the volume of the ionic liquid, and ρ is the density of the ionic liquid. A value $\alpha = 5 \cdot 10^{-4}$ K^{-1} was obtained from this equation. The molecular volume of [MMIM][MeSO$_4$] at 298.15 K was calculated from the experimental density using the following equation:

$$V_{\text{molec}} = \frac{M}{N\rho} \tag{7}$$

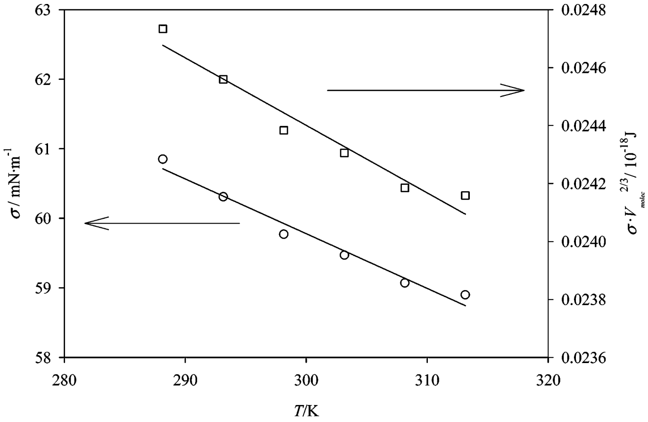

Figure 5. Plot of experimental values of surface tension σ (○) and $\sigma \cdot V_{\text{molec}}^{2/3}$ (□) against T and fitted curves for [MMIM][MeSO$_4$].

where M is the molar mass (208.27 g·mol^{-1}), N is Avogadro's number, and V_{molec} is the molecular volume. The molecular volume at 298.15 K for [MMIM][MeSO$_4$] is 0.2606 nm^3.

In general, σ of many liquids almost linearly decreases while temperature increases, and the relationship is expressed in the Eötvös equation:[8]

$$\sigma \cdot V_{\text{molec}}^{2/3} = k(T_c - T) \tag{8}$$

where V_{molec} is the molecular volume of the liquid, T_c is the critical temperature, and k is an empirical constant. The linear regression of $\sigma \cdot V_{\text{molec}}^{2/3}$ obtained from this experimental values against T was made, and the equation $\sigma \cdot V_{\text{molec}}^{2/3}/10^{-18} \cdot J = 0.0314 - 0.00002\ (T/\text{K})$ was obtained. The standard deviation of the linear regression is 0.001. The value of k is $0.2 \cdot 10^{-24}$ J·K^{-1}. The fused salts have large polarity, and their values of k are low, for example, k is $0.6 \cdot 10^{-24}$ J·K^{-1} for fused NaCl.[8] This implies that [MMIM][MeSO$_4$] has a similar polarity than the fused salts. Therefore, the magnitude of k can represent the polarity of ionic liquids. Figure 5 shows the experimental and adjustable values of $\sigma \cdot V_{\text{molec}}^{2/3}$ against T.

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