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Density, excess properties, electrical conductivity and viscosity of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide + γ-butyrolactone binary mixtures

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A B S T R A C T

Density, electrical conductivity and viscosity of binary liquid mixtures of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [bmim][NTf$_2$], with γ-butyrolactone (GBL) were measured at temperatures from (293.15 to 323.15) K and at atmospheric pressure over the whole composition range. Excess molar volumes have been calculated from the experimental densities and were fitted with Redlich–Kister polynomial equation. Other volumetric properties, such as isobaric thermal expansion coefficients, partial molar volumes, apparent molar volumes and partial molar volumes at infinite dilution have been also calculated, in order to obtain information about interactions between GBL and selected ionic liquid.

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1. Introduction

Ionic liquids (ILs) are molten salts consisting of a large, asymmetric organic cations and organic or inorganic anions with a melting point below 100 °C [1,2]. Numerous combinations of different anions with structurally modified cations can affect their physical and chemical properties. Increasing attention has been paid to room-temperature ionic liquids (RTILs) and their application as green solvents, since many of them are non-volatile, biodegradable and recyclable materials [3]. RTILs became one of the most rapidly growing areas in green chemistry because of their remarkable and tunable physical and chemical properties, such as high thermal [4] and electrochemical stability [5], negligible vapor pressure [6], large liquidus range [7], flame retardant [8] and good ability to dissolve organic and inorganic compounds [9]. Thus, these physicochemical properties are making them interesting solvents for electrolytes in lithium-ion battery production [10–12]. Exchange of common organic solvents by RTILs can enhance the safety of lithium-ion batteries [13]. However, pure ionic liquids are highly viscous which impedes their application [14]. The high viscosity of RTILs can be overcome by mixing with some molecular solvents [15–17].

Good solvent candidates for improving volumetric and transport properties of ILs are cyclic carbonates or lactones which are usually applied as solvents in the lithium batteries and electrochemical devices due to some of their fundamental characteristics such as a large electrochemical window, a high solvating power for lithium salts and a high relative permittivity [18]. An aprotic solvent which can be used as a component in the lithium-ion batteries is γ-butyrolactone, since the polarity of GBL provides excellent solvation of lithium ions and thus the increasing conductivity. GBL has a strong dipolar moment, a sufficiently high dielectric constant, a relatively low viscosity, a low fusion point (−45 °C) and a high boiling point (204 °C) [19]. The mixture of GBL with selected ILs can improve both the performance and thermal stability of the electrolytes [20,21]. Due to these reasons, further physicochemical characterization of GBL binary mixtures with different ILs is required.

In this study, volumetric, thermal and transport properties of different binary mixtures of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquid, [bmim][NTf$_2$], with γ-butyrolactone have been presented as a function of temperature and composition.

2. Experimental section

2.1. Materials

Ionic liquid [bmim][NTf$_2$] and GBL were purchased from Merck. Mass fraction purity of both chemicals was ⩾0.99. The water

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content was less than $1 \cdot 10^{-4}$ mass fraction, as determined by Karl Fisher titration using a 831 Karl Fischer coulometer. GBL was used without purification. All the chemicals were kept above 0.4 nm molecular sieves for 1 week to remove any trace of water. Chemicals were stored in a desiccator above P_2O_5. In order to remove remaining amounts of water and other volatile impurities, we kept the ionic liquid under vacuum for 24 h with constant stirring. The summary of the provenance and purity of the samples is given in table 1.

Binary mixtures covering the whole composition range of [bmim][NTf$_2$] and GBL were prepared by measuring appropriate amount of the components on a Denver analytical balance. The standard uncertainty of mass fraction is less than $\pm 5 \cdot 10^{-5}$.

2.2. Apparatus and procedure

2.2.1. Density measurements

The vibrating tube densimeter, Rudolph Research Analytical DDM 2911 with the accuracy and precision of $\pm 0.00001 \text{ g} \cdot \text{cm}^{-3}$ was used for density measurements. Density measurements with a vibrating tube are based on the dependence of oscillation period of a unilaterally fixed U-tube on its mass. Prior the injection of the samples into U-tube they were kept for one hour in an ultrasonic bath. The total volume of the samples used for density measurements was approximately 1 cm^3. Special attention has been paid to the injection of the samples with no air bubbles which would give wrong results. The instrument was thermostated (Peltier-type) within ± 0.01 K and viscosity was automatically corrected. Before each series of measurements calibration of the instrument was performed at the atmospheric pressure. The calibration was made using ambient air and bi-distilled ultra pure water in the temperature range (293.15 to 323.15) K. Densimeter already has incorporated moisture adsorbent. Each experimental density value is the average of at least three measurements at temperatures from (293.15 to 323.15) K. Repeated experimental measurements showed reproducibility within 0.001%, and an average value is presented in this paper. The standard uncertainty of determining the density is less than $2.0 \cdot 10^{-5} \text{ g} \cdot \text{cm}^{-3}$.

2.2.2. Electrical conductivity measurements

Mixtures for the conductivity measurements were prepared by mixing the appropriate amounts of [bmim][NTf$_2$] and GBL. These measurements were carried out in a Pyrex cell with platinum electrodes in the temperature range (293.15 to 323.15) K on a conductivity meter Jenco 3107, using DC signal. The conductometric cell with a total volume of 14 cm^3 was initially dried in the atmosphere of nitrogen and thermostated for twenty minutes with the external flow with an accuracy of ± 0.01 K. At least 10 measurements were performed at 5 s intervals, in order to eliminate the self-heating and ionization in the electrodes [22]. The experimental cell was calibrated with standard 0.1000 mol $\cdot$ dm^{-3} KCl solution by the same experimental procedure. The resulting cell constant amounted to 1.0353 cm^{-1}, and it was checked from time to time to control any possible evolution. The relative standard uncertainty for electrical conductivity was less than 1.5%. All obtained experimental values represent the mean of three measurements.

2.2.3. Viscosity measurements

Viscosity was measured using a Brookfield Viscosimeter DV II + Pro thermostated with an accuracy of ± 0.01 K and filled with

TABLE 1
Provenance and purity of the samples.

Chemical name	Provenance	Mass fraction purity
[bmim][NTf$_2$]	Merck	$\geqslant 0.99$
γ-Butyrolactone	Merck	$\geqslant 0.99$

about 8 cm^3 of tested binary mixtures or pure components. The principal of operation of the DV-II + Pro is to drive a spindle (which is immersed in the test fluid) through a calibrated spring. The viscous drag of the fluid against the spindle is measured by the spring deflection. Spring deflection is measured with a rotary transducer. The measurement range is determined by the rotational speed of the spindle, the size and shape of the spindle, the container the spindle is rotating in, and the full scale torque of the calibrated spring. The spindle type (SC4-18), which is attached to the rotating cylinder, was immersed and rate per minute (RPM) was set in order to obtain a suitable torque (20% to 80%). A viscometer cell protected from moisture with the compartment made by the manufacturer was calibrated using the liquids of different viscosities purchased from the manufacturer. Viscosity was measured in the temperature range from (293.15 to 323.15) K with the rotation speed of 60 RPM for pure ionic liquid to 180 RPM for pure GBL. Presented experimental values are the mean of three measurements and the measurement relative standard uncertainty was found to be about 1%.

3. Results and discussion

3.1. Densities

Densities of pure components and ([bmim][NTf2] + GBL) mixtures were measured as a function of temperature in the range from (293.15 to 323.15) K and the results are shown in tables 2 and 3 and also in figure S1 in the supporting information. From these results it can be concluded that the density decreases with the increasing temperature and increases with the ionic liquid mole fraction in the binary mixture. Obtained data were fitted as a function of temperature using a linear fit. These parameters are given in table S1 in the supporting information.

Values of the excess molar volume, V^E, were calculated from the experimental density of the mixture, d, densities of the pure components, d_i, the corresponding mole fractions, x_i, and molar masses, M_i, using the following equation:

$$V^E = x_1 M_1 \left(\frac{1}{d} - \frac{1}{d_1} \right) + x_2 M_2 \left(\frac{1}{d} - \frac{1}{d_2} \right), \tag{1}$$

where x_1, M_1 and d_1 relate to [bmim][NTf$_2$] whereas x_2, M_2 and d_2 relate to GBL.

Values of the excess molar volumes are given in table 3 and graphically presented in figure 1 using a Redlich–Kister-type equation [43] where Y^E represents the excess property:

$$Y^E = x_1 x_2 \sum_{i=0}^{n} A_i (1 - 2x_1)^i. \tag{2}$$

Values of the excess molar volumes were fitted by a method of the least squares. Here, A_i refers to the adjustable parameters and n is the number of the coefficients in the equation. The standard deviation of the fit is given as:

$$\sigma Y^E = \left[\sum_1^m \left(Y^E_{exp} - Y^E_{calc} \right)^2 \Big/ (m - n) \right]^{\frac{1}{2}}, \tag{3}$$

where m denotes the number of experimental points. The coefficients of the Redlich–Kister's equation, as well as the standard deviations of the fit are given in table S2 as the supporting information.

Figure 1 shows that the values of excess molar volumes are negative in the whole composition range with a minimum at x(IL) = 0.5. Negative values of excess molar volumes indicate that the interaction between the IL and the GBL becomes significant. This will lead to a volume contraction of the mixture. Comparing