



Ideal and non-ideal behaviour of {1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide + γ -butyrolactone} binary mixtures



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ABSTRACT

Density, electrical conductivity and viscosity of binary liquid mixtures of 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [bmpyr][NTf₂], 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 fitted with the Redlich–Kister polynomial equation. These values are positive over the whole range of ionic liquid mole fraction and at all temperatures. In the range between 0.55 and 0.6 [bmpyr][NTf₂] mole fraction, an ideal behaviour of the ionic liquid mixture with molecular solvent was observed for the first time. Other volumetric properties, such as isobaric thermal expansion coefficients, partial 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. Positive values of these properties for both components also indicate weaker interactions between GBL and IL compared to the pure components. From the viscosity results, the Angell strength parameter was calculated and found to be 3.24 indicating that [bmpyr][NTf₂] is a “fragile” liquid. From the volumetric and transport properties obtained, formation of the [bmpyr]⁺ micellar structures was also discussed. All the results are compared to those obtained for imidazolium-based ionic liquid with GBL.

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1. Introduction

Ionic liquids (ILs) have been described as molten salts with a melting point below 100 °C, consisting of a large asymmetric organic cations and organic or inorganic anions [1]. Room temperature ionic liquids (RTILs) are designed solvents with physicochemical properties that can be easily tuned simply by changing the structure of the cations and/or anions [2]. Cation variation is essential for physicochemical properties such as polarity, density, viscosity and ionic diffusion. Ionic liquids possess remarkable properties, such as high thermal and electrochemical stability [3,4], large liquidus range [5] and the ability of dissolution and extraction of inorganic and organic components [6,7]. In addition to the favourable physical and chemical properties of ionic liquids, their negligible vapour pressure [8,9], non-flammability [10], biodegradability and recyclability [11], make them interesting for a wide range of applications as potentially green solvents associated with little waste, risk and hazard problems. Since the ionic liquids are essentially ionic conductors, their utilisation as novel electrolytes for electrochemical devices, such as lithium-ion batteries

[12–14], electric double layer separators, dye-sensitised solar cells and fuel cells has also been the subject of intense studies. Exchange of common organic solvents by RTILs can enhance the safety of lithium-ion batteries [15]. The high viscosity of RTILs, which is limiting factor for their practical and industrial application [16] can be overcome by mixing RTILs with selected molecular solvents [17–19].

Solvents such as propylene carbonate (PC) and γ -butyrolactone (GBL) have a high boiling point, low melting point and low vapour pressure. The GBL is also a non-corrosive liquid suitable for electrochemical cells, operating over a wide temperature range for a long time. These properties make GBL a good solvent candidate to be used to improve volumetric and transport properties of ILs, due to its biodegradability, low toxicity [20] and large electrochemical window [21]. Thus, GBL is usually applied as a solvent in the new generation of lithium-ion batteries and electrochemical devices since the polarity of GBL provides excellent solvation of lithium ions and thus the increasing conductivity.

Comprehensive study of the properties of electrolytes in aprotic solvents has been undertaken in order to understand the factors and interactions which limit the performance of the batteries [22,23]. GBL has a strong dipole moment, a sufficiently high relative permittivity ($\epsilon = 39$), a relatively low viscosity and a high

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boiling point (204 °C) [24]. The mixture of GBL with selected ILs can improve both the performance and thermal stability of the electrolytes [25,26]. For potential use of these mixtures in various chemical processes, it is of immense importance to understand their mixing behaviour and gather accurate physicochemical data.

In this study, volumetric and transport properties of different binary mixtures of 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ionic liquid ([bmpyrr][NTf₂]) with γ -butyrolactone are presented as a function of temperature and mixture composition.

2. Experimental

2.1. Materials

The ionic liquid [bmpyrr][NTf₂] and GBL were purchased from Merck. The mass fraction purity of both chemicals was $\omega \geq 0.99$. The summary of the provenance and purity of the samples is given in table 1. 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 water content was less than $1 \cdot 10^{-4}$ mass fraction, as determined by Karl Fisher titration using a 831 Karl Fischer coulometer. GBL was kept under 0.4 nm molecular sieves for one week to remove traces of water. Chemicals were stored in a desiccator above P₂O₅. Binary mixtures covering the whole composition range of [bmpyrr][NTf₂] and GBL were prepared by measuring appropriate amounts 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. This mass consists of the U-tube material and the mass of the fluid filled into the U-tube. 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 $\pm 0.01 \text{ K}$ 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 within the temperature range (293.15 to 323.15) K. The densimeter already had 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 $5.0 \cdot 10^{-5} \text{ g} \cdot \text{cm}^{-3}$.

TABLE 1

Provenance and purity of the samples.

Chemical name	Provenance	Mass fraction purity
[bmpyrr][NTf ₂]	Merck	$\omega \geq 0.99$
γ -Butyrolactone	Merck	$\omega \geq 0.99$

2.2.2. Viscosity measurements

Viscosity was measured using a Brookfield Viscosimeter DV II + Pro thermostated with an accuracy of $\pm 0.01 \text{ K}$ and filled with 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%.

2.2.3. Electrical conductivity measurements

Mixtures for the conductivity measurements were prepared by mixing the appropriate amounts of [bmpyrr][NTf₂] and GBL. These measurements were carried out in a Pyrex cell with platinum electrodes in the temperature range (298.15 to 323.15) K on a conductivity metre 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 $\pm 0.01 \text{ K}$. At least 10 measurements were performed at 5 s intervals, in order to eliminate the self-heating and ionisation in the electrodes [27]. The experimental cell was calibrated with standard $0.1000 \text{ mol} \cdot \text{dm}^{-3}$ 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 experimental values obtained represent the mean of three measurements.

3. Results and discussion

3.1. Volumetric parameters

Densities of pure components, [bmpyrr][NTf₂] and GBL, were measured within the temperature range from (293.15 to 323.15) K and the experimental results are plotted in figure 1, together with the available literature values for these compounds [20,28–49]. It is found that deviations of our experimental results obtained for IL (figure 1(a)) from the literature values are less than 0.2% over the whole range of temperature. The highest deviation was found to be in the case of the values measured by Kato and Gmehling [39] where deviation exceeds 0.2%, while the best match of our experimental data is with those reported by Pereiro *et al.* [29] and Harris *et al.* [36] (deviations in the whole temperature range does not exceed 0.07%). Experimental densities for GBL (figure 1(b)) deviate from the literature values up to 0.075%, except in the case of the values obtained by Boodida *et al.* [44] and Yang *et al.* [42] especially at higher temperatures.

Densities of ([bmpyrr][NTf₂] + GBL) mixtures as a function of temperature are shown in table 2 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.

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