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A systematic study on physicochemical and transport properties of imidazolium-based ionic liquids with γ-butyrolactone

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ABSTRACT

Densities, viscosities and electrical conductivities were determined and discussed for γ-butyrolactone (GBL) with 1,3-dimethylimidazolium *bis*(trifluoromethylsulfonyl)imide ionic liquid ([mmim][NTf$_2$]) binary mixtures as a function of temperature at atmospheric pressure over the whole composition range. From the experimental density data the related excess molar volumes were calculated and fitted using Redlich–Kister's polynomial equation. The thermal expansion coefficients were also calculated from the acquired experimental density values. Electrical conductivity data were correlated using Casteel–Amis and Arrhenius equations. The influence of viscosity on electrical conductivity was discussed within the scope of Walden rule. Volumetric and transport properties of GBL binary mixtures with selected ionic liquid are compared with available literature data for the corresponding 1-methyl-3-alkylsupstituted imidazolium based ILs.

1. Introduction

With increasing development of industrial and commercial applications of ionic liquids (ILs), the systematic study of their thermal [1], transport [2], electrochemical [3,4], separation [5] and environmental [6] properties became especially important and required, since the physicochemical properties directly determine the choice and purpose of ILs [7]. The physicochemical properties of ionic liquids (ILs) depend on the nature, size and shape of both of their structural elements – cations and anions [8,9]. Properties of ILs can be fine tuned over a wide range by adjusting the structure and chemical composition of the constituting ions [10–13]. Additionally, the cation symmetry and/or length of the supstituent on cation provides a different structural organization which also allows the fine tuning of IL's physicochemical properties [14–17].

Nevertheless, the utilization of ILs is usually limited by their high viscosity [7], which could be overcome by mixing ILs with different molecular liquids [18–21]. An aprotic, non-corrosive, polar solvent with high permittivity ($\varepsilon = 39.1$ [22]), γ-butyrolactone (GBL) is usually applied as a co-solvent in the mixtures with suitable ILs in the new generation of lithium-ion batteries [21]. Addition of GBL into ionic liquids maintains the electrochemical and thermal stability of the mixtures. To understand the properties of such binary mixtures and rationally expand their applications, accurate data on their physicochemical properties are required.

During our systematic research on the thermodynamic properties of ILs binary mixtures with molecular solvents, 1-alkyl-3-methylimidazolium-based ILs were studied both pure and in the mixtures with GBL [23–25]. Therefore, as an extension of our previous studies towards the understanding the ILs fundamental properties, the volumetric and transport properties of 1,3-dimethylimidazolium *bis*(trifluoromethylsulfonyl)imide, ([mmim][NTf$_2$]), binary mixtures with GBL were investigated in the temperature range from (298.15 to 323.15) K. Selected IL is especially interesting since it contains the shortest alkyl substituent on both nitrogen atoms of the imidazole, making this cation highly symmetric. It is also known that selected IL exhibits anomalously low value of melting point and high viscosity values [14,16] comparing to the values of other 1,3-dialkylimidazolium ionic liquids with higher number of C atoms in the alkyl chains. Therefore, physicochemical properties of [mmim][NTf$_2$] binary mixtures with GBL are studied extensively to check whether these deviations remain upon addition of GBL. Influence of the alkyl side chain length on the imidazole are discussed from the obtained volumetric and transport properties data. A comparative discussion of these properties was performed taking into account literature available data for GBL binary mixtures with corresponding 1-alkyl-3-methylimidazolium based ionic liquids [23–26].

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2. Experimental

2.1. Materials

The ionic liquid [mmim][NTf_2] was purchased from IoLiTec and molecular liquid GBL was purchased from Aldrich. The summary of the provenance and purity of the samples is given in Table 1.

Prior to use, GBL was distilled and middle fraction was collected and kept above 0.4 nm molecular sieves for 1 week. Ionic liquid was gently heated under vacuum (p = 10 Pa) for 12 h at temperature T = 373.15 K. After that, ionic liquid and GBL were kept in vacuum desiccator over P_2O_5 for 24 h. Upon drying chemicals were stored in the dry box under nitrogen atmosphere. The water content was determined by Karl Fischer titration using a 831 Karl Fischer coulometer. Water content in each chemical is given in Table 1.

Binary mixtures covering the whole composition range of {[mmim][NTf_2] + GBL} were prepared by measuring appropriate amounts of the components on a Sartorius analytical balance. The standard uncertainty of mole fraction was found to be less than $\pm 7.5 \times 10^{-4}$.

2.2. Apparatus and procedures

2.2.1. Density measurements

The densities of pure components and binary mixtures were measured at atmospheric pressure of p = .1 MPa using a vibrating tube Anton Paar DMA 5000 densimeter with a declared reproducibility of $1 \cdot 10^{-4}$ g·cm^{-3}. Before each series of measurements calibration of the instrument was performed at the atmospheric pressure using triple distilled ultra pure water in the temperature range from (298.15 to 323.15) K. The instrument was thermostated within ±0.001 K and viscosity related errors in the density were automatically corrected over full viscosity range. To avoid gas bubbles entrapped in the measuring cell filled with a sample, the cell was filled carefully to minimize the probability of such error. The total volume of the samples used for density measurements was approximately 1 cm^3. Densimeter already has incorporated moisture adsorbent. The standard uncertainty of determining the density was estimated to be 2.3×10^{-3} g·cm^{-3}.

2.2.2. Viscosity measurements

The viscosities of the solutions were determined with a micro Ubbelohde viscometers (SI Analytics GmbH, Mainz, Germany, type No. 526 10 capillary I and type No. 526 20 capillary II) and an automatic flow time measuring system ViscoSystem® AVS 370. The viscometer was immersed in a transparent thermostat bath where the temperature was maintained from (298.15 to 323.15) K ± 0.01 K. Each measurement was automatically repeated at least five times and yielded a reproducibility of the flow time of <0.2%. The kinematic viscosity of solutions, v (m^2·s^{-1}), was calculated from the equation $v = K \cdot t$ [27], where t (in seconds) is the flow time and K is the constant characteristic for the viscometer. The absolute (dynamic) viscosity, η (Pa·s = kg·m^{-1} s^{-1}), was obtained from the relation $\eta = v \cdot d$, where d (in kg·m^{-3}) is density of the investigated solution. The errors from calibration and temperature control yield an relative standard uncertainty of 2% of absolute viscosity.

2.2.3. Electrical conductivity measurements

Conductivity was measured with a set of capillary cells, which were built with platinum electrodes in plastic clip, with different cell constants, B', as these are required for concentrated solutions [28], $B' = (\approx 3\text{–}85)$ cm^{-1}. An assembly lid equipped with nine conductivity cells and switch equipment connecting them to the PC-interfaced LCR Meter Agilent 4284 A permits conductivity to be measured at nine different concentrations at each temperature.

The cells were calibrated with diluted potassium chloride solutions and immersed in the high-precision thermostat described previously [29]. An alternating current was used for the electrical conductivity measurements with working frequencies from 500 Hz to 10 kHz. The oil bath was set to each temperature of a temperature program with the reproducibility within 0.005 K. The temperature was checked with a calibrated Pt-100 resistance thermometer (MPMI 1004/300 Merz) connected to an HP 3458 A multimeter. Solutions of different mole fractions, known by weight, were transferred under nitrogen into the capillary cells and measurements were carried out over a temperature cycle beginning and ending at T = 298.15 K. The cell arrangement permits conductivity to be measured at nine concentrations at each temperature. A home-developed software package was used for temperature control and acquisition of conductance data. The measuring procedure and the extrapolation of the sample conductivity to infinite frequency are as described [29].

3. Mathematical approach

From the experimental density of the mixture (d) and density of the pure components (d_i), the excess molar volume (V^E) can be calculated:

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

here x_1, M_1 and d_1 relate to ionic liquid [mmim][NTf_2] and x_2, M_2 and d_2 to GBL. Obtained values of the excess molar volumes are fitted using a Redlich–Kister's equation [30] where Y^E is the excess property and A_i are the adjustable parameters:

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

The values of A_i are obtained applying the method of least-squares.

The experimental reduced excess molar volumes are expressed by Eq. (2a) proposed by Desnoyers and Perron [31]:

$$Y^{\mathrm{E}}(x_1) = V^{\mathrm{E}} \big/ x_1 x_2 = V^{\mathrm{E}} \big/ x_1 (1 - x_1) \qquad (2a)$$

Apparent molar volumes $V_{\Phi 1}$ and $V_{\Phi 2}$ for both components of the mixture (1 refers to ionic liquid and 2 to GBL) can be also calculated using the experimental density:

$$V_{\Phi 1} = \frac{(d_2 - d)}{m_1 d d_2} + \frac{M_1}{d} \qquad (3)$$

$$V_{\Phi 2} = \frac{(d_1 - d)}{m_2 d d_1} + \frac{M_2}{d} \qquad (4)$$

Table 1
Provenance and purity of the samples.

Chemical name	Provenance	CAS Number	Purification method	Final mass fraction as stated by the supplier	Water content by Karl-Fischer titration
[mmim][NTf_2][a]	IoLiTec	174899-81-1	Vacuum drying	$\omega \geq 0.99$	83×10^{-6}
γ-butyrolactone	Aldrich	96-48-0	Distillation	$\omega \geq 0.99$	96×10^{-6}

[a] [mmim][NTf_2] = 1,3-dimethylimidazolium *bis*(trifluoromethylsulfonyl)imide.