



# Solubility, volumetric properties and viscosity of the sustainable systems of liquid poly(ethylene glycol) 200 with imidazolium- and phosphonium-based ionic liquids: Cation and anion effects



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## ABSTRACT

In this work, solubility, volumetric and viscosity behavior were studied for the systems containing the environmentally acceptable compounds: liquid poly(ethylene glycol) (PEG200) and three ionic liquids: 1-butyl-3-methylimidazolium dicyanamide ([C<sub>4</sub>mim][dca]), trihexyltetradecyl phosphonium dicyanamide ([P<sub>6,6,6,14</sub>][dca]) and 1-hexyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)amide ([C<sub>6</sub>mim][NTf<sub>2</sub>]). The studies were performed in a temperature range (288.15 to 328.15) K and at a pressure of 0.1 MPa. For the only system that evidenced limited miscibility, namely (PEG200 + [P<sub>6,6,6,14</sub>][dca]), the temperature–composition phase diagram at 0.1 MPa was determined, mapping the existing one- and two-phase regions. In the homogeneous region of this diagram, densities and viscosities were measured and the excess molar volumes, as well as deviations in viscosity were calculated. For the other two systems, as they are always homogeneous in the temperature ranges of the present work, these measurements and calculations were performed in the full range of compositions. The molecular interactions in the studied systems were scrutinized using the obtained excess molar volumes, deviations of viscosity, as well as Kamlet–Taft parameters of PEG200 and the ionic liquids. In addition, the excess molar Gibbs free energies of activation of viscous flow and the related enthalpies and entropies were calculated and introduced to take into consideration the differences in size of the molecules.

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## 1. Introduction

The present study is a continuation of the previous ones, carried out by some of the authors, related to the volumetric, viscosity and liquid phase behavior of the environmentally acceptable solutions of the liquid poly(ethylene glycol) (PEG) and imidazolium- and phosphonium-based ionic liquids with bistriflamide and triflate anions [1,2]. In those recent contributions, the sustainability of the studied compounds was thoroughly described and reviewed along with their good and diverse solvent properties. In particular, PEG is highly polar [3] and is simultaneously good hydrogen bond acceptor and donor [4], which is also the case for ionic liquids [5–8]. Nevertheless, both PEG [9] and ionic liquids [10,11] can also dissolve well (practically) non-polar arenes. This is explained by PEG's specific ability to sometimes adjust its structure to the polarity of the other compound [12] and by the dual nature of ionic liquids (existence of polar/non-polar domains) [13]. Due to these diverse properties, the solutions of liquid PEG and ionic liquids

are appealing sustainable homogenous [2] or biphasic solvents [14], potentially applicable on a wide range of target molecules.

In this work we present novel solubility, volumetric and viscosity studies, in a temperature range (288.15 to 328.15) K and at a pressure of 0.1 MPa, of the solutions containing liquid PEG200 (average molar mass of 0.200 kg · mol<sup>-1</sup>) and ionic liquids. The latter are 1-alkyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)amide ([C<sub>6</sub>mim][NTf<sub>2</sub>]), 1-butyl-3-methylimidazolium dicyanamide ([C<sub>4</sub>mim][dca]) and trihexyltetradecyl phosphonium dicyanamide ([P<sub>6,6,6,14</sub>][dca]), which were not previously studied with PEG200. From all the studied systems only (PEG200 + [P<sub>6,6,6,14</sub>][dca]) exhibited partial solubility—thus the related temperature–composition phase diagram at 0.1 MPa was determined. For this system, the measurements of densities and viscosities as well as the subsequent calculations of the related excess molar volumes and deviations in viscosity were carried out for the compositions at which the solution is homogeneous. For the other studied systems, which are completely soluble, these measurements and calculations were performed in the full range of compositions.

The excess molar volumes, deviations of viscosity, as well as Kamlet–Taft parameters [5,6] of the pure compounds were used

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to analyze and discuss the molecular interactions existing in the studied solutions. For this purpose, resort has been made to the Eyring theory of liquid viscosity. In this respect we have calculated and made use of theoretical parameters like the excess molar Gibbs energy of activation of viscous flow, and the related excess entropy and enthalpy.

It is noteworthy that the [dca]<sup>−</sup> anion showed an advantage over the [NTf<sub>2</sub>]<sup>−</sup> in the formation of strong, oriented interactions – hydrogen bonds and (ion-dipole) – with PEG200 that provided negative excess molar volumes for the systems PEG200 + [C<sub>4</sub>mim][dca]. Also, this ability of the [dca]<sup>−</sup> anion is thought to play a major role for the good solubility of PEG200 with the comparatively less interactive [P<sub>6,6,6,14</sub>][dca] ionic liquid.

## 2. Experimental

### 2.1. Chemicals and preparation of solutions

In [table 1](#) the studied chemicals, their suppliers, stated purities, purification (drying) procedure applied in each case and the average post-drying water contents are given. The purification methods were those previously described for ionic liquids [2,10,15] and PEGs [2,9,16].

Solutions were prepared gravimetrically using a Mettler Toledo MS205DM analytical semi-microbalance with a stated accuracy (repeatability) of  $\pm 2 \cdot 10^{-5}$  in mass fraction – nonetheless, the real average experimental uncertainty, from repeated measurements, was found to be  $\pm 1 \cdot 10^{-4}$  in mass fraction.

### 2.2. Apparatuses and experimental procedure

#### 2.2.1. U-tube density measurements

Densities of the pure substances and the corresponding binary mixtures were measured in the temperature range (298.15 to 328.15) K, using an Anton Paar DMA 5000 digital vibrating U-tube densimeter (with automatic viscosity correction). The temperature in the cell was controlled within  $\pm 0.001$  K by a built-in solid-state thermostat. The apparatus was calibrated using ambient air and Milipore™ quality water. The calibration was verified, prior to the introduction of each sample. A set of measurements were subsequently performed at several temperatures. The average experimental uncertainty in density – estimated from repeated measurements – was  $\pm 1 \cdot 10^{-2}$  kg · m<sup>−3</sup>. The overall uncertainty of the present density measurements is estimated to be within  $\pm 0.1\%$ , at a 95% confidence level. These estimates were based on previous sensitivity studies [17,18].

#### 2.2.2. Capillary viscosity measurements

Viscosity measurements were performed using an automatic Schott ViscoSystem® AVS 440 measuring unit, fitted with two micro-Ubbelohde capillary viscometers of type 537 23/IIIC and 537 30/III. The latter were manufactured and calibrated by SI Analytics GmbH, carried out by comparison with reference viscometers, of which the constants were determined at the Physikalisch-Technische Bundesanstalt (PTB), Germany. The calibration constants of the micro-Ubbelohde capillaries have an uncertainty of  $\pm 0.8\%$  at a 95% confidence level.

The experimental setup and procedure were similar to those described previously by Diogo et al. [17,18]. All of the inlets used for air admission to the micro-capillaries were fed with dry nitrogen gas. The filling of the capillaries was always made inside a glove-box in a dry nitrogen atmosphere. The automatic filling controller Schott ViscoSystem® AVS 440 was placed inside a glove-box in a dry nitrogen-gas atmosphere. The venting and pressure tubes of the micro-capillaries were connected to the filling controller,

inside the glove-box, by silicone tubes, in order to avoid contact with humid air, during all capillary viscosity measurements.

Once filled with the sample, the capillaries were immersed in a silicone oil thermostatic bath (Schott-Geräte CT1445). A Thermo NESLAB RTE7 cryostat was used as a circulating cooling source. The temperature of the thermostatic oil was measured, with a 100 Ω-platinum resistance thermometer, calibrated by EIA (Portugal) with an overall estimated uncertainty of  $\pm 0.05$  K [17], at a 95% confidence level. The temperature was stable to within  $\pm 0.01$  K during a series of measurements. The results of the measurements were accepted when two sets of five measurements were performed, having deviations from the mean smaller than  $\pm 0.2\%$ .

Based on previous sensitivity studies [17–19] and taking into account the characteristics of the samples measured in this work, the overall maximum uncertainty of the viscosity measurements, without consideration of eventual water contamination during the measurements, was estimated as  $\pm 1.0\%$ , at a 95% confidence level.

#### 2.2.3. Liquid-liquid equilibria (LLE) experiments

Liquid-liquid equilibria (LLE) experiments were performed at 0.1 MPa and in a temperature range of (283.15 to 373.15) K. For this purpose a visual cloud-point method was applied, including dynamic and titration techniques. The details of the method, techniques and the procedure of cloud-point determination were described in our previous studies [2,9,15,20]. Pyrex-glass cell, introduced earlier [21], was used to carry-out the experiments – the design and operation of the cell were explained thoroughly elsewhere [15,20]. The expanded uncertainty of the present LLE measurements, estimated from repeated experimental runs, is  $\pm 0.6$  K (95% level of confidence).

## 3. Results

All the results listed herein were obtained at a pressure of 0.1 MPa.

[Table 2](#) shows the densities and viscosities of the pure components of the solutions studied herein, at nominal temperatures. Values taken from the literature are also shown for comparison purposes. The viscosity of [C<sub>6</sub>mim][NTf<sub>2</sub>] has been measured by a large number of researchers. To the best of our knowledge the most recent data have been published by Diogo et al. [18]. Although those measurements are of high quality, we decided to include in [table 2](#) the results of a round-robin promoted by IUPAC Project (2002-005-1-100) [22,23], noticing that the latter project has proposed [C<sub>6</sub>mim][NTf<sub>2</sub>] to be a reference for several properties, including density and viscosity. The values shown in [table 2](#) were obtained by the correlation equation published by Chirico et al. [23], in the sequence of three round-robin measurements. The choice of the same source [23] for the literature density data is justified because the densimeter used in the present work is the same as the one used in our previous work [18], which could be thought to bias the comparison. The comparisons for both properties are excellent, with the deviations being well within the estimated uncertainties of our data. The literature density and viscosity data for [C<sub>4</sub>mim][dca] [24] were selected because they are thought to be the most recently published quality measurements of these two properties. Density and viscosity data from Reference [17] were compared before with [P<sub>6,6,6,14</sub>][dca] data from Pereira et al. [25]. The two density data sets from References [17,25], show a very good mutual agreement. We have chosen to use density data from Reference [17], which were obtained with the same sample of [P<sub>6,6,6,14</sub>][dca], except for the temperature of 288.15 K, which is outside the range of those measurements, and used the datum published by Pereira et al. [25] instead. For

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