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Physicochemical properties of low viscous lactam based ionic liquids

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ABSTRACT

Lactam based ionic liquids were synthesized by an atom economization process between a lactam such as caprolactam or butyrolactam with a Brønsted acid such as formic acid, acetic acid or hexanoic acid. The density, speed of sound and viscosity were measured at atmospheric pressure and as a function of temperature from $T = (293.15$ to $333.15)$ K. The experimental density and viscosity values were fitted with linear and Vogel–Tamman–Fulcher (VTF) equations, respectively and found to be fitting well within the experimental error. Thermodynamically important derived properties such as the coefficient of thermal expansion (α) and isentropic compressibility (β_s) were calculated from the experimental density and speed of sound values. Lattice potential energy (U_{POT}) has been calculated to understand the strength of ionic interaction between the ions and the standard entropy (S^o) has been estimated to assess the disorder within the fluids. The remarkably low values of viscosity of ionic liquids studied are discussed on the basis of activation energy estimated from the Arrhenius equation. Furthermore, the effect of alkyl chain length on the anion, geometry of the cation and temperature has been analysed for the properties studied.

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1. Introduction

The ionic liquid (IL), a molecular puzzle in the hand of scientific community, has witnessed an exceptional growth of research activity over the last decade. Researchers from all disciplines related to chemistry have now kicked off the studies to improve the molecular design required for the specific application. Unlike molecular solvents, their unmatched characteristic properties which include low volatility, high range in the liquid state, good thermal stability, and high solvating capacity put together, make it a potential alternative solvent. The applications span optical [1], electrical [2], chemical [3] to thermal [4] and mechanical [5].

To date, most work has been focused on the imidazolium based ionic liquid [6,7]. Even so, some work also has been centred on pyridinium, pyrrolidinium and piperidinium [8–10], triazolium [11,12], ammonium and phosphonium [13–16] based ionic liquid. Always there has been an inquisitive search to develop a novel ionic liquid that can meet the new challenges and extend the potential applications. In this context, ionic liquids based on ε-caprolactam and γ-butyrolactam (*i.e.* 2-pyrrolidone) are relatively new as compared to the ionic liquids mentioned above. Compared to imidazolium based ionic liquids, caprolactam ionic liquid (CPIL)

and butyrolactam ionic liquid (BTIL) are relatively cheap and have lower intrinsic toxicity [17,18]. CPIL and BTIL can be potentially used for gas sweetening as they have high affinity towards NO, NO_2 [19], SO_2 [20,21] and H_2S [22]. Also caprolactam hydrogen sulfate ionic liquid is being used as catalyst and reaction media for more than a decade in large scale industrial processes for Beckmann rearrangement of cyclohexanone oxime to caprolactam [23,24]. In addition, the presence of the carbonyl group in the lactam based ionic liquid might encourage specific interaction while being used as reaction media or catalyst.

It is evident that carboxylate based ILs are suitable for the dissolution of cellulose [25,26] and lignocellulose [27] during biofuel production. The carboxylate ion having high hydrogen bond basicity (Kamlet–Taft parameter, β) can strongly coordinate with the hydroxyl group of carbohydrates and help in dissolution [27]. Moreover the viscosity of ILs plays an important role for the dissolution of biomass composites. The undesirable viscosity slows down the rate of enzyme catalysed hydrolysis [28] and also the dissolution of cellulose [29–31].This work may open a new window as it satisfies both the condition of low viscosity and the presence of the carboxylate ion for cellulose processing.

The knowledge of the physicochemical properties is essential for the design of reaction and processing units, which influence directly equipment performance. Except for the work by Deng *et al.* [32] who discussed the thermophysical properties of lactam based ionic liquids only at room temperature, there is no open literature

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available that describes the effect of temperature upon thermophysical properties of lactam based ILs. In this work, we measured the density (ρ), viscosity (η) and speed of sound (u) over a range of temperature from T = (293.15 to 333.15) K at atmospheric pressure for six novel lactam based ILs. The effects of the ring size of the cation and alkyl chain length of anion upon the properties are also discussed.

2. Experimental

2.1. Synthesis of ionic liquids

The source and purity of all the organic acids, amides used in this study are summarized in table 1 and used without further purification. The typical synthetic procedure adopted for caprolactam formate is illustrated in scheme 1 and can also be used as an example for the synthesis of the remaining ionic liquid. Benzene/water (30 mL) was added to the double necked round bottom flask containing caprolactam (11.32 g, 0.1 mol) equipped with a reflux condenser. During vigorous stirring, formic acid (11.4 g, 0.1 mol) was added slowly through a dripping funnel. The temperature of the bath was kept below 10 °C during the addition and then elevated subsequently to room temperature. The reaction lasted for another 24 h under a nitrogen atmosphere. The Benzene/water mix was then removed using a rotary evaporator and further dried by high vacuum for 2 h. The name, abbreviations, the respective cations and anions used in this work, are shown in table 2.

2.2. Characterizations

Proton NMR was recorded on a Brukar Avance 500 MHz spectrometer. For BTF (CDCl$_3$) δ = 2.14 ppm (qn, 2H), δ = 2.39 ppm (t, 2H), δ = 3.45 ppm (t, 2H), δ = 7.34 ppm (s, 1H), δ = 8.04 ppm (s, 1H), δ = 9.08 ppm (s, 1H). For BTAc (DMSO-d$_6$) δ = 1.91 ppm (s, 3H), δ = 1.96 ppm (qn, 2H), δ = 2.06 ppm (t, 2H), δ = 3.2 ppm (t, 2H), δ = 7.49 ppm (s, 1H). For BTH (DMSO-d$_6$) δ = 0.86 ppm (t, 3H), δ = 1.26 ppm (m, 4H), δ = 1.49 ppm (qn, 2H), δ = 1.96 ppm (qn, 2H), δ = 2.06 ppm (t, 2H), δ = 2.18 ppm (t, 2H), δ = 3.20 ppm (t, 2H), δ = 7.50 ppm (broad, 1H), δ = 11.96 ppm (broad, 2H). For CPF (CDCl$_3$) δ = 1.67 ppm (m, 4H), δ = 1.77 ppm (qn, 2H), δ = 2.47 ppm (t, 2H), δ = 3.22 ppm (qr, 2H), δ = 7.53 ppm (broad, NH), δ = 8.05 ppm (s, 1H). For CPAc (CDCl$_3$) δ = 1.65 ppm (m, 4H), δ = 1.75 ppm (qn, 2H), δ = 2.04 ppm (s, 3H), δ = 2.45 ppm (t, 2H), δ = 3.20 ppm (qr, 2H), δ = 7.46 ppm (broad, NH). For CPH (CDCl$_3$) δ = 0.88 ppm (t, 3H), δ = 1.31 ppm (m, 4H), δ = 1.63 ppm (m, 4H), δ = 1.68 ppm (qn, 2H), δ = 1.75 ppm (qn, 2H), δ = 2.30 ppm (t, 2H), δ = 2.46 ppm (t, 2H), δ = 3.21 ppm (qr, 2H), δ = 7.37 ppm (broad, NH).

2.3. Measurement technique

The density and speed of sound were measured with an Anton Paar (DSA 5000 M) instrument which employs the well-known oscillating U-tube principle (for density measurement). The instrument has a number of features for easy sample handling and to produce reliable results. It can measure the density in the range

TABLE 1
Provenance and mass fraction purity for each chemical sample used during this work.

Chemical name	Source	Mass fraction purity
ε-Caprolactam	Sigma Aldrich	0.99
γ-Butyrolactam	Sigma Aldrich	0.99
Formic acid	Sigma Aldrich	$\geqslant$0.95
Acetic acid	Sigma Aldrich	0.99
Hexanoic acid	Sigma Aldrich	0.99
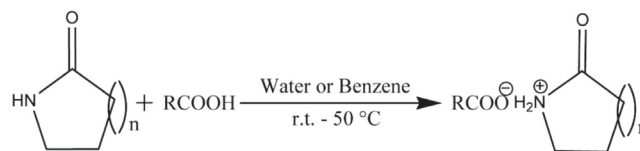
SCHEME 1. Synthesis of lactam based ionic liquid. n = 1, Butyrolactam; n = 3, Caprolactam; R=H, CH$_3$, C$_5$H$_{11}$.

of (0 to 3) g · cm^{-3} and speed of sound from (1000 to 2000) m · s^{-1}, simultaneously at temperatures from T = (273.15 to 343.15) K, with a pressure variation from (0 to 0.3) MPa. A Lovis 2000 ME (Anton Paar) was used to measure the dynamic viscosity of the ionic liquid. It can measure the viscosity from (0.3 to 10,000) mPa · s using the rolling ball technique. The temperature is controlled by a built-in precise Peltier thermostat with an accuracy of T = 0.02 K. At regular intervals of time, the density meter was calibrated with dry air and Millipore water as described in the manual and the Lovis instrument was calibrated with the reference liquid (S3, N26, N100 liquid for (1.59, 1.8 and 2.5) mm capillary, respectively) supplied by the Anton Paar Co., Austria. The samples were loaded into the density, speed of sound cell as well as the Lovis capillary in one cycle and the measurements were carried out by the slow equilibration mode, simultaneously. The values reported here are the average of three consecutive measurements carried out between the temperatures T = (293.15 to 333.15) K with an interval of T = 5 K at atmospheric pressure. To verify the instrument, we measured all the intended properties of the reference IL, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C$_6$mim][Tf$_2$N] [33,34]. The standard uncertainties associated with the measurements were estimated to be less than T = 0.002 K for temperature, 0.007 kg · m^{-3} for density, 0.005 mPa · s for viscosity and 0.5 m · s^{-1} for the speed of sound.

The Karl Fischer Titrator from Analab (Micro Aqua Cal 100) was used to measure the water content. The instrument operates on the conductometric titration principle using dual platinum electrodes that permits detection of water content from less than $10 \cdot 10^{-6}$ to 100%. The instrument was calibrated with Millipore quality water.

Thermograms are recorded using the TGA instrument (TA instruments Hi-Res. TGA Q500) with a weighing precision of ±0.01% at a heating rate of 10 °C · min^{-1} under a nitrogen atmosphere with an open aluminium pan. Simultaneous measurement of sample temperature and heating rate control were carried out accurately and precisely by the two thermocouples, positioned immediately adjacent to the sample. The Curie point temperature calibration was carried out with Nickel metal.

3. Results and discussion

Before the measurement of thermophysical properties, samples were dried under high vacuum for 24 h, water content was then measured and reported in table 3. The experimental density of ILs was measured from T = (293.15 to 333.15) K at 0.1 MPa and values summarized in table 4. As shown in figure 1, the structural and temperature dependence on density cover a wide range from 967.34 kg · m^{-3} for CPH at T = 333.15 K to 1140.78 kg · m^{-3} for BTF at T = 293.15 K. As expected, increase in carbon chain length, ring size upon anion and cation, respectively shows decreasing effect over the density. For instance, ILs having same butyrolactam cation, at T = 303.15 K the density decreases from 1131.51 kg · m^{-3} for formate (BTF) to 1010.57 kg · m^{-3} for hexanoate (BTH) type ILs. Similarly for the same acetate anion at T = 303.15 K, there is decrease in density from 1090.91 kg · m^{-3} for butyrolactam (BTAc) to 1051.83 kg · m^{-3} for caprolactam (CPAc) type ILs. This decrease in density can be attributed to the difficulties in the formation of