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Measurement and correlation for the thermophysical properties of novel pyrrolidonium ionic liquids: Effect of temperature and alkyl chain length on anion

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ABSTRACT

In this work, a new series of low viscous protic ionic liquids based on *N*-methylpyrrolidone cation and carboxylate anions with different chain length has been synthesized and characterized. Density, speed of sound and viscosity have been measured for these ionic liquids in the temperature range from 293.15 to 343.15 K. The density data have been fitted to linear equation as well as correlated with group contribution method developed by Gardas and Coutinho. From the density correlation, molecular volume data for cation and anion constituents of studied ionic liquids have been proposed. By using experimental density and speed of sound data, the isentropic compressibility, coefficient of thermal expansion, standard entropy, intermolecular free length and lattice energy have been calculated for studied ionic liquids. Viscosity data were correlated with the Vogel–Tammann–Fulcher equation. To understand the nature of the ionic liquids and structure–property relationship, the effect of anion alkyl chain length has been studied and correlated. Ionic liquids studied in this work are comparatively cheaper in price and can be promising in bio-macromolecule solubilization and other commercial fields.

1. Introduction

Since the time of its introduction to the chemical community, ionic liquid (IL) has made a distinct place by its unique properties and promising applicability. The incomparable physical characteristics as low volatility, large liquidus range, and good electrical conductivity have opened unlimited opportunities to the scientists from all branches for further exploration. The expedition has shown ILs to have amazing applicability in the fields as solvent medium [1,2], catalysis [3], biomass processing [4], petroleum refining [5], electrochemistry [6], as magnetic fluid [7] and energetic materials [8].

ILs are generally composed of a bulky organic cation and relatively small anion, so it is theoretically possible to get innumerous number of combinations. As it is practically impossible to study all of them, an accurate and systematic investigation of physicochemical properties of selected systems is necessary, which can help to build structure property correlation and enhance predictive modeling [9]. These studies are useful for both fundamental and applied research as the primary screening to find a suitable material for an application is based on its thermophysical properties. Furthermore, to understand and relate the macroscopic and microscopic behavior of ILs, a detailed knowledge of the thermophysical properties is of utmost importance.

Over the past few decades, to fulfill the work specific demand or academic quest, many new ILs have been discovered and studied. Though the number of publications on ILs is enormous, most of the researches are centered on imidazolium, pyridinium, pyrrolidinium, piperidinium and phosphonium [10–13] with some recent works on ammonium [14] and triazolium [15] based ILs. The primary factor for an extensive research and application is the high cost of the ILs; therefore search for cheaper species is always economically preferable. The high viscosity of the ILs is another burden which narrows down the field of applicability in the industrial processes. Water solubility and toxicity are among other criteria confining the applicability to bio-related fields. In other words, there is always a scope to study new ILs, as the presently available data or correlations are not exhaustive anyways.

In this retrospect, ionic liquids based on *N*-methylpyrrolidone (NMP) can present a blend of new properties as well as low toxicity, less viscosity and cheapness. Carboxylates anions, on the other hand, can fulfill both the research demand of studying nature of ILs as well as can be applicable in cellulose and lignin treatment [16,17]. To the best of our knowledge, there are only few open literature available on NMP based ILs with inorganic anions [18–20], but no literature on ILs with organic acid anions.

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List of symbols

N	Avogadro number
α	Coefficient of thermal expansion
ρ	Density
L_f	Inter molecular free length
β_s	Isentropic compressibility
K	Jacobson's constant
U_{POT}	Lattice potential energies
M	Molecular weight
V_m	Molecular volume
V_a	Molecular volume of the anion
V_c	Molecular volume of the cation
P	Pressure
u	Speed of sound
S^0	Standard Entropy
T_d	Thermal decomposition temperature
η	Viscosity

Furthermore, none of the literature reports the thermophysical properties of NMP based ILs. Therefore, in the present work, we have synthesized a series of NMP carboxylate ILs as listed in Scheme 1 in which only the anion carbon chain length varies. Densities, ultrasonic sound velocities and viscosities of this series have been experimentally measured as a function of temperature. Some important thermodynamic properties such as molecular volume, isobaric expansion coefficient, isoentropic compressibility, standard molar entropy, lattice energy have been calculated for these ILs. The present work attempts to understand the molecular interaction as well as the effect of alkyl chain length in the anion on the physicochemical properties of the ILs. These data have a potential to add in developing structure-property correlation and molecular modeling. Furthermore, these carboxylate ILs can be applicable in various fields such as ammonia based refrigeration systems and others.

2. Experimental

2.1. Synthesis of ILs

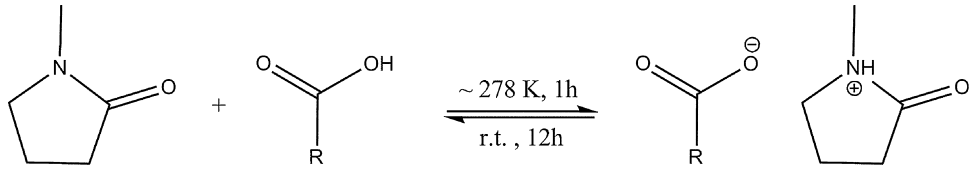
The source and purity of all the chemicals used in this experiment are summarized in Table 1. The detailed synthetic procedure has been described elsewhere [21]. The general procedure involves the exothermic neutralization of the base with equimolar amount of different acids as shown in Scheme 1. The synthesis of *N*-methylpyrrolidonium acetate ionic liquid is given here. Similar procedure has been followed for the synthesis of other ILs. 9.9 g (0.1 mol) of *N*-methylpyrrolidone (NMP) was taken in a 250 mL double necked round bottomed flask fitted with a reflux condenser, a thermometer and a pressure equalizing dropping funnel and kept in an ice bath. 6.0 g (0.1 mol) acetic acid was added drop wise from the dropping funnel with vigorous stirring by a magnetic stirrer. During addition, the temperature was maintained at ~278 K to dissipate the heat generated in the reaction. After complete addition, the flask was taken out from the ice bath and stirring was continued in room temperature for 12 h. The flask was then connected to high vacuum for 24 h with heating at 313.15 K to remove any unreacted starting materials as well as moisture. The structures of the synthesized ILs along with their abbreviations are summarized in Table 2.

2.2. Characterization

The ^{1}H and ^{13}C NMR was recorded in a Bruker Avance 500 MHz spectrometer with $CDCl_3$ as solvent and TMS as internal standard. The IR data were recorded in a JASCO FT/IR-4100 spectrometer using NaCl disk. The ^{13}C and IR data has been given in supporting information S1. ^{1}H-NMR ($CDCl_3$, δ ppm): [NMP][For] δ = 2.32 (m,4H) 2.93(s,3H) 3.34(t,2H) 6–8(broad NH^+ and $HCOO^-$); [NMP][Ace] δ = 2.04(q,2H) 2.44(t, 2H) 2.49(s,3H) 2.86(s,3H) 3.4(t,2H) 6.4 (broad NH^+); [NMP][Pro] δ = 1.10(t,3H) 2.01(m,2H) 2.29(m,2H) 2.37 (t,2H) 2.83(s,3H) 3.42(t,2H) 6.1(broad NH^+); [NMP][But] δ = 0.94 (t,3H) 1.64(q,2H) 2.00(m,2H) 2.28(m,2H) 2.38(m,2H) 2.83(s,3H) 3.38(t,2H) no broadening; [NMP][Pen] δ = 0.88 (t,3H) 1.32(m,2H) 1.56(m,2H) 1.99(m,2H) 2.29(m,2H) 2.38(q,2H) 2.82(s,3H) 3.36 (t,2H) (no broad peak for NH^+); [NMP][Hex] δ = 0.89(t,3H) 1.31 (m,4H) 1.63(q,2H) 2.01(m,2H) 2.35(m,4H) 2.83(s,3H) 3.38(t,2H) (no broad peak for NH^+)

2.3. Measurement technique

The density and speed of sound of the ionic liquids were measured with an Anton Paar (DSA 5000M) in the temperature range of 293.15–343.15 K and at atmospheric pressure. For density measurement, the instrument uses the vibrating U-shaped cell kept inside a cavity of a metallic block with peltier devices allowing precise temperature control and stability. The sound velocity measurement cell is connected to one end of the U tube so that the same liquid can pass to it without sample loss and the same metallic block can control the temperature. The viscosity measurements were done by Anton Paar Lovis 2000ME instrument. It uses the rolling ball in a capillary method and temperature is kept constant through a built-in peltier device with an accuracy of 0.02 K. Approximately 4 mL of sample was inserted to the inlet port carefully (in bubble free condition) of density meter which also fills the sound velocity cell and viscometer capillary respectively. Prior to measurements, the internal calibration was verified by the measurements with double distilled water and atmospheric air. Similar to our earlier work [21], the instrument was also calibrated with reference ionic liquid namely, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide, [C_6Mim][Tf_2N] for density, speed of sound and viscosity measurements. The data reported here is the average value of three consecutive measurements. The



Where R = -H, -CH3, -$(CH_2)_n$CH3; (n=1,2,3)

Scheme 1. General procedure for the synthesis of *N*-methylpyrrolidone based ionic liquids.