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Thermophysical properties of ammonium and hydroxylammonium protic ionic liquids

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ABSTRACT

In this work, five protic ionic liquids having propylammonium, 3-hydroxy propylammonium as cations and formate, acetate, trifluoroacetate as anions have been synthesized. Thermophysical properties such as density (ρ), viscosity (η) and sound velocity (u) have been measured at various temperatures ranging from (293.15 to 343.15) K at atmospheric pressure. The experimental density and viscosity were fitted with second order polynomial and Vogel–Tamman–Fulcher (VTF) equations, respectively. Also experimental densities were correlated with the estimated density proposed by Gardas and Coutinho model. The coefficient of thermal expansion (α) and isentropic compressibility (β_s) values have been calculated from the experimental density and sound velocity data using empirical correlations. Lattice potential energy (U_{POT}) has been calculated to understand the strength of ionic interaction between the ions. Thermal decomposition temperature (T_d) and glass transition temperature (T_g) along with crystallization and melting point were investigated using TGA and DSC analysis, respectively. The effect of alkyl chain length and electronegative fluorine atoms on anionic fragment as well as hydroxyl substituent on cationic side chain in the protic ionic liquids has been discussed for studied properties. The effect of ΔpK_a over the studied properties has also been analyzed.

1. Introduction

Ionic liquids (ILs) are organic salts generally composed of ions and having melting points below 100 °C [1]. It draws extensive attention during last few decades due to their fascinating properties like low volatility, high solvation capacity, large electro-chemical window, high thermal and electrical conductivity both in academia and industry. Protic ionic liquids (PILs) are subgroup of ILs formed by proton transfer from a Brønsted acid to a Brønsted base [2]. The presence of an available proton which is responsible for hydrogen bonding makes PILs different from other ILs. Till date, PILs have not received much more attention as compared to their counterpart aprotic ionic liquids [3]. Nevertheless, these ILs have many beneficial properties and potential applications, basically due to their protic nature, such as self-assembly media [4–9], catalysts in chemical reactions [10–12], biological applications [13], and proton conducting electrolytes for polymer membrane fuel cells [14].

Hydroxylammonium ionic liquid can be used to dissolve zein, an industrially important natural polymer [15]. Many insoluble polymers such as polyaniline and polypyrrole are found to be highly soluble in this class of ILs [16]. The effect of the hydroxyl (−OH) group in this type of ionic liquid for the solvation with polar solvents has been revealed by the determination of solvato -chromic parameter [17]. Currently, aqueous monoethanolamine has been used for CO_2 removal from natural gas in industrial processes [18]. Due to its serious environmental concerns related to volatility, recovery and corrosiveness [19–23], ILs seem to be better alternative solvents which can surpass the above difficulties along with high efficiency for CO_2 absorption [24]. Ionic liquids having imidazolium and pyridinium cations are the most studied classes of ionic liquids for gas separation [25–31]. Recently, ammonium and hydroxylammonium ionic liquids have also drawn considerable attention towards CO_2 absorption both from natural and flue gas [12,32,33]. Knowledge of thermophysical properties such as density, viscosity and thermal stability are important to determine the possible application of ionic liquids for gas sweetening. In spite of their importance and easy preparation technique there are very few literature available on the thermophysical properties of pure hydroxylammonium and ammonium ionic liquids [34–37].

There may exist a possible equilibrium due to incomplete proton transfer during neutralization reaction, resulting in the formation of neutral ion-pairs. MacFarlance et al. suggested that ΔpK_a (the difference in pK_a [38,39] value for the acid and base determined in dilute aqueous solutions) > 4 is sufficient for complete

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List of Symbols

ρ	Density	T_d	Thermal decomposition temperature
η	Viscosity	T_g	Glass transition temperature
u	Sound velocity	V_m	Molecular volume
α	Coefficient of thermal expansion	L_f	Inter molecular free length
β_s	Isentropic compressibility	K	Jacobson's constant

proton transfer [40]. However the nature of ionic liquids which depends upon the difference in pK_a values between the acid and the base is still a matter of debate in the scientific community. Specifically Angell et al. demonstrated that $\Delta pK_a > 10$ is required for complete proton transfer [41].

In this work, we have synthesized, purified and characterized five ammonium and hydroxylammonium based PILs. The density, viscosity and sound velocity have been measured at atmospheric pressure with temperature variation from (293.15 to 343.15) K. The sound velocity and hence the isentropic compressibility can be regarded as thermodynamic properties, as the ultrasonic absorption is negligible due to the use of low frequency (3 MHz) and low amplitude of the acoustic waves [42,43]. The experimental density and viscosity have been correlated with second order polynomial and Vogel–Tamman–Fulcher (VTF) equations, respectively. The coefficient of thermal expansion and isentropic compressibility have been calculated using the density and sound velocity data. Thermal decomposition temperature (T_d) and glass transition temperature (T_g) of studied ionic liquids have been analyzed by TGA and DSC, respectively.

2. Experimental section

2.1. Chemicals

Acetic acid (⩾99%), formic acid (⩾95%), trifluoroacetic acid (99%), 3-amino-1-propanol (99%) and propyl amine (⩾99%) were obtained from Sigma Aldrich and were used without further purification.

2.2. Synthesis of ionic liquids

All the five ILs were synthesized by exothermic neutralization of equimolar bases with different acids [16]. The bases were taken in a two necked round bottom flask equipped with reflux condenser and dropping funnel. Acids were then added drop wise under vigorous stirring to the round bottom flask kept in ice bath, maintaining the reaction mixture temperature below 10 °C. After complete addition, the temperature was raised to room temperature with further stirring up to 24 h. The resulting viscous liquid obtained was then connected to high vacuum for 48 h at room temperature with continuous stirring, to remove the water content and residual amine, taken in excess to ensure complete consumption of acid. The ionic liquids were then stored under N_2 atmosphere. Their structure and abbreviations are shown in table 1.

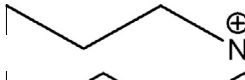
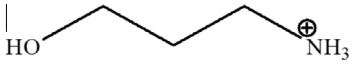
2.3. Characterizations

Proton, carbon NMR was recorded (see figure in the Supporting Information) on Brukar Avance 500 MHz spectrometer using deuterated DMSO as solvent. For 3-HPAF δ = 8.44 ppm (s, 1H, $HCOO^-$), δ = 5.96 ppm (broad, 4H, OH and NH_3^+), δ = 3.46 ppm (t, 2H, CH_2—N), δ = 2.79 ppm (t, 2H, CH_2—O), δ = 1.66 ppm (qn, 2H, CH_2—C). For 3-HPAAc δ = 5.29 ppm (broad, 4H, OH and NH_3^+), δ = 3.46 ppm (t, 2H, CH_2—N), δ = 2.73 ppm (t, 2H, CH_2—O), δ = 1.71 ppm (s, 3H, CH_3—C), δ = 1.61 ppm (qn, 2H, CH_2—C). For 3-HPATFAc δ = 5.28 ppm (broad, 4H, OH and NH_3^+), δ = 3.46 ppm (t, 2H, CH_2—N), δ = 2.77 ppm (t, 2H, CH_2—O), δ = 1.64 ppm (qn, 2H, CH_2—C). For PAF δ = 8.44 ppm (s, 1H, $HCOO^-$), δ = 3.56 ppm (broad, 3H, NH_3^+), δ = 2.68 ppm (t, 2H, CH_2—N), δ = 1.53 (sx, 2H, CH_2—C), δ = 0.88 ppm (t, 3H, CH_3—C). For PAAc δ = 5.12 ppm (broad, 3H, NH_3^+), δ = 2.60 ppm (t, 2H, CH_2—N), δ = 1.72 ppm (s, 3H, CH_3—CO) δ = 1.47 ppm (sx, 2H, CH_2—C), δ = 0.87 ppm (t, 3H, CH_3—C). IR spectra were recorded by JASCO FT/IR-4100 spectrometer using NaCl disk. The device has a maximum resolution of 0.9 cm^{-1} and have 22,000:1 signal to noise ratio. For all PILs the broad band appeared in (3600 to 2600) cm^{-1} range exhibits the characteristic ammonium peak and O—H stretching vibration. A combined broad band of the N–H plane bending vibrations and carbonyl stretching is observed around 1600 cm^{-1}.

2.4. Apparatus and procedure

Density and sound velocity of the studied ionic liquids were measured using Anton Paar (DSA 5000 M) vibrating tube digital density and sound velocity meter. It uses an inbuilt oscillating glass U tube for density measurement and stainless steel cell for sound velocity measurement. To ensure accurate and reproducible results as well as highly convenient sample handling, the instrument has a number of unique features like: (i) Density (in the range from (0 to 3) $g \cdot cm^{-3}$) and sound velocity (in the range from (1000 to 2000) $m \cdot s^{-1}$) can be measured simultaneously in the temperature range from (273.15 to 343.15) K with pressure variation from (0 to 3) bar. (ii) Sample filling errors are detected automatically. (iii) A PT-100 sensor is used to measure the temperature with an accuracy of ±0.01 K. (iv) It provides automatic viscosity correction across the sample's entire viscosity range and (v) It has the facility

TABLE 1
Ionic liquids names and abbreviations used in this work.

Cation	Anion	Name	Abbreviation
	$HCOO^-$	Propylammoniumformate	PAF
	CH_3COO^-	Propylammonium acetate	PAAc
	$HCOO^-$	3-Hydroxypropylammonium formate	3-HPAF
	CH_3COO^-	3-Hydroxypropylammonium acetate	3-HPAAc
	CF_3COO^-	3-Hydroxypropylammonium trifluoroacetate	3-PATFAc