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Synthesis, spectroscopic characterization and acoustic, volumetric, transport and thermal properties of hydroxyl ammonium based ionic liquids

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ABSTRACT

In the present work, solvent-free synthesis of two hydroxyethyl ammonium-based ionic liquids (ILs) at room temperature was carried out namely, N-butyl-(N-hydroxyethyl) ammonium trifluoroacetate ([BHEA][TFA]) and N-butyl-(N-hydroxyethyl) ammonium nitrate ([BHEA][NO_3]). The synthesized ionic liquids were characterized by various spectroscopic techniques such as ^{1}H-NMR, ^{13}C-NMR and FTIR. Furthermore, density (ρ), speed of sound (u), electrical conductivity (σ) and viscosity (η) have been measured within the temperature range from T = (303.15 to 343.15) K and at 0.1 MPa pressure. The measured density and viscosity values were fitted to the linear and Vogel–Tammann–Fulcher (VTF) equation, respectively. The temperature dependence conductivity of the measured ILs was fitted to a similar equation type of viscosity (VTF). Furthermore, the refractive index was measured at T = 303.15 K, in turn molar refraction (R_m) and free volume (f_V) were calculated using the Lorentz–Lorenz equation. The thermodynamic properties such as thermal expansion coefficient (α), isentropic compressibility (β_S) and intermolecular free length (L_f) were calculated by using the experimental values of density and speed of sound. The thermal decomposition temperature (T_d) was investigated using TGA analysis. Finally, thermophysical properties of pure ILs were analyzed in terms of different kind of anions present in the ionic liquids.

1. Introduction

Ionic liquids (ILs) are an important new class of solvents that have received significant interest due to their potential as replacements for traditional organic solvents and due to their unique solubility characteristics [1]. The ILs have many fascinating properties such as chemical stability, non-flammability, negligible vapor pressure [2,3], a broad liquid range [4], rich and complex behavior as a solvent [5–7], and also electrical [8], chemical [9], and mechanical [10] strengths. These ILs have many commercial applications due to their protic nature such as absorption media for gas separations [11], separating agents in extractive distillation, heat transfer fluids [12], biomass processing, working fluids in a variety of electrochemical devices for example batteries, capacitors, solar cells [13] and biocatalysts [14].

Protic ionic liquids (PILs) are a subset of ionic liquids formed by the stoichiometric (equimolar) combination of a Brønsted acid with a Brønsted base [15,16]. The proton-transfer process can be improved through the use of stronger acids and/or stronger bases, hence leading to a greater driving force for the proton transfer. The presence of an available proton which is responsible for hydrogen bonding makes PILs different from other ILs. The pK_a values of acids and bases may be considered as an indication of how strongly a proton will be transferred from the acid to a base [17]. When a PIL is synthesized by mixing a strong acid with a strong base, the proton is located very strongly on the base; the PIL is most likely composed entirely of ions with possible ion complexation and aggregate formation [18].

Hydroxyl ammonium ionic liquids have been used to dissolve zein polymer as well as many insoluble polymers such as polyaniline and polypyrrole. 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 solvatochromic parameter [19]. ILs are an alternative solvent for the removal of gases such as CO_2, H_2S, and SO_2 from fossil fuel burning, electric power plant emissions etc. using the unique absorption and low volatility characteristics. Aqueous hydroxyl amines have been used for CO_2 absorption in current industrial process, but it causes serious

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environmental concerns due to its volatility and corrosiveness. Therefore, a non-volatile and non-corrosive solvent that can absorb CO_2 may be advantageous [20,21]. Yuan *et al.* [22] reported the gas solubility in hydroxyl ammonium ionic liquids. These results show that ionic liquids have high possibilities as solvents for CO_2 removal processes. Kurnia *et al.* [21] investigated the solubility of CO_2 in six hydroxyl ammonium ionic liquids and showed the increase with an increase in pressure and decrease with an increase in temperature. Yuan *et al.* [22] compared the CO_2 solubility between [emim][Ac] and [emim][TFA] and concluded that the presence of the CF_3 group reduced CO_2 solubility dramatically. This is due to the fact that the CF_3 group withdraws the electron density reducing the Lewis basicity of the anion. Thus, the overall chemical complexation of CO_2 with IL is reduced owing to a lower CO_2 solubility. The most common room-temperature ILs are relatively complex due to bulky and often asymmetric molecular cations and anions. However, less complex constituents can offer advantages, for example ionic liquids containing the chloride anion possess remarkably solubilizing power for cellulose, presumably because this anion is a strong H-bond acceptor [23]. The smaller fluoride anion is an even better H-bond acceptor and Maiti *et al.* [24] recently proposed ILs with this anion as powerful solvents for materials with a high degree of inter and intramolecular H-bonding.

The determination and understanding of basic physical and transport properties of ILs, such as density, viscosity (for fluid flow and diffusion of gases) refractive index, thermal decomposition (to set the feasible temperature operating range) and thermal expansion are vital for the process design and development of contacting equipment. Pratap *et al.* [25] reported density, speed of sound, viscosity, decomposition temperature and glass transition temperature of hydroxyethyl ammonium based ILs at various temperatures. Kurnia *et al.* [26] explored density, viscosity, refractive index and decomposition temperature of various hydroxyethyl ammonium based ILs at different temperatures and Andre *et al.* [27] experimentally determined density, viscosity and electrical conductivity of alkanol ammonium based ionic liquids.

The aim of our work is to synthesize new PILs, hydroxyethyl amine as a cation with trifluoroacetate and nitrate as the respective anions, namely (N-butyl-(N-hydroxyethyl) ammonium trifluoroacetate and N-butyl-(N-hydroxyethyl) ammonium nitrate. The various thermodynamic properties such as density, conductivity, viscosity, speed of sound, refractive index, coefficient of thermal expansion, isentropic compressibility were measured. To the best of our knowledge, there is no literature available regarding this work. Finally, volumetric, acoustic, transport and spectroscopic properties were analyzed in terms of size and interactions of the ions in ionic liquid.

2. Experimental methods

2.1. Synthesis of ILs

In this work, all the chemicals were used to synthesize ILs without further purification. The general procedure involves exothermic a neutralization process between bases with stoichiometric quantity of different kinds of acids as shown in scheme 1. We are mentioning the procedure for trifluoroacetic acid and a similar procedure was followed for the synthesis of the other IL.

A total of 15 mL (0.116 mol) of 2-(butylamino) ethanol (BAE) was taken in a 250 mL double necked round bottomed flask fitted with a pressure equalizing dropping funnel. This total setup was arranged in an ice bath. Trifluoroacetic acid, 8.9 mL (0.116 mol) was added drop wise through the dropping funnel at (5 to 10) °C, within an inert atmospheric condition (nitrogen gas). After the addition of the acid, the solution was stirred at room temperature for 24 h. The unreacted starting materials as well as moisture were removed under high vacuum at about 40 °C for 24 h. The appearance of the reaction mixture changed from colorless to a yellowish and viscous liquid. Dried ionic liquids were characterized by ^1H NMR, ^{13}C NMR and FTIR spectroscopic techniques which confirmed that no residual amine or acid was present in the IL. Hence the probable impurity in dried IL could be water only. From the spectroscopic techniques used, the mass fraction purity of each synthesized ionic liquid was estimated to be more than 0.97. The structures of the synthesized ILs along with their abbreviations and purities are listed in table 1.

2.2. Characterization

The ^1H and ^{13}C NMR were recorded using a Bruker Avance 500 MHz spectrometer with $CDCl_3$ as an external solvent and relevant spectra are given in figures S1 to S4:

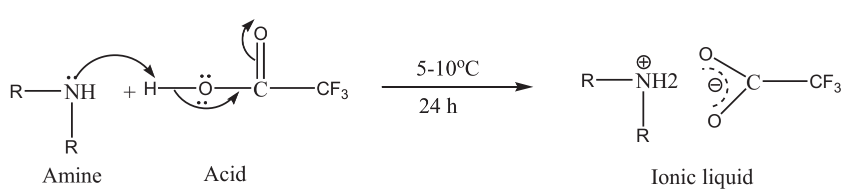
^{1}HNMR ($CDCl_3$):**[BHEA][TFA]:** $\delta = 0.914 \times 10^{-6}$ (*t*, 3H); $\delta = (1.326 \text{ to } 1.400) \cdot 10^{-6}$ (*m*, 2H); $\delta = (1.640 \text{ to } 1.702) \cdot 10^{-6}$ (*m* 2H); $\delta = 2.956 \times 10^{-6}$ (*t*, 2H); $\delta = 3.087 \times 10^{-6}$ (*t*, 2H); $\delta = 3.852 \times 10^{-6}$ (*t*, 2H); $\delta = 4.725 \times 10^{-6}$ (*s*, 1H; OH-group); $\delta = 8.905 \times 10^{-6}$ (*br.s*, 2H, NH_2^+) ^{13}CNMR): (13.39, 19.74, 27.77, 48.03, 49.96, 57.18, 115.38 and 162.50) $\cdot 10^{-6}$. **[BHEA][NO$_3$]:** $\delta = 0.900 \times 10^{-6}$ (*t*, 3H); $\delta = (1.319 \text{ to } 1.394) \cdot 10^{-6}$ (*m*, 2H); $\delta = (1.642 \text{ to } 1.704) \cdot 10^{-6}$ (*m*, 2H); $\delta = 3.019 \times 10^{-6}$ (*t*, 2H); $\delta = 3.134 \times 10^{-6}$ (*t*, 2H); $\delta = 3.831 \times 10^{-6}$ (*t*, 2H); $\delta = 6.319 \times 10^{-6}$ (*br.s*, 3H; NH_2^+, OH). ^{13}CNMR: (13.78, 20.04, 28.46, 48.44, 50.36 and 57.93) $\cdot 10^{-6}$.

FTIR spectra were recorded on a FTIR spectrophotometer (JASCO FT-IR-4100, Japan; wave number range (7800 to 400) cm^{-1}; wavelength range (1282 to 25,000) nm using a NaCl disk. The instrument has a maximum resolution of 0.9 cm^{-1} and has a 22000/1 signal-to-noise ratio.

2.3. Measurements

The water content of the synthesized ionic liquids was measured using the Karl Fischer Titrator supplied by Analab (Micro Aqua Cal 100) and the measured values are listed in table 1. The instrument follows the conductometric titration principle with dual platinum electrodes that permit the measurement of water content from less than 10×10^{-6} to 100%. The instrument was calibrated using Millipore water according to the supplier's guidelines.

The Anton Paar, DSA 5000 M digital densitometer was used to measure the density (ρ) and speed of sound (u) of synthesized PILs within the temperature range from T = (303.15 to 343.15) K and at



SCHEME 1. Synthesis of hydroxyl ammonium ionic liquids: proton exchange reactions between acids and amines.