Uncommon structure making/breaking behaviour of cholinium taurate in water

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A B S T R A C T

Synthesis, volumetric and transport properties of the new third generation ionic liquid cholinium taurate, [Chol][Tau], are reported. Density, viscosity and electrical conductivity measurements of diluted aqueous solution of [Chol][Tau] were performed, while from the theoretical aspects density functional theory (DFT) calculations and molecular dynamics (MD) simulations have been applied in order to understand the nature of interactions and water structuring in the studied system. DFT approach was used to understand geometry and non-covalent interactions between $[Chol]^+$ and $[Tau]^-$ ions, while radial distribution functions (RDFs) obtained after MD simulations were applied in order to determine the parts of the ionic liquid that are most responsible for the interaction with water.

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1. Introduction

In the recent years ionic liquids (ILs) have attracted growing scientific interest in various areas due to their excellent thermal and chemical stability, outstanding ability to dissolve various inorganic or organic compounds and the fact that their properties can be tuned by changing the anion or by introducing different functional groups to the cation part [1,2]. They are widely used in organic synthesis [3], catalysis and biocatalysis [4], chromatography [5], CO_2 apsorption [6], cellulose dissolution [7] etc. ILs are claimed to be "perfect green solvents" based on their negligible vapour pressure and low flammability [8]. Such statements promoted a series of new scientific research based on their impact on the environment, toxicity and biodegradability [9,10]. Obtained results showed that commonly used imidazolium and pyrrolidinium based ILs are not so benign as previously thought [11,12]. These ILs generally express toxicity to enzymes, microorganisms and cells as well as to whole animals and plants. Also, most of the commercially available imidazolium and pyrrolidinium ILs could not be considered as "readily biodegradable", since the resulting products can be more toxic then the starting compounds. It has been widely shown that the cation of IL, especially presence of the substituents, plays a major role in determine wether IL is toxic or not [13]. Based

on the available and limited knowledge about the relationship between structure and properties of ILs, a TSAR (Thinking in terms of Structure-Activity Relationships) strategy has been proposed for rational design of novel and "greener" ILs [14]. According to this strategy, cholinium ion is a good candidate for the synthesis of non-toxic ILs, since the cholinium contains the quaternary ammonium cation with a polar hydroxyl group.. Also, choline is biologically widespread micronutrient, which is completely degradable under aerobic conditions [15]. Recently, numerous cholinium based ILs have been synthesized [16–18] and have been reported to have low toxicity [19–21] and high biodegradability [22,23].

The anion also plays a significant role in the overall toxicity of ILs, although its effect has been often overlooked possibly due to the limited anion types reported. One of the most promising strategies for synthesis of non-toxic ILs is the use of the amino acids as an anion, in so called amino acid based ionic liquids (AAILs) [24]. These new ILs are expected to be green solvents having chiral centers, biodegradable properties, low cost and high biocompatibility [25,26].

Because of these reasons the goal of this work is to obtain new taurate based IL. Taurine is a pseudo amino acid containing sulfonate instead of a carbonyl group showing significant biological activity and has an essential impact in certain aspects of mammalian development. Low levels of taurine are associated with various pathologies including cardiomyopathy, retinal degeneration and growth retardation [27]. In addition, it is well known that

sodium and potassium taurate have significant capacity for CO_2 capture, but this process has several disadvantages owing to high energy cost, corrosion effects and difficult regeneration [28,29]. ILs containing taurate are promising in this regard as they can form complexes with CO_2 and can be used in carbon capture applications because they possess non-volatility, thermal and chemical stability and recycling ability.

Understanding interactions with water is of great importance, especially in the case of molecular structures with potential application as biologically active molecules. In this case we investigated ionic liquid that contains both biologically active ions. Thus, interactions with water are useful tool to understand how this IL could act in the organism. The nature of the interactions with water of synthesized [Chol][Tau] will be discussed from the calculated volumetric parameters derived from the experimental densities, conductometric and viscosimetric measurements and molecular modeling.

2. Experimental

2.1. Synthesis of [Chol][Tau]

All chemicals were used without further purification. The summary of the provenance and purity is given in Table 1. Millipore ultrapure water for preparation of the solution is applied. [Chol][Tau] is synthesized by a potentiometric acid–base titration of cholinium hydroxide, [Chol][OH], and taurine. The reaction is conducted by slow addition of aqueous solution of cholinium hydroxide ($c = 1.7524$ mol·dm^{-3}). The [Chol][OH] is added in a small excess and then back titrated by adding a taurine solution until desired pH value of 9.01. Obtained titration curve is presented in Fig. S1 in the Supplementary Material of this manuscript.

From synthesized IL water is removed at 343.15 K using a rotational evaporator. Then, [Chol][Tau] is heated under vacuum until constant mass was achieved and stored with P_2O_5 under the vacuum for the next 72 h. After drying, water content in the IL was found to be 215 ppm using the Karl-Fisher titration.

For additional characterization, the IR and NMR spectra of the [Chol][Tau] were recorded (Figs. S2 and S3 in the Supplementary Material). NMR spectrum was recorded in D_2O at 298 K on a Bruker Advance III 400 MHz spectrometer. Tetramethylsilane was used as accepted internal standard for calibrating chemical shift for ^1H and ^{13}C. Infrared spectrum was recorded from (4000 to 650) cm^{-1} on a Thermo-Nicolet Nexus 670 spectrometer fitted with a Universal ATR Sampling Accessory.

2.2. Densimetry and volumetric properties

The vibrating tube Rudolph Research Analytical DDM 2911 densimeter with the accuracy and precision of ±0.00005 g·cm^{-3} was used for density measurements. The instrument was thermostated within ±0.01 K and viscosity was automatically corrected. Before each series of measurements calibration of the instrument was performed at the atmospheric pressure using ambient air and bi-distilled ultra-pure water in the temperature range from (293.15 to 313.15) K. Each experimental density value is the average of at least five measurements at selected temperatures. Repeated experimental measurements showed reproducibility within 0.01% and an average value is presented in this paper. Standard uncertainty of determining the density is less than $7.8 \cdot 10^{-4}$ g·cm^{-3}. Obtained experimental values are presented graphically in Fig. S4 and also tabulated in Table S1.

From the experimental densities the apparent molar volumes, V_Φ, were calculated using the following equation:

$$V_\phi - \frac{1000(d_o - d)}{mdd_o} + \frac{M_2}{d} \tag{1}$$

where M_2 is the molar mass of ionic liquid, d_o and d are the experimental densities of water and mixtures, respectively, and m is the molality. The results are tabulated in Table S1 and graphically presented in Fig. S5.

Also, the partial molar volumes of water (V_1), and [Chol][Tau] (V_2), were calculated using the procedure described elsewhere [30]. Calculated values of the partial molar volumes are given in Table S1 and their variations with temperature and [Chol][Tau] concentration are presented in Fig. 1.

2.3. Viscosity

The viscosity of the {[Chol][Tau] + H_2O} binary mixtures was measured using Ubbelohde viscosimeter by measuring the flow rate of the liquid. Viscosimeter was calibrated using 0.1 mol·dm^{-3} KCl solution (NIST reference) and bi-distilled deionized water in a temperature range from (293.15 to 313.15) K. Viscosimeter was filled with experimental liquid and placed vertically in glass sided thermostat maintained constant to ±0.01 K, with standard uncertainty of controlled temperature of ±0.02 K. After thermal equilibrium is attained, the flow time of liquids was recorded with a digital stopwatch with an accuracy of ±0.01 s. Presented results were obtained as the mean value of at least ten viscosity measurements. Viscosity of the studied binary mixtures was measured in the molality range up to 0.0907 mol·kg^{-1} of [Chol][Tau]. Experimental values are graphically presented in Figs. S6 and S7 and given in Table S2.

Dynamic viscosity was calculated using the following equation:

$$\eta = (Kt - L/t) \tag{2}$$

where K and L are the constants of the viscosimeter, t is a flow time and d experimental density of the liquid. Relative standard uncertainty of determining the viscosity with Ubbelohde viscosimeter was found to be less than 1%.

2.4. Electrical conductivity

The measurements were carried out in a Pyrex-cell with platinum electrodes on a conductivity meter Jenco 3107 using DC signal. Dried conductometric cell with a total volume of 14 cm^3 was thermostated with an accuracy of ±0.01 K for 20 min with the external flow. At least ten measurements were performed at 5 s intervals in order to eliminate the self-heating and ionization in

Table 1
Provenance and purity of the samples.

Chemical name	Provenance	CAS number	Purification method	Final mass fraction, ω	Water content
Choline hydroxide (water solution)	Sigma-Aldrich	123-41-1	None		54%[***]
Taurine	Sigma Aldrich	107-35-7	None	ω ⩾ 0.99	
[Chol][Tau]	Synthesis		Rotary evaporation followed by vacuum	ω ⩾ 0.96[**]	215 ppm[*]

[*] Determined by Karl-Fischer titration.
[**] Determined by NMR.
[***] Mass percentage is stated by supplier.