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Kosmotropism of newly synthesized 1-butyl-3-methylimidazolium taurate ionic liquid: Experimental and computational study

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ABSTRACT

For the first time the synthesis and characterization of the new third generation ionic liquid containing taurate anion is reported. The goal of this study was to understand interactions between ions and their interaction with water molecules, from both experimental and theoretical aspects. 1-Butyl-3-methylimidazolium taurate ionic liquid, [bmim][Tau], was synthesized and fully characterized. Density, electrical conductivity and viscosity measurements were performed, while from the theoretical aspects, density functional theory (DFT) calculations and molecular dynamics (MD) simulations have been applied in order to additionally understand the fundamental properties of [bmim][Tau] and its interaction with water. DFT approach was used to understand non-covalent interactions between $[bmim]^+$ and $[Tau]^-$ ions, while radial distribution functions (RDFs) obtained after MD simulations were applied in order to determine the molecule sites that are principally responsible for the interaction with water.

1. Introduction

Ionic liquids (ILs) are modern neoteric and designed solvents with remarkable properties usually considered as green alternatives for conventional volatile organic compounds suitable for the application in many technological and industrial processes [1–7]. The first generation of ILs includes those liquids with desirable physical properties such as negligible vapor pressure and high thermal stability. Second generation of ILs has been used as functional energetic materials, lubricants, and metal ion complexing agents. Recently, the new generation of ionic liquids was prepared using active pharmaceutical ingredients to improve their biological activity [8–10].

A special group of the third generation ionic liquids are so-called task-specific ionic liquids (TSILs) with functional groups designed to provide specified properties and reactivity of the ILs [11,12]. One of the most promising TSILs are amino acid-based ionic liquids (AAILs). These new ILs are expected to be green solvents having chiral centers, biodegradable properties, low cost and high biocompatibility. AAILs show potential application in many technologies such as gas purification (CO_2 or SO_2 absorption) [12–15], biomass dissolution [16,17], separation processes [18], metal scavenging [11] and catalysts for aqueous chemical reactions [19].

It's well known that amino acid salts have been widely used as a absorbents in the field of CO_2 capture due to their low volatility and resistance to oxygen degradation in the absorption process [20,21]. It was shown that aqueous solutions of sodium and potassium taurate possess a high potential for CO_2 storage [22–24]. However, this process has some major disadvantages, such as high energy costs, loss of solvent, corrosion effects and difficult regeneration. AAILs are promising in this regard as they can form complexes with CO_2 and can be used in carbon capture applications because they possess properties such as non-volatility, thermal and chemical stability and recycling ability [25].

In addition, taurine is a pseudo amino acid containing sulfonate instead of a carbonyl group with significant biological activity. Taurine has shown to be essential in certain aspects of mammalian development. Low levels of taurine are associated with various pathologies including cardiomyopathy, retinal degeneration and growth retardation [26]. Also, physico-chemical properties of taurine-based AAILs are not investigated yet. Thus, the main goal of this work was to synthesize new taurine-based AAIL and to determine volumetric and transport parameters for the pure ionic liquid, but also to investigate nature of the interactions in the aqueous AAIL solutions.

Since the water has a unique properties and a wide range of applications in many chemical processes, but also is included in various physiological phenomena, it is of the crucial importance further investigation of the solvation processes and the interactions of water molecules with solute particles. Ions that have

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strong interactions with water molecules can increase the structuring of water; they are called structure-makers or kosmotropes. Other ions that decrease the structuring of water are structure-breakers or chaotropes [27]. Actually, kosmotropes are usually small and highly charged ions, while chaotropes are large and low charged. Structure making/breaking properties of newly synthesized AAIL (1-butyl-3-methylimidazolium taurate, ([bmim][Tau]) will be discussed from the calculated volumetric parameters, conductometric and viscosimetric measurements together with molecular modeling.

2. Experimental

All chemicals were used without further purification: [bmim][Cl] (Merck, $\omega \geqslant 0.98$); taurine (Sigma Aldrich, $\omega \geqslant 0.99$); sodium hydroxide (Lachner; $\omega \geqslant 0.999$); acetone (Lachner; $\omega \geqslant 0.99$). The summary of the provenance and mass fraction purity of the samples is given in table 1.

For the newly synthesized [bmim][Tau] ionic liquid, nuclear magnetic resonance (NMR) data were recorded in $CDCl_3$ at $T = 298.15$ K on a Bruker Advance III 400 MHz spectrometer and the solvent peak was used as reference. Infrared spectra were recorded as neat samples from (4000 to 650) cm^{-1} on a Thermo-Nicolet Nexus 670 spectrometer fitted with a Universal ATR Sampling Accessory. Thermogravimetric analysis of [bmim][Tau] was performed on a TA Instruments SDT Q600 in the nitrogen atmosphere.

Density measurements. The vibrating tube Rudolph Research Analytical DDM 2911 densimeter with the accuracy and precision of ±0.00001 $g \cdot cm^{-3}$ was used for density measurements. The instrument was thermostated (Peltier-type) within $T = \pm 0.01$ K and viscosity was automatically corrected. Before each series of measurements calibration of the instrument was performed at the atmospheric pressure. The calibration procedure is described in our previous papers [28]. Each experimental density value is the average of at least three measurements at temperatures from (293.15 to 313.15) K. Repeated experimental measurements showed reproducibility within 0.01%, and an average value is presented in this work. Standard uncertainty of determining the density is less than $8.1 \cdot 10^{-4}$ $g \cdot cm^{-3}$.

Electrical conductivity measurements. Binary mixtures for the electrical conductivity measurements were prepared by mixing the appropriate amounts of [bmim][Tau] and water. These measurements were carried out in a Pyrex-cell with platinum electrodes in the temperature range (293.15 to 323.15) K for pure IL, and from (293.15 to 313.15) K for binary mixtures on a conductivity meter Jenco 3107 using DC signal. The experimental procedure was described elsewhere [28]. The cell constant amounted to 1.0353 cm^{-1} was checked from time to time to control any possible evolution. The relative standard uncertainty for electrical conductivity was less than 1.5%. All obtained experimental values represent the mean of three measurements.

Viscosity measurements. The viscosity measurements of the binary mixtures and pure water were performed using Ubbelohde viscosimeter by measuring the flow rate of the liquid. The viscosimeter was calibrated applying 0.1 $mol \cdot dm^{-3}$ KCl solution (NIST reference) and bi-distilled deionized water in the temperature range (293.15 to 313.15) K. Prior to each series of measurements viscometer was washed twice with distilled water and acetone and dried. Viscosimeter was filled with experimental liquid and placed vertically in glass sided thermostat maintained constant to $T = \pm 0.01$ 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. Dynamic viscosity was calculated using the following equation:

$$\eta = (Kt - L/t)d, \quad (1)$$

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 about 1%.

Viscosity of pure IL was measured using a Brookfield Viscosimeter DV II + Pro thermostated with an accuracy of $T = \pm 0.01$ K and filled with about 8 cm^3 of pure liquid. The spindle type (SC4-18) was immersed and rate per minute (RPM) was set in order to obtain a suitable torque. A viscometer cell protected from moisture with the compartment made by the manufacturer was calibrated using the liquids of different viscosities purchased from the manufacturer. Viscosity for pure IL was measured in the temperature range from (293.15 to 323.15) K with the rotation speed of 2 RPM. Presented experimental values are the mean of three measurements and the measurement uncertainty was found to be about 1%.

2.1. Synthesis of [bmim][Tau]

Equimolar amounts of taurine and sodium hydroxide were mixed and dissolved in water. After two hours of stirring in a round-bottom flask, water was removed under vacuum at $T = 373.15$ K. After achieving a constant mass, in order to remove remaining content of water, obtained sodium taurate was kept for 24 h under the vacuum in the presence of P_2O_5. Then, equimolar amounts of sodium taurate and 1-butyl-3-methylimidazolium chloride were mixed and dissolved in acetone. The mixture was stirred under reflux for another 12 h. The resulting white precipitate (sodium chloride) was removed and the clear red liquid is obtained. The ionic liquid was heated for 30 min at $T = 343.15$ K under vacuum to remove remains of the acetone. Achieving a constant mass, the ionic liquid was additionally dried under the vacuum for the next 72 h. Water content in a dried IL was found to be 263 ppm by the Karl Fischer titration and chloride content less than 1.8 ppm determinated using ion chromatography. For

TABLE 1
Provenance and purity of the samples.

Chemical name	Provenance	CAS number	Purification method	Final mass fraction from supplier	$\omega_{H2O}/10^{-6}$	$\omega_{H2O}/10^{-6}$
1-Butyl-3-methylimidazolium chloride	Merck	79917-90-1	None	$\omega \geqslant 0.98$		
Taurine	Sigma Aldrich	107-35-7	None	$\omega \geqslant 0.99$		
Sodium hydroxide	Lachner	1310-73-2	None	$\omega \geqslant 0.999$		
Acetone	Lachner	67-64-1	None	$\omega \geqslant 0.99$		
1-Butyl-3-methylimidazolium taurate	Synthesis		Rotary evaporation followed by vacuum	$\omega \geqslant 0.96$[a]	263[b]	1.8[c]

[a] Confirmed by NMR spectroscopy (figure S2).
[b] Determined by Karl-Fischer titration.
[c] Determined by ion chromatography.