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Structure making properties of 1-(2-hydroxylethyl)-3-methylimidazolium chloride ionic liquid

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ABSTRACT

Diluted aqueous solutions of 1-(2-hydroxylethyl)-3-methylimidazolium chloride ionic liquid, [C_2OHmim][Cl], were investigated and fully characterized. Density, viscosity and electrical conductivity were measured experimentally, while from the theoretical aspects molecular dynamics (MD) simulations and radial distribution functions (RDFs) have been applied in order to understand the nature of interactions and water structuring in the studied system. Radial distribution functions were used to determine the ion sites that are principally responsible for the interaction with water.

1. Introduction

Imidazolium-based ionic liquids containing hydroxyl group in the alkyl chain exhibit different physico-chemical features comparing to non-functionalized ionic liquids. They have better solubility and miscibility with water and may dissolve numerous inorganic salts [1–6]. Also, electron donor properties of hydroxyl group increase coordinating ability of imidazolium cation making these liquids suitable medium for the study of complex formation and thermochromism of some transition metals [7,8]. Polar OH-group in the alkyl chain induces stronger (ion + dipole) interactions and hydrogen bonds with ionic liquid anion, increasing viscosity and decreasing electrical conductivity comparing to corresponding conventional ionic liquids [9–17].

Such ionic liquids were firstly synthesized and applied for the absorption of the greenhouse gases [2,18,19]. Due to their excellent hydrophilic properties they are used instead of polar volatile organic solvents in (liquid + liquid) extractions, synthesis, electrochemical processes and catalysis as fluidic support for catalyst or reactant [19–24]. Also, these liquids may be used for the stabilization and the reduction of the nanoparticles during the synthesis [25,26]. Low lipophilicity and low toxicity of hydroxyl-functionalized ionic liquids was also observed [27–29].

Aqueous solution of [C_2OHmim][Cl] was applied in the absorption pump technology as excellent working fluid [30,31]. In such aqueous solutions of hydrophilic ionic liquids two distinct regions as a function of composition may be defined: (1) ionic liquids in water-rich solutions with strong electrolyte-like behavior; and (2) water in ionic liquid-rich solutions, in which water shows a disrupting effect on the interionic interactions. The extension and properties of these two regions are strongly dependent on the nature of involved ions. Nie at al [31] were investigated highly concentrated {[C_2OHmim][Cl] + H_2O} binary mixtures. Thus, in this work transport and volumetric properties of diluted aqueous [C_2OHmim][Cl] solutions were investigated in order to get more information about solvation processes and structuring of water in the studied system. Some important properties and constants for $[C_2OHmim]^+$ cation will be calculated which are currently not available in the literature. Molecular dynamics (MD) and radial distribution function (RDF) will be applied for the investigation of the nature of interactions in the solution.

2. Experimental and mathematical approach

The summary of the provenance and purity of the samples is given in table 1. All chemicals were used without further purification. Millipore ultrapure water for preparation of solution is applied. Synthetic path of [C_2OHmim][Cl] is described elsewhere [7].

For additional characterization, the IR and NMR spectra of the [C_2OHmim][Cl] were provided (figures S1 and S2 in the Supplementary material). NMR spectra were recorded in D_2O at T = 298 K on a Bruker Advance III 400 MHz spectrometer. Tetramethylsilane

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TABLE 1
Provenance and purity of the samples.

Chemical name	Provenance	CAS number	Purification method	Final mass fraction	Water content in ppm
N-Methylimidazole	Sigma-Aldrich	616-47-7	None	$\omega \geqslant 0.99$	
2-Chloro-1-ethanol	Fluka	107-07-3	None	$\omega \geqslant 0.995$	
Ethyl acetate	Backer	141-78-6	None	$\omega \geqslant 0.996$	
1-(2-Hydroxethyl)-3-methylimidazolium chloride[a]	Synthesis		Re-crystallization	$\omega \geqslant 0.99$	296

[a] Commercially available under CAS number: 61755-34-8.

was used as accepted internal standard for calibrating chemical shift for ^{1}H and ^{13}C.

^{1}H homodecoupling and 2D COSY method were used routinely for the assignation of obtained NMR spectra. ^{13}C NMR spectra were assigned by selective decoupling technique. 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.

2.1. Densimetry and volumetric properties

The vibrating tube Rudolph Research Analytical DDM 2911 densimeter with the accuracy and precision of ±0.00005 $g \cdot cm^{-3}$ was used for density measurements. The instrument was thermostated 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 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 $7.6 \cdot 10^{-4}$ - $g \cdot cm^{-3}$. Obtained experimental values are presented graphically in figure S3 and also tabulated in table S1.

From the experimental densities the apparent molar volumes, V_{Φ}, were calculated using the following equation

$$V_{\Phi} = \frac{1000(d_o - d)}{mdd_o} + \frac{M_2}{d} \quad (1)$$

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 figure S4.

Also, the partial molar volumes of water (V_1), and [C_2OHmim][Cl] (V_2), were calculated using the procedure described elsewhere [32,33]. Calculated values of the partial molar volumes are given in table S1 and their variations with [C_2OHmim][Cl] concentration are presented in figures S5 and S6.

2.2. Viscosity measurements

The viscosity measurements of the binary mixtures were performed using Ubbelohde viscosimeter by measuring the flow rate of the liquid. Viscosimeter was calibrated using 0.1 $mol \cdot dm^{-3}$ KCl solution (NIST reference) and bi-distilled de-ionized 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 $T = \pm 0.01$ 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. Viscosity of the studied {[C_2OHmim][Cl] + H_2O} binary mixtures was measured in the molality range up to 0.0868 $mol \cdot kg^{-1}$ of [C_2OHmim][Cl]. Experimental values are graphically presented in figure S7 and given in table S2.

Dynamic viscosity was calculated using the following equation:

$$\eta = (Kt - L/t)d \quad (2)$$

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%.

2.3. Electrical conductivity

The measurements were carried out in a Pyrex-cell with platinum electrodes on a conductivity meter Jenco 3107 using DC signal. The conductometric cell with a total volume of 14 cm^3 was initially dried in the atmosphere of nitrogen and thermostated for twenty minutes with the external flow with an accuracy of $T = \pm 0.01$ K. At least ten measurements were performed at 5 s intervals, in order to eliminate the self-heating and ionization in the electrodes [34]. The experimental cell was calibrated with standard 0.1000 $mol \cdot dm^{-3}$ KCl solution by the same experimental procedure. The resulting cell constant amounted to 1.0353 cm^{-1}, and it 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.

The electrical conductivity of {[C_2OHmim][Cl] + water} binary mixtures were measured in the temperature range from (293.15 to 313.15) K. The results are listed in table S3. Based on the experimental density and electrical conductivity data, molar conductivity was calculated (figure S8 and table S4).

TABLE 2
Masson's equation fitting parameters for the {[C_2OHmim][Cl] + H_2O} solutions in the temperature range from (293.15 to 313.15) K with the deviations of their fit (σ) and regression coefficient (R^2).

T/(K)	V_{ϕ}^{o}/($cm^3 \cdot mol^{-1}$)	S_v/($cm^{9/2} \cdot mol^{-3/2}$)	σ	R^2
293.15	143.36	−75.87	0.0025	0.9990
298.15	144.56	−79.18	0.0033	0.9991
303.15	145.67	−83.29	0.0022	0.9993
308.15	146.66	−86.81	0.0019	0.9997
313.15	147.75	−90.61	0.0020	0.9997