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Interactions in aqueous solutions of imidazolium chloride ionic liquids [$C_n$mim][Cl] (n = 0, 1, 2, 4, 6, 8) from volumetric properties, viscosity *B*-coefficients and molecular dynamics simulations

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ABSTRACT

In this work a systematic study of aqueous diluted solutions (~0.005 < *m*/mol·kg^{-1} < ~0.1) of six imidazolium based ionic liquids (IL) [$C_n$mim][Cl] with different alkyl chain lengths (n = 0, 1, 2, 4, 6, 8) was carried out. Densities and viscosities were measured as a function of IL concentration in the temperature range between 278.15 K and 313.15 K in steps of 5 K. From experimental data, apparent molar volumes, standard partial molar volumes, and viscosity *B*-coefficients of ILs were derived. The effect of the alkyl chain length on the estimated properties was discussed in terms of ion-ion and ion-solvent interactions. It turned out that the studied cations with longer alkyl side chain (n = 4, 6, 8) can be regarded as structure makers; cations with shortest side chain (n = 0, 1) as structure breakers, whereas [C_2mim]$^+$ can be considered as a border line ion. In order to obtain more information about interactions and influence of studied ILs on water structure, computational simulations were performed. For this purpose, DFT calculations using B3LYP-D3 functional and molecular dynamic simulations with OPLS 2005 force field, were applied. Obtained results show that the increase in length of alkyl substituent in imidazolium ring leads to weakening of interactions with water molecules.

1. Introduction

Thermodynamic and transport properties of ionic liquids (ILs) solutions are highly influenced by their structure, *e.g.* from the alkyl chain length on the cation. Recently, a systematic study on ion mobility and association in aqueous diluted solutions of nine imidazolium based chlorides, [$C_n$mim][Cl] with different alkyl chain lengths (n = 0 to 12), from 1-methyl-imidazolium chloride, [C_0mim][Cl] to 1-dodecyl-3-methylimidazolium chloride, [C_{12}mim][Cl], with two isomers 1,2- and 1,3-dimethylimidazolium chloride, [C_1mim][Cl] has been carried out [1]. By help of conductivity experiment and molecular dynamics simulations it was found that the mobility/diffusion coefficients of imidazolium cations in the limit of infinite dilution decrease with an increasing length of the cation alkyl chain, but not linearly. In addition, binding free energies of imidazolium cations with chloride anion, estimated by statistical mechanics calculations, molecular dynamics simulations and experimental association constants reveal that the association of investigated ILs as model 1-1 electrolytes in water solutions is weak but evidently dependent on the molecular structure (alkyl chain length), which also strongly affects the mobility of imidazolium cations.

Experimental data on physical properties such as density and viscosity of imidazolium based chlorides ILs in aqueous solutions also give information on the existence of specific molecular interactions. A survey of literature data reveals that volumetric and viscometric properties belong probably to the most investigated characteristics of ILs systems. Surprisingly only some investigations of volumetric properties were carried out on imidazolium based chlorides in diluted aqueous solutions [2–7], but not in a systematic manner. Whereas viscosity *B*-coefficients of [$C_n$mim][Br] (n = 4, 6, 8) in alcohols at 298.15 K were reported recently [8], similar study in water solutions is still missing. Therefore, we decided to carry out the systematic investigation on volumetric and viscometric properties for a number of aqueous solutions of imidazolium based chlorides [$C_n$mim][Cl] with n = 0, 1, 2, 4, 6 and 8 (Fig. 1). Due to the micellization in water in the investigated concentration range imidazolium chlorides [$C_n$mim][Cl] with n = 10 and 12 were not included in the investigation.

In present study, measurements of density and viscosity were performed in the temperature range between 278.15 K and 313.15 K in steps of 5 K at concentration ~0.005 < *m*/mol·kg^{-1} < ~0.1. From experimental values of densities, the apparent molar volumes and the partial molar volumes of solute and solvent were calculated as a function of

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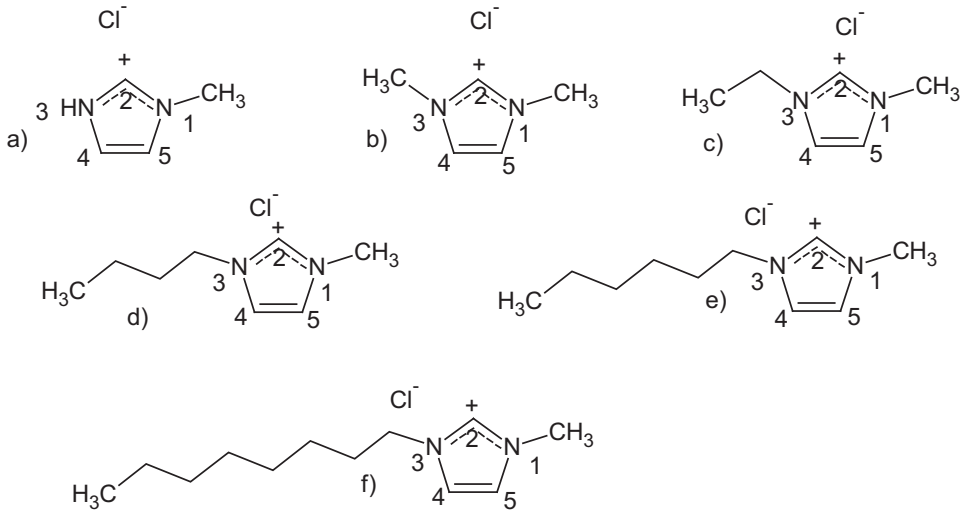

Fig. 1. Structures of investigated ionic liquids, with numerations of imidazolium ring: a) [C_0mim][Cl]; b) [C_1mim][Cl]; c) [C_2mim][Cl]; d) [C_4mim][Cl]; e) [C_6mim][Cl] and f) [C_8mim][Cl].

concentration and temperature, whereas viscosities served to determine the *B*-viscosity coefficients. Derived parameters were discussed and interpreted in terms of IL-IL and IL-water interactions. The reported volumetric and viscometric properties are related to changes in the structure of water caused by dissolved [$C_n$mim][Cl] depending on the temperature and the length of the cation alkyl chain. In addition, molecular dynamics simulations were carried out also in order to get more insight in the interactions of imidazolium based chlorides [$C_n$mim][Cl] with water.

2. Experimental section

2.1. Materials

All imidazolium chlorides were purchased from Ionic Liquids Technologies (io-li-tec Germany, the details are given Table S1 in Supplementary data) and were used without further purification. They were dried for 24 h at ~40 °C with a vacuum line ($p < 5$ Pa) and stored in a desiccator over P_2O_5 before use. Stock solutions were prepared by mass from the pure compounds and demineralized and distilled water, and the working solutions were obtained by mass dilution. Demineralized water was distilled two times in a quartz bidestillation apparatus (Destamat Bi 18E, Heraeus). The final product with the specific conductivity $<6 \cdot 10^{-7}$ S cm^{-1} was distilled into a flask under an atmosphere of nitrogen permitting storage under an atmosphere of nitrogen. The molality, *m*, of the stock solution for each imidazolium chloride in water was checked by potentiometric titration with a standard solution of $AgNO_3$. Molality is related to the corresponding (temperature-dependent) molar concentration, *c*, *via* $c = 1000 \cdot m \cdot \rho / (1000 + m \cdot M_2)$, where M_2 is the molar mass of IL and ρ is the density of solution.

2.2. Density and viscosity measurements

The densities of aqueous imidazolium chloride solutions were measured at atmospheric pressure of 0.1 MPa using a vibrating tube Anton Paar DMA 5000 densimeter with a declared reproducibility of ~$5 \cdot 10^{-3}$ kg·m^{-3}. Before each series of measurements calibration of the instrument was carried out at the atmospheric pressure using demineralized and distilled ultra-pure water in the temperature range from (278.15 to 313.15) K. The instrument was thermostated within ±0.005 K and viscosity related errors in the density were automatically corrected over full viscosity range. To avoid gas bubbles entrapped in the measuring cell filled with a sample, the cell was filled carefully to minimize the probability of such error. The total volume of the sample used for density measurements was approximately 1 cm^3. Densimeter already has incorporated moisture adsorbent. The relative standard uncertainty of determining the density was estimated to be 0.4%.

The viscosities of the solutions were determined with a micro Ubbelohde viscometers (SI Analytics GmbH, Mainz, Germany, type no. 526 10 capillary I) and an automatic flow time measuring system ViscoSystem® AVS 370. The viscometer was immersed in a transparent thermostat bath where the temperature was maintained from (278.15 to 313.15) ± 0.01 K. Each measurement was automatically repeated at least five times and yielded a reproducibility of the flow time of <0.02%. The kinematic viscosity of solutions, ν (m^2·s^{-1}), was calculated from the equation $\nu = C \cdot t - E/t^2$, where t (s) is the flow time, $C = 1.00669 \cdot 10^{-8}$ m^2·s^{-2} and $E = 1.3785 \cdot 10^{-5}$ m^2·s are constants characteristic for the viscometer and were determined by calibration of the viscometer with water at 293.15 and 298.15 K. The absolute (dynamic) viscosity, η (Pa·s = kg·m^{-1}·s^{-1}), was obtained from the relation $\eta = \nu \cdot \rho$, where ρ is density of the investigated solution. The errors from calibration and temperature control yielded an uncertainty <0.1% of absolute viscosity. For more details about density and viscosity measurements see Ref. [9].

2.3. Computational details

Computational analysis of the interaction of imidazolium based chlorides [$C_n$mim][Cl] with water was performed employing molecular dynamics simulations with Desmond 14.2 [10–13]. In order to make simulations more realistic, charges were obtained using *ab initio* calculations with Jaguar 8.8 program [14,15]. *Ab initio* calculations were performed for several configurations of $[C_nOHmim]^+$ and $[Cl]^-$ with B3LYP-D3 exchange-correlation functional with 6–31 + G(d,p) basis set.

In order to investigate the interactions with water radial distribution functions (RDFs) were calculated. For these purposes Optimized Potential for Liquid Simulations (OPLS) 2005 force field [16] was used within NPT ensemble class for all MD simulations. Temperature was set to 300 K, while pressure was 101325 Pa. Eight [$C_n$mim][Cl] ion pairs were placed in a cubic box, filled with water molecules, which corresponds to the concentration in experimental conditions which were used. Water was treated within statistical process control (SPC) solvent