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The role of water in cholinium carboxylate ionic liquid's aqueous solutions

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ABSTRACT

Binary systems composed of water and cholinium carboxylate ionic liquids, namely cholinium lactate ([Ch][Lac]), cholinium propanoate ([Ch][Prop]) and cholinium malonate ([Ch][Mal]) were studied from the neat ionic liquid to very diluted aqueous solutions. Densities and viscosities were measured and atypical behaviors were observed, such as the increasing density of the binary [Ch][Prop] + H_2O mixtures with increasing water content. In order to get molecular level insights on the IL + H_2O solvation schemes, ^1H NMR studies were performed. Large deviations were obtained in the anionś resonances when compared to those of the cation suggesting that water interacts preferentially with the anion counter-part of the ionic liquid. The increasing density of [Ch][Prop] + H_2O system with increasing water content can be related to the orientation of the alkyl chains, as a result of their nanoscale organization. This behavior was confirmed through the study of the thermophysical properties of [Ch][Hex] + H_2O mixtures, where this phenomenon is known to occur.

1. Introduction

It has been claimed that one of the first steps towards green chemistry practice is assessing materials that are unsustainable in order to replace them with safer chemicals. In this context, ionic liquids (ILs) are largely recognized as alternatives for replacing highly toxic organic solvents [1] due to their negligible vapor pressure [2,3], high thermal and chemical stability [4] and low flammability [5], not to mention their amazing solvation capacity [4,6]. Nevertheless, the most commonly used ILs are based on imidazolium or pyridinium cations that do not meet the biodegradable and biocompatible aspects required by the green chemistry concepts [7] and the regulations [8] enforced therein.

The need to meet the established green solvents criteria encourages the development of new and greener families of ILs. One example of a possible green IL is the cholinium-based IL family, that has been gaining considerable attention since 2007, due to their particular features, namely biocompatibility [9], biodegradability and low toxicity [10]. The cholinium cation has already been used to synthesize ionic liquids through its combination with amino acids [4,11,12] and carboxylic acids [13–15], resulting in ILs wholly composed of materials derived from renewable sources. In terms of applications, these compounds, particularly those containing carboxylated anions, have been tested in the implementation of benign extraction schemes, such as in aqueous biphasic systems [16,17] and suberin extraction [6,9], or as liquid phases for CO_2 separation processes [18]. However, concerning the thermophysical properties of cholinium-based ILs, only a few studies are reported in the literature [4,19,20]. On the other hand, cholinium-based ILs have an acute hydrophilic character, which is well evidenced by the partial miscibility of cholinium bis(trifluoromethylsulfonyl)amide IL with water at room temperature [21]. Consequently, the combination of the cholinium cation with carboxylated anions clearly enhances the water affinity of the resulting ILs. Moreover, it is well known that both hydrophobic and hydrophilic ILs show large affinity for water, and as some authors point out, water can be considered the major impurity found in some families of ILs [22]. The understanding of how water interacts with ionic liquids and how their properties are affected by the presence of water is important in the most common applications of these fluids, so that a true assessment of their applicability can be made.

In the last few years, (water + IL) interactions and the role of water on the nanostructural organization [23] of ILs have been studied from both the experimental and the theoretical point of view. For instance, the properties of mixtures containing water and distinct hydrophilic ILs such as 1-(2-hydroxyethyl)-3-methylimidazolium trifluoroacetate ([OHC$_2$mim][TFA]) [24], 1-ethyl-3-methylimidazolium hydrogen sulfate ([C$_2$mim][HSO$_4$]) [24], 1-ethyl-3-methylimidazolium methanesulfonate ([C$_2$mim][CH$_3$SO$_3$])

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[24,25] and 1-ethyl-3-methylimidazolium ethyl sulfate ([C_2mim][C_2SO_4]) [26,27] were investigated. Different techniques ranging from vibrational spectroscopy, NMR experiments, calorimetry or molecular dynamics simulations have been used to answer questions regarding on how water changes the behavior of ILs and accommodates in the IL milieu. The main conclusion, unanimously stated, is that water molecules are preferentially hydrogen bonded to the ILs anions [25], even at higher water concentration. When increasing the water content, the polar network progressively collapses and water aggregates are formed, leading to a well defined hydrogen-bonded network [27]. The small differences observed from this behavior have been correlated with the different chemical structures of the ILs. MD simulations suggest that (water + IL) systems are highly structured media containing nonpolar domains [23,28]. This indication can be used to understand the decreasing of (water + IL) interactions when changing the cation structure from 1-butyl-3-methylimidazolium tetrafluoroborate ([C_4mim][BF_4]) to 1-butyl-3-methylpyridinium tetrafluoroborate ([C_4mpy][BF_4]), as observed by Brennecke's group [24]. Overall, these studies yield valuable insights on the behavior of imidazolium-based ILs in water. However, for other IL families, such as cholinium, there is still a lack of information on this subject. Only one recent work [29] reports activity coefficients of cholinium ILs aqueous solutions, showing that hydrogen bonding is the driving force in these systems. Despite the unquestionable interest in this kind of systems, the absence of data, either at the macroscopic or molecular level, motivated us to study the properties of aqueous solutions of ILs comprising cholinium cations combined with small chain carboxylated anions. This type of knowledge is the key to a successful implementation of several sustainable technologies [24,30,31] since equipment such as pumps, stirrers or flow meters heavily depend on the ILs thermophysical properties, that are largely influenced by the presence of water.

In this work, cholinium carboxylate ILs, namely cholinium lactate ([Ch][Lac]), cholinium propanoate ([Ch][Prop]), cholinium malonate ([Ch][Mal]) and cholinium hexanoate ([Ch][Hex]) (see figure 1 for chemical structures) were synthesized and the density and the viscosity of their mixtures with water were measured as a function of temperature, at a pressure of 0.1 MPa. The first three ILs were chosen to study (water + IL) interactions because they are liquid at room temperature [10,18,19]. Also due to their similar structure, fixing the cholinium cation and changing the carboxylate anion but still maintaining the number of carbon atoms. The [Ch][Prop] has a small linear anion, and the effect of the introduction of one hydroxyl or one carboxyl functional group was studied using the [Ch][Lac] and [Ch][Mal], respectively. [Ch][Hex] was further prepared in order to establish a direct comparison with the behavior obtained for [Ch][Prop]. Furthermore, NMR experiments were performed to get molecular level insights on the solvation of these ionic liquids by the water molecules.

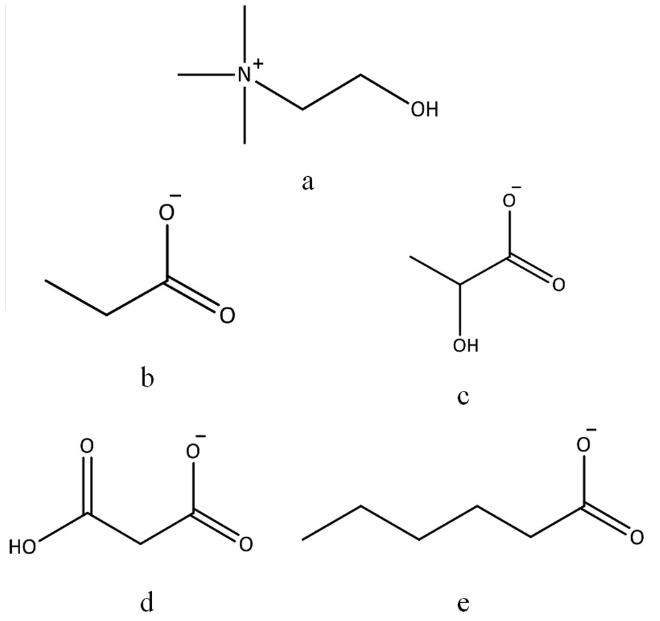

FIGURE 1. Chemical structures of cholinium cation (*a*) and propanoate (*b*), lactate (*c*), malonate (*d*) and hexanoate (*e*) anions.

2. Experimental

2.1. Materials

L(+)lactic acid (≈81 wt% in water) was purchased from Fluka. Cholinium bicarbonate (≈80 wt% in water), malonic acid (≈99%), propanoic acid (≈99%) and hexanoic acid (≈99%) were purchase from Sigma–Aldrich. Deuterium oxide, D_2O and DMSO-d_6 99.9%, were supplied by Cambridge Isotope Laboratories, Inc., as shown in table 1. Double distilled water, passed through a reverse osmosis system and further treated with a Milli-Q plus 185 water purification equipment, was used in all experiments.

2.2. ILs synthesis

Cholinium-based ILs ([Ch][Lac], [Ch][Prop], [Ch][Mal] and [Ch][Hex]) were prepared by dropwise addition of the corresponding acid to aqueous cholinium bicarbonate in equimole quantities, following an established procedure [13]. The mixtures were stirred at ambient temperature and pressure for 12 h. The resulting products were washed with diethyl ether to remove unreacted acid. Excess of water and traces of other volatile substances were removed first by rotary evaporation and then by freeze-drying. The obtained ILs were stirred and heated at $T = 318$ K for at least three days under vacuum ($p = 1$ Pa). The washing and removing of trace solvents were repeated until the chemical structure and the absence of impurities were confirmed by ^{1}H and ^{13}C NMR.

2.3. (Water + ILs) mixtures preparation and density and viscosity measurements

Aqueous binary mixtures were prepared by adding a specific amount of water to each ionic liquid. After the removal of air using a nitrogen stream, the vials were closed and immediately sealed. To minimize the water uptake, the vials were transferred to a glove box and the water content determined by Karl-Fischer titration. Density (ρ) and viscosity (η) were measured at $p = 0.1$ MPa in the temperature range between $T = (293.15 \text{ and } 343.15)$ K, using an SVM 3000 Anton Paar rotational Stabinger viscometer-densimeter. The precision of the dynamic viscosity measurements is ±0.5%, temperature is controlled within a precision of ±0.02 K and the absolute uncertainty of the density is $\pm 0.0005 \text{ g} \cdot \text{cm}^{-3}$. These cholinium salts are stable until $T = (457 \text{ to } 496)$ K [10].

2.4. NMR capillary studies

Degassed aliquots of the (water + IL) mixtures, prepared for the density and viscosity measurements, were transferred to melting capillary tubes, which were flame sealed under a reduced nitrogen pressure. Simultaneously, Karl-Fisher titrations were performed to measure the water content of the samples. Afterwards, each sealed melting tube was placed into a standard 5 mm NMR tube filled with deuterium oxide, D_2O (99.9%, Cambridge Isotope Laboratories,