



Ionic association and interactions in aqueous methylsulfate alkyl-imidazolium-based ionic liquids



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ARTICLE INFO

Article history:
Available online 14 February 2014

Keywords:
Ionic liquids
Conductivity
Viscosity
Diffusion
Ionicity
IR spectroscopy

ABSTRACT

Several experimental techniques were used to study ionic association and interactions in aqueous $[C_1C_2Im][MeSO_4]$, 1-ethyl-3-methylimidazolium methylsulfate, and $[C_1C_4Im][MeSO_4]$, 1-butyl-3-methylimidazolium methylsulfate. Two transport properties, viscosity and electrical conductivity, were determined for these two binary mixtures. For a better assessment of the ionic association and the perturbation of water into the molecular structure of the ionic liquid, diffusion coefficients of ions and water molecules were obtained by NMR spectroscopy while molecular interactions were probed by IR spectroscopy.

The comparison of the two ionic liquids shows that for the shorter alkyl chain the viscosity was lower and the electrical conductivity was higher. While the viscosity of the mixture drops already with small additions of water, the electrical conductivity of the solution is only significantly increased for high water concentrations. A maximum is observed for compositions around $x_{water} = (0.90 \text{ to } 0.95)$. The SO_3 asymmetric stretching band of the IR spectrum can be used as a probe to observe the evolution of the structure around the anion which was mainly occurring for high concentrations of water. Several experimental techniques show that the main change in the ionic association was only observed for high water contents (water mole fraction > 0.8).

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1. Introduction

Ionic liquids constitute a class of promising compounds for the development of innovative technologies in a wide range of engineering and material science with applications both in processes (synthesis, catalysis, separations, electrochemistry) and in devices (optical, lubricants, batteries, photovoltaic cells) [1]. These liquids are typically not used pure but in presence of a cosolvent, in mixtures or as additives. Their high viscosity can be easily lowered by the addition of a small quantity of molecular component. As additives, they can improve enantioselective hydrogenations [2] and break azeotropes [3]. For these reasons the knowledge of their properties in presence of a molecular neutral compound is of key significance for industrial applications.

A specificity of ionic liquids is that they are composed entirely of ions and thus are ionic by nature. They can be present as charged cations and anions but also as neutral ion pairs or larger aggregates. Their ionicity (or degree of dissociation) corresponds to the fraction of ions available for ionic conduction [4]. It is not easily

quantified but it has been proved that it can be modified by the presence of a non-electrolyte [5]. Moreover, ionic liquids can exhibit a nanostructuration with polar and apolar domains [6]. The neutral component, depending on its polarity and size will be present in the polar and/or apolar domain. As a consequence, these nanodomains will be modified with the addition of a co-solvent [7]. The main objective of the present work is to understand how the presence of a neutral component, namely water, will affect the anion–cation association and interactions of two alkyl-imidazolium methylsulfate ionic liquids. These molecular modifications are associated with variations of the macroscopic physico-chemical properties of the system necessary for the development of applications with ionic liquids. These two ionic liquids were selected for their total miscibility with water, allowing to analyze the whole composition range, from the pure ionic liquid, entirely composed of ions, to the pure water. In the ionic liquid-rich region, the molecular component will act as a diluted solute, aggregating in one of the region of the ionic liquid. After a certain water quantity and the disruption of the ionic network, the liquid will be comparable to a diluted electrolyte [7].

Some information on the effect of the presence of water on sulfate based ionic liquids can be found in literature both using

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experimental and simulation approaches. Experimentally, the molecular organization and the interactions in aqueous ionic liquids have been analyzed by several techniques. The viscosity of various alkylsulfate based ionic liquids mixed with water was determined by Bhattacharje *et al.* [8] ($[C_1C_2Im][MeSO_4]$ and $[C_1C_4Im][MeSO_4]$) and Rodriguez *et al.* [9] ($[C_1C_2Im][EtSO_4]$) as a function of the composition, a dramatic decrease being observed with the increase of the water content. Electrical conductivity of aqueous $[C_1C_4Im][MeSO_4]$ was measured for mixtures between $0.2 < x_{water} < 0.8$ [10]. No maximum of the electrical conductivity as a function of composition was observed, as the entire composition was not studied. Rilo *et al.* have focussed on the effect of the alkyl chain length (from 2 to 6 carbons) of the sulfate anion on the electrical conductivity of $C_1C_4Im^+$ based ionic liquids with water [11]. The conductivity was found to decrease when the alkyl chain of the anion increased which is coherent with an increased viscosity. It is the simultaneous measurement of the electrical conductivity and of the viscosity that gives qualitative information on the ionic association from the position in the Walden plots (logarithm of the molar conductivity as a function of the logarithm of the fluidity), as studied on aqueous pyrrolidinium based ionic liquids [12] or on aqueous $[C_1C_4Im][NTf_2]$ (bis(trifluoromethylsulfonyl)imide) [13]. On this last system, we observed that the mixtures have a similar position on the Walden graph to that of the pure ionic liquid indicating that water has no influence on the dissociation of the ionic component. It should be noticed the limited composition range studied due to the poor miscibility between $[C_1C_4Im][NTf_2]$ and water.

Excess enthalpy and heat capacity were measured for a set of binary systems ionic liquid + water including $[C_1C_2Im][EtSO_4]$ and $[C_1C_2Im][MeSO_4]$ [14]. Excess enthalpy of several aqueous imidazolium alkylsulfate shows that the increase of the alkyl chain in the anion from $[HSO_4]$ to $[EtSO_4]$ is correlated with an increase of the excess enthalpy probably due to an increase hydrophobicity of the ionic liquid [15]. Surface tension of aqueous ionic liquids was also measured to observe the organization of ions in water [16,17].

Spectroscopic techniques are particularly relevant to access molecular information on ionic liquid + water mixtures. IR spectroscopy has been especially used to detect interactions between the different components of a complex system like ionic liquid. Water molecules diluted in ionic liquids have been particularly studied, since ionic liquids are often hygroscopic and adsorption of water has a strong impact on several properties of ionic liquids. Using ATR (attenuated total reflection) IR spectroscopy Cammarata *et al.* demonstrated that at low concentration, water molecules are bonded via two hydrogen bonds to two anions; anion $\cdots HOH \cdots$ anion [18]. More recently, the understanding of highly diluted water in ionic liquid was improved using together IR and Raman spectroscopy as well as quantum calculations on dry and wet ion pair dimers [19]. The impact of water on CH stretching bands of several ionic liquid has also been analyzed for various systems [20,21]. The rest of the IR spectrum of aqueous ionic liquids has been much less studied. For ionic liquids with a sulfate anion, Zhang *et al.* have investigated molecular interactions of aqueous solutions with $[C_1C_2Im][EtSO_4]$ by ATR-IR spectroscopy including the fingerprint region of the IR spectrum [22]. Aqueous solutions of $[C_1C_2Im][EtSO_4]$ were also recently analyzed by Raman spectroscopy to study molecular interaction and specifically the existence of H-bonds between anion, cation and water [23]. In a similar manner, the evolution of NMR shifts of aqueous $[C_1C_2Im][EtSO_4]$ was also used to detect the changes in molecular interactions with the concentration of water [22].

The evolution of the self-diffusion coefficients of cation, anion and water can be a tool to understand how the presence of a molecular component will affect the structure, interactions and association of ionic liquids. Menjoge *et al.* [24] have used pulsed

field gradient NMR to measure the diffusion coefficients of ions and water in $[C_1C_2Im][EtSO_4]$ + water mixtures. Rollet *et al.* [25] have studied the self diffusion properties of $[C_1C_2Im][NTf_2]$ + water system by PFG NMR as a function of the composition of the mixture. In both studies, the authors observed an increase of the self diffusion coefficient of anion and cation with the addition of water in the ionic liquid. Moreover according to these authors, the presence of water disturbs the ionic liquid organization but does not induce a significant increase in ionic dissociation [25].

The molar conductivity ratio [5] is the conductivity measured by the electrochemical method divided by the conductivity estimated by PFG NMR spectroscopy. It constitutes a quantitative measurement of the ionicity of the medium. This parameter was estimated by Ueno *et al.* for several mixtures [5]. These authors have observed an enhanced ionic association with the dilution of the ionic liquid by a molecular component (propylene carbonate or 1,2-dichloroethane). In contrast, in the case of conventional electrolyte solutions, the dissociation is generally promoted by the dilution with a molecular compound (decrease of the concentration of salts).

In the present work, two transport properties (viscosity and electrical conductivity) were measured in the aqueous mixtures. From these data, the evolution of the ionic association and its modifications in presence of water were qualitatively observed using the Walden plot. Then, the diffusion coefficients of the ions (and of water) were measured by NMR spectroscopy and the ionicity concept used to quantify anion–cation association. Finally, a molecular approach (ATR-IR spectroscopy) was considered to study the interactions in the mixtures.

2. Experimental methods

2.1. Chemicals

The ionic liquids were purchased from Solvionic with a purity of 0.995. After treating the samples for 15 h under vacuum, they were considered as dried. To avoid any contact of the sample with atmosphere, a Schlenk tube was used to load the samples into the different apparatus. A coulometric Karl Fisher titration (Mettler Toledo DL31) on water was performed to test variations of the water quantity in the samples. Typical water quantities of 50 ppm were measured. A particular attention was paid to a possible degradation of the sulfate-based ionic liquids in presence of water as this phenomenon is mentioned in literature [26,27]. The samples used in this work were always kept dried and their stability was regularly checked by NMR analysis.

2.2. Samples preparation

All the binary mixtures were prepared by weighing the components using an AE240 Mettler Toledo balance with an accuracy of ± 0.1 mg. The vials were always nearly totally filled to minimize the vapor phase and thus an uncontrolled change in the liquid phase composition. The estimated uncertainty on the mole fraction composition is ± 0.0001 .

2.3. Viscosity measurements

The dynamic viscosity, η , has been measured using an Anton Paar Microviscosimeter (AMVn) based on a falling-ball principle. A sensor detects the time, t_1 , taken by the ball to fall a given distance in a capillary tube of calibrated diameter filled with the mixture. The viscosity of the mixture, η , is calculated from the values of t_1 , the capillary calibration constant, K , and the densities of the ball and of the ionic liquid, ρ_b and ρ_l , respectively:

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