Aust. J. Chem. 2015, 68, 420–425 http://dx.doi.org/10.1071/CH14240

The Influence of Water and Metal Salt on the Transport and Structural Properties of 1-Octyl-3-methylimidazolium Chloride

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The addition of diluents to ionic liquids (ILs) has recently been shown to enhance the transport properties of ILs. In the context of electrolyte design, this enhancement allows the realisation of IL-based electrolytes for metal–air batteries and other storage devices. It is likely that diluent addition not only impacts the viscosity of the IL, but also the ion–ion interactions and structure. Here, we investigate the nano-structured 1-methyl-3-octylimidazolium chloride (OMImCl) with varying water concentrations in the presence of two metal salts, zinc chloride and magnesium chloride. We find that the choice of metal salt has a significant impact on the structure and transport properties of the system; this is explained by the water structuring and destructing properties of the metal salt.

Manuscript received: 14 April 2014. Manuscript accepted: 31 May 2014. Published online: 26 August 2014.

Introduction

The development of metal-air batteries is gaining momentum for applications in next-generation electronics and energy storage devices.^[1-4] This is driven largely by the remarkably high theoretical energy output that can be achieved.^[2,5] A major challenge in the development of metal-air batteries is the electrolyte. Recently, ionic liquids (ILs) have been investigated as possible electrolyte materials,^[6] however, the conductivity of IL electrolytes remains a major drawback. To address this issue, the addition of diluents, including water, has been investigated.^[7,8] It has been shown that the addition of water to trihexyl (tetradecyl)phosphonium chloride, [P_{6,6,6,14}][Cl], is extremely beneficial in reducing the viscosity, increasing the conductivity, and enhancing the discharge performance of a studied magnesium anode.^[8] It has been shown that the presence of water, even minor traces, can have an impact on the structural organisation or the molecular arrangement of ILs, which subsequently affects the physical properties of the system.^[9-11] The interaction of water with ILs depends greatly on the nature and association of anion and cation of the IL. While it is generally accepted that at low water concentrations water interacts preferentially with the anion, the extent of that interaction can be IL dependent. Wu et al. investigated intermolecular interactions in 1-butyl-3methylimidazolium tetrafluoroborate (BMImBF₄) and 1-ally-3methylimidazoliun chloride (AMImCl)-water mixtures using near-infrared spectroscopy.^[9] The authors showed that in the case of the BF₄-based IL, water interacted almost exclusively with the anion, whereas in the chloride-based IL, interactions with both the chloride anion and the imidazolium cation were

observed. The water interacted preferentially with the C2 proton on the imidazole ring; the C2 proton is known to be the most acidic proton in the ring.^[9,12] As such, depending on the nature of the interaction of the IL with the water, the supramolecular structure of the IL can be either enhanced or destroyed upon addition of water.^[9,13,14] Furthermore, it has been shown that for a class of imidazolium-based ILs typically with the chloride anion and a sufficiently long alkyl chain length (usually eight and above), the formation of a liquid crystalline phase is likely.[12,15-20] We recently demonstrated that 1-methyl-3octylimidazolium chloride exhibits a liquid crystalline phase, with water content of 69-82 mol-%.^[20] Here, we aim to investigate what role the addition of a metal salt may have on how the water is structured. We have investigated the impact of two different metal salts, MgCl₂ and ZnCl₂, that were selected because they have different water structuring and water destructuring properties^[21,22] as well as being relevant to metalair devices.

Experimental

Synthesis of 1-Methyl-3-octylimidazolium Chloride

1-Methyl-3-octylimidazolium chloride (OMImCl) was synthesised according to the following procedure. In a 250-mL roundbottom flask with a magnetic stirrer and a water-cooling system, 1-methylimidazole (35.57 g, 0.433 mol) and 1-chlorooctane (70.86 g, 0.476 mol) were added. The mixture was stirred at 80°C for 72 h under a nitrogen atmosphere and subsequently washed three times with 80 mL of ethyl acetate and dried under high vacuum for 4 h at 80°C. Water was added to OMImCl for the washing step to decrease the viscosity, thereby affording more efficient mixing.

 $\delta_{\rm H}$ (CDCl_3, 500 MHz) 10.17 (1H, s), 7.51 (1H, s), 7.27 (1H, s), 3.97 (2H, t), 3.78 (3H, s), 1.56 (2H, m), 0.92 (10H, m), 0.49 (3H, t).

Materials Methodology

The ionic liquid, 1-methyl-3-octylimidazolium chloride (OMImCl) was dried under high vacuum for 2 h at 80°C before all sample preparation. Milli-Q water was added to OMImCl at the following concentrations: 0, 6, 11.5, 20.8, 28.40, 34.8, 40.3, 45, and 69.35 mol-%. Both zinc chloride and magnesium chloride were dried in the oven at 120°C for 2 h and added at the following concentrations: 0.1, 0.25, and 0.5 mol kg⁻¹. Salt addition was performed in a nitrogen dry box.

Characterisation

Chemical Shift NMR

¹H NMR chemical shift measurements were performed using a Bruker Ultrashield 500 MHz NMR spectrometer. All samples were introduced into a 5-mm OD NMR. An inner capillary, containing CDCl₃ with 1 % TMS acted as the reference and lock. All measurements were performed at 295 K.

Pulsed Field Gradient (pfg) Diffusion NMR

¹H pfg NMR diffusion measurements were performed on a Bruker Ultrafield 300 MHz NMR spectrometer using the pulsed field gradient stimulated echo (PGSte) sequence. A 90-degree pulse, P1, of 12 μ s was employed. The gradient, G, was varied between 500 and 2000 G cm⁻¹ with 24 experiments consisting of 24 scans at each gradient step. The interval between the two gradient pulses, Δ , was 40 ms. The diffusion coefficients were calculated according to the following equation:

$$\ln(I/I_{g=0}) = -D * (2 * \pi * \gamma * g * \delta)^{2} * (\Delta - \delta/3) * 1e4$$

where *I* is the spin-echo signal intensity, γ is the gyromagnetic ratio, δ is the duration of the field gradient, which was in the range of 1–2 ms.

Fourier Transform Infrared (FT-IR) Spectroscopy

All infrared spectra (64 scans; 4 cm^{-1} resolution) were collected using a Bruker Alpha Platinium FT-IR spectrometer.

Raman Spectroscopy

Raman spectra were measured at 25°C on a Raman spectrometer equipped with a near-IR (infrared) diode laser. An excitation line of 785 nm was used for the measurement.

Density Functional Theory (DFT) Calculations

As an approximation to the experimental system, the complex between OMIm cation and the MeCl₃ unit (Me = Zn or Mg) was modelled within a micro-solvated environment of six water molecules. To explore likely arrangements of the OMIm and MeCl₃ unit, we first investigated the non-solvated system, generating over a dozen of different candidate minima via geometry optimisation at the PBE0/6–31G*^[23] level of theory, probing different initial configurations of the OMIm ring and the MeCl₃ unit, including coordination of the metal ion with the chloride ions (single, double, and triple coordinated). Of these resulting structures, 10 structures that were lowest in energy were selected for further investigation. To each of these 10 structures, we added six water molecules in different arrangements, and re-optimised the geometry in each case at the same level of theory. The *Gaussian09*^[24] software package was used, with analytic derivatives used throughout the geometry optimisations. Vibrational frequencies were calculated for each structure to ensure true minima identification. A selection of configurations were chosen for single-point energy calculations at the MP2/aug-cc-pVDZ level of theory; the energy differences resulting from these calculations showed good agreement, as that demonstrated for more simple systems.^[25]

Results and Discussion

Intermolecular Interactions in the OMImCl/H₂O Systems

The ¹H chemical shift data for the OMIm cation at varying water concentrations are shown in Fig. 1. For simplicity, the chemical shift of the C2 proton is chosen as a representative of the ring and the C12 proton as a representative for the alkyl chain. It can be seen that the addition of water, from 0 to 96.7 mol-%, results in a 1.72 ppm shift to lower ppm for the C2 proton, whereas the C3 and C4 ring protons displayed a shift of 0.76 ppm and 0.69 ppm, respectively. The largest chemical shift observed for the C2 proton is consistent with previous reports^[9,19] and is likely due to the acidic nature of the C2 proton resulting in an increased interaction with the water molecules.^[10] In contrast to the ring protons, the chemical shift of the alkyl chain protons is not impacted by the addition of water; no chemical shift was measured for the C12 proton, Fig. 1.

The chemical shift for the water peak, also shown in Fig. 1 and further highlighted in the inset, shows interesting behaviours across the concentration region. It can be seen that at low water concentrations (<70 mol-% and before liquid crystalline formation), the chemical shift of the water proton decreases by 0.20 ppm to lower ppm. This is in agreement with previous experimental reports and molecular dynamics simulations that indicates an increase in water–anion interactions.^[9,13,26]

The chemical shift for the water peak is at its lowest ppm, 4.37 ppm relative to TMS, in the liquid crystalline phase. Interestingly, water additions beyond the liquid crystalline phase result in the water peak shifting to higher ppm; a shift of 0.27 ppm was measured. The shift to higher ppm at water concentrations beyond 84 mol-% is likely due to increased water–water interactions as the number of water–anion interactions possible is now saturated.^[9,13] It has been also reported that at high water concentrations, a water percolation cluster is present in these imidazolium ILs.^[27,28]

Effect of Zn^{2+} and Mg^{2+} lons on the OMImCl/H₂O System

The addition of metal ions to this system is expected to change the nature of the interaction between the water molecules and the IL cation and/or anion. An insight into the type of likely structures and coordination environments for the Zn^{2+} and Mg^{2+} cations can be obtained from theoretical calculations. DFT calculations indicated a profound difference in the energy landscape that governs the behaviour of these two systems. For the ZnCl₂ case, we found several different structures, incorporating either a single- or triple-coordinated metal centre (Fig. 2a, b), where in the former case, the two remaining $Cl^$ ions were loosely complexed via water molecules to the ring. The energies of three such structures were found within k_BT (Boltzmann constant) at room temperature, even allowing for



Fig. 1. Schematic of OMImCl with proton labelling. ¹H Chemical shift (δ_{H}) of OMIm and water protons as a function of water concentration. The black line represents the ring protons (e.g. C2 proton), the red line represents the alkyl chain protons (e.g. C12 protons), and the blue line represents the water protons. The green box indicates the liquid crystalline region.



Fig. 2. Examples of the most energetically favourable structures of the micro-solvated complex between OMIm⁺, Me^{2+} (Me = Zn, Mg), three Cl⁻, and six water molecules obtained from DFT calculations: (a) ZnCl₂ system, single-coordinated with Cl⁻, (b) ZnCl₂ system, triple-coordinated with Cl⁻, and (c) MgCl₂ system, double-coordinated with Cl⁻.

uncertainties in the DFT calculations. This indicates that all three structures should be thermally accessible. In contrast, the favoured structure for the MgCl₂ case involves a doubly coordinated metal centre (Fig. 2c). In energetic terms, the difference between this structure and alternative structures is too great to render other structures thermally accessible ($\sim 5 k_BT$ and greater). Taken together, these data suggest that within the approximations imposed by our micro-solvated model, the ZnCl₂ system is favoured entropically, with a predicted greater Cl⁻ lability (in terms of number of thermally accessible states), when compared with the MgCl₂ case. Thus, we explore the OMIm and H₂O environments using NMR techniques, as described for the OMImCl/H₂O systems.

Fig. 3a presents the ¹H chemical shift data for the OMIm cation with addition of varying salt (ZnCl₂ and MgCl₂) concentrations at a fixed water content of 45 mol-% (before the formation of the liquid crystalline phase). No shifts for either the ring or the alkyl chain protons were measured as a function of MgCl₂ concentration, whereas a small shift of 0.25 ppm to lower ppm was seen for the ring protons as a function of ZnCl₂ concentration (0–0.5 mol kg⁻¹). This suggests that a stronger interaction between the Zn²⁺ ions and IL is present when compared with that in the Mg²⁺ case. This proposed difference

in interaction strengths is supported by our DFT calculations. The lowest energy structures in each case (Fig. 2b, c) yielded Zn^{2+} -ring distances of 5.1, 4.1, and 4.5 Å for N1, C2, and N3, respectively. In contrast, the corresponding Mg²⁺-ring distances are greater, at 5.7, 5.0, and 5.2 Å, respectively.

The chemical shift of the water peak was also measured as a function of salt addition, shown in Fig. 3b, from 0 to 0.5 mol kg⁻¹. The chemical shift of the water peak shows a different trend for the two salts investigated here. In the presence of Zn^{2+} ions, a small decrease in chemical shift of 0.15 ppm is measured for the water proton, whereas an increase of 0.93 ppm is observed with the addition of MgCl₂. These differences observed in the chemical shift of water suggest the presence of stronger water-Mg²⁺ ion interactions in contrast to water- Zn^{2+} interactions, and this is consistent with the coordination ability of these two divalent ions.^[29] Due to an ionic radius of 0.74 Å, the divalent Zn^{2+} ion can be considered as both a hard and a soft cation, and therefore can be coordinated with nitrogen, oxygen, and halogen atoms, thus likely explaining the slight shift seen in the ring protons with ZnCl₂ addition. It is probable that the Zn^{2+} ions preferentially interact with the Cl^{-} anion to form species such as Z_nCl_4 .^[21,22] In contrast, divalent Mg^{2+} (i.e. ionic radius = 0.65 Å) is a hard cation, and therefore prefers



Fig. 3. (a) ¹H Chemical shift (δ_{H}) of OMIm protons as a function of salt concentration for zinc chloride and magnesium chloride systems at 45 mol-%. (b) ¹H Chemical shift (δ_{H}) of water as a function of salt type and concentration at different water concentrations: 28 mol-% water + MgCl₂ (orange line), 45 mol-% water + MgCl₂ (bright red line), 35 mol-% water + ZnCl₂ (blue line), 40 mol-% water + ZnCl₂ (burgundy line), and 45 mol-% water + ZnCl₂ (pale purple line).



Fig. 4. ¹H Diffusion coefficient ($D_{\rm H}$) of (a) OMIm and water protons as a function of water concentration, (b) OMIm and water protons as a function of salt concentration at 45 mol-% water for both MgCl₂ and ZnCl₂ systems, and (c) OMIm (solid lines) and water protons (dashed lines) as a function of zinc chloride concentration at 28 (green line), 40 (red line), and 45 (black line) mol-% water.

to be coordinated with oxygen, suggesting that formation of an $Mg(H_2O)_x^{2+}$ species is more likely.^[29] This is supported by DFT calculations and our findings that suggest a clear difference in the coordination preferences of the two metal ions. The lowest energy structure for the ZnCl₂ case (Fig. 2b) featured close co-ordination of only two water molecules, whereas for the MgCl₂ case (Fig. 2c), a four-coordinate configuration is favoured.

To determine the influence of these interactions on the transport properties of the IL/water system, we used ¹H pfg-NMR to measure the diffusion of the IL and the water as a function of water concentration (mol-%) and salt at a fixed water content of 45 mol-%. As can be seen in Fig. 4a, the diffusivity of the system, both for the IL cation and the water molecule, increases with increasing water concentration. Interestingly upon addition of MgCl₂, the diffusivity of these species decreased dramatically, further supporting the presence of strong water-MgCl₂ interactions, hypothesised from the chemical shift data and the DFT calculations. The behaviour of the OMImCl/water system with MgCl₂ addition is in contrast to previous work done by our group, investigating the impact of metal salts on the water saturated [P_{6,6,6,14}][Cl].^[8] For the $[P_{6,6,6,14}]$ [Cl], no difference in the diffusivity of the IL/water system was measured with MgCl₂ addition. To understand the role of the IL cation in interacting with metal salts, we measured the diffusivity of the shorter chain BMImCl with 0.1 mol kg⁻ MgCl₂ at 45 mol-% water and found a similar trend to the OMImCl, that is, a reduction in the diffusion of the cation in the presence of MgCl₂. This suggests that the inherent stacking organisation of these imidazolium-based ILs^[30,31] and how the Mg interacts with the ring and/or anion account for the differences observed between the two different classes of ILs.

The diffusivity trend measured with the addition of $ZnCl_2$ to the OMImCl/water system is different to that measured with the addition of MgCl₂. The diffusivity values of both the water and the OMIm cation are only slightly reduced with ZnCl₂ addition, with the lowest diffusivity measured for the system at 0.1 mol kg⁻¹ of ZnCl₂. Fig. 4c shows the diffusivity values of both the water and the OMIm cation as a function of ZnCl₂ at water concentrations of 28, 40, and 45 mol-%. Again at all water concentrations and across all ZnCl₂ concentrations, the diffusivity values of the water and OMIm cation remain the same. As the water content increased, the diffusivity also increased, further supporting the hypothesis that weak water–Zn²⁺ interactions exist in this system. This was further supported by the absence of any liquid crystalline phase formation in the presence of ZnCl₂.

To characterise the metal salt complexes that may be present in the OMImCl/water system, we have used a combination of FT-IR and Raman spectroscopies. Fig. 5a shows the Raman spectra of OMImCl at 45 mol-% water (black line), OMImCl at 45 mol-% water with 0.5 mol kg⁻¹ ZnCl₂ (blue line), and OMImCl at 45 mol-% water with 0.5 mol kg⁻¹ MgCl₂ (red line). An additional peak at 274 cm⁻¹ is observed for the ZnCl₂ system, characteristic of the complex ZnCl₄²⁻ ion. ^[32,33] The presence of ZnCl₄²⁻ ions has previously been shown to have a structurebreaking effect on water by disrupting the hydrogen bond



Fig. 5. (a) Raman spectra and (b) FT-IR spectra of OMImCl-45 mol-% water (black line), OMImCl-45 mol-% water with 0.5 mol kg^{-1} zinc chloride (blue line), and OMImCl-45 mol-% water with 0.5 mol kg^{-1} magnesium chloride (red line).

network.^[21,22] The presence of this complex may also explain the ¹H chemical shift and ¹H pfg-NMR data with reduced hydrogen bonding, leading to a reduced degree of deshielded ¹H resonance. No significant difference in the vibrational spectrum upon addition of MgCl₂ was observed. Fig. 5b shows the FT-IR spectra of OMImCl at 45 mol-% water (black line), OMImCl at 45 mol-% water with 0.5 mol kg⁻¹ ZnCl₂ (blue line), and OMImCl at 45 mol-% water with 0.5 mol kg⁻¹ MgCl₂ (red line). For both systems, OMImCl at 45 mol-% water without salt and with ZnCl₂ (0.5 mol kg⁻¹), a characteristic O–H absorption band is observed at 3382 cm⁻¹, due to the presence of water. For the MgCl₂ system, a shift of the O–H stretching band to 3347 cm⁻¹ is observed, as consistent with the formation of a hydrated magnesium chloride complex.^[34,35]

Conclusion

We have assessed the influence of ZnCl₂ and MgCl₂ addition on the nano-structured OMImCl system at varying water concentrations. The addition of water to this system is known to enhance the supramolecular structure resulting in a more ordered system. We showed that the addition of the metal salt could either disrupt or enhance the supramolecular structure of the IL that was most likely due to the interactions of the metal salt with water. For example, in the ZnCl₂ case, we observed a destructing effect explained by the presence $ZnCl_4^{2-}$ that destroyed the π stacking of the imidazolium-based ILs. This directly influenced the transport properties; no reduction in diffusivity was measured in the presence of ZnCl₂. In contrast, a dramatic decrease in the diffusivity of both the water and the OMIm cation resulted with the addition of MgCl₂. This has important implications for the use of ILs in metal–air batteries.

Acknowledgements

The authors thank the Australian Research Council (ARC) for support of this work through the Australian Laureate Fellowship scheme. The ARC is also acknowledged for funding the Magnetic Resonance Facility at Deakin University through LIEF grant LE110100141.

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