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Coordination and interactions in a Li-salt doped ionic liquid

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ABSTRACT

We report on the coordination and interactions in the LiTFSI doped ionic liquid PyR₁₄TFSI over a large concentration range, $0.01 \leq x \leq 0.4$, using Raman spectroscopy. We find that the concentration dependence of the average number of TFSI anions coordinating to one Li-ion ($N_{\text{TFSI/Li}}$) can be divided into three regimes. For low concentrations, $x \leq 0.05$, we find that a large number TFSI anions coordinate each Li-ion, $N > 2$. The number decreases with increasing salt concentration and the interaction between the Li-ion and the TFSI anions is rather weak in this concentration range. At intermediate concentrations, $0.1 \leq x \leq 0.2$, the number of TFSI anions coordinating each Li-ion ($N_{\text{TFSI/Li}}$) is ~ 2 pointing towards the formation of $[\text{Li}(\text{TFSI})_2]^-$ ionic clusters. At higher concentrations, $x > 0.2$, $N_{\text{TFSI/Li}}$ decreases further indicating the transition to more complex structures with Li-ions bridging TFSI anions. We also show that the evolution of the microscopic structure as a function of Li-salt concentration is mirrored in the behaviour of macroscopic properties such as the ionic conductivity and the glass transition temperature, which also show a crossover in the same concentration range.

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1. Introduction

The interest in ionic liquids (ILs) as electrolyte materials for Li-batteries has boosted in the last years [1–4]. Properties such as low vapour pressure, non-flammability, and high thermal and electrochemical stability make them superior to the organic solvents used in conventional electrolytes. For application in Li-batteries, ILs are doped with a suitable lithium salt and commonly used Li-salts are based on the same anion as in the IL, e.g. BF_4^- , PF_6^- , and TFSI⁻ [bis(trifluoromethanesulfonyl)imide]. However, the addition of the Li-salt leads to an increase in viscosity and a decrease in ionic conductivity, limiting the concentration range for practical applications [5–8]. In addition, the transport number decreases pointing towards the formation of various $\text{Li}^+ \text{X}^-$ complexes, where X^- is the ionic liquid's anion [6]. Thus, to further develop and optimize these systems, knowledge about the microscopic structure and interactions, such as the Li^+ solvation directly connected to the Li-ion transport in the electrolyte, is important.

In this paper, we use Raman spectroscopy to investigate the interactions and coordination in the LiTFSI doped ionic liquid PyR₁₄TFSI [N-butyl-N-methyl pyrrolidinium bis(trifluoromethanesulfonyl) imide]. We obtain quantitative results over a wider salt concentration range, especially expanding to very dilute concentrations, compared to previous investigations [9–11]. In addition, in the analysis of the data, we also take into account the conformational state of the TFSI anion, previously not considered, and directly compare the

concentration dependence of the coordination to that of the macroscopic properties the ionic conductivity and the glass transition temperature.

Different IL based electrolytes have been investigated for battery applications, the most common being based on the imidazolium cation due to a high ionic conductivity of these systems and a large variety of ILs being commercially available [12]. However, imidazolium based ILs suffer from electrochemical instability towards common anode materials [13]. To overcome these problems, the flexibility in the molecular design of ILs has been exploited [14–17]. In particular, ILs based on the pyrrolidinium cation family, PyR_{ab} (where $a = 1, 2$ and $b = 3, 4$ are the lengths of the alkyl side-chains on the cation) have shown improved electrochemical stability and have been used as electrolytes for Li-batteries [16,17]. We have previously investigated the influence of the addition of LiTFSI on the ionic conductivity and the phase behaviour PyR-TFSI ILs [18].

Raman spectroscopy and DFT calculations have previously been applied to investigate Li-ion coordination in LiTFSI doped ILs [9,10,19,20]. In electrolytes based on the LiTFSI salt, the strong Raman band around 740 cm^{-1} has been used to identify “free” anions and ion-pairs [9,19–21]. This mode is the expansion–contraction mode of the entire TFSI anion and is particularly sensitive to interactions [22,23]. For anions fully solvated and weakly interacting with cations from the IL, a spectral component is found at $738\text{--}742 \text{ cm}^{-1}$. For anions interacting with Li-ions, the band shifts to higher frequencies and a spectral component appears in the range $744\text{--}748 \text{ cm}^{-1}$ [6,9,10,19,21]. Here one should note that the band is also sensitive to the conformational state of the anion. The TFSI anion exists in two conformations: [22–24] the cisoid form (C_1 symmetry) with the two CF_3 groups on the same side of the S–N–S plane and the transoid form (C_2 symmetry) with

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the two CF₃ groups on opposite sides of the S–N–S plane, as shown in Fig. 1. Ab initio calculations have predicted that the frequency difference of these two conformers is 3 cm⁻¹ and that the corresponding Raman cross sections are practically the same [23]. Thus, the spectral feature of the anions that weakly interact with the cations of the IL should be a sum of the contributions from C₁ and C₂, respectively, which has also been observed experimentally [22–24].

In previous studies for moderate salt concentrations ($x \approx 0.1$ – 0.2 , where x is the mole fraction of LiTFSI added to the IL), the average number of TFSI anions surrounding a Li-ion ($N_{\text{TFSI/Li}}$) has been found to be approximately 2, suggesting the presence of [Li(TFSI)₂]⁻ complexes [9–11], slightly decreasing with increasing LiTFSI concentration [9,10]. There have also been attempts to reveal the solvation structure of the Li-ion from diffusion experiments. Saito et al. suggested the formation of [Li(TFSI)₃]²⁻ complexes in LiTFSI doped BMImTFSI and BDMImTFSI ILs, where BMIm and BDMIm are 1-butyl-3-methylimidazolium and 1-butyl-2,3-dimethylimidazolium, respectively [25]. Also the formation of [Li(TFSI)₄]³⁻ and [Li(TFSI)₂]⁻ complexes has been suggested for LiTFSI doped EMImTFSI, where EMIm is 1-ethyl-3-methylimidazolium [26]. From molecular dynamics simulations of LiTFSI doped pyrrolidinium ILs, complexes with four TFSI anions surrounding a Li-ion have been suggested [27]. In our work we show that the actual speciation is concentration dependent. All the suggested species can be present but in different concentration ranges.

2. Experimental details

2.1. Materials

Ionic liquid Pyr₁₄TFSI (purity > 99%) and LiTFSI salt (purity > 99.95%) were purchased from Sigma-Aldrich and used as received. The xLiTFSI/(1-x)IL solutions were prepared by mixing the proper mole fraction (x) of LiTFSI in the neat ionic liquids under stirring at 323–333 K until homogeneous solutions were obtained. All sample preparations were performed in an argon dry box with oxygen and water content < 1 ppm, and the water content in the samples is conservatively estimated to be < 50 ppm.

2.2. Raman spectroscopy

Raman spectra were recorded on a Bruker IFS66 Fourier Transform spectrometer, equipped with a FRA106 Raman module. The 1064 nm line of a Nd:YAG laser was used as excitation source. The laser power was set to 200 mW, the resolution was 2 cm⁻¹, and the spectra were averaged over 1000 scans. All the Raman spectra were recorded at room temperature.

In the analysis the 720–760 cm⁻¹ spectral region was fitted with three Voigt functions to describe the two “free” anion species, corresponding to the C₁ and C₂ conformations respectively, and the TFSI anions coordinated to Li-ions. In addition, side bands in the ranges 700–730 cm⁻¹ and 760–770 cm⁻¹, associated to vibrations from the pyrrolidinium cation, were included in the fitting procedure.

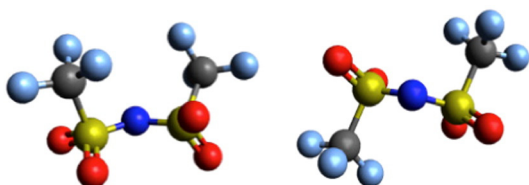


Fig. 1. Conformations of the TFSI anion: C₁ (left) and C₂ (right).

3. Results and discussion

Raman spectra in the range of the expansion–contraction mode of the entire TFSI anion, 720–760 cm⁻¹, for the solutions xLiTFSI/(1-x)Pyr₁₄TFSI at different concentrations are displayed in Fig. 2 as an example. The experimental data are shown together with the best fits, and the fitted spectral components. For the pure IL ($x = 0$), the expansion–contraction band of the TFSI anion is found at 740 cm⁻¹, in agreement with previous results for weakly coordinating TFSI anions in ionic liquids [6,9,10,19,21]. Here, a fit with two components, corresponding to the C₁ and the C₂ conformations (labelled as bands I and II, respectively) is sufficient to reproduce the experimental data, as expected. From the areas of the two components, it is clear that the TFSI anion is predominantly found in the C₂ conformation, in agreement with previous results for other ionic liquids [24]. Upon addition of LiTFSI, a shoulder at ~745 cm⁻¹ grows on the high-frequency flank and at high salt concentrations the band clearly becomes bimodal. In the fits a third component (band III) has thus to be introduced to reproduce this shoulder, accounting for TFSI anions coordinated to Li-ions.

In Fig. 3, the results from the analysis are shown, providing quantitative information on the position and the relative integrated intensities of the spectral components as a function of LiTFSI concentration. In the pure IL the two components corresponding to the C₁ and C₂ conformation are found at ~739 cm⁻¹ (C₁) and ~741 cm⁻¹ (C₂) respectively, in agreement with theoretical predictions and previous experimental results for other ionic liquids [10,19,21,22]. For these components we observe a slight increase in frequency with LiTFSI concentration. In contrast, the spectral component related to the TFSI anions coordinated to Li-ion (C_{coord}) shows a stronger frequency shift with increasing LiTFSI concentration. For the lowest salt concentration ($x = 0.01$), this band is found at 744 cm⁻¹ and the frequency increases rapidly up to 746 cm⁻¹ at $x = 0.05$, whereafter it increases more slowly with salt concentration. The relative integrated intensities related to the weakly coordinated anions (components I and II) decrease whereas the intensity of the Li-ion coordinated component (III) increases with LiTFSI concentration, as expected. This reflects that the population of weakly coordinated TFSI anions decreases and transfer to the Li-ion coordinated state when the LiTFSI concentration increases.

From the relative integrated intensities of the three components we can estimate the population of weakly coordinated TFSI anions and TFSI anions coordinated to Li-ions, expressed as the fractions:

$$C_{\text{weak}} = \frac{(A_I + A_{II})}{A_{\text{Tot}}} \quad (1)$$

$$C_{\text{coord}} = \frac{A_{III}}{A_{\text{Tot}}} \quad (2)$$

where A_I , A_{II} , and A_{III} are the integrated intensities of the bands I, II, and III respectively, and A_{Tot} is the total integrated intensity of all three bands. This is based on the assumption that the Raman scattering cross section is the same for the two conformers C₁ and C₂ as well as for the Li-ion coordinated TFSI anion. This has previously been shown to be the case for ionic liquids with the imidazolium cation and the TFSI anion [10,19].

The fraction of weakly coordinated TFSI anions, as a function of LiTFSI concentration, x , is shown in Fig. 4 (top). In this plot format, a linear dependence with x corresponds to a constant number of TFSI anions interacting with one Li-ion, as indicated in the figure. For low concentrations, $x \leq 0.05$, C_{weak} decreases rapidly with increasing concentration, whereas it decreases much slower at higher concentrations. This indicates that there is a rapid change in the coordination of Li⁺ by TFSI⁻ as a function of LiTFSI concentration for low concentrations. For intermediate concentrations, $0.1 \leq x \leq 0.2$, the data agree well with a configuration of two TFSI anions interacting with one

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