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Inelastic neutron scattering study on boson peaks of imidazolium-based ionic liquids

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ABSTRACT

Low energy excitations of 1-alkyl-3-methylimidazolium ionic liquids (ILs) have been investigated by means of neutron spectroscopy. In the spectra of inelastic scattering, a broad excitation peak referred to as a “boson peak” appeared at 1–3 meV in all of the ILs measured. The intensity of the boson peak was enhanced at the Q positions corresponding to the diffraction peaks, reflecting the in-phase vibrational nature of the boson peak. Furthermore the boson peak energy (E_{BP}) was insensitive to the length of the alkyl-chain but changed depending on the radius of the anion. From the correlation among E_{BP} , the anion radius, and the glass transition temperature T_g , we conclude that both E_{BP} and T_g in ILs are predominantly governed by the inter-ionic Coulomb interaction which is less influenced by the alkyl-chain length. We also found that the E_{BP} is proportional to the inverse square root of the molecular weight as observed in molecular glasses.

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1. Introduction

Ionic liquids (ILs) are defined as salts in liquid states near room temperature. ILs have gained much attention in a past decade due to their unique properties, such as negligible vapor pressure, non-flammability, high ionic conductivity, and high solubility in a wide range of inorganic, organic, and polymeric materials. It is remarkable that their physicochemical properties are tunable by varying cations and anions, which make them much more versatile and useful for applications. They consist of bulky and asymmetric organic cations and common anions. The cations of ILs have positively charged core parts and hydrophobic alkyl-chains. On the other hand, a wide range of anions are employed, ranging from halogens (Cl^- , Br^- , I^-) to inorganic/organic ionic groups (e.g. BF_4^- , PF_6^- , $(\text{CF}_3\text{SO}_2)_2\text{N}^-$, CH_3COO^-). The most investigated ILs are based on imidazolium cations, in particular, 1-alkyl-3-methylimidazolium salts which are investigated in this work. They are usually abbreviated as C_nmimX , where n is the alkyl-carbon number and X is the anion.

Another interesting aspect is that some classes of ILs are “good” glass formers. The supercooled liquid undergoes a glass transition at the glass transition temperature, T_g , which is typically around 200 K [1]. Beside

the glass transition, there is an interesting dynamical phenomenon observed by inelastic neutron and Raman scatterings. In glasses and (sometimes) supercooled liquids, one can observe excess vibrational excitations over the Debye level, which is called “boson peak”. The boson peak appears at typically 1–5 meV irrespective of the type of chemical bonding. The peak intensities at different temperatures can be normalized with Bose factors in spite of intrinsic broadness of the peak shape, hence the name. The presence of the boson peak is universal for glass-forming materials and the origin of the boson peak is one of the major subjects in glass researches. The question arises as to what kind of vibrational mode contributes to the boson peak. Recently, some spectroscopic and computer simulation studies suggested that the boson peak has a transverse character [2–6] which can be related to the libration of molecules [7,8] or structural fragments such as SiO_4 tetrahedrons [9,10]. Furthermore it is discussed that the boson peak energy is associated with the van Hove singularity [5] or Ioffe-Regel limit [3] for the transverse acoustic (TA) mode. However, the origin of the boson peak is still under debate [11–13].

As for the ILs, the boson peak has been investigated mainly by Raman spectroscopy [14–16]. Ribeiro et al. have investigated several types of ILs and found that the boson peak frequency is insensitive to the length of the alkyl-chain but depends on anions [16]. On the other hand, only C4mimCl and C4mimFeCl_4 were investigated by neutron scattering [17,18]. Neutron scattering has an advantage that the scattering intensity is directly related to the vibrational density of states, whereas for light scattering, a photon-phonon coupling constant, which is frequency dependent, makes it difficult to make a quantitative comparison of the boson peak among substances.

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In the paper, we report our systematic studies of the boson peak for imidazolium-based ILs at glassy states, using an inelastic neutron scattering (INS) technique. We aim at investigating (i) how the feature of the boson peak changes with anions or cations in more detail and (ii) what kind of vibrational mode contributes to the boson peak in ILs. For the purpose, we have measured twelve ILs, eight protonated and four deuterated ones, comprising six anions and four cations with different alkyl-chain lengths. The scattering intensity of protonated ILs predominantly comes from incoherent scattering from H atoms, which enables us to investigate the density of states. On the other hand, the deuterated samples will provide information for the collective dynamics. Although the boson peak usually appears as dispersionless mode in the Q range studied in this work, it is of interest to see how the boson peak intensity varies as a function of momentum transfer Q .

2. Experimental

The cations chosen in this work are 1-alkyl-3-methylimidazolium ions ($C_n\text{mim}$, $n = 3, 4, 6, 8$), while the anions are chloride (Cl), bromide (Br), iodide (I), tetrafluoroborate (BF_4), hexafluorophosphate (PF_6), and bis(trifluoromethylsulfonyl)imide (TFSI) ions with a wide range of ionic size. The protonated $C_n\text{mimI}$ ($n = 3, 4, 6$) were provided by Prof. M. Nakakoshi in Yokohama National University. All other protonated samples were purchased from commercial sources; $C_4\text{mimX}$ ($X = \text{Cl}, \text{BF}_4, \text{PF}_6, \text{TFSI}$) from Kanto Chemical Co., Inc. and $C_4\text{mimBr}$ from Solvent Innovation GmbH. The nominal purities of the samples were specified as $>99\%$ and they were used without further purification. The deuterated samples were the same as used for the previous quasielastic neutron scattering studies and their synthesis methods are reported in Refs. [19,20]. The samples were loaded into concentric double-cylinder Al cans with He gas, which facilitates thermal equilibration inside the cans. The thickness of the sample confined between the two Al walls was 0.3 mm for the protonated samples and 2 mm for the deuterated analogues, giving a neutron transmission of 85–90%, in order to reduce multiple scattering effects.

The INS experiments were performed using two time-of-flight spectrometers, the AGNES spectrometer [21], which is owned by ISSP, University of Tokyo and located at the research reactor JRR-3 in Japan Atomic Energy Agency, and the CNCS spectrometer [22] at the spallation neutron source SNS at Oak Ridge National Laboratory in the USA. All of the protonated samples were measured on AGNES. While the deuterated ones were investigated using CNCS, taking advantage of the high neutron flux at the SNS facility. The incident neutron energies used were 4.6 meV at AGNES and 6.6 meV at CNCS, giving rise to energy resolutions (full width at half maximum of the elastic peak) of $\Delta E = 0.12$ meV and $\Delta E = 0.2$ meV, respectively. The deuterated $C_8\text{mimTFSI}$ was measured on CNCS also with the incident energy of 1.55 meV ($\Delta E = 0.025$ meV). The data reduction was performed using an in-house software at AGNES and the Mantid software at CNCS.

3. Results and discussion

3.1. Incoherent scattering

Incoherent INS spectra were measured using the AGNES spectrometer for the protonated samples. Fig. 1 shows the energy spectra of inelastic scattering intensity, $S(E)$, of the glassy $C_4\text{mimCl}$ at $T = 100$ K. The polycrystalline $C_4\text{mimCl}$, which was obtained by annealing the sample at $T = 290$ K, is also presented for comparison. The present data are different from those previously reported in Ref. [18]; the AGNES instrument was upgraded in 2005 and the present data were measured after that. The plotted $S(E)$ values are estimated by summing up the intensity of the detectors with Q values between 1 and 2.5 \AA^{-1} at elastic positions and then is normalized by the elastic intensity. Assuming that the scattering intensity comes from the incoherent scattering

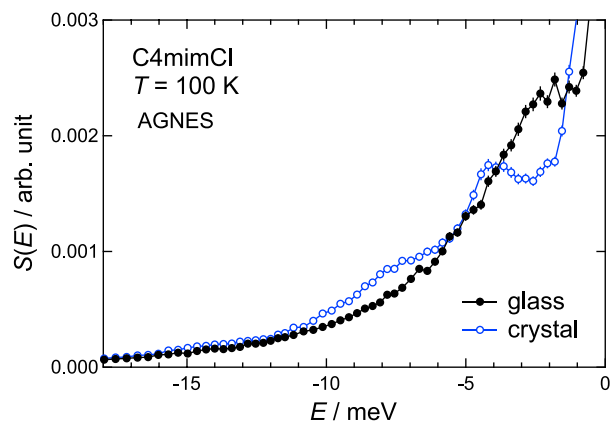


Fig. 1. Energy dependence of scattering intensity averaged over $1 < Q < 2.5 \text{ \AA}^{-1}$ for $C_4\text{mimCl}$ at both glassy and crystalline states measured at $T = 100$ K.

from H atoms, this normalization procedure allows us to compare $S(E)$ of the different samples quantitatively.

Apparently, the vibrational spectrum at the glassy state is quite different from that in the crystalline phase. The glassy $C_4\text{mimCl}$ exhibits an excess vibrational excitation around 2 meV, demonstrating the presence of a boson peak. On the other hand, two vibrational peaks were observed at 4 and 8 meV in the crystalline phase. Penna and co-workers [16] observed Raman peaks around 3.8 and 10 meV at 300 K but could not identify the origin of the peaks. Their peaks may be essentially the same as those observed by us. We speculate that the peak at 4 meV arises mainly from the TA branch while the broad band at 8 meV involves the contribution from the longitudinal acoustic (LA) mode and/or some optical phonons.

It is known that the boson peaks are more visible in a $g(E)/E^2$ plot. Here $g(E)$ is the vibrational density of states (VDOS) and E^2 expresses the Debye contribution. Here $G(E)$ was estimated from $G(E) \propto S(E) \times E/\langle n \rangle$ in the incoherent and one-phonon approximations, where $\langle n \rangle$ is the Bose factor. Since a standard sample was not measured, we cannot obtain the absolute value of $g(E)$ and show it in an arbitrary unit. Fig. 2 displays the $g(E)/E^2$ for glassy $C_4\text{mimX}$ ($X = \text{Cl}, \text{Br}, \text{I}, \text{BF}_4, \text{PF}_6, \text{TFSI}$) taken at $T = 100$ K. Interestingly, the position of the boson peak changes depending on the anion. In order to evaluate the boson peak energy, the spectrum was fitted to the combination of a log-normal function, $1/E$, and a constant,

$$\frac{g(E)}{E^2} = I_{\text{BP}} \exp \left[-\frac{\{\ln(E/E_{\text{BP}})\}^2}{\sigma^2} \right] + \frac{A}{E} + C. \quad (1)$$

Here E_{BP} is the peak-top energy of the boson peak, I_{BP} is the intensity of the boson peak, σ is associated with the peak width. The log-normal function has often been used to describe the boson peak [23–26]. The term A/E is added to reproduce the tail near the elastic line. The constant expresses the contribution from the Debye phonon. The solid curves are the results of the fits and dashed ones correspond to the individual components in Fig. 2. The $g(E)/E^2$ plot for $C_n\text{mimI}$ ($n = 3, 4, 6$) at glassy state are presented in Fig. 3. The boson peak did not change much with changing the alkyl-chain length. The same fitting procedure was carried out for these data. The width parameter σ is about 1 meV and unchanged for all of the measured samples.

3.2. Coherent scattering

Fig. 4 shows the $S(Q, E)_{\text{red}}/Q$ map of the inelastic neutron scattering from d- $C_8\text{mimTFSI}$ at 40 K. Here $S(Q, E)_{\text{red}}$ is the reduced dynamic structure factor and given by $S(Q, E)_{\text{red}} (= S(Q, E)/E\langle n \rangle)$. The background including a spurious scattering due to multiple scattering events involving

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