Raman Spectroscopic Study on Alkaline Metal Ion Solvation in 1-Butyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)amide Ionic Liquid

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The Raman spectra for 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide [BMI][TFSA] containing alkaline metal salts of TFSA⁻, MTFSA (M = Li, Na, K and Cs), were recorded in the frequency range of 200 – 1800 cm⁻¹, with varying salt concentrations at 298 K. With Li⁺ and Na⁺ ions, at the frequency range of 730 – 760 cm⁻¹, new Raman bands ascribable to the anion bound to the ions appeared at higher frequency relative to that found in the neat ionic liquid. On the other hand, with K⁺ and Cs⁺ ions, single Raman bands were solely observed. According to the difference Raman spectra for the ionic liquids containing K⁺ and Cs⁺, evaluated by subtracting Raman spectra for the neat ionic liquid, it turned out that two-state approximation, *i.e.*, bulk TFSA⁻ and TFSA⁻ bound to K⁺ and Cs⁺ ions, could hold, as Li⁺ and Na⁺ ions. By careful analyses of Raman band intensity arising from bulk TFSA⁻ as a function of the salt concentration, the solvation numbers for the respective ions were successfully evaluated to be 1.95 for Li⁺, 2.88 for Na⁺, 3.2 for K⁺ and 3.9 for Cs⁺, respectively. By taking into account that TFSA⁻ acts as a bidentate ligand, the atomic coordination numbers are proposed to be 4, 6, 6 and 8 for Li⁺, Na⁺, K⁺ and Cs⁺, respectively. Raman shifts for the TFSA⁻ bound to the metal ions relative to that of the bulk TFSA⁻ were plotted against the ionic radii for the solvated alkaline metal ions estimated *via* Shannon's ionic radii, to yield a straight line with a slope of almost unity, suggesting that the electrostatic interaction predominantly operates in the ion-ion interaction between the alkaline metal ions and TFSA⁻, as expected. Moreover, the Raman spectra in the frequency range of 370 – 450 cm⁻¹ strongly depend on the alkaline metal ions, indicating that *cis* TFSA⁻ is favored in the first solvation sphere of the Li⁺ ion of a relatively small ionic radius, and that such a preferred conformational isomerism of TFSA⁻ diminishes with an increase of the ionic radii of the central metal ions.

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Introduction

Room temperature ionic liquids have recently attracted much attention as environmentally favorable solvents owing to their practically negligible vapor pressure. The non-volatility, and thus non-flammability of ionic liquids stimulate researchers to develop high-energy density electrochemical devices of high safety,¹ such as fuel cells,² lithium ion secondary batteries,³ electric double-layer capacitors⁴ and dye-sensitized solar cells.⁵ On the other hand, one of the promised applications of ionic liquids is alternative solvents instead of conventional volatile organic solvents for separation and extraction. Some useful reviews on separation and extraction using ionic liquids have been published.⁶ The efforts to develop new ionic liquids for the purpose is still continued.⁷ Though numerous numbers of ionic liquid applications, particularly those using metal ions, as mentioned above, have been published, studies from the viewpoint of fundamental science seem to be scarce in ionic liquid chemistry. Nishi and Kakiuchi *et al.* successfully applied the ion transfer voltammetry across the electrochemically

polarized micro liquid-liquid interface between water and ionic liquids, and found that the transfer of alkali metal ions (Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺) across the interface between an aqueous solution and a highly hydrophobic ionic liquid, *N*-octadecylisoquinolinium-tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ([C18Iq][TFPB]), can be facilitated by dibenzo-18-crown-6 (DB18C6).⁸ They evaluated the formation constants for a complex formation between alkaline metal ions and DB18C6 in the [C18Iq][TFPB] ionic liquid, and found that the ionic liquid provides a unique solvation environment for the complexations of DB18C6 with alkaline metal ions.

As is well established, solvation plays a key role in chemical reactions in solutions particularly ion-pair formation, complex formation and electron-transfer reactions. Therefore, it should be indispensable to reveal solvation in ionic liquids from thermodynamic and structural viewpoints. Hardacre reviewed EXAFS (extended X-ray absorption fine structure) studies on ionic liquids containing metal ions, including those of conventional room temperature molten salts.⁹ On the other hand, structural aspects on alkylimidazolium-based salts containing fluoro-anions have recently been reviewed, while focusing on the solid state.¹⁰ Jensen *et al.* reported structures of Sr²⁺ and Eu³⁺ complexes in ionic liquids by EXAFS and HES (high-energy X-ray scattering) techniques.¹¹ However, little has

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been reported on the “naked” solvation structure of metal ions in ionic liquids,¹² though those in aqueous and non-aqueous solvents were accumulated.¹³ EXAFS is a useful technique to determine the structural parameters for heavy metal ions, while it is not so easy to apply to prove ions of small atomic number. With regard to alkaline metal ions, a few Raman spectroscopic studies on lithium ion solvation have been published in connection with lithium ion secondary batteries using ionic liquids composed of bis(trifluoromethanesulfonyl)amide.^{14–16} However, the lithium ion solvation number in ionic liquids was not clear, because the Raman spectra for ionic liquids containing lithium ion, and even neat ionic liquids, themselves, are quite complicated, *i.e.*, according to our previous studies, the components 1-ethyl-3-methylimidazolium (EMI⁺),¹⁷ *N*-butyl-*N*-methylpyrrolidinium (P₁₄⁺)¹⁸ and bis(trifluoromethanesulfonyl)-amide (TFSA⁻)¹⁹ ions have conformational isomerism, and two or three predominant conformers of the respective ions exist in equilibrium in the corresponding ionic liquids.

Recently, we reported on the lithium ion solvation structure in [EMI][TFSA] and [P₁₄][TFSA] ionic liquids by means of Raman spectroscopy and DFT calculations,²⁰ and elucidated that the lithium ion is coordinated by two TFSA⁻ anions as a bidentate ligand, and that the anion in the first coordination sphere of the lithium ion prefers the *cis* conformation (two CF₃ groups locate at the *cis* position with respect to the S–N–S plane), though the *trans* one is a slightly favorable isomer in neat ionic liquids. In order to understand the ion-ion interactions for metal ion solvation in ionic liquids in detail, it is needed to reveal the ionic radii dependence of the ion solvation. Thus, we extended our study on the solvation structure of metal ions in ionic liquids to other alkaline metal ions (Na⁺, K⁺ and Cs⁺). It should be noted that the ionic radii for the solvated alkaline metal ions can be reasonably specified by knowing the atomic coordination numbers in ionic liquids.

In this paper, the Raman spectra of 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide [BMI][TFSA] ionic liquid containing alkaline metal salts MTFSA (M = Li, Na, K, and Cs) were recorded with varying the metal ion concentration. The integral intensity of the Raman band for the bulk TFSA⁻ anion in the respective metal ion solution was quantitatively analyzed as a function of the metal ion concentration. The solvation numbers for the alkaline metal ions in the ionic liquid were successfully evaluated. The ion-ion interactions between TFSA⁻ and the alkaline metal ions were discussed in terms of the dependence of the $\Delta\nu$ values ($\Delta\nu = \nu_M - \nu_{\text{bulk}}$, ν_M and ν_{bulk} stand for the peak positions for the Raman bands arising from TFSA⁻ bound to the alkaline metal ion and the bulk one, respectively) on the ionic radii of the solvated metal ions. Moreover, we found that the anion conformations in the first solvation spheres of the metal ions depend on the ionic radii of the central alkaline metal ions. The conformations of the anion bound to the alkaline metal ions are also discussed with the aid of MD simulations for similar systems.

Experimental

Materials

LiTFSA and KTFSA salts (Morita Chemical Industries) dried *in vacuo* at 423 K for 48 h were used without further purification. NaTFSA and CsTFSA salts were prepared by treating the corresponding carbonates with an aqueous solution of HTFSA (Morita Chemical Industries), and recrystallized 3 times from water, then dried *in vacuo* at 423 K for 48 h. The solvent [BMI][TFSA] was obtained by treating [BMI][Br] with

an HTFSA aqueous solution, followed by repeated recrystallization from water and drying *in vacuo* at 348 K. The residual Br was checked to be negligible by the AgNO₃ test. [BMI][Br] was synthesized according to the literature from *N*-methylimidazole (Nippon Synthetic Chemical Industry) and bromobutane (Tokyo Chemical Industry), which were distilled in advance.²¹ The water content was checked by a Karl Fischer method to be below 100 ppm for all samples examined. Sample solutions were prepared by dissolving a given amount of the alkaline metal salts in the ionic liquid [BMI][TFSA] at ambient temperature. All samples used in this study were treated and stored in a high-performance glove box (Miwa), in which the water and oxygen contents were kept below 1 ppm.

Raman spectra measurements

Raman spectra were obtained using an FT-Raman spectrometer (Perkin Elmer GX-R) equipped with an Nd:YAG laser operating at 1064 nm. The laser power was kept at 800 mW throughout measurements. The optical resolution was 2.0 cm⁻¹ and spectral data were accumulated 1024 times to obtain data of a sufficiently high signal-to-noise ratio. The sample liquid in a quartz cell was stirred and thermostated at a given temperature within ± 0.3 K. No appreciable damage to the sample was detected after irradiation. The measured Raman intensities were normalized using the 826 cm⁻¹ band ascribable to BMI⁺,²² and the concentrations of ions in sample liquids were corrected for the density. The densities of sample solutions were measured using a density-meter (Kyoto Electronics DA 300).

Raman spectra were deconvoluted to extract single Raman bands. A single Raman band is assumed to be represented as a *pseudo*-Voigt function, $f_V(\nu) = \gamma f_L(\nu) + (1 - \gamma) f_G(\nu)$, where $f_L(\nu)$ and $f_G(\nu)$ stand for the Lorentzian and Gaussian components, respectively, and the parameter γ ($0 < \gamma < 1$) is the fraction of the Lorentzian component. To avoid any uncertainty in obtaining the γ value of the peaks, the value was fixed to that obtained at the highest molarity alkaline metal ions. The intensity I of a single Raman band is evaluated according to $I = \gamma I_L + (1 - \gamma) I_G$, where I_L and I_G denote integrated intensities of the Lorentzian and Gaussian components, respectively. A nonlinear least-square curve-fitting program, based on the Marquardt-Levenberg algorithm,^{23,24} was developed in our laboratory and used throughout the analyses.

MD simulations

Lennard-Jones (LJ) and Coulomb terms were taken into account for intermolecular interactions. For the neat ionic liquid, the force field constructed by Lopes and Pádua *et al.*²⁵ was employed, which means that all simulations reported in this work were based on the OPLS-AA²⁶ convention. With regard to Li⁺, we used two kinds of intermolecular potential parameters, *i.e.*, one was that proposed by Soetens *et al.*²⁷ for the molecular simulations of carbonates solutions containing Li⁺, and the other was CFF force fields.²⁸ In our simulations, Gear's predictor-corrector algorithm²⁹ was employed for the integrals of the equation of motion. The system temperature and pressure were controlled by Nose's³⁰ and Parrinello-Rahman's³¹ methods. The Coulombic long-range interactions were treated by Ewald's method with a cutoff distance of 11 Å.

As the first step in the simulations, *NTP* ensembles at 2000 K and 10000 atm were employed, with 38 Li⁺, 218 EMI⁺ and 256 TFSA⁻ ions for the mole fraction of an $x = 0.15$ solution (and also 82 Li⁺, 174 EMI⁺ and 256 TFSA⁻ for $x = 0.32$) set at low density inside a cubic box with periodic boundary conditions. These ensembles were simulated until near-equilibrium conditions were achieved, a process that took a few hundred

Fig. 1 Raman spectra in the frequency range of 730 – 760 cm^{-1} for [BMI][TFSA] ionic liquid solutions containing *ca.* 0.5 mol dm^{-3} MTFSA (M = Li, Na, K and Cs), measured at 298 K.

picoseconds. Then, the ensembles were changed to *NVT*, and the system volumes were fixed to the average values obtained from the previous *NTP* ensemble runs. These second-step equilibrations were typically calculated during 500 ps. The obtained trajectories were analyzed to check if the ions were fully mixed, and the final configurations were employed as the initial sets for the final *NTP* ensemble simulations at 1 atm and 298 K. The final simulations typically consisted of a 1-ns equilibration period, followed by 1 ns production runs. The trajectories in the last 500 ps of the production runs were then analyzed.

The density values as ensemble averages were 1.614(6) and 1.663(6) g cm^{-3} for $x = 0.15$ and 0.30, respectively. The experimentally determined values were 1.55981(5) g cm^{-3} and 1.61235(3) g cm^{-3} at 298.15 K for the respective ionic liquid solution. The predicted densities agreed with the measured ones within *ca.* 3% accuracy in this work.

All simulations were carried out using Fujitsu Materials Explorer 4.0 on a Fujitsu PRIMEQUEST 580 at the Computing and Communications Center, Kyushu University.

Results and Discussion

Solvation structure in $\text{BMI}^+\text{TFSA}^-$

Raman spectra for [BMI][TFSA] ionic liquid solutions containing alkaline metal ions at the frequency range of 730 – 760 cm^{-1} are shown in Fig. 1, and the dependence on the alkaline metal ion concentration is also shown in Fig. 2. In this frequency region, it is well established that the Raman band assigned to the CF_3 bending vibration $\delta_s(\text{CF}_3)$ coupled with the S–N stretching one $\nu_s(\text{SNS})$ of TFSA^- appears at 743 cm^{-1} .³² The Raman band is accompanied by that of a higher frequency ascribable to the anion bound to the Li^+ ion, dissolving LiTFSA salt.^{14–16,20} In the frequency range, the Raman spectra for the ionic liquid containing Li^+ were similar to those previously reported for [EMI][TFSA], as expected.²⁰ As can be seen in Fig. 2, with the Na^+ ion, a new Raman band ascribable to the anion bound to Na^+ ion is clearly found at the higher frequency side relative to that of the neat ionic liquid, like the Li^+ ion. Such a higher frequency shift has been found in Raman spectra for a polymer electrolyte system containing NaTFSA salt.³³ On the other hand, with K^+ and Cs^+ ions of relatively large ionic radii, single Raman bands solely appeared with peak positions of slightly higher frequency. It should be noted that, strictly speaking, even the Raman band observed at 743 cm^{-1} for neat [BMI][TFSA] is also affected by the ion-ion interaction with the BMI^+ cation in

Fig. 2 Raman spectra of [BMI][TFSA] ionic liquid solutions containing MTFSA (M = Li, Na, K and Cs) at 298 K with varying MTFSA concentration.

Fig. 3 Difference Raman spectra of [BMI][TFSA] ionic liquid solutions containing KTFSA (a) and CsTFSA (b) salts, respectively.

ionic liquids. The higher frequency shifts found in Raman bands for ionic liquids containing K^+ and Cs^+ ions may be due to the superposition of those for TFSA^- ions bound to the metal ions and bulk one. Thus, Raman difference spectra for ionic liquids containing K^+ and Cs^+ ions were evaluated by subtracting the Raman spectrum for the neat ionic liquid (Fig. 3). As clearly shown in Fig. 3, asymmetric Raman difference spectra, like differential ones, with the obvious iso-scattering points of *ca.* 744 and 743 cm^{-1} for K^+ and Cs^+ solution, respectively, were obtained, indicating that the Raman bands ascribable to the anions bound to K^+ and Cs^+ ions are seriously overlapped with that arising from the bulk anion, and observed as single Raman bands, because the higher frequency shifts are quite small. This is plausible by taking into account the small charge density of singly charged K^+ and Cs^+ ions of relatively large ionic radii. This will be discussed in a later section more quantitatively.

As can be seen in Fig. 2, with Li^+ and Na^+ ions, the Raman bands from the bulk TFSA^- evidently decreased in intensity with increasing the metal ion concentration. On the other hand, the minimum of the negative value found in the Raman difference spectra for ionic liquids including K^+ and Cs^+ ions (Fig. 3) decreased in intensity (the negative peak height becomes lower more negatively) with practically unchanged peak positions, which indicates that the intensity of the Raman bands for the bulk TFSA^- in the ionic liquid solutions decreased as the

Fig. 4 Typical extracted single Raman bands in the frequency range of 720–770 cm^{-1} for [BMI][TFSA] ionic liquid solutions for *ca.* 0.5 mol dm^{-3} MTFSA ($M = \text{Li, Na, K and Cs}$), measured at 298 K.

increase of the concentration of K^+ and Cs^+ ions, like Li^+ and Na^+ ions. As previously reported,²⁰ a quantitative analysis of the decrease in the integral intensity of the Raman band for bulk TFSA^- can yield the solvation numbers for the dissolved metal ion, when a two-state approximation, one in bulk and the other bound to the metal ion, can be reasonably held. As discussed above, we assumed that the two-state approximation could hold adequately, even in the case of K^+ and Cs^+ ions. Thus, we attempted to extract single Raman bands from the observed Raman spectra to yield the integral intensity of the Raman band for bulk TFSA^- . During the course of analysis, we employed some transcendental criteria, *i.e.*, the peak position and the molar Raman scattering coefficient for bulk TFSA^- in the respective solution should be independent from the dissolving metal ions, and the band shape should remain practically unchanged. Typical results for Raman band deconvolution of the nonlinear least squares are shown in Fig. 4. As can be seen from this figure, the Raman band intensity for the bulk TFSA^- in the ionic liquid solutions containing almost the same concentration of *ca.* 0.5 mol dm^{-3} alkaline metal ions obviously decreases in the order of $\text{Li}^+ > \text{Na}^+ \approx \text{K}^+ > \text{Cs}^+$, implying that the solvation numbers for the alkaline metal ions increases with the ionic radii. Thus, a more quantitative analysis was carried out while varying the alkaline metal salts concentration.

The integral intensity I_f of an extracted single Raman band of the bulk TFSA^- anion can be represented as $I_f = J_f c_f$, where J_f and c_f stand for the molar Raman scattering coefficient and the molarity of the TFSA^- anion in the bulk, respectively. c_f is given as $c_f = c_T - c_b = c_T - n c_M$, where c_T , c_b , c_M and n denote the molarities of the total and bound TFSA^- anions, and the molarity and the solvation number of the alkaline metal ions, respectively. Taking into consideration the above two relationships, we obtained the following relationship: $I_f/c_M = J_f(R - n)$, where $R = c_T/c_M$. A plot of I_f/c_M against R thus yields a straight line, and the n value is obtained as $n = -\beta/\alpha$ from a slope of $\alpha = J_f$ and an intercept of $\beta = -J_f n$. I_f/c_M vs. R plots for the respective alkaline metal ion are shown in Fig. 5. As can be seen from this figure, plots for all of the alkaline metal ions examined here fall on straight lines, which suggests that the solvation numbers for the alkaline metal ions hardly depend on the concentration examined here. In addition, almost the same slope for the respective alkaline metal ion (the slope yields the Raman scattering coefficient for the bulk TFSA^-), indicating that Raman band deconvolution was made adequately throughout this work, and thus the obtained solvation numbers could be reliable. The evaluated values for the solvation numbers for the alkaline metal ions are listed in Table 1, accompanied by the Raman spectroscopic parameters. The values of the solvation numbers

Fig. 5 Plots of I_f/c_M vs. R . Solvation numbers of alkaline metal ions in ionic liquid were evaluated from the slope and the intercept for linear least squares (see text).

Table 1 Solvation numbers n in [BMI][TFSA] ionic liquids at 298 K, Shannon's ionic radii r/pm for alkaline metal ions and Raman spectroscopic parameters such as $\Delta\nu/\text{cm}^{-1}$, Raman scattering coefficients J_f and J_b , and the ratio J_b/J_f

	n	r	$\Delta\nu$	J_f	J_b	J_b/J_f
Li^+	1.95(3)	59	5.9	1.930(6)	1.3	0.68(6)
Na^+	2.88(2)	102	3.4	1.952(2)	1.6	0.86(2)
K^+	3.2(1)	138	2.1	1.89(1)	1.4	0.82(9)
Cs^+	3.9(2)	174	1.6	1.92(3)	1.4	0.77(6)

are 1.95 for lithium ion, 2.88 for sodium ion, 3.2 for potassium ion and 3.9 for cesium ion, respectively. Taking into consideration the experimental errors, the numbers of solvated TFSA^- anions could be 2 for Li^+ , 3 for Na^+ and K^+ , and 4 for Cs^+ , respectively. Moreover, it is plausible that, in the liquid state, the TFSA^- anion predominantly acts as a bidentate ligand with one oxygen atom in each SO_2 group. Consequently, it is plausible that the atomic coordination numbers for Li^+ , Na^+ , K^+ and Cs^+ are 4, 6, 6 and 8, respectively, in the ionic liquid.

It is worth comparing with the coordination numbers or the solvation structures of the alkaline metal ions in conventional molecular liquids. With regard to lithium ion, the hydration structure revealed by various techniques was recently reviewed.³⁴ The hydration numbers of Li^+ ion distribute from 4 to 6, depending on the counter anion and the concentrations of the salts. However, we recently demonstrated that lithium ion predominantly exists as a 4-coordinated structure in propylene carbonate solutions by neutron diffraction with the ^6Li isotope substitution technique.³⁵ According to previously reported neutron scattering studies, 4-coordinated structures of Li^+ ion would be favorable species in aqueous solutions³⁶ and in non-aqueous solutions.³⁷ Compared with the solvation structures in conventional molecular solvent solutions, the similar 4-coordinated structure of Li^+ ion in ionic liquids seems to be reasonable. With the Na^+ ion, the hydration numbers seem to depend on the salt concentration, *i.e.*, 6 and 4 in dilute and concentrated solution, respectively.³⁸ On the other hand, experimental investigations on the Na^+ ion solvation structure in non-aqueous solution are scarce.³⁹ With K^+ and Cs^+ , recent experimental and theoretical studies on the hydration structures can be found in the literature,⁴⁰ while, as far as we are aware, there is no published experimental work on the solvation structures in non-aqueous solvents. We believe that the solvation structures of Na^+ , K^+ and Cs^+ ions in non-aqueous solvents are not clear at

the present stage.

To the best of our knowledge, no neutron/X-ray scattering experiments for the alkaline metal ions solvation in the ionic liquid has been reported until the present, while a few theoretical studies were published. Borodin *et al.* investigated the lithium ion solvation structure and transport property in *N*-alkyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide by MD simulations based on a many-body polarizable model.⁴¹ According to their simulations, the Li⁺ ion is coordinated by 4 oxygen atoms, and 65% of the Li⁺ ions exist as the oligomer, in which two Li⁺ ions are bridged by three TFSA⁻ ions in a bidentate manner, *i.e.*, two oxygen atoms in a SO₂ group coordinate to a Li⁺ ion. Such a solvation structure agrees with the LiTFSA crystal structure,⁴² while differing from that of Li₂[EMI][TFSA]₃.⁴³ On the other hand, according to MD simulations based on the effective pair potentials,⁴⁴ three TFSA⁻ ions solvate to a Li⁺ ion, which is surrounded by five oxygen atoms, *i.e.*, two of bidentate TFSA⁻ and one mono-dentate. In addition, the Li⁺ ion solvation structure depends on its concentration, *i.e.*, with an increase of the Li⁺ ion concentration, the average number of solvated TFSA⁻ increases, whilst the average number of donating oxygen atoms decreases. Sieffert and Wipff have so far studied alkaline metal ions of Na⁺, K⁺, Rb⁺ and Cs⁺ by quantum chemical calculations and MD simulations in connection with solvent extraction and/or a liquid-liquid interface.⁴⁵ They evaluated the interaction energy for the aggregates [Na⁺(TFSA⁻)_{*n*}] (*n* = 1 – 3) in the gas phase by quantum chemical calculations, and found that the interaction energy shows a minimum at *n* = 2. In addition, in their simulations, Na⁺ is surrounded by 4.0 TFSA⁻ *via* O atoms of 5.7, corresponding to two bidentate and two mono-dentate TFSA⁻ ions. Cs⁺ is coordinated by 5 TFSA⁻ anions *via* 6.2 oxygen atoms on the average, one anion being bidentate and the others being mono-dentate. Thus, it would be necessary to make more experimental and theoretical efforts to draw more accurate pictures of alkaline metal ion solvation at a molecular level.

Ion-ion interaction between alkaline metal ion and TFSA⁻ ion

It is difficult to obtain information on the M-O bond length in solvated alkaline metal ions in solution by Raman spectroscopy directly. Nevertheless, though rough, information related to the bond length can be obtained from careful insight into the Raman spectra, if we take into account the well-accepted relationship between the coordination number and the bond length, *i.e.*, the larger is the coordination number, the longer is the bond length. As indicated above, the solvation numbers (and thus the atomic coordination number) of the alkaline metal ions were evaluated, so that we could know the ionic radii of the solvated alkaline metal ions in ionic liquids. According to Shannon,⁴⁶ the ionic radii are 59, 102, 138 and 174 pm for Li⁺, Na⁺, K⁺ and Cs⁺ of the 4-, 6-, 6- and 8-coordinated structure, respectively. By using these values, the relationship between $\Delta\nu$ and the ionic radii *r* of the solvated alkaline metal ions in the ionic liquid can be directly discussed. As the ionic radius of the alkaline metal ion is smaller, the higher frequency shift of the Raman band arising from the anions bound to the metal ions is larger. In other words, $\Delta\nu$ may be proportional to the *n*th power of the reciprocal ionic radii *r*. Thus, assuming that the relationship $\Delta\nu = (ar)^{-n}$ can hold, where *a* represents parameters for the effective ionic radii of the metal ions, plots of $\log(\Delta\nu/\text{cm}^{-1})$ vs. $\log(r/\text{pm})$ yield the value of *n* as their slope. Furthermore, if the ion-ion interactions between the alkaline metal ions and the anion are electrostatic, it is expected that a value close to unity, because $\Delta\nu$ is proportional to the reciprocal *r*. As shown in Fig. 6, the plot falls on a straight line, suggesting that the TFSA⁻ non

Fig. 6 Plots of $\log(\Delta\nu/\text{cm}^{-1})$ vs. $\log(r/\text{pm})$; *n* was evaluated from the slope for linear least squares, according to the relationship $\Delta\nu = (ar)^{-n}$.

coordinates to all alkaline metal ions examined here with practically the same binding mode, *i.e.*, the bidentate one *via* one oxygen atom from each SO₂ group. Moreover, the value of the slope was evaluated to be 0.999(5). Therefore, it can be deduced that the ion-ion interactions between the alkaline metal ions and TFSA⁻ ion are essentially electrostatic, as expected.

In addition, we could discuss the ion-ion interaction between the alkaline metal ions and TFSA⁻ in terms of the Raman scattering coefficient. When the alkaline metal ions are coordinated by TFSA⁻ *via* oxygen atoms, the S-O bond, and probably also the C-F bond, should be polarized. The Raman scattering coefficient (scattering cross section) is proportional to the polarizability, and it is thus expected that the Raman scattering coefficient of the vibration mode including the motions of the S-O group would vary from the value for the bulk TFSA⁻, when coordinating to the alkaline metal ions. The relationship $I_b = J_b c_b = J_b n c_{\text{Li}}$ also holds for the TFSA⁻ anion bound to the metal ion, and the molar Raman scattering coefficient J_b is obtained from the I_b vs. c_M plot for the Raman bands arising from the bound anion. In fact, the J_b/J_f values for all of the alkaline metal ions examined here are smaller than unity, as shown in Table 1. Moreover, though large uncertainties exist, the smallest value was obtained for the Li⁺ ion of the smallest ionic radius, as expected. However, *ab initio* calculations of high levels sufficient to predict correct polarizability are necessary to discuss more quantitatively.

Conformation of TFSA⁻ in the first solvation sphere of alkaline metal ion

Figure 7 displays Raman spectra for ionic liquids containing alkaline metal ions of *ca.* 0.5 mol dm⁻³ in the frequency range of 370 – 450 cm⁻¹, where a specific Raman band arising from *cis* TFSA⁻ (407 cm⁻¹) and those from *trans* TFSA⁻ (398 and 413 cm⁻¹) can be observed for the neat ionic liquid.¹⁹ As previously reported,²⁰ when dissolving the Li⁺ ion, the 407 cm⁻¹ band increases relative to the other two Raman bands from *trans* TFSA⁻ anion. The same can be observed in this work. Moreover, as can be seen in Fig. 7, similar enhanced Raman bands of 407 cm⁻¹ were evidently found in the Raman spectra for ionic liquids containing Na⁺ and K⁺ ions. On the other hand, such an increase of the 407 cm⁻¹ Raman band in intensity could not be observed for ionic liquid containing Cs⁺. This observation strongly suggests that the TFSA⁻ ion prefers the *cis* conformation, when it coordinates to alkaline metal ions of relatively small ionic radii. It should be noted that, in a neat ionic liquid, *trans* TFSA⁻ is a more favorable isomer relative to *cis* one, as shown both experimentally^{19,47} and theoretically.⁴⁸

Fig. 7 Raman spectra in the frequency range of 360 – 450 cm^{-1} for [BMI][TFSA] ionic liquid solutions *ca.* 0.5 mol dm^{-3} MTFSA (M = Li, Na, K and Cs), measured at 298 K.

The more stabilized *cis* TFSA[−] bound to metal ions relative to the *trans* one can also be found in crystals. According to our survey of the Cambridge Structure Database (CSD),⁴⁹ 137 molecular structures of the TFSA[−] ion in crystals have been reported except the disordered ones, in which there are 81 and 56 anions bound to metal ions and non-metal cations, respectively. With the former, the C–S··S–C dihedral angle distribution corresponding to the anions bound to metal ions are rather different from those interacting with non-metal ions, as shown in Fig. 8.

This is also supported by quantum mechanical calculations. With regard to the Li⁺ ion, the binding energy for [Li(*cis* TFSA)₂] is slightly larger than that for [Li(*trans* TFSA)₂] in the gas phase, as previously shown by our DFT calculations at the B3LYP/6-311+G(d,p) level of theory.²⁰ On the other hand, according to DFT calculations at the B3LYP/6-31G(d) level of theory by Sieffert and Wipff,^{45a} the binding energy for [Na(*cis* TFSA)₂] is smaller than that for [Na(*trans* TFSA)₂]. From these calculations, it can be deduced that *cis* TFSA[−] is stabilized relative to *trans* TFSA[−], when it coordinates to the Li⁺ ion of small ionic radius, however, there is no such stabilization when it binds to the larger Na⁺ ion.

In order to shed more light on the conformation of a TFSA[−] anion bound to alkaline metal ions, we performed MD simulations for [EMI][TFSA] ionic liquids containing the Li⁺ ion. We adopted two different Li⁺–O intermolecular potentials, as described above. The solvation structures of the Li⁺ ion in our simulations will be described elsewhere, compared with other experimental evidences. Here, we focus only on the conformational isomerism of TFSA[−]. For a discussion of the conformational isomerism of TFSA[−], it is useful to extract the dihedral angle distributions with respect to the *pseudo*-dihedral angle of the CS··SC ϕ in the anion, *i.e.*, $\phi \approx 40^\circ$ and 170° represent *cis*- and *trans* TFSA[−], respectively.^{25,48} Figure 9 shows the CS··SC dihedral angle distributions derived from MD simulations for the respective force field with varying LiTFSA salt mole fractions in ionic liquid solutions. As can be seen, it is evidently found that *trans* TFSA[−] (peak at *ca.* 165°) decreased, and oppositely the *cis* isomer (peak at *ca.* 30°) increased with an increase of the LiTFSA mole fractions. Moreover, the conformational behavior of increasing LiTFSA mole fraction is independent from the two kinds of Li⁺–O intermolecular

Fig. 8 CS··SC dihedral angle distribution for TFSA[−] bound to metal ions (●) and non-metal ions (○) in crystals found in the CSD database.

Fig. 9 CS··SC dihedral angle distribution of TFSA[−] derived from MD simulations for [BMI][TFSA] ionic liquid containing LiTFSA. *x* stands for the mole fraction of LiTFSA in [Li₁BMI_(1-x)TFSA]. Employed inter-molecular potential for Li⁺–O (TFSA[−]) was that proposed by Sohtens *et al.* (a) and CFF force fields (b), respectively.

potentials employed in this study. It should be noted that our simulations are classic ones and are based on the effective pair potentials of simple LJ and Coulombic interactions. The preferred conformation of *cis* isomer around the Li⁺ ion of small ionic radius could be attributable to a larger dipole moment for the isomer relative to the other.^{19,20} In fact, similar preferred conformational isomerism in the first coordination sphere of the Li⁺ ion was found in non-aqueous solvent solutions of dimethyl carbonate.²⁷ Though we have no thermodynamic data for ion solvation in ionic liquids, such a preferred conformational isomerism may stabilize the central metal ion of small ionic radius relative to a larger one, as was previously shown by our systematic studies on the ion solvation in non-aqueous solvent solutions of amides.⁵⁰

Conclusion

Raman spectra for 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide containing alkaline metal salts of TFSA[−], MTFSA (M = Li, Na, K and Cs), were recorded in the frequency

range of 200 – 1800 cm^{-1} , with varying salt concentration at 298 K. Quantitative analyses of Raman spectra with sufficient care yielded the solvation numbers to be 1.95 for Li^+ , 2.88 for Na^+ , 3.2 for K^+ and 3.9 for Cs^+ , respectively. 4-, 6-, 6- and 8-coordinated structures for Li^+ , Na^+ , K^+ and Cs^+ , respectively, in an ionic liquid were proposed based on the thus-evaluated solvation numbers and the bidentate binding mode of TFSA $^-$. Relative Raman shifts for the bound TFSA $^-$ to that for the bulk one show a good linear correlation with the reciprocal ionic radii for the solvated alkaline metal ions, according to Shannon's ionic radii corresponding to the atomic coordination numbers proposed here.

From the Raman spectra in the frequency range of 370 – 450 cm^{-1} , the conformation of TFSA $^-$ in the first solvation sphere of the alkaline metal ions were discussed. Experimental evidence for the preferred conformational isomerism of *cis* TFSA $^-$ bound to Li^+ and Na^+ ions of the relatively small ionic radii was provided, and well supported by DFT calculations and MD simulations. The preferred conformational isomerization of *cis* TFSA $^-$ bound to small alkaline metal ions was ascribed to its larger dipole moment relative to *trans* TFSA $^-$.

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