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Coordination structures of transition-metal ions in ionic liquids.

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Introduction

Ionic liquids are nowadays attracting considerable attention owing to their potential use in a wide range of applications. Particularly, they have successfully been employed in the preparation of inorganic materials. We have been studying the preparations of alkylpolyaminium protic ionic liquids (= PILs) and of ionic liquids of silver(I) complexes (= AgILs) [1, 2] and the interactions of transition metal ions in the ILs. In this study, we have prepared a series of the PILs containing transition-metal ions and measured EXAFS for the coordination structures around the transition-metal ions.

Experimental

The PILs were obtained by the neutralizations of hexylethylenediamine (= Hexen) with HTFSA (= bis(trifluoromethanesulfonyl)amide acid) or HTFA(= trifluoroacetic acid) and of hexylamine (= Hexam) with HTFSA. These PILs are hereafter abbreviated as HHexen(TFSA), HHexen(TFA), and HHexam(TFSA), respectively. HHexen(TFSA) and HHexen(TFA) ILs significantly dissolve many kinds of metal salts while HHexam(TFSA) does only copper(II) salts. We studied the interactions of metal(II) ions in the PILs with an addition of metal compounds such as chlorides, bromides, and bis-TFSA complexes of Mn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}, and tetraammine complex of Cu^{2+}.

EXAFS measurements were performed at room temperature in a transmission mode at BL-9C. The solid samples were mixed with boron nitride to make a tablet specimen. The PILs and other liquids were sealed into polyethylene bags for measurements; the metal concentrations were 0.04-0.15 mol kg^{-1}. In order to extract the backscattering amplitude and phase shift functions for the curve-fitting, the reference compounds (MnO, [Ni(en)$_3$]SO$_4$, [Cu(en)$_3$]SO$_4$) were used in this experiment. The structural parameters for the respective metal(II) samples were determined referred to those for the corresponding metal(II) reference compounds.

Results and Discussion

Figure 1 shows typical Fourier transformed EXAFS spectra for the solid and concentrated solutions of copper(II) salts. For all the samples except Cu(TFSA)$_2$ solid, the peak around 0.23 nm assigned to the bond of copper(II)-N appears with the same height.
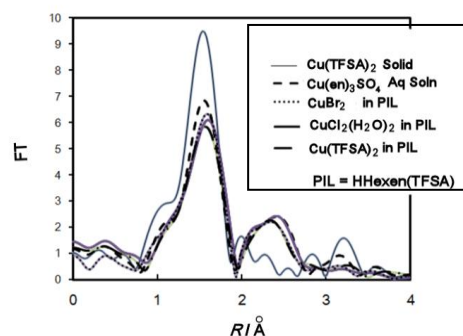

Figure 1. Fourier transformed $|F(r)|$ of the $k^3 \chi(k)$ curves for copper(II) ions. (uncorrected for the phase shift)

The en complex shows a characteristic peak due to a weak second shell contribution of carbon as well as a single monatomic first shell of nitrogen.[3] The relative magnitude of the second peak to the first one is useful to monitor the extent of the interaction of the copper(II) ion with the en chelate in the HHexen(TFSA) PIL system in comparing with [Cu(en)$_3$]SO$_4$. The spectra showed that copper(II) ions strongly coordinate to the en-chelate ring in the HHexen cation rather than the TFSA anion; the coordination mode around the copper(II) ion is close to that in 0.05 mol kg^{-1} [Cu(en)$_3$]SO$_4$ aqueous solution. The selective interaction occurs against the electrostatic disadvantage and is almost independent on the kinds of copper(II) salts. On the other hand, in the HHexam(TFSA) PIL (not described here), copper(II) ions prefer the TFSA anion rather than the hexylaminium cation. The other metal ions (Mn^{2+}, Co^{2+}, Ni^{2+}) also prefer the HHexen cation over the TFSA anion in the PIL; the selectivity to the HHexen cation is the largest for copper(II) ion. These selective interactions of the metal ions with the PILs and analogous liquids are consistent with the results obtained by paramagnetic NMR relaxation methods.

References
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