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Coordination structures of transition-metal ions in ionic liquids.

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Introduction

Our research group focuses on the interactions of transition-metal ions in the ionic liquids having polyamine chelate. A series of alkyl-polyaminium protic ionic liquids (= PILs) have been prepared and the interactions of various transition metal ions in the PILs have been studied. We herein prepared a series of the PILs, where some kinds of nickel(II) salts were dissolved, and then determined the coordination structure around the nickel(II) ion using EXAFS.

Experimental

The PILs were obtained by a neutralization of *N*-hexylethylenediamine (= Hexen) or 2-ethylhexylethylenediamine (= EtHexen) with HTf_2N (= bis(trifluoromethanesulfonyl)amide acid) or with HTFA(= trifluoroacetic acid). [1] The PILs thus obtained are abbreviated as HHexen(Tf_2N), HHexen(TFA), HEtHexen(Tf_2N), and HEtHexen(TFA) hereafter. Nickel salts of $NiCl_2$, $Ni(Tf_2N)_2$, and $Ni(TFA)_2$ were added to the PILs or to the neat liquid of Hexen (or EtHexen), and the interactions of Ni^{2+} with the PILs were compared with those of the neat Hexen (or EtHexen) liquid.

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 were sealed into polyethylene bags for measurements; the metal concentration was adjusted to 0.10 mol kg^{-1}. In order to extract the backscattering amplitude and phase shift functions for the curve-fitting, the reference compound ($Ni(en)_3SO_4$ in solid) was used in this experiment. The structural parameters for the respective nickel(II) samples were determined referred to those for the corresponding nickel(II) reference compounds and to the results of UV-vis absorption spectra.

Results and Discussion

The Fourier transformed $|F(r)|$ of the $k^3\chi(k)$ curve was obtained for $Ni(en)_3SO_4$ in solid state as a standard, whose structure has been well established. The nickel(II) ion in the en PILs shows a characteristic peak due to a weak second shell contribution of carbon as well as a single monatomic first shell of nitrogen. For some nickel(II) salts in the above four kinds of PILs and in the two kinds of the neat ethylenediamine liquids the similar FT curves were obtained, whereas the main peak height of the FT spectra of the nickel ion only in the HHexen(Tf_2N)-PIL was significantly lower than those in the other systems.

Curve-fittings for the FT curves were performed by fixing the coordination numbers which were determined by the VIS absorption spectra; the results are listed in Table 1. The selective interaction was almost independent on the kinds of added nickel(II) salts. The lower intensity of the main peak of the FT spectrum in the HHexen(Tf_2N) system can be attributed to the larger D-W parameter for the four nitrogen atoms of the en..

The obtained r and σ values indicate that the en-headgroups of the PILs coordinate to the nickel(II) ion with the nearly octahedral configuration, which is consistent with the result of the VIS absorption spectra.

Table 1. EXAFS parameters determined from the curve-fittings of the FT spectra.

Medium	System	Bond	10 *r* / nm	10 σ (D-W) / nm	*CN* (fix)	*R*(%)
STD	$[Ni(en)_3](SO_4)$ Solid	Ni-N	2.13	0.09	6	2.2
		Ni-C	2.94	0.09	6	
Free-Ligand	Ni^{2+} in Hexen	Ni-N	2.11	0.08	4	2.3-2.7
		Ni-O	2.19	0.07	2	
		Ni-C	3.02	0.10	6	
	Ni^{2+} in EtHexen	Ni-N	2.11	0.09	4	2.0-2.8
		Ni-O	2.17	0.08	2	
		Ni-C	2.97	0.10	6	
Hexen-PILs	Ni^{2+} in HHexen (Tf_2N)	Ni-N	2.11	0.12	4	2.6-3.3
		Ni-O	2.12	0.08	2	
		Ni-C	3.00	0.11	6	
	Ni^{2+} in HHexen (TFA)	Ni-N	2.13	0.08	4	1.8-1.9
		Ni-O	2.15	0.14	2	
		Ni-C	2.97	0.10	6	
EtHexen-PILs	Ni^{2+} in HEtHexen (Tf_2N)	Ni-N	2.14	0.08	4	1.4-3.3
		Ni-O	2.19	0.15	2	
		Ni-C	2.97	0.08	6	
	Ni^{2+} in HEtHexen (TFA)	Ni-N	2.13	0.08	4	2.2-2.6
		Ni-O	2.10	0.15	2	
		Ni-C	2.96	0.10	6	

References

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