Nuclear Science and Techniques **23** (2012) 129–133

XAFS study of Cu^{2+} in aqueous solution of $CuBr_2$

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Abstract Copper ion is the essential microelement to many organisms. In this paper, the local structure of Cu^{2+} in $CuBr_2$ aqueous solutions with different concentrations are investigated by using X-ray absorption fine structure (XAFS) technique. XANES (X-ray Absorption Near Edge Structure) spectra indicate that charge transfer from Br^- to Cu^{2+} decreases with the solution concentration, which lead to a shift of the absorption edge. The shoulder appearing at the rising edge proves to be characteristic of a tetragonal distortion. The Fourier transform magnitudes of EXAFS (Extended X-ray absorption fine structure) data of Cu species suggest that more Cu-Br bonds may exist in high concentrations. A fivefold coordination configuration like a pyramid is used as the fitting parameters. From the analysis of the coordination numbers, the proportion of Cu-O and Cu-Br is 4:1 in the saturated solution. The Br atom is on the equatorial plane of the model. The fitting results agree well with the experiment data.

Key words $CuBr_2$, Aqueous solution, XAFS, coordination

1 Introduction

Aqueous fluids not only exist throughout the Earth's crust, but also in organisms. And many physical and chemical reactions are done in solutions. So, it is of significance to study structure and coordinate of chemical species in solutions. For the past a few years, a large number of authors studied metal ionic solutions, such as zinc (II)[1], calcium (II)[2], copper (II)[3] and so on. It has been demonstrated that many kinds of metal ions existed in aqueous solution in the form of hydrated ions.

Copper (II), as one of divalent transition metals, is the essential microelement to many organisms. For humans, excessive or lack of copper ions would bring on inflammation, anemia, cancer and other diseases[4-6]. Besides, its geometric and electronic structure play an important role in a number of systems, such as metalloproteins, enzyme[7], high-TC superconductors[8] and so on. Especially, the strong electric field near Cu^{2+} in aqueous solution would lead to the orientation arrangement of water molecules and forming hydrated copper ions. It is important to study Cu^{2+} coordination structure for understanding the physical and chemical properties.

In the past thirty years, a great number of researches about Cu^{2+} coordination structure in aqueous solution were reported[3,9-12]. However, there is still not enough information about its structure. A large number of authors support a Jahn-Teller distorted six-coordinate structure[13,14]. A few groups proposed a five-fold coordination based on neutron diffraction findings and theoretical simulations[15-17]. Recently, Bryantsev, *et al.*[18]. recommended coexist of five- and six-coordinate hydrate structure of Cu^{2+} in solution

Copper（II) bromide, as one of the copper compounds, is an efficient reagent for catalyses[19], bromination[20] and other reactions[21]. In this work, $CuBr_2$ aqueous solutions at different concentrations (from saturation to 0.28 mol/L) were studied, and the

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Supported by National Natural Science Foundation of China (Grant No. 11005148, 10705046, 11135008), National Basic Research Program of China (Grant No. 2010CB934501), Special Presidential Foundation of the Chinese Academy of Science (Grant No. 29) and Science and Technology Commission of Shanghai Municipality (Grant No. 11JC1414900)

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Received date: 2012-03-19

hydration shell of cooper ions was investigated by XAFS at Cu-K and Br-K edge.

2 Experimental

$CuBr_2$ (analytical degree) was purchased from Sinopharm Chemical Reagent Co., Ltd. The saturated solution of $CuBr_2$ was obtained by dissolving it in deionized water at room temperature and filtering it. Other samples were simply prepared by diluting part of the solution into concentrations of 2.82, 1.13, 0.56 and 0.28 mol/L.

Both Cu and Br K-edge X-ray absorption spectra were recorded at the BL14W1 beamline of Shanghai Synchrotron Radiation Facility (SSRF). The electron storage ring was operated at 3.5 GeV with a current of 150 mA during experiment runs. The data were collected in unfocused and transmission mode by using a double-crystal Si (311) monochromator. Two ionization chambers were used to measure intensities of the incident X-ray (I_0) and the transmitted X-ray from the samples (I_1). The X-ray energy had been calibrated by recording the Cu and Pb characteristic X-ray spectra with their metal foils respectively. All the samples were measured at room temperature. For Cu K-edge measurements, the front and back ionization chambers were filled with nitrogen. For Br K-edge measurements, the front chamber was filled with 15% argon and 85% nitrogen while the back one was filled with argon.

Analyses of the XAFS data were performed using the software Iffefit. First, all the raw spectra in the pre-edge region were fitted with a linear function and the background was subtracted. Then the spectra were normalized to the absorption coefficient at 50 eV above the edge to eliminate thickness dependence. For Cu K-edge spectra, the normalized data were transformed from energy space to k-space, where the EXAFS function $\chi(k)$ data were multiplied by k^3-weight. The $\chi(k)$ data were Fourier transformed to R space, which suggest the different coordination shells, subsequently. The data in R space ranging from 0.9 to 2.5 Å^{-1} were applied to the fitting work.

3 Results and discussion

Spectra of the Cu K-edge XAFS of $CuBr_2$ aqueous solutions of different concentrations are shown in Fig.1. The signal of main peak is attributed to a Cu 1s → 4p transition. The weak peak at low energy (8978 eV) is assigned as a 1s→3d transition[7]. As the concentration decreases, a 1.3-eV shift to high-energy direction is seen at the absorption edge. At the main peak (Fig.2), there is a 1.5-eV shift to high-energy. This indicates that the ligand-to-metal charge transfer is reduced. In addition, the intension of white line peak increases with the concentration, implying a bigger degree of structural disorder at high concentrations.

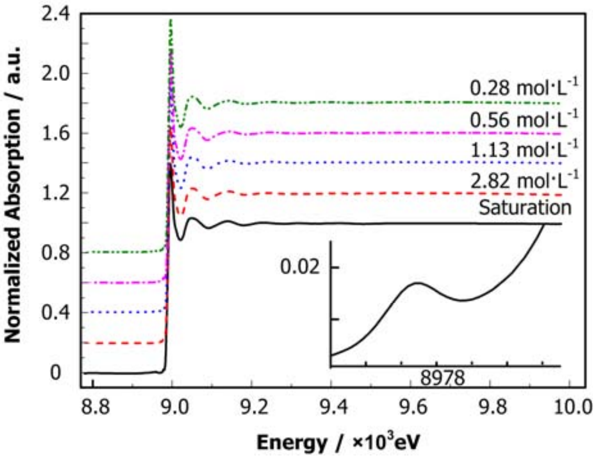

Fig.1 XAFS spectra of CuBr2 aqueous solution with different concentrations at Cu K-edge.

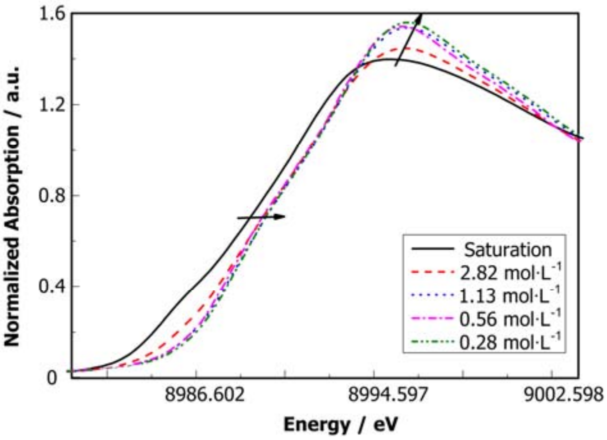

Fig.2 Comparison of XANES spectra of CuBr2 aqueous solution with different concentrations at Cu K-edge.

All the spectra exhibit a shoulder at the absorption edge, which can be clearly indentified in the derivative spectra (Fig.3)[22]. Peak A and B correspond to the shoulder and absorption crest, respectively[23]. Peak A proves to be characteristic of a tetragonal distortion[13]. In spectra of the solutions in saturation and 2.82 mol/L concentration, a shift of peak A can be seen, while its amplitude decreases with the concentration. This indicates that the contribution from Br$^-$ to Cu^{2+} is greater in high concentrations. This phenomenon can also be observed in the *k*-space. Small discrepancy can be seen at 8−12 Å^{-1} from the normalized k^3-weighed spectra in Fig.4a. Fig.4b shows the Fourier transform magnitudes of EXAFS data of Cu species with different concentrations. The data are weighted by k^3. The Cu-Br coordination number is greater in high concentration solutions. Due to electro-negativity of H_2O over Br$^-$, more Cu-O bonds exist, instead of Cu-Br bonds, with decreasing concentrations.

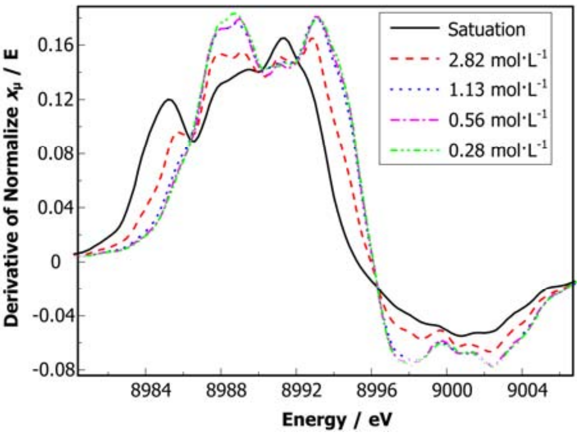

Fig.3 Derivative spectra of CuBr$_2$ aqueous solution with different concentrations at Cu K-edge.

The EXAFS spectra for Cu K-edge were fit using theoretical phases from the Artemis code. The Cu $\chi(k)$ data were windowed between 2.6 and 13 Å^{-1} using a Hanning window with d*k*=0.5. We set the fitting parameters according to the fivefold coordination model of Cu^{2+} aqua complex, which has been evidenced[15,16,24]. The amplitude reduction factor (S_0^2) was set to 0.9 based on Cu metal foil fitting work. In order to get the best-fit results, we tried to use a Cu-Br and two Cu-O paths. The calculation results are listed in Table 1.

In CuBr$_2$ saturated solution, the proportion of Cu-O and Cu-Br is 4:1. Because of the two different Cu-O paths, the average lengths of Cu-O are 1.95(4) Å and 2.40(0) Å, respectively. The Cu-Br distance is 2.39(9) Å. The model corresponds to a distorted pyramid with one axial O at 2.40(0) Å and three equatorial O and one equatorial Br$^-$. The weak peak at 13467 eV in the XANES spectra of CuBr$_2$ (Fig.5) indicates this asymmetry of equatorial plane.

From Table 1, at concentrations below 1.13 mol/L, no obvious Cu-Br bond can be seen, and the hydrated Cu^{2+} is bound to five water molecules. The structural parameters suggest the model of a square pyramid. From the analysis, the calculation results agree well with the experiment data.

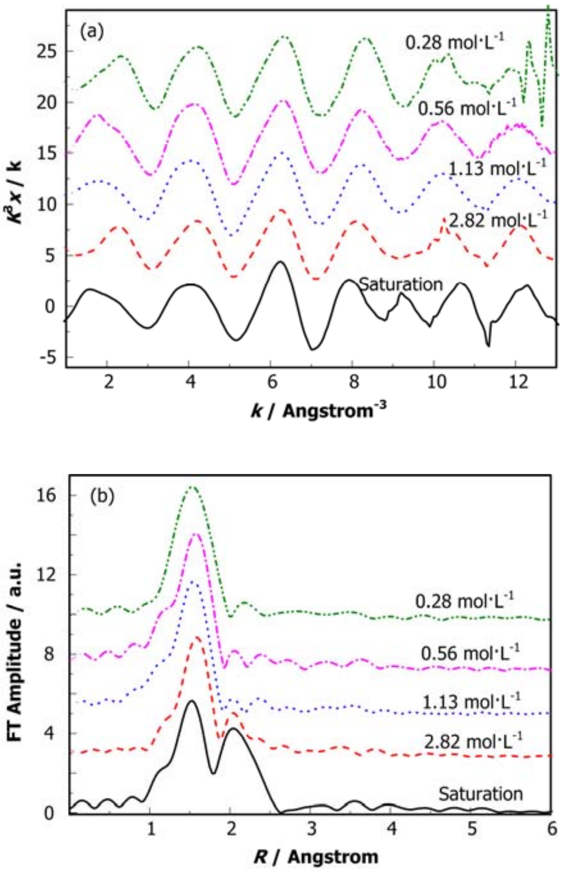

Fig.4 Comparison of EXAFS signals at Cu K-edge in *k*-space (a) and in R space (b).

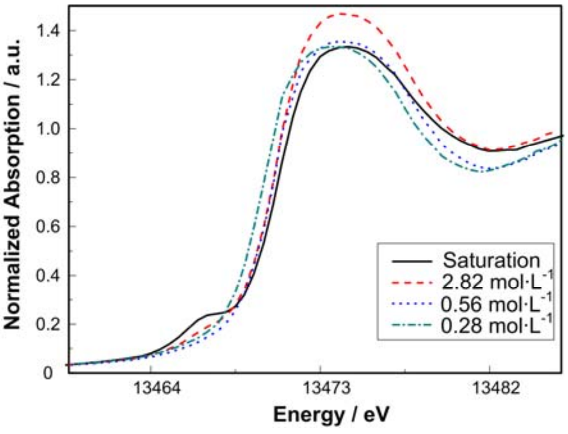

Fig.5 Comparison of XANES spectra of CuBr$_2$ aqueous solution with different concentrations at Br K-edge.

Table 1 Local structure parameters of $CuBr_2$ aqueous solution with different concentrations

Concentration / mol·L^{-1}	Coordination	N	R0 (Å)	σ_S^2(Å^2)	E_0 Shift	R factor
Saturation	Cu-O1	2.9(7)	1.95(4)	0.0053	−1.76	0.0018
	Cu-O2	1.1(3)	2.40(0)	0.0610	−1.76	0.0018
	Cu-Br	0.9(0)	2.39 (9)	0.0044	−1.76	0.0018
2.82	Cu-O1	3.6(4)	1.95(6)	0.0053	−1.20	0.0043
	Cu-O2	1.1(8)	2.37(7)	0.0390	−1.20	0.0043
	Cu-Br	0.1(8)	2.39(5)	0.0010	−1.20	0.0043
1.13	Cu-O1	4.0(2)	1.94(9)	0.0054	−1.78	0.0058
	Cu-O2	0.9(6)	2.39(9)	0.0416	−1.78	0.0058
	Cu-Br	0.0(2)	/	/	/	/
0.56	Cu-O1	4.0(0)	1.94(9)	0.0053	−2.00	0.0064
	Cu-O2	1.0(0)	2.36(3)	0.0497	−2.00	0.0064
	Cu-Br	/	/	/	/	/
0.28	Cu-O1	4.0(0)	1.95(4)	0.0053	−1.06	0.0067
	Cu-O2	1.0(0)	2.31(6)	0.0286	−1.06	0.0067
	Cu-Br	/	/	/	/	/

4 Conclusion

XAFS measurements were performed to investigate $CuBr_2$ aqueous solution at different concentrations. By comparing the shape of spectra and analyzing Cu ions coordination environment, we obtained its electron local atomic structures, and also the proportion, distance and location of Cu-O bonds and Cu-Br bonds. The results are different from those in Refs.[25,26]. Due to the stronger ligand field from H_2O over Br^-, more Cu-O bonds exist instead of Cu-Br bonds in low concentrations. Although a recent research suggested both five- and six-coordinate configuration may coexist[18], we support five-coordination pyramidal model, which is more stable. In addition, the fitting results agree well with the experiment data.

Acknowledgements

Thank to the members of XAFS beamline in Shanghai Synchrotron Radiation Facility for the XAFS beam time.

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