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THE EXAFS STUDY OF Cu(II) AQUEOUS SOLUTION USING A POSITION SENSITIVE DETECTOR

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Extended X-ray absorption fine structure (EXAFS) spectroscopy has been applied to the study of an aqueous solution. An X-ray spectrum for 0.32 M $Cu(ClO_4)_2$ was measured by a multi-detection apparatus of laboratory scale with a usual X-ray tube and a position-sensitive detector and analyzed preliminarily by Fourier transformation method to give the Cu - O distances of 1.94 and 2.46 Å (assuming α = 0.39 Å), in agreement with the X-ray diffraction result.

Recent experimental and theoretical advances have made the X-ray absorption spectroscopy a promising new method for the study of local structure around a specific atom in many compounds of interest, such as metalloproteins, catalysts, amorphous materials, where conventional diffraction methods are not feasible.¹⁾ However, since the technique of EXAFS is very subtle, it has been difficult to obtain EXAFS spectra with an apparatus of laboratory scale. In this paper, we report the EXAFS of an aqueous $Cu(ClO_4)_2$ solution obtained by an apparatus equipped with a usual X-ray tube and a position-sensitive detector. The purpose of the present investigation is to test the availability of our apparatus by determining the structure of Cu^{2+} ions in aqueous solution from the measured EXAFS spectrum.

Ohtaki et al.2) obtained metal ion - water molecule distances of 1.94 Å (equatorial) and 2.43 Å (axial) for a concentrated $Cu(ClO_4)_2$ solution by an X-ray diffraction study. Eisenberger and Kincaid3) reported that the nearest Cu - O distance was 1.97 Å in a dilute $CuBr_2$ solution on the basis of their EXAFS study.

A high resolution X-ray absorption spectrum was obtained for a 0.32 M aqueous solution of $Cu(ClO_4)_2$ with an energy-dispersive-type apparatus equipped with a tungsten X-ray tube and a self-scanning photodiode array (SSPA).4) The SSPA consisting of 512 photodiodes and MOS switches is used for a one-dimensional X-ray detector. The continous radiation emitted at an acceleration voltage of 14 kV with a tube current of 30 mA was diffracted by a (200) reflection from a LiF single crystal. A plastic cell contained a small volume of the sample solution between mylar windows spaced 1.0 mm apart. The obtained apectrum was an average of five measurements, each of which required 3000 seconds, i.e. 1000 seconds each for the photocurrent of the transmitted beam of the sample, I_s, and of water, I_0, and for the dark current withour X-ray, I_d. The absorption spectra were taken over a photon energy range extending from approximately 8920 up to 9660 eV, Cu K absorption edge being 8980 eV. The energy correction was done with CuZn alloy.

Figure 1 shows μX $(=\ln[(I_0-I_d)/(I_s-I_d)])$ as a function of photon energy. This spectrum was analyzed as follows. All the X-ray absorption due to all causes other than photoemission from the Cu K shell is removed by subtracting the extrapolated absorption below the K edge from the rest of the spectrum. The absorption modulations are isolated by the cubic spline technique to remove the smooth background. The resulting EXAFS amplitude, $\chi(k)$, is plotted against the photoelectron wave vector, k, as shown in Figure 2. Then a Fourier transformation from k space to r space is applied to $k\chi(k)$ values in the k range of 3.5-11.0 Å^{-1}. The result is given in Figure 3.

As discussed by Stern et al.,$^{5)}$ the presence of an atomic-scattering phase-shift term gives rise to a complication in deducing coordination distances from peak positions in the Fourier transform. The effect of a phase shift is to shift all peaks toward the origin by an amount α. The main peak appearing in the transform at 1.55 Å may correspond to the Cu - O distnace of 1.94 Å reported by Ohtaki et al.$^{2)}$ from their X-ray diffraction experiment. Then, the α value is 0.39 Å, with which the second peak at 2.07 Å corresponds to 2.46 Å in agreement with the previous result (2.43 Å).$^{2)}$ Interpretation of the peak at 0.58 Å and determination of the second-sphere Cu - O distances will be deferred, until a better spectrum is obtained with an improved apparatus to be constructed.

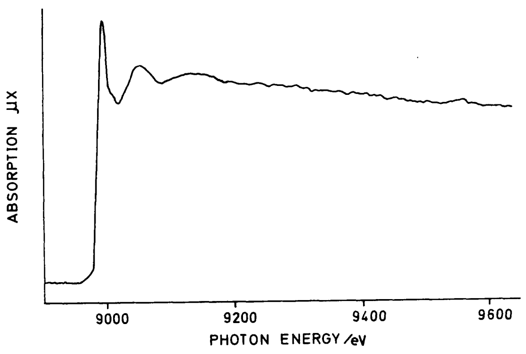

Fig. 1 X-ray absorption spectrum of an aqueous $Cu(ClO_4)_2$ solution

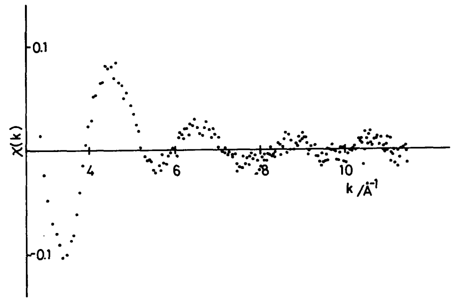

Fig. 2 EXAFS spectrum of an aqueous $Cu(ClO_4)_2$ solution

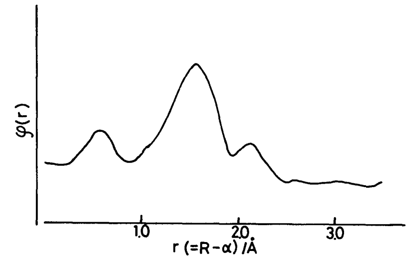

Fig. 3 Fourier transform of the EXAFS spectrum

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