New insight on the local structure of Cu$^{2+}$ ion in the solution of CuBr$_2$ by EXAFS studies

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Abstract. CuBr$_2$ solutions at different concentrations were studied by extended X-ray absorption fine structure (EXAFS) at the Cu K edge. In the saturated solution Cu$^{2+}$ ions have chemical bonds with 3.0 oxygen atoms and 0.9 Br ion at about 1.96 Å and 2.42 Å, respectively. It indicates that the CuBr$_4^{2-}$ configuration exists with a ratio of 25% under this condition. In the dilute solutions no evidence of Br ions contributions in the first shell around Cu$^{2+}$ ions occurs. The almost identical X-ray absorption near edge structure (XANES) and EXAFS characters address similar local environments around Cu$^{2+}$ in agreement with results of the EXAFS fit taking into account only the contributions of Cu-O bonds.

1. Introduction

Structural and coordination information of chemical species in solution are significant in many areas such as electrochemistry, solution chemistry and homogeneous catalysis [1]. In particular the configurations of cations, 3d transition metals in strong II-I electrolyte solutions such as NiCl$_2$, ZnCl$_2$, ZnBr$_2$, CuBr$_2$, at different concentrations have been investigated for many years [2-6] and a well-established understanding of the physical chemistry of solutions is available [4, 5]. The existence of strong correlations between nickel ions was raised by Howe et al. using the neutron scattering technique with isotope ions [6, 7]. Moreover, on the basis of thermodynamic calculations and a vast body of physico-chemical evidences it is generally accepted that in highly concentrated solutions complexes of MBr$_4^{2-}$ ions exist together with [M(aq)]$^{2+}$ ions [3, 8]. A lot of techniques, such as X-ray scattering [9, 10], neutron scattering [6, 11], Raman scattering [12], extended X-ray absorption fine structure (EXAFS) [3, 13-15], and anomalous X-ray scattering (AXS) [16] have been applied to investigate chemical species in solution.

In this work, we focus on CuBr$_2$ solutions, a typical strong II-I electrolyte solution already studied for more than thirty years. Nevertheless, is still not clear the ratio of the two complexes (CuBr$_4^{2-}$ and Cu(aq)$^{2+}$) in highly concentrated solutions and also the question whether the CuBr$_4^{2-}$ complex exists in dilute solutions remains open. This work investigated these two aspects by means of XAFS (X-ray
absorption fine structure) analysis at the Cu-K edge in different CuBr$_2$ solutions (0.1 M, 0.5 M and at saturation).

We have used in this investigation the XANES and EXAFS techniques which represent the best spectroscopical methods to investigate metal ions in solution at high spatial resolutions. XANES is very sensitive to the oxidation states of a selected atom, the coordination species and their local geometries. It can be used to reconstruct the local environments around a photo-absorber with a qualitative and quantitative analysis in the framework of MS calculations that can be combined with EXAFS, a powerful technique usually applied to obtain accurate bond distances and coordination numbers (CN). The combined analysis may also return reliable information at the molecular level.

2. Experiment

CuBr$_2$ was purchased from SCRC (Sinopharm Chemical Reagent Beijing Co., Ltd). Aqueous solution samples were simply obtained dissolving weighted amounts of CuBr$_2$ in deionized water while the saturated solution has been filtered to remove any dissolved material.

XAS measurements were performed at the X-ray absorption station of the 1W1B beamline at Beijing Synchrotron Radiation Facility (BSRF). The typical energy of the storage ring was 2.5 GeV with a current decreasing from 180 to 120 mA during experimental runs. A Si (111) double crystal monochromator was used, minimizing the high harmonics content with a 20% detuning of the two crystals. The absolute energy position was calibrated using a Cu metal foil. The Cu K edge of the 0.1 M solution sample was recorded in the fluorescence mode while the 0.5 M solution sample, the saturated solution and the reference CuBr$_2$ powders were measured in the transmission mode. For the experiments, solutions were kept in a sample cell of polyethylene while CuBr$_2$ standard was ground into subtle grains and then a well-proportioned distribution was deposited on Kapton films for the measurements. An ion chamber flowed by 25% argon and 75% nitrogen was used to monitor the incident beam intensity ($I_0$) while another ion chamber flowed also by 25% argon and 75% nitrogen was used to monitor the beam intensity after sample ($I_1$) in the transmission geometry and a Lytle detector flowed by pure Ar was used to record the fluorescence signal ($I_f$). Data analysis of the experimental XAS spectra was performed using WinXAS3.1 [16] and FEFF 8.0 [17] packages.

3. Results and discussion

![Figure 1. Comparison of the Cu K edge XANES (a) and EXAFS signals in the k space (b) of the CuBr$_2$ powder and of the solutions at concentrations of 0.1 M, 0.5 M and at saturation.](image)

Cu K edge XANES spectra of both 0.1 M and 0.5 M solutions in figure 1(a) are almost identical and this behaviour is also shown by their corresponding EXAFS signals exhibiting the same frequency and
amplitude in the K space [figure 1(b)]. Increasing the concentration of the CuBr$_2$ solution from 0.1 M to 0.5 M no configuration changes occur. Moreover, no common features can be recognized with the CuBr$_2$ spectrum. On the contrary, at saturation, some differences with the XANES spectra of the diluted solutions exist. At saturation the EXAFS signal presents features similar to that of the CuBr$_2$ standard, in particular in the range 7-11.5 Å$^{-1}$ suggesting the presence of CuBr$_4^{2-}$ ions in this sample.

Table 1. EXAFS parameters around Cu ions for the CuBr$_2$ standard and the three solutions at different concentrations.

| Samples   | Bond Type | CN | R(Å) | σ$^2$ (Å$^2$) | ΔE$_0$ (R) | R (%) |
|-----------|-----------|----|------|---------------|------------|-------|
| CuBr$_2$  | Cu-Br     | 4.0| 2.41 | 0.0056        | 1.8        | 1.7   |
| 0.1 M     | Cu-O      | 4.0| 1.97 | 0.0065        | -1.8       | 8.0   |
| 0.5 M     | Cu-O      | 4.1| 1.96 | 0.0065        | -1.8       | 6.4   |
| Saturation| Cu-O      | 3.0| 1.96 | 0.0065        | -2.8       |       |
|           | Cu-Br     | 0.9| 2.42 | 0.0058        | 2.6        | 3.6   |

To identify the local structural differences of CuBr$_2$ solutions at different concentrations, EXAFS fits of all spectra were performed with the WinXAS3.1 code [16] and theoretical modes generated by FEFF8.0 [17]. Indeed, CuBr$_2$ solutions have been studied many years ago with other techniques, such as differential anomalous scattering-DAS, X-ray diffraction-XRD, Raman [2, 5, 14]. However, due to limited experimental conditions and analytical methods, no consensus exists regarding the Cu local structure configuration of solutions at different concentrations. Indeed, previous researches indicated that CuBr$_4^{2-}$ occurs with a high proportion even in diluted solutions [3, 8]. The Fourier transform of each spectrum was performed on the $k^3$-weighted EXAFS oscillations in the range of 2.9–12.8 Å$^{-1}$. The amplitude reduction factor ($S_0^2$) was set to 0.9, the bond distance error has been estimated to be ~ 0.02 Å while coordination numbers were obtained within 20%. The Cu-O coordination number of the 0.1 M solution was fixed as 4, i.e., only 4 equatorial atoms were considered and the more distant axial oxygen atom was neglected according to the model suggested by Benfatto et al. [18]. Because of their similarity, the achieved Debye-Waller factor was then used in the EXAFS fitting of the 0.5 M solution, obtaining the same Cu-O coordination number of 4. This value is then reasonable and the Debye-Waller factor can be used as a fixed parameter in the EXAFS analysis also of the saturated solution in order to determine the Cu-O coordination number in this sample. Results are compared in figure 2 and summarized in table 1. The distance of the Cu-O and Cu-Br bonds obtained by the fit are about 1.96 Å and 2.41 Å, respectively, values in good agreement with previous studies of Cu(aq)$^{2+}$ and CuBr$_2$ [18, 19]. There is no obvious contribution of Br ions at about 2.41 Å (including the phase shift) for CuBr$_2$ solutions at concentrations of 0.1 M and 0.5 M, while a distribution of O atoms at about 1.96 Å (including the phase shift) is observed in both samples. Data demonstrate that the presence of CuBr$_4^{2-}$ in solutions with concentration <0.5 M can be ruled out and that a saturated CuBr$_2$ solution presents features of both O atoms and Br ions, according to the coordination numbers with a 3:1 ratio. Data indicate also that Cu ions in the saturated solution exist as Cu(aq)$^{2+}$ and CuBr$_2^{2-}$ with the same ratio of 3:1. The proportion of CuBr$_4^{2-}$ obtained is smaller than 50% [5] and in agreement with previous investigations [3, 14].
4. Conclusions
For the saturated solution, a clear contribution of Br ions around Cu ions has been observed and the structural parameters obtained are in agreement with both DAS and X-ray diffraction data [2, 14]. On the contrary, XAFS analysis of solutions with concentrations of 0.1 M and 0.5 M does not show the presence of Br ions in the first shell around Cu ions. This result is different from that obtained in other dilutes solutions where CuBr$_4$$^{2-}$ is present with a high proportion [3, 8].

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