

Complexation of Cu^{2+} in hydrothermal (25–175°C) NaCl brines: results from *in situ* EXAFS spectroscopy

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It has long been realized that complexation of Cu by Cl ligands is responsible for the solubility of Cu sulphide phases in hydrothermal solutions. It is essential that we

know the speciation of such CuCl_n^{2-n} complexes at high temperature in order to make thermodynamic predictions of the relation between Cl concentration and Cu mineral solubility. To this end, we have measured the speciation of Cu^{2+} complexes from 25 to 175°C in NaCl brines of 0, 2.0 and 5.0 M.

Experimental

EXAFS spectra of 0.1 M CuCl_2 with 0, 2.0 and 5.0 M NaCl were measured at Daresbury Laboratory station 8.1 in fluorescence mode. Solutions were heated in a titanium high-temperature cell with Kapton windows. Spectra were measured at 25, 75, 125 and 175°C. EXAFS spectra out to 11 \AA^{-1} were fit using the EXCURV92 code which calculates potentials and phase shifts for a given model using density functional theory.

Results

A spectrum of 0.1 M CuCl_2 is shown in Fig. 1. Fits to the CuCl_2 spectra are given in Table 1 and show that, at least up to 125°C, there is no Cl complexation in

this solution. We interpret the Cu coordination environment as having 4 H_2O or OH ligands in a square planer arrangement with two unresolved OH or H_2O (or Cl ?) ligands at a longer axial distance and with a much greater Debye-Waller factor. Such a tetragonal coordination environment is expected because of the Jahn-Teller distortion of the $\text{Cu}(\text{OH}, \text{H}_2\text{O})_6$ complex due to the $t_{2g}^6 e_g^3$ configuration of the Cu d-electrons. Note that a recent EXAFS study (at 25°C) by D'Angelo *et al.* (1997) suggested that there are also Cl ligands at the axial positions with Cu-Cl bond lengths of 2.83–2.86 Å. However, we cannot find any statistically significant shell corresponding to such Cl atoms in our data.

With increasing temperature, there is a systematic increase in the Cu-O bond length. At high temperature (175°C) there is a dramatic change in the Cu coordination environment with evidence for 1.7 Cl at 2.109 Å. However, the O shell Debye-Waller factor at 175°C was constrained (by extrapolation) to 0.019.

Spectra of 0.1 M CuCl solutions in 2.0 M NaCl were very similar to those of 0.1 M CuCl_2 . The same transition was found suggesting a transition to $\text{CuCl}_2(\text{aq})$ between 125 and 175°C. This suggests that $\text{CuCl}_2(\text{aq})$ is the dominant species of Cu in mesothermal brines.

Spectra of CuCl_2 solutions at 5M NaCl concentra-

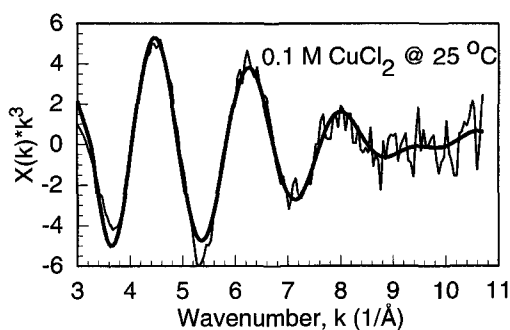


FIG. 1.

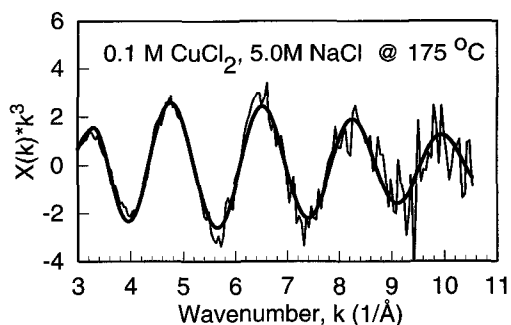


FIG. 2.

TABLE 1. Model fit of 0.1 M CuCl₂ EXAFS spectra

T(°C)	N(O)	R(Cu-O)	2σ ²	N(Cl)	R(Cu-Cl)	2σ ²
25	3.7	1.945	0.011	0	–	–
75	4.1	1.95	0.015	0	–	–
125	4.1	1.965	0.017	0	–	–
175	1.4	2.025	0.019*	1.7	2.109	0.012

TABLE 2. Model fit of 0.1 M CuCl₂ + 5M NaCl EXAFS spectra

T(°C)	N(O)	R(Cu-O)	2σ ²	N(Cl)	R(Cu-Cl)	2σ ²
25	2.5	1.945	0.010	1.1	2.28	0.01
75	1.9	1.95	0.007	1.4	2.29	0.01
125	0	–	–	3.5	2.24	0.019
175	0	–	–	1.7	2.16	0.014

tion, however, show Cl complexation at low temperatures increasing to CuCl₄²⁻ at 125°C. (Some complexation by Cl at 25°C is evidenced by the colour change of the solution). The Cu-Cl distance is close to that (2.29 Å) observed in solid CuCl₂·H₂O. Between 125 and 175°C, however, the dominant Cu complex appears to change from CuCl₄²⁻ to CuCl₂ as in the NaCl-free system. This, again, suggests that

CuCl₂ (aq) is the dominant Cu species in mesothermal brine solutions.

References

- D'Angelo, P., Bottari, E., Festa, M.R., Nolting, H.F. and Pavel, N.V. (1997)
J. Chem. Phys., **107**, 2807–12.