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# Complexation in the Cu(II)–LiCl–H<sub>2</sub>O system at temperatures to 423 K by UV-Visible spectroscopy

Liliana Trevani<sup>a</sup>, Jana Ehlerova<sup>b</sup>, Josef Sedlbauer<sup>b</sup>, Peter R. Tremaine<sup>c,\*</sup>

<sup>a</sup> Faculty of Science, University of Ontario Institute of Technology, Oshawa, Canada L1H 7K4

<sup>b</sup> Department of Chemistry, Technical University of Liberec, 46117 Liberec, Czech Republic

<sup>c</sup> Department of Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

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## ABSTRACT

Thermodynamic data for the solubility and formation of copper(I) and copper(II) species are required to model innovative designs of the electrolysis cells used in the thermochemical copper-chloride hydrogen production process. Cumulative formation constants of Cu<sup>2+</sup>(aq) complexes with Cl<sup>−</sup>(aq) were determined by Principal Component Analysis of UV-spectra, obtained over a very wide range of solution compositions and temperature, coupled with an appropriate model for activity coefficients of the solution species. Shortcomings in the existing database and future work to extend these studies to higher temperatures and much higher copper concentrations are discussed.

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## 1. Introduction

The Super-Critical-Water-Cooled Reactor (SCWR) is a concept for a novel, extremely energy-efficient advanced nuclear reactor that has been chosen by Canada as its major R&D contribution to meet the targets of the Generation IV International Forum treaty. A requirement of all the SCWR concept designs is an ability to co-generate hydrogen from high-temperature steam at temperatures below 823 K. The reactor would be separated from the hydrogen production plant, but coupled through an intermediate heat exchanger that supplies heat to the thermochemical cycle.

Over 200 processes for thermal hydrogen production have been evaluated by the US Department of Energy and three

have been selected for use at temperatures below 823 K [1]. As yet, only one of these, the copper-chloride cycle, has been shown to have promise as a practical process. The laboratory-scale copper chloride process involves an electrochemical step at temperatures up to 348 K, with chloride concentrations up to ~6 mol kg<sup>−1</sup>. The Canadian research program is investigating novel electrochemical processes, higher acid concentrations, and the use of temperatures up to 423 K and pressures of 15 MPa, to achieve efficiencies in the electrolysis reactions and the compression of produced hydrogen gas [2,3]. Copper (I) and copper (II) chloride solubilities and data for complex formation are required to model speciation in the aqueous phase and copper transport mechanisms under these conditions [3].

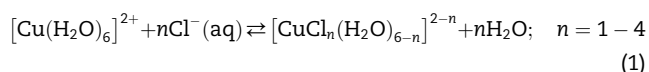
\* Corresponding author. Tel.: +1 519 824 4120(56076); fax: +1 519 766 1499.

E-mail address: [tremaine@uoguelph.ca](mailto:tremaine@uoguelph.ca) (P.R. Tremaine).

Fritz and Königsberger [4] have compiled solubility data for cuprous and cupric chloride, CuCl and CuCl<sub>2</sub>, in several chloride media including concentrated hydrochloric acid solutions. Unfortunately, there is only one set of data in this compilation that reaches 373 K, and the uncertainty is larger than that for data at lower temperatures. Most of the solubility studies at high-temperature were intended to understand the transport and deposition of copper in ore-forming systems or concentrated brines [5–10]. As a consequence, hydrochloric acid is only present at very low concentrations to avoid the hydrolysis of copper and the formation of hydroxyl-copper species. Cumulative formation constants for chloride with copper (I) and copper (II) have been reported by Liu et al. [9,10] and Brugger et al. [11].

In the case of CuCl<sub>2</sub>, extensive work has been done in the field of hydrometallurgy, mainly in concentrated CuCl<sub>2</sub>–NaCl solutions at moderate temperatures [12–14]. Much less has been done on the electrodeposition of copper from CuCl<sub>2</sub>–HCl solutions, due to the difficulties associated with the use of concentrated HCl solutions [15]. The complexation of copper(II) with chloride was studied by Brugger et al. [11] in LiCl solutions up to 363 K and, according to the authors, there is evidence for the formation of up to four or even five copper complexes. There are no other accurate data for polynuclear copper complexes above 298 K.

In the first phase of this study, we have used the high-temperature UV-visible flow system developed by Trevani et al. [16] to measure the spectra of Cu(II)–LiCl–H<sub>2</sub>O solutions at 373 K and 423 K, at a pressure of 9 MPa. The spectra were obtained for solutions with constant initial loading of copper and at different concentrations of LiCl, from 0 mol kg<sup>-1</sup> to 15 mol kg<sup>-1</sup>. A small excess of hydrochloric acid was used to prevent the precipitation of hydroxides. Under these conditions, complexation is expected to take place by successive displacement of water molecules according to the reaction:



These measurements are part of a broader project involving the study of complexation reactions in concentrated HCl solutions up to 6 mol kg<sup>-1</sup>, and Cu(II) concentrations up to the solubility limit. The experimental information will be used to model the solubility of copper in the electrochemical step of the copper thermochemical cycle. LiCl was chosen as the source of chloride because at our experimental conditions this electrolyte is more benign compared to other salts, and is consistent with other experimental studies in the literature [11,12]. This point is important because the high number of absorbing species in the solution requires the use of factor analysis methods in the data treatment and a very wide range of concentrations [17].

## 2. Experimental

### 2.1. Chemicals

All chemical materials were used without further purification. The list of chemicals includes: lithium chloride, LiCl (Sigma-Aldrich, 99+%, A.C.S. reagent); sodium hydroxide, NaOH (50%

w/w solution, Fisher ACS certified); hydrochloric acid, HCl (ACS reagent-grade); copper(II) chloride dihydrate, CuCl<sub>2</sub>·2H<sub>2</sub>O (Sigma-Aldrich, 99.99+%); silver nitrate, AgNO<sub>3</sub> (Fisher ACS certified); potassium chromate, K<sub>2</sub>CrO<sub>4</sub> (Fisher ACS certified); potassium thiocyanate, KSCN (BDH, 98%, analytical reagent); sodium thiosulphate pentahydrate, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O (Fisher ACS certified); sodium carbonate, Na<sub>2</sub>CO<sub>3</sub> (Fisher-Scientific); potassium iodate, KIO<sub>3</sub> (Caledon, 99.4%); potassium iodide, KI (Fisher, Reagent A.C.S.); starch (Fisher-Scientific, starch solution stabilized); sodium chloride, NaCl (Sigma Ultra, 99.5%). Solutions were prepared by mass using nanopure water (resistivity > 18 MΩ cm).

The concentrations of the CuCl<sub>2</sub>, LiCl, and HCl stock solutions used to prepare the final CuCl<sub>2</sub>–HCl–LiCl solutions were determined by titration against standard Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, AgNO<sub>3</sub>, and NaOH solutions, respectively [18,19]. All titrations were done by mass. The molality of the Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution was determined by titration against a primary standard KIO<sub>3</sub> solution using the starch indicator. AgNO<sub>3</sub> solution was standardized against a primary standard NaCl solution using a K<sub>2</sub>CrO<sub>4</sub> indicator. The NaCl salt was dried for at least 48 h at 393 K before preparing the solution. The molality of the HCl stock solution was determined by titration against a secondary standard NaOH(aq) solution that was previously standardized by titration against a primary standard, potassium hydrogen phthalate (Fisher-Scientific), which was dried for at least 48 h at 393 K before preparing the solution. The acid-base titrations were done by mass using a Metrohm794 basic Titrino titrator.

LiCl–HCl solutions with chloride concentrations from ~0 to 15 mol kg<sup>-1</sup> were prepared by mass from standard LiCl and HCl solutions and with deionized nanopure water. Each solution was divided in two parts. CuCl<sub>2</sub>–HCl stock solution was added to one of the fractions to obtain a total copper concentration of ~10<sup>-4</sup> mol kg<sup>-1</sup> while the other without copper was used to run the baseline experiments.

### 2.2. Experimental measurements

UV-visible spectra were measured in a high-temperature, high-pressure titanium cell with sapphire windows (1.72 cm optical path length; 0.34 cm<sup>3</sup> volume) described by Trevani et al. [16]. The sample injection system was modified to allow the automatic injection of the solutions (see Fig. 1). The current design is based on a system developed by Mendez de Leo and Wood [20] for high-temperature and high-pressure conductance measurements. In our system, the only materials in contact with the solutions were PEEK (polyaryletheretherketone), PTFE (polytetrafluoroethylene), titanium (Grade 2), sapphire, and Pyrex glass. In this system, the low-pressure peristaltic pump was used to fill the sample loop through a low-pressure 12 port valve connected by PTFE tubing to 12 different glass bottles containing the solutions. A high-performance liquid chromatography pump (HPLC Gilson 305) was used to inject the solutions contained in the sample injection loop into the cell (low rate ~0.5 cm<sup>3</sup> min<sup>-1</sup>). A high-pressure 6 port valve allowed the operator to select deionized water or the solution in the injection loop (copper chloride or baseline solution). In our design and because of the temperature range, the solutions were not pressurized before injecting them into the system. The second high-pressure 6 port valve

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