EUROPEAN SYNCHROTRON RADIATION FACILITY

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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Speciation control in thermochromic cobalt and nickel complexes and their effect on electrodepostion in Deep Eutectic Solvents	**Experiment number**: CH 4855
Beamline: BM25A	**Date of experiment**: from: 26.01.2017 to: 31.01.2017	**Date of report**:
Shifts: 15	**Local contact(s)**: Eduardo Salas-Colera	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

EXAFS spectra were acquired for nickel and cobalt salts dissolved in either Ethaline or Reline (1:2 molar mixtures of choline chloride, with ethylene glycol or urea, respectively). Spectra of nickel and cobalt metal foils were used for reference purposes.

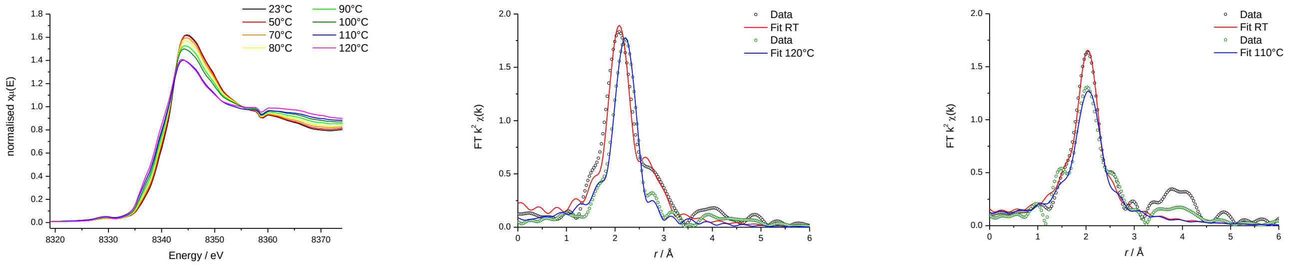
All heated samples were measured in transmission mode only, due to the window dimensions of the heated cell, and carried out between room temperature and 120°C. Data for the nickel samples was generally very good, except for glitches at approximately 8359, 8440, 8681, 8746 and 9003 eV. Data for the cobalt samples was generally noisier, but still of reasonable quality.

Samples of nickel chloride in Ethaline containing various amounts of the additives ethylenediamine, boric acid and dimethyl hydantoin were measured. Speciation changes were only observed for the ethylenediamine solutions, despite observed colour changes (all shades of green) with the other additives. At the moment this observation is incosistent with the EXAFS data and cannot be explained yet. Variation of temperature with the ethylenediamine samples indicated a slight speciation change with 1 molar equivalent, but less with 2-3 equivalents. This would suggest that ethylenediamine coordinates more strongly than chloride, even at higher temperatures.

Metal-ligand distances were calculated to be 2.09 Å for Ni-O, 2.9 Å for Ni-C, and 2.3 Å for Ni-Cl and Co-Cl, which is consistent with both the solid reference samples and previous experimental data. Path lengths for Ni-N are closer to 2.1 to 2.2 Å. As the temperature of the nickel solutions was increased, a corresponding change in the speciation was observed, from 6xO to 4xCl per Ni atom – similar speciation to that of nickel chloride in [C6mim][Cl] at room temperature.

For the nickel samples, the change in speciation determined by EXAFS is consistent with the UV-vis data discussed in the proposal. A major change in coordination number is observed around 90-100°C, where a predominantly octahedral complex turns to predominantly tetrahedral. Bond lengths also become slightly shorter with this structural change. It was observed that the thermochromic reaction was not fully complete at 120°C for the solution of nickel sulphate in Ethaline. Linear combination fitting of the XANES spectra suggests this solution would require 130-140°C to fully complete the transition. The signal at approx. 3-4 Å in the Reline samples is most likely due to multiple scattering from coordination to the urea. At higher temperatures, this peak decreases in intensity, possibly due change in coordination as the urea decomposes.

Cobalt chloride in Ethaline displays a coordination of 4xCl for at all temperatures studied. The addition of ethylenediamine produces complex spectra, which we are still analysing.



XANES of $NiCl_2 \cdot 6H_2O$ in Ethaline (left), and Fourier transforms of the EXAFS data (circles) and fits (line) for $NiCl_2 \cdot 6H_2O$ in Ethaline (middle) and Reline (right).

We attempted to measure the EXAFS of leaching solutions of copper(I)- and copper(II)-sulphide ores in Ethaline. The data we obtained were good, despite the relatively low solute concentrations, compared to the main nickel and cobalt samples. Unfortunately, one of the computers at the beamline broke down, preventing us from fully utilising our beamtime (approx. 12 hrs lost).

These results have allowed us to determine how the speciation of nickel changes with temperature in two different deep eutectic solvents. Combined with other techniques, the presence of intermediate species is anticipated, instead of a simple transition from one species to the next. Cobalt chloride does not display speciation change with temperature, indicating that any change in redox behaviour is related to other factors.

The results will complement our fundamental studies on speciation origins of electrochemical behaviour and contribute to the development of novel electroplating electrolytes.