



Experiment title:
Cu, Ni and Cr Speciation in Deep Eutectic Solvents

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CH-2984

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Report:

EXAFS spectra were acquired for nickel salts in the deep eutectic solvents ethaline (ethylene glycol and choline chloride) and reline (urea and choline chloride) as well as solid reference samples. The chloride samples were also measured with added complexing agents (ethylene diamine and EDTA).

Spectra of copper chlorides were recorded in ethaline and reline as well as solid reference samples.

EXAFS for the type 3 eutectic solvent chromline ($\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$ and choline chloride) has been obtained including different pre-treatments of the liquid. A solid reference sample was measured.

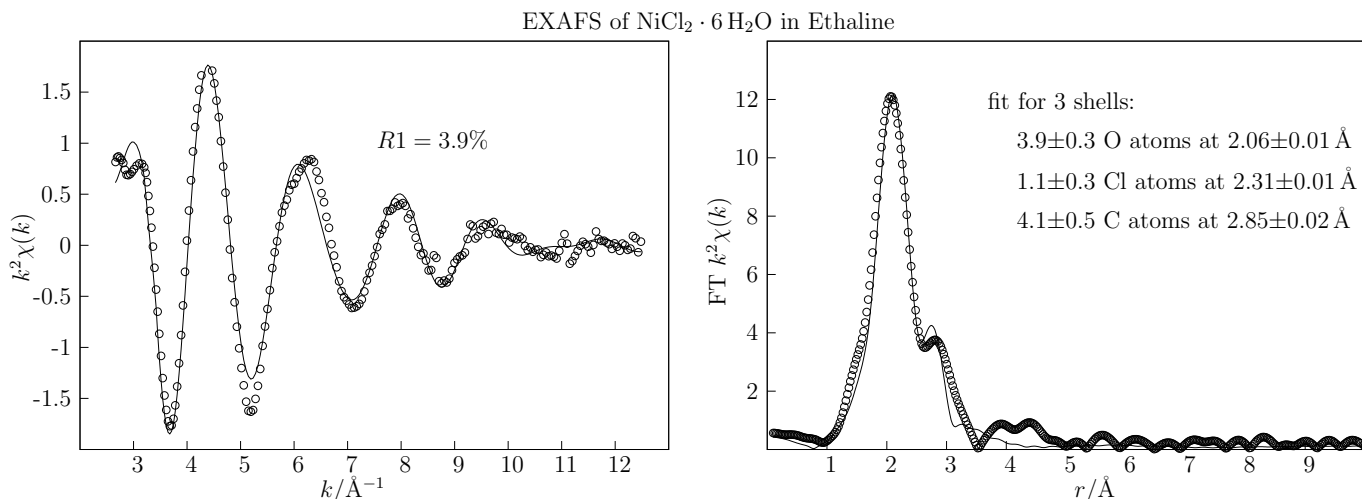
In total EXAFS spectra of 27 samples could be obtained and speciation of the investigated metal complexes could be determined from most of these spectra. Liquid samples were investigated using fluorescence detection. Solid samples were diluted in BN matrix and recorded in transmission mode.

We can clearly distinguish between chloride based coordination and coordination with lighter atoms as well as mixed coordination using scattering factors and bond-length analysis. Metal-ligand distances are 1.9 to 2.1 Å for O and N and 2.2 to 2.5 Å for Cl. This is consistent with the solid references. Chelate ligands like ethylene diamine could clearly be identified by a second peak in the fourier transform originating from the C atoms at distances of 2.8 to 3.0 Å. For Ni and Cu there seems to be a slight edge shift depending on the donor strength of the ligand (i.e. effective oxidation state of the metal). A systematic study with more accurate data of the edge region could be beneficial for future experiments.

We found that Cu(II)-chloride and Cu(II)-chloride-dihydrate both exhibit pure chloride coordination (CN=4) in Ethaline whilst some of the hydrate water remains in the first coordination shell in Reline. This is consistent with the empirical experience that Ethaline has the higher chloride activity.

Experiments with various Ni salts in the same solvents showed that anions from the salt were found in the first coordination shell for OAc^- and NO_3^- . Ethylene diamine forms a 4-coordinated complex with Ni over a range of en concentrations.

It was commonly held belief that in Deep Eutectic Solvents the hydrogen bond donor (ethylene glycol or urea) binds only to chloride. Metal ions would be coordinated by either chloride, water or the anion from the dissolved metal salt. Suprisingly, $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$ in Ethaline exhibits the typical peak for chelate ligands, indicating that ethylene glycol binds to the metal in these samples. Reline samples also show a broad peak between 3.0 and 4.5 Å which could originate from urea being part of the first coordination shell. This opens a new perspective on the current development of type 4 eutectic solvents consisting only of a metal salt and a hydrogen bond donor.



EXAFS for chromline has been obtained including different pre-treatments of the liquid. Spectra show mixed Cl/O coordination depending on the amount of water added, confirming that addition of water has indeed an effect of Cr speciation. A second group of peaks between 400 and 600 pm indicates that some of the ligand may be bridging two Cr atoms but these could not be refined reasonably. There is no significant difference between heated and non-heated samples within the limitations of the measurement. The quality of the data is probably affected by self-absorption. Since the liquid cannot be diluted without possible changes in speciation, we are planning to construct a thin cell (1-10 microns) to measure in transmission mode for further experiments.