

Chapter 7

Summary

A new liquid setup has been build which allows us to investigate solid and liquid samples with soft x-rays regime at atmospheric pressure. Two techniques can be applied using this setup, namely NEXAFS and EXAFS. The experiments carried out include the study of the behavior of ions in solution as a function of concentration, solvent, and pH. Alkaline earth metals in aqueous solution have been investigated using NEXAFS, and have been modeled theoretically using the DFT technique (StoBe DeMon package). A clear evidence for direct ion-pairing between the cations and the anions has been observed at high concentration, which is decreasing upon decreasing concentration. Replacing water by ethanol in a 1 M NaI electrolyte solution, the ion-pairing is sterically hindered by the solvent molecules. As a third parameter, which can affect the ion interaction in solution, the pH of the solvent is investigated. Varying the pH between 1 and 11, does not show no significant effect on the white line intensity of the sodium K-edge. In contrast, going to pH = 13, a significant decrease of the white line is observed and gives evidence for an interaction of more than one OH^- ion with one Na^+ ion. Quantitatively, the experiment shows that there are approximately 2.4 Na^+ interacting with one OH^- . Molecular dynamic studies of the same system support our observations and suggest the existence of extended clusters between the Na^+ and the OH^- .

The investigations were extended to transition metal ions in solution, in particular Ni^{2+} . Simulating the NEXAFS L-edge of open shell transition metal is not possible by the one electron picture DFT technique. For this, a Multiplet approach has been used. Direct ion interaction in this system generates a clear charge transfer peak in the NEXAFS spectra, which appears only in the hydrated powder, and disappears upon dissolving the powder in water. Upon diluting the $NiCl_2$ solution, a systematic change of the triplet state relative

to the singlet ones is observed and reproduced in multiplet calculations. The reason for this is the existence of another kind of interaction between the ions in solution, known as a solvent-shared ion pair. Their existence decrease upon diluting the $NiCl_2$ solution from 1 M to 50 mM. We confirmed our NEXAFS observation using the RIXS experiments, and performed EXAFS to obtain direct structure information. The EXAFS results - modeled using the FEFF8 program package - could not support the solvent-shared ion pair argument directly.

Amino acids at different pH were investigated by XPS. We have shown that individual nitrogen and carbon atoms of aqueous lysine can be identified by their respective core-level binding energies. The C1s energies of carbon atoms next to the ammonium moiety are identified by a 0.5–0.3 eV chemical red-shift upon protonation. These experiment observations have been supported by Gaussian simulation for the Lysine molecule. Another study for amino acids in solution combined with ions was carried out using NEXAFS technique. The effect of cysteine and histidine upon complex formation with Zn^{2+} was investigated at the L-edge of Zn^{2+} . Significant differences in the spectra are observed upon complex formation with Hys and Cys. This different behavior is due to the SH group of the Cys, which is absent in His.

In the last part of this study, charge transfer in wet polymer/acceptor system was studied by NEXAFS experimentally, and modeled by DFT simulation. The charge transfer interaction between the acceptor tetrafluoro-tetracyanoquinodimethane (F4TCNQ) and the polymer poly(3-hexylthiophene) (P3HT) turned out to be very strong, leading to significant molecular conformation changes. The charge transfer is rather localized on approximately four repeat units of a single donor polymer chain. The HOMO and LUMO levels of the charge transfer complex (CTC), which are relevant for charge transport, are formed by hybridization of the donor HOMO and the acceptor LUMO, and due to the finite energy gap the complex is non-metallic. Most notably, only one specific CTC conformation predominates, where F4TCNQ is strongly bent out of its neutral planar form due to pronounced electron donation from P3HT chain segments. These results have been supported by conductivity measurements, where high conductivity is observed upon formation of a charge transfer complex. Currently we are investigating different polymers and follow the charge transfer complex formation; furthermore complement our findings by modeling the system with different theoretical packages.

Recently, the possibility to carry out soft x-ray spectroscopy for wet samples

or even liquids attracted many research groups to BESSY for a variety of applications. A new line of experiments has been started recently in the LIQUIDROM setup were a group of Uppsala university in collaboration with us investigating the behavior of gel materials in collaboration with us. To further expand the options given by the LIQUIDROM, a stop-flow cell will be implemented. This will open the way to new research areas in chemistry and applied sciences. An additional extension of the setup will enable time resolved measurements, where we plan to apply pump-probe techniques to the liquid using a laser as a pumping source and synchrotron as a probing source. This application is in part motivated by future use in free electron laser facilities (FEL).

