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EXAFS-STUDY OF THE Zn^{2+} COORDINATION IN AQUEOUS HALIDE SOLUTIONS

P. DREIER and P. RABE*

*Institut für Experimentalphysik, Universität Kiel,
Olshausenstrasse 40, D-2300 Kiel 1, F.R.G.*

**Fachhochschule Ostfriesland, Fachbereich
Naturwissenschaftliche Technik, Constantiaplatz 4,
D-2970 Emden, F.R.G.*

Abstract

Aqueous solutions of $ZnCl_2$, $ZnBr_2$ and ZnI_2 in the concentration range from 0.1 molal up to saturation have been studied by EXAFS experiments at the zinc K-edge. EXAFS spectra of the crystalline compounds of $ZnCl_2$, $ZnBr_2$, ZnI_2 and $ZnSO_4 \cdot 7H_2O$ have been used as references. In the low concentration range up to 0.5 molal a complete hydration of the zinc ions by 6 - 7 water molecules is observed. At high concentrations above 5 molal the mean local coordination around the zinc ions consists of halide ions and water molecules.

The structure of electrolytic solutions at high concentrations and especially the behaviour of the metal ion between ionic hydration (e.g. $SrCl_2$) and formation of anionic complexes (e.g. $ZnCl_2$, $CdCl_2$) has received considerable interest (1). Coordination numbers play a dominant role in the interpretation of the structural data but their determination in an EXAFS-analysis demands reliable reference data. So we started our analysis with a measurement of EXAFS-spectra from crystalline zinc halides.

The absorption experiments have been performed with a focussing monochromator (2) using a rotating anode x-ray generator. The measurement of the reference spectra of crystalline $ZnCl_2$, $ZnBr_2$ and ZnI_2 is made difficult by the very hygroscopic nature of these compounds. The fact that four anhydrous modifications and (below 40°C) at least five modifications of hydrates of $ZnCl_2$ exist, requires a clear identification of the reference compound. We have constructed a special sample cell for sample preparation, characterization and subsequent absorption experiments. The samples are prepared by the crystallization of a thin film of the aqueous solution on polyimide foil. The sample cell is provided with windows to enable diffraction experiments in reflection geometry in the angular range $0^\circ < 2\theta < 120^\circ$. The diffraction spectra have been compared to spectra calculated from the known crystal structure of the anhydrous zinc halides (3), (4), (5). By variation of the growth parameters homogeneous films of anhydrous $ZnCl_2$, $ZnBr_2$ and ZnI_2 could be produced. In these compounds the zinc atoms are surrounded tetrahedrally by 4 halide atoms. After the characterization the absorp-

tion experiments have been performed using another pair of windows in the sample cell. As reference spectrum for the Zn-H₂O coordination a spectrum of crystalline ZnSO₄*7H₂O was used. In this compound zinc is surrounded by 6 H₂O molecules.

The fine structures of the crystalline reference compounds ZnCl₂, ZnBr₂, ZnI₂ and ZnSO₄*7H₂O are shown in fig. 1. The spectrum of ZnCl₂ shows a

single oscillation with a monotonically falling envelope produced by the four chlorine neighbours of the zinc atoms.

The spectrum of ZnBr₂ shows an oscillation with a maximum in the envelope at $\sim 6\text{\AA}^{-1}$

typically for medium sized backscatterers as bromine.

The absorption spectrum of ZnI₂ has a poorer quality due to the high background absorption of iodine and the low amplitude of the oscillation at $k > 5\text{\AA}^{-1}$.

The structure at 9\AA^{-1} originates from the characteristic WLB₂ line in the emission spectrum of the x-ray generator. So this reference spectrum can only be used up to 9\AA^{-1} .

The reference spectrum of ZnSO₄*7H₂O shows the contribution of several shells with light backscatterers. The scattering phases and the backscatterer amplitudes have been extracted by the Fouriertransform - backtransform method (6). These data are used in the analysis of the absorption spectra of the aqueous solutions.

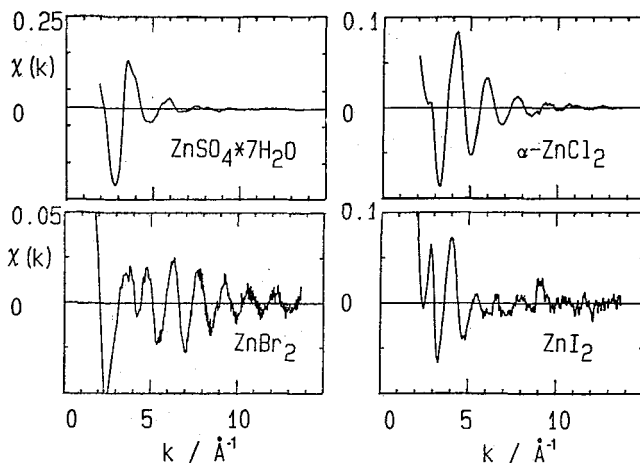


Fig. 1 EXAFS-spectra of the crystalline reference compounds.

Fig. 2a shows the k-weighted fine structures of the absorption spectra of the aqueous ZnBr₂-solutions. For comparison the reference spectra for the Zn-Br coordination and the Zn-H₂O coordination are included. At the concentration 0.1 m the fine structure is very similar to the Zn-O reference spectrum. This indicates that at low concentrations the zinc ion is coordinated by water molecules.

At the highest concentration (20 m) the spectrum in the large wavenumber range ($> 6\text{\AA}^{-1}$) is similar to the Zn-Br reference spectrum with a smaller amplitude. In the low wavenumber part ($< 6\text{\AA}^{-1}$) it resembles the Zn-O reference spectrum. This comparison shows that at high concentrations the zinc ions are surrounded by bromine ions and water molecules. The other spectra show how the fine structure gradually changes with concentration. The k-weighted EXAFS-spectra of the ZnI₂ solution are displayed in fig. 2b. As in the case of the ZnBr₂ solutions the spectrum of the dilute solution points to a water-like environment of the zinc ions. With increasing concentration details of the Zn-I reference spectrum appear in the fine structure of the solutions indicating a mixed coordination of the zinc ions with water molecules and iodine ions. In the case of the ZnCl₂ spectra (fig. 2c) the concentration dependence is not so pronounced. This is due to the small difference between the Zn-Cl and the Zn-H₂O reference spectra. Nevertheless a characteristic indication of a change in the environment of the zinc ions is the shift of the first peak from 3.8\AA^{-1} in the 0.1 m solution to 4.1\AA^{-1} in the 30 m solution. For a numerical evaluation the spectra have

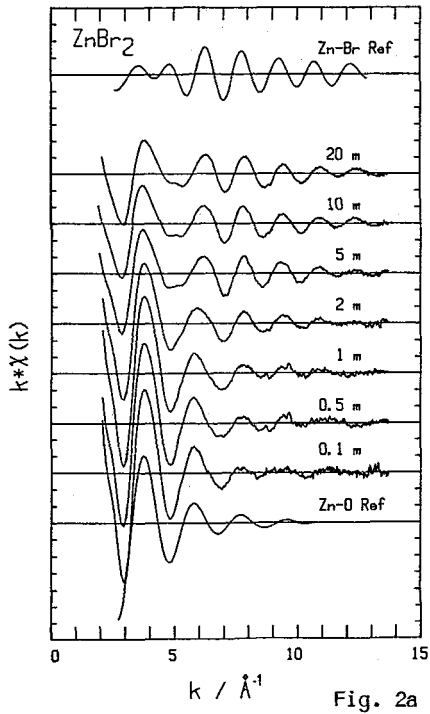


Fig. 2a

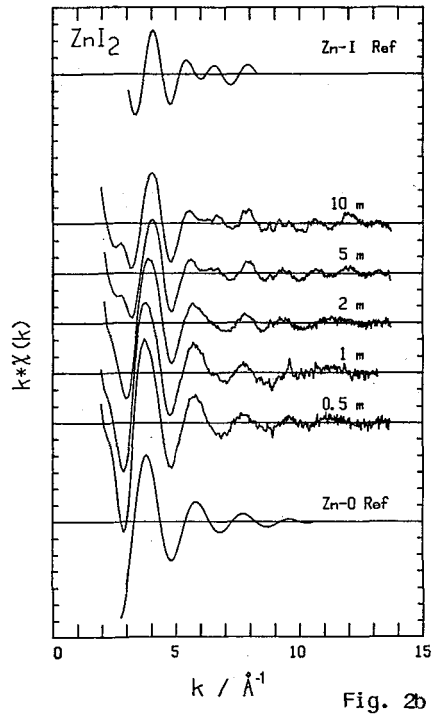


Fig. 2b

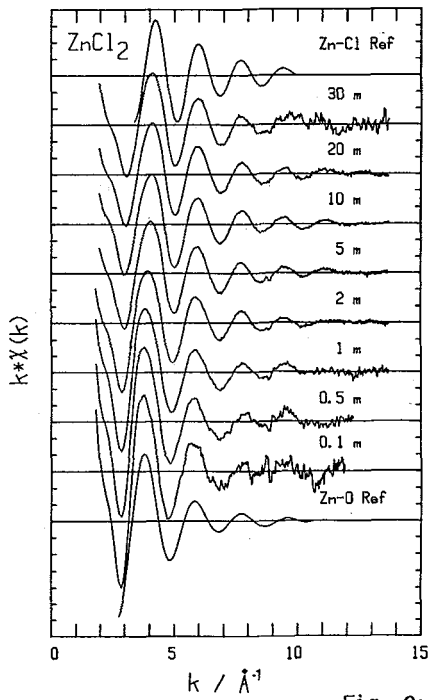


Fig. 2c

Fig. 2 EXAFS spectra of aqueous solutions of ZnCl_2 , ZnBr_2 and ZnI_2 . Fourier-filtered reference spectra are included for comparison.

been Fouriertransformed. The first coordination shells due to water and halides are too close to each other to be separated in real space, so that they are commonly backtransformed. A least-squares fit procedure using the phase shifts and the backscattering amplitudes from the reference spectra enables the determination of structural parameters. The parameters used in the fit procedure were the coordination numbers N , the interatomic distances r , the Debye-Waller factors and a shift ΔE_0 in the zero of the k -scale. Values of ΔE_0 were very small, typically a few eV. At the concentrations 0.5 m and 0.1 m the contribution of the zinc-halide coordination is too weak to be analysed and one shell was sufficient for a good fit. The results of the fits for r and N are shown in tab. 1.

	$ZnCl_2$				$ZnBr_2$				ZnI_2			
	N_o	r_o	N_{Cl}	r_{Cl}	N_o	r_o	N_{Br}	r_{Br}	N_o	r_o	N_I	r_I
30m	2.0	1.99	2.5	2.31	--	--	--	--	--	--	--	--
20m	2.5	2.01	2.6	2.34	2.4	2.00	1.9	2.38	--	--	--	--
10m	3.2	2.03	2.4	2.30	3.1	2.03	1.9	2.38	2.7	2.02	3.2	2.59
5m	2.8	2.02	2.2	2.32	3.2	2.05	2.0	2.38	3.1	2.02	2.9	2.61
2m	4.2	2.03	1.6	2.31	4.3	2.05	1.4	2.38	6.4	2.03	1.0	2.65
1m	4.9	2.02	0.9	2.34	5.9	2.06	0.3	2.38	6.4	2.05	0.5	2.65
0.5m	5.7	2.05	--	--	6.3	2.05	--	--	7.4	2.05	--	--
0.1m	7.1	2.07	--	--	7.0	2.05	--	--	--	--	--	--
Ref	6	2.03	4	2.30	6	2.03	4	2.41	6	2.03	4	2.62

Tab.1 Structural parameters of the aqueous zinc halide solutions determined by a two shell fit. N_o , N_{Cl} , N_{Br} , N_I : number of water molecules, chlorine, bromine and iodine ions in the zinc environment. r_o , r_{Cl} , r_{Br} , r_I : Distance from zinc ions to water, chlorine, bromine and iodine neighbours (in Angstroms).

The most interesting result of the analysis is the concentration dependence of the coordination numbers which appears in all solutions in a similar manner. In the high concentration range the zinc ions are surrounded by 2-3 halide ions and 2-3 water molecules. In the range from 5 m to 0.5 m the halide ions disappear from the zinc environment and the number of water molecules rises to about 7. The change of the zinc coordination takes place in a concentration range where 1-2 hydration shells can be built up around each ion. In all solutions the Zn-H₂O distance enlarges with falling concentration. Zn-Cl distance and Zn-Br distance do not vary systematically with concentration whereas the Zn-I distance tends to increase at low concentration. It should be emphasized that the distances in the solution do not differ strongly from the corresponding distances in the crystalline reference compounds.

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