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Structure of zirconium complexes in aqueous solutions

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Two types of zirconium(IV) complexes with the different Zr–Zr distances were detected by EXAFS in the aqueous solutions of $ZrOCl_2 \cdot 8H_2O$, $ZrO(NO_3)_2 \cdot 2H_2O$ and $Zr(SO_4)_2 \cdot 4H_2O$ salts.

Zirconium oxides are traditionally prepared starting from the solutions of zirconium salts, which contain various polynuclear complexes. The composition and properties of the precipitate can be controlled by varying the composition of solutions.[1,2]

Zirconium oxychloride solutions were studied using various spectroscopic techniques.[3–9] It was found that, in such solutions, zirconium occurs as complexes structurally similar to the base unit of crystalline zirconium oxychloride.[10–13] The complex exhibits the structure of a slightly distorted square with zirconium atoms arranged at its corners (Zr–Zr_1 is 3.6 Å; Zr–Zr_2 is 5.1 Å) and with the distances Zr–OH of 2.14, 2.22 and 2.35 Å and Zr–OH_2 of 2.09, 2.13 and 2.37 Å. The tetrameric complexes form larger polynuclear complexes in the course of ageing.[7,11] Unfortunately, the structure of both tetrameric and polynuclear complexes is still not clearly understood. However, it was well established that eight oxygen atoms are coordinated to a zirconium atom, and the interatomic distances range from 2.1 to 2.24 Å. We believe that the solutions of $ZrOCl_2 \cdot 8H_2O$, $ZrO(NO_3)_2 \cdot 2H_2O$ and $Zr(SO_4)_2 \cdot 4H_2O$ also contain polynuclear complexes.

In this work, we studied aqueous solutions of zirconium salts by EXAFS. The 0.5 M solutions were prepared using chemically pure $ZrOCl_2 \cdot 8H_2O$ and $ZrO(NO_3)_2 \cdot 2H_2O$ salts and $Zr(SO_4)_2 \cdot 4H_2O$ crystallised from a concentrated sulfuric acid solution according to the published procedure.[14] In addition, we also studied zirconium oxychloride solutions aged at room temperature for 12 months.

The X-ray absorption spectra at the zirconium K-edge were measured according to the standard method[15] at the EXAFS Station of the Siberian Synchrotron Radiation Centre (Novosibirsk). For this purpose, the sample thickness was chosen to obtain $\Delta\mu x = 0.8$ for zirconium.

For all samples, the oscillating parts of absorption spectra $[\chi(k)]$ were analysed as $k^3\chi(k)$ in the wavenumber range $k = 3–16$ Å^{-1}. The VIPER[16] and EXCURV92[17] programs were used for data processing.

Figure 1 shows the radial distribution functions obtained from the EXAFS spectra of the initial solutions by Fourier transform. Table 1 summarises the calculated structural data. In all samples, the measured average Zr–O distance is close to 2.2 Å, a typical average distance for the oxygen environment of zirconium. We observed two pairs of Zr–Zr distances: 3.6 and 5.1 Å and 3.3 and 4.7 Å. Upon ageing of the chloride solution, the intensity ratio at the distances 3.3 and 3.6 Å changed from 1:3 to 1:1.

Because interatomic distances in all complexes are similar, it is believed that their structure is similar to that of the zirconium oxychloride solution; that is, all complexes are tetramers with the structure described above. The presence of two sets of Zr–Zr distances (3.3 and 4.7 Å and 3.6 and 5.1 Å) and the change in the peak intensity ratio with changing the anion or ageing the solution suggest the presence of two different zirconium tetramers with the above Zr–Zr distances. For both complexes, a Zr–Zr distance is greater than the other distance by about $2^{1/2}$; this fact suggests that the above complexes exhibit a square-planar configuration. The Zr–Zr distances equal to 3.6 and 5.1 Å are typical of zirconium hydroxide, cubic zirconium oxide and the majority of basic zirconium(IV) salts, including solid zirconium oxychloride.

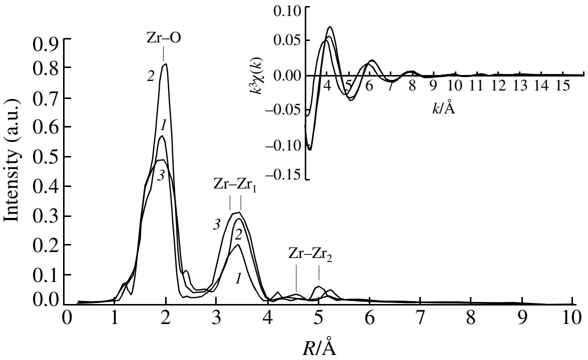

Figure 1 Radial distribution functions obtained from the EXAFS spectra of the solutions of (*1*) zirconium oxynitrate, (*2*) zirconium oxychloride and (*3*) zirconium sulfate. Inset: the oscillating part of the absorption coefficient $\chi(k)$ for $k = 3–16$ Å^{-1}.

Previously,[7] it was found by SAXS that complexes may contain different numbers of chloride ions in their structure and hence exhibit different ionic charges. A change in the ionic charge can be responsible for a change in the Zr–Zr distance. We believe that the occurrence of two pairs of interatomic distances in the test solutions of zirconium sulfate, oxychloride and oxynitrate is also associated with the different numbers of anions coordinated to the square-planar framework of zirconium cations. It is likely that the Zr–Zr distance changes on varying the charge of the complex ion, which is determined by the number of coordinated anions and weakly depends on the nature of anions. This distance is equal to 3.38 Å in $ZrO(NO_3)_2 \cdot 2H_2O$ or $ZrOCl_2 \cdot 8H_2O$, whereas it is 3.25 Å in the case of $Zr(SO_4)_2 \cdot 4H_2O$. The reason for this difference will be studied later on.

Table 1 Structure of the local environment of zirconium according to EXAFS.

Sample	Distance/Å		Coordination number	Debye–Waller factor/Å^2
$ZrO(NO_3)_2$	Zr–O	2.189	4.1	0.009
	Zr–Zr	3.377	0.3	0.002
		3.627	0.3	0.005
		4.590	1.4	0.028
		5.176	0.9	0.018
$ZrOCl_2$	Zr–O	2.172	6.1	0.011
	Zr–Zr	3.373	0.2	0.002
		3.649	0.6	0.006
		4.769	0.4	0.022
		5.220	1.0	0.017
$ZrOCl_2$[a]	Zr–O	2.151	5.9	0.007
	Zr–Zr	3.325	1.4	0.010
		3.568	1.7	0.013
		4.710	1.2	0.019
		5.108	0.9	0.011
$Zr(SO_4)_2$	Zr–O	2.222	5.3	0.015
	Zr–Zr	3.251	1.1	0.016
		3.607	1.6	0.012
		4.653	0.5	0.010
		5.112	0.7	0.011

[a] The solution was aged for 12 months at room temperature.

Thus, the complexes formed in the aqueous solutions of zirconium oxychloride, zirconium oxynitrate and zirconium sulfate are structurally similar. They exhibit a square-planar configuration of zirconium ions. Two types of zirconium complexes different in the Zr–Zr distance were detected in aqueous solutions. We believe that the difference in complex structures is associated with different numbers of anions entering the complex and, consequently, with the difference in the charge of the complex.

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