

Investigation of Zr(IV)-hydroxide Solubility with LIBD and EXAFS

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Zr(IV) gained increasing attention in recent literature as homologue of Pu(IV), due to its similar hydrolysis and colloid formation [1, 2]. In addition, Zr is an important material in reactor technology and a fission product of high yield and long lifetime (⁹³Zr). In the present work, the solubility of Zr(OH)₄(am) in 0.5M HCl/NaCl solution is determined. Conventionally, solubility data is obtained by measuring the equilibrium amount of solvated species in the presence of a precipitate starting from undersaturation. In the present case, a different approach is chosen, similar to a previous study with Th(IV) [3]. In the acidic range, the "Zr(OH)₄(am)"-solubility decreases with increasing *pH*. As the *pH* is increased, eventually the solubility limit is exceeded and some fraction of the Zr will precipitate. However, precipitation is difficult to observe at low concentration. Prior to precipitation, oligomers or colloids form in the solution which remain suspended by Brownian motion due to their small size (10-100nm) and serve as a very sensitive indicator of exceeding the solubility limit. They are detected by laser induced breakdown detection (LIBD) [4, 5]. From a concentrated stock solution ([Zr] = 5 · 10⁻³ M in 0.5 M HCl), 12 starting solutions are prepared below the solubility limit at Zr concentrations between 10⁻³ M and 2.5 · 10⁻⁸ M, at 1 < *pH* < 3, at constant ionic strength I=0.5 M (addition of NaCl). *pH* is increased very slowly by coulometric titration. Current control of the CT, *pH* detection and LIBD measurements are fully automated and operated remote-controlled continuously up to several weeks for one series. The *pH* is increased by predefined steps (≤ 0.1 *pH* units). After each step the current is turned off, and after a 30 minute equilibration time, the LIBD measurement is performed and the colloid size distribution is obtained [6]. After the LIBD measurement has finished, the current is switched on again and the *pH* is increased further. Close to the expected solubility limit, the *pH* is increased even more slowly by reducing the electric current down to 10 μA (~ 3 · 10⁻⁹ mol OH⁻s⁻¹). The onset of colloid formation is depicted in Figure 1 (▲).

In order to calculate the solubility product, hydrolysis has to be taken into account. The first hydrolysis constant for the complex ZrOH³⁺ is taken from potentiometric studies [7] and the other formation constants of Zr(OH)_n⁽⁴⁻ⁿ⁾⁺ (n = 2–6) are estimated by using the semi-empirical ligand repulsion model [8]. Based on the assumption of colloid formation from mononuclear species, which is most likely valid for low concentrations, the calculated solubility product, logK_{sp}^o, is 52.9 ± 0.6. The data of the present work is in qualitative agreement with a similar method using light scattering for detection (○ from [1]). Deviations at low concentration are due to the low sensitivity of light scattering, as the authors state themselves. The data of Kovalenko

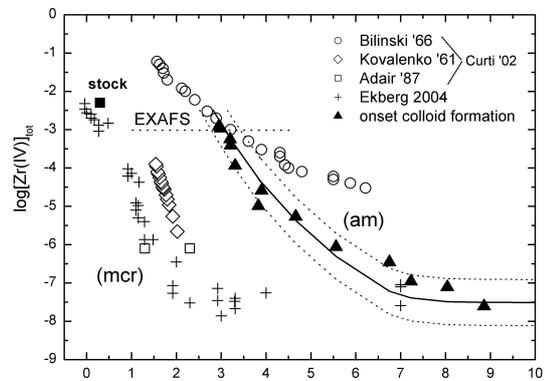


Figure 1: Solubility data for Zr(IV). Present work (▲) and a similar method using light scattering (○) refer to amorphous hydroxide. The data at low *pH* most likely refer to a microcrystalline phase (mcr)

(◇, from [1]) and Ekberg (+) [2] deviate by six orders of magnitude and seem to refer to microcrystalline ZrO₂ and not to amorphous hydroxide.

The most concentrated solution ([Zr] = 1 · 10⁻³ M) is studied by EXAFS in order to characterize polynuclear species and the structure of the colloids. Polynuclear Zr-species were reported earlier in the literature [9, 10] and confirmed at high concentrations ([Zr] = 1 · 10⁻² M) by strong Zr-Zr interactions even at very acidic conditions *pH* = 0.3. At [Zr] = 1 · 10⁻³ M no Zr-Zr interaction is found for *pH* < 2. As the solubility limit is approached close to *pH* 3, oligomers form. Colloids which form at higher *pH* are observed to have a higher disorder in their Zr-O coordination shell. The long term stability of these colloids and their agglomeration are also investigated with LIBD and a "single particle counter".

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