Application of LIBD to the determination of the solubility product of thorium(IV)-colloids

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Summary. A new experimental method is presented for the determination of solubility data, which is based on the laser-induced breakdown detection (LIBD). The method is capable of monitoring the initial colloid generation when the metal ion concentration reaches or just exceeds the solubility at given pH. The application is made to determine the solubility of Th(IV) in acidic solutions at $I = 0.5$ M (NaCl) and 25 °C. The initial colloid formation is determined as a function the H^+ concentration in a series of 2.8×10^{-2}–8.9×10^{-5} M thorium solutions. The conditional solubility product ($\log K'_{sp} = -49.54 \pm 0.22$) obtained in this study corresponds to an equilibrium between solution and colloidal thorium dioxide particles. The solubility product at $I = 0$ ($\log K°_{sp} = -52.8 \pm 0.3$) is calculated with the SIT coefficients of the NEA-TDB. It corresponds to the known value for crystalline $ThO_2(cr)$, in particular if the small particle size of about 20 nm is taken into account. The present results indicate that the high thorium solubilities measured in the previous studies for amorphous Th(IV) hydroxide or hydrous oxide are primarily caused by the inclusion of polynuclear species or Th(IV) colloids of very small size.

1. Introduction

The laser induced breakdown detection (LIBD) is a very sensitive method for the detection of small colloids down to a diameter of 1 nm [1, 2]. For colloids smaller than 50 nm in diameter, the detection limit is found to be in the lower ppt-concentration range [2]. This makes the method specially suitable to monitor the actinide colloid formation by hydrolysis and polynucleation. As discussed in the previous paper on the solubility of Pu(IV) [3], the initial incitement of colloid formation provides the possibility to determine the solubility. The formation of colloids indicates that the An(IV) concentration exceeds the solubility limit at given pH. Small colloids of diameter < 20 nm thus formed do not undergo precipitation but remain in solution as colloidal dispersion. The applicability of LIBD to investigate the generation of Th(IV) colloids by increasing pH of acidic thorium solutions has been tested previously [4, 5].

The aim of the present study is to determine the solubility product of $ThO_2 \cdot x\,H_2O$ colloids. For this purpose the thorium concentration in acidic solutions is varied in a wide range and pH is increased in small steps. In order to avoid local oversaturation during titration, pH is increased coulometrically. The initial incitement of colloid formation at given pH and Th(IV) concentration is considered as the solubility of small $ThO_2 \cdot x\,H_2O$ particles of given size. When the results are compared to the solubility of bulk $ThO_2 \cdot x\,H_2O(s)$ the effect of particle size must be taken into account.

2. Experimental

2.1 Experimental setup of LIBD

The experimental setup of LIBD is schematically illustrated in Fig. 1. A pulsed Nd-YAG laser (Continuum; Surelite I) is used with frequency doubled at $\lambda_{em.} = 532$ nm and a repetition rate of 20 Hz. After passing through a variable attenuator, the laser beam is focused by a plano-convex lens of 50 mm focal length into the sample dispersion in a rectangular flow through cuvette (Vol. 3 ml). The incident laser pulse energy is monitored by a pyroelectric detector and adjusted below the breakdown threshold of ultra pure water (Milli-Q-academic). The breakdown induced acoustic wave is measured laterally to the laser beam by a piezo electric detector (PZT) contacted to a sample cell wall. The plasma light emission magnified by a macro-microscope is recorded by a triggered Charge-Coupled-Device Camera. Laser pulse
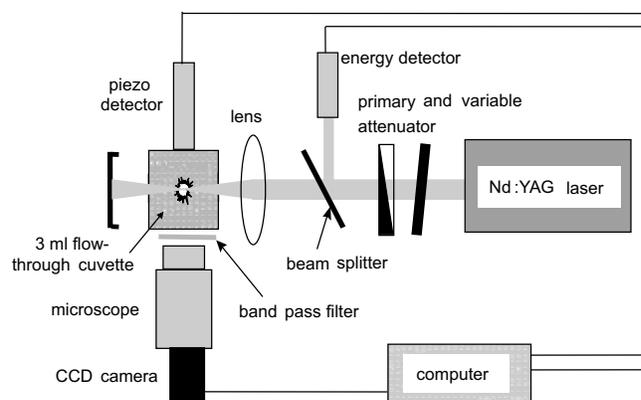

Fig. 1. Experimental setup of LIBD.

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energy and piezo electric signal are digitized and computed by a PC. The processing of data from the Charge-Coupled-Device Camera goes via a frame grabber card by special software. The distribution of 8000 plasma events is measured in the coordinate of the beam direction. The distribution width is correlated to the mean particle size. By calibration of LIBD with polystyrene reference particles, a mean particle diameter and a number density of given colloids can be derived. The particle size distribution cannot be determined with the present equipment.

2.2 Coulometric pH titration

The pH of 2.8×10^{-2}–8.9×10^{-5} M thorium nitrate solutions in 0.5 M HCl/NaCl is increased in small steps until the formation of colloids is detected by LIBD. All experiments are performed in a double walled titration vessel thermostated at 25 °C which is equipped with a Pt-electrode, a salt bridge (filled with 0.5 M NaClO$_4$ solution) as external electrode, a pH electrode, inlet and outlet for the solution. The coulometer shown in Fig. 2 is controlled by a constant current source type Digistan 6706 (Burster Co.) at a current of 0.1–1 mA.

2.3 Chemicals and analytical methods

Th(NO$_3$)$_4$ · 5H$_2$O (p.a.), NaCl (p.a.) and HCl (ultrapure) are purchased from Merck. For further purification, NaCl is re-cristallized twice. The sample solutions are prepared with ultrapure water from a water purification apparatus (Milli-Q-academic, Millipore). Colloid-free thorium solutions are obtained by double filtrations through Amicon 10 KD ultra-filters (pore size about 1 nm). The thorium concentration is determined photometrically by the arsenazo-method [6] and by ICP-AES analysis.

A combined ROSS electrode (Orion Co.) is used for the pH measurement. In order to determine the H$^+$ concentration in 0.5 M NaCl the calibration is made against standard solutions x M HCl/(0.5 − x) M NaCl, with x in the range 0.001 − 0.1. Since the experimental results depend strongly on the accuracy of the measured H$^+$ concentration, the calibration procedure is repeated before and after each experiment. The concentration of log [OH$^-$] is calculated from log [H$^+$] applying the known ion product of water (log $K_W' = -13.73$ in 0.5 M NaCl [7]).
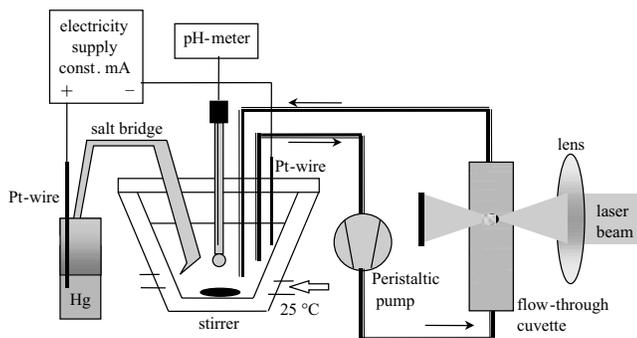

Fig. 2. Experimental setup of the coulometric pH titration cell.

3. Results and discussion

3.1 Detection of ThO$_2$ reference colloids by LIBD

The calibration of LIBD for polystyrene reference colloids in the size range of 19–1072 nm and a developed theoretical model based on binomial statistics are described elsewhere [1, 2]. This model is capable to predict the dependence of breakdown probability on colloid number, size and material. The breakdown probabilities of inorganic reference colloids of different chemical compositions, i.e. alumina, silica and thoriasol are compared to the calibration with polystyrene reference colloids. By calculation according to the previous work [1, 2] the colloid size is normalized to a diameter of 30 nm taking into account the densities of different materials. In Fig. 3. the results of the normalized breakdown probabilities for colloids of different materials are compared as a function of the particle number density. The shift of curves for various colloid materials is due to differences in the dielectric properties of the materials. No difference is observed between thoriasol and polystyrene particles. This ensures that the basis of the LIBD calibration made with polystyrene particles can be directly used for the study of actinide colloid formation caused by hydrolysis and polynucleation.

3.2 Colloid formation and solubility of thorium(IV)

Fig. 4 shows the results of LIBD measurements along with pH titration in 0.5 M HCl/NaCl. Up to a certain pH value, the breakdown probability remains at the constant background value of the initial solution. At pH where the given Th(IV) concentration exceeds the solubility, colloids are formed and the breakdown probability increases sharply. The higher the thorium concentration, the lower is the H$^+$ concentration for the incitement of colloid formation. The results obtained from 7 separate experiments with varying thorium concentration are summarized in Table 1. The mean diameter of the thorium colloids formed in the titration experiments shows no systematic variation and is found to be in the range of 16–23 nm.

The solubility data obtained with Th(IV) colloids as solid phase are compared with the literature solubilities of Th(OH)$_4$(am) and ThO$_2$ · xH$_2$O(s) in solutions of compa-
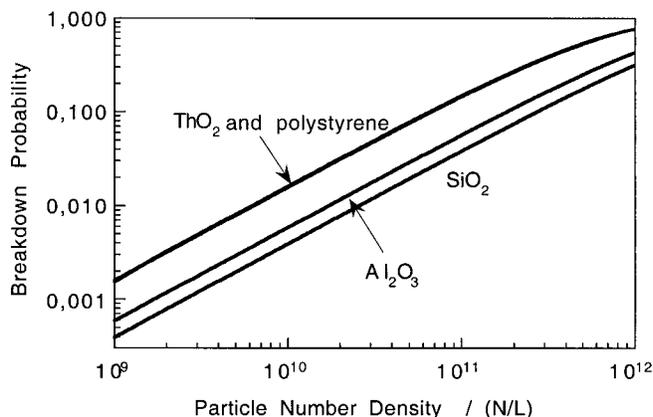

Fig. 3. Calculated breakdown probabilities as a function of the particle number density for different materials, normalized to a particle diameter of 30 nm.
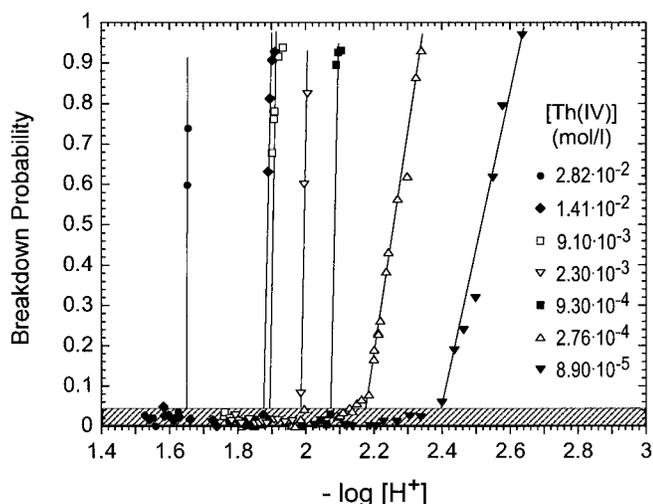
Fig. 4. Breakdown probabilities after background subtraction during the coulometric pH titration of 2.8×10^{-2}–8.9×10^{-5} M Th in 0.5 M HCl/NaCl at 25 °C.

Table 1. The H^+ concentration for the incitement of colloid formation at given Th(IV) concentrations and the solubility product $\log K'_{sp}$ for $ThO_2 \cdot x\,H_2O$ (colloids) (in 0.5 M HCl/NaCl at 25 °C).

$\log [Th(IV)]$	$\log [H^+]_{coll}$	$\log K'_{sp}$
-1.55 ± 0.02	-1.65 ± 0.02	-49.87 ± 0.08
-1.85 ± 0.02	-1.88 ± 0.02	-49.25 ± 0.08
-2.04 ± 0.02	-1.90 ± 0.02	-49.36 ± 0.08
-2.64 ± 0.02	-1.99 ± 0.02	-49.60 ± 0.08
-3.03 ± 0.02	-2.08 ± 0.02	-49.63 ± 0.08
-3.56 ± 0.02	-2.19 ± 0.03	-49.72 ± 0.12
-4.05 ± 0.02	-2.40 ± 0.03	-49.37 ± 0.12
		mean value: -49.54 ± 0.23

rable ionic strength (Fig. 5). The amorphous Th(IV) precipitates, considered as either amorphous Th(IV) hydroxide (Moon [8]) or Th(IV) hydrous oxide (Rai *et al.* [9–11]), are not treated at higher temperature but only washed with water. Within the scattering of experimental data, the results of these authors agree fairly with one another. However, the reported solubilities are higher than the present results of Th(IV) colloids by many orders of magnitude. Since both Moon [8] and Rai *et al.* [9, 10] determined the thorium concentration after filtration at a pore size of about 2 nm, the high thorium concentrations measured for amorphous Th(IV) precipitates [6, 8–11] may be ascribed primarily to polynuclear species or small Th(IV) colloids (< 2 nm). This assumption is corroborated by potentiometric titration studies in the pH range of $2.5 - 4$ [12–14], in which the pH of a given Th(IV) solution above 10^{-4} mol/l is carefully increased. The conditions (pH and thorium concentration) applied in these studies are between the two solubility curves in Fig. 5. The potentiometric titration studies demonstrate that polynuclear species, possibly colloidal particles, are predominant under these conditions [12–14].

Östhols *et al.* [6] investigated the solubility of microcrystalline $ThO_2 \cdot x\,H_2O(s)$ at 25 °C. Their solid was dried at room temperature for one week in a vacuum desiccator. X-ray powder diffraction indicated a low degree of crystallinity and the water content was determined to be $x \approx 2.5$.
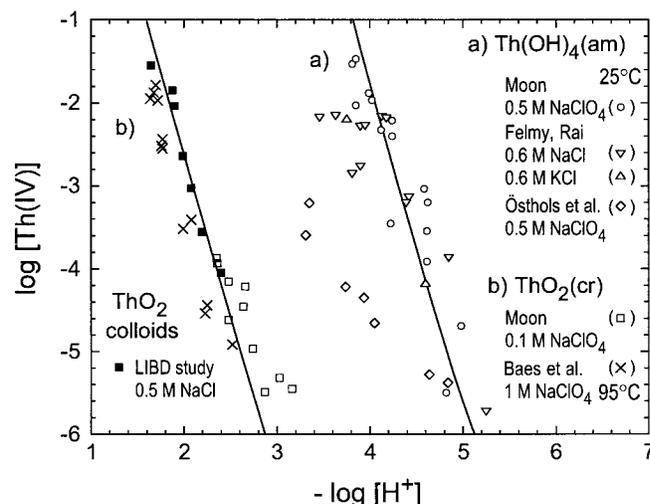

Fig. 5. Comparison of the literature solubilities with those of the present LIBD method; (**a**) amorphous precipitates in 0.5 M $NaClO_4$ (Moon [8], Östhols *et al.* [6]) and 0.6 M NaCl or KCl (Rai *et al.* [10, 11]) at 20–25 °C. (**b**) crystalline ThO_2(cr) in 0.1 M $NaClO_4$ at 20 °C (Moon [8]) and in 1 M $NaClO_4$ at 95 °C (Baes *et al.* [12]) The solid lines are calculated with $\log K'_{sp}$ ($ThO_2 \cdot x\,H_2O$(colloids)) $= -49.54$ in 0.5 M NaCl, and the thermodynamic constants selected in our recent review [18]: hydrolysis constants from [14] and $\log K°_{sp}$ ($ThO_2 \cdot x\,H_2O$(am)) $= -47.2$.

The authors observed no effect on the measured solubilities when the filter pore size was varied from 10–220 nm. The solubilities in the acidic pH region are considerably below those of Moon [8] and Rai *et al.* [9, 10]. However, they are still much different from the results of the present study. The solubility of Th(IV) colloids determined by LIBD is comparable with the experimental data determined by Moon [8] in 0.1 M $NaClO_4$ with crystalline ThO_2(cr) prepared at 700 °C. The solubility data of Baes *et al.* [12] measured at 95 °C after addition of crystalline ThO_2(cr) to oversaturated Th(IV) solutions in acidic 1 M $NaClO_4$ are also comparable with the present results (Fig. 5). At the recent conference Migration '99, Rai *et al.* reported similar solubility data for ThO_2(cr) at 25 °C and 90 °C.

3.3 Evaluation of the solubility product

According to the hitherto published literature data on the hydrolysis of Th(IV) [12–14] the Th^{4+} ion is the predominant aqueous species at $-\log[H^+] < 2.5$. This explains the slope of -4 when $\log[Th(IV)]$ is plotted vs. $-\log[H^+]$ of the initial colloid formation (Fig. 5). The solubility data of the present LIBD study (Table 1) are used to calculate the average value for the conditional solubility product K'_{sp} of colloidal Th(IV) particles in 0.5 M NaCl:

$$K'_{sp} = [Th^{4+}][OH^-]^4 \qquad (1)$$

with

$$\log K'_{sp} (ThO_2 \cdot x\,H_2O \text{ (colloids)}) = -49.54 \pm 0.22$$
in 0.5 M NaCl

In order to evaluate the thermodynamic constant $K°_{sp}$ at $I = 0$, the activity coefficients γ_i are calculated with the SIT

coefficients given in the NEA-TDB [7]:

$$K^\circ_{sp} = K'_{sp}\, \gamma_{Th^{4+}}\, (\gamma_{OH^-})^4 \tag{2}$$

With $\log\{\gamma_{Th^{4+}}(\gamma_{OH^-})^4\} = -3.30$ in 0.506 m NaCl [7], we obtain

$$\log K^\circ_{sp}\, (ThO_2 \cdot x\,H_2O\,(colloids)) = -52.8 \pm 0.3$$

A considerably lower solubility product of $\log K^\circ_{sp} = -54.7$ is calculated, if the set of Pitzer parameters proposed by Rai *et al.* [11] is used for the activity coefficients in 0.506 m NaCl. However, the corresponding value of $\log\{\gamma_{Th^{4+}}(\gamma_{OH^-})^4\} = -5.13$ [11] seems to be too negative as compared to the analogous values of $\log\{\gamma_{U^{4+}}(\gamma_{OH^-})^4\} = -2.83$ [11] and -3.37 [15], which are calculated with the Pitzer parameters reported by the same authors and Plyasunov *et al.* [15], respectively.

It appears somewhat surprising that the solubility product of the freshly formed thorium colloids is relatively close to the value of $\log K^\circ_{sp}\,(ThO_2(cr)) = -54.2 \pm 1.3$ [16] calculated from thermochemical data for $ThO_2(cr)$. It may be assumed that the observed colloids have a crystalline thorium dioxide structure. This conclusion is supported by the results of Dzimitrowicz *et al.* [17], who investigated Th(IV) precipitates by transmission electron microscopy and X-ray powder diffraction. The precipitates include small $ThO_2(cr)$ crystallites < 30 nm.

As the particle size of the thorium colloids formed in the present pH titration experiments is only about 20 nm their solubility product is expected to be somewhat increased compared to a bulk $ThO_2(cr)$. As shown e.g. for $SrSO_4$, $BaSO_4$, ZnO, CuO and $Cu(OH)_2$ [19–21], the solubility product of particles < 300 nm depends noticably on the particle size. The difference in Gibbs energy when either small solid particles with the molar surface S or large crystals with negligible molar surface ($S \to 0$) are suspended in water is given by [13, 19–21]:

$$\Delta G = RT \ln \frac{K^\circ_{sp}\,(S \to 0)}{K^\circ_{sp}\,(S)} = \frac{2}{3}\overline{\gamma}S \tag{3}$$

where $\overline{\gamma}$ denotes the mean free surface energy per unit surface area of the solid-liquid interface (interfacial tension) and S the surface area per mole of solid:

$$S = \frac{M\,\alpha}{\rho\,d} \tag{4}$$

M is the molecular weight and ρ the density of the solid, d describes the particle size and α is a geometrical factor which depends on the shape of the particles. For approximately spherical particles with diameter d the geometry factor is $\alpha \approx 6$. According to Schindler [21] the mean free surface energy of the solid-liquid interface can be estimated by

$$\overline{\gamma} = -\frac{3RT \ln K^\circ_{sp}\,(S \to 0)}{2N_A \sum 4\pi r_i^2} \tag{5}$$

Using the known data for crystalline $ThO_2(cr)$ ($\log K^\circ_{sp} = -54.2$ [16], $M = 264.04$ g mol^{-1}, $\rho = 10.0$ g cm^{-3} [22], the ionic radii $r_{Th^{4+}} = 0.105$ nm, $r_{O^{2-}} = 0.140$ nm [23]), and $RT \ln 10 = 5.708$ kJ mol^{-1} at 25 °C, $\overline{\gamma}$ is calculated to be

1.22 J m^{-2}. The difference between the solubility products of ThO_2 colloids and a large crystal ($S \to 0$) of the same chemical composition and structure is thus given by

$$\log K^\circ_{sp}\,(colloids) - \log K^\circ_{sp}\,(S \to 0) = 23/d\,(nm) \tag{6}$$

Accordingly the solubility product of the observed ThO_2 colloids ($d = 16$–23 nm) is expected to be about 1.0–1.4 orders of magnitude higher than the solubility product of the corresponding bulk solid. This estimation of the particle size effectis in fair agreement with the difference between $\log K^\circ_{sp}\,(colloids) = -52.8 \pm 0.3$ evaluated in the present study and $\log K^\circ_{sp}\,(ThO_2(cr)) = -54.2 \pm 1.3$ [16] calculated from thermochemical data for crystalline $ThO_2(cr)$, and supports the assumption that the thorium colloids formed in the present pH titration experiment consist of crystalline thorium dioxide.

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