

Electrophoretic characterization of thorium species in very dilute solutions containing humic acid

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Abstract. Electrophoretic mobility of thorium was measured in aqueous solutions ($\text{HClO}_4 + \text{NaClO}_4$, $I = 0.01$) as a function of thorium concentration ($\ll 10^{-7} - 10^{-5}$ M), pH (2 – 10) and solution composition (Aldrich humic acid, NaHCO_3) using free-liquid electrophoresis. Results have shown that negatively charged thorium humate complexes can prevail at pH 2 – 10 even in solutions containing very low concentration of humic acid (0.1 – 1 mg/L) and medium concentration of carbonates (0.001 M). The mobilities determined can serve for analysis of formation of the humate complexes in aqueous solutions and natural or wastewaters.

Introduction

Complexation of natural radionuclides with humic substances present in surface and ground waters can strongly affect speciation and migration of the radionuclides. Although the strong interaction of humic substances with thorium in natural waters has been documented (Wahlgren and Orlandini 1982, Miekeley and Kuechler 1987, Zeh et al. 1995, Kim and Marquardt 1999), formation and properties of humic complexes of tetravalent thorium and uranium are not well known (Reiller 2005). It is due to the strong hydrolysis and other complexation reactions of the tetravalent metals as well as easy precipitation of their hydroxides, extensive sorption on surfaces and, in the case of uranium, also to redox reactions. Most of the data on the complexation on of thorium with various humic and fulvic acids were obtained at pH 3.95-6.5. Only recently was formation of thorium humate studied in the neutral pH region (6.75-7.9, Reiller et al. 2003). No experimental data on the formation of similar complexes of tetravalent uranium are available.

Thorium can be used as model for other tetravalent actinides (Choppin 1999), therefore basic knowledge on its complexation with humic substances is also ap-

plicable for uranium (Reiller 2005). In this paper, thorium complexation with well characterized Aldrich humic acid is studied in a broad range of experimental conditions using free-liquid electrophoresis. Among principal advantages of the method (Benes and Majer 1980) belongs that it can be applied for very low concentrations of thorium and thus precipitation of thorium hydroxide can be avoided. Furthermore, electrophoretic mobilities measured by the method characterize the charge of the complexes formed and can serve for analysis of the effects of saturation of humic acid with the metal. The electrophoresis can also be used for analysis of speciation of thorium in natural waters, if mobilities of typical thorium species are known. Determination of such mobilities is one of the aims of the paper.

Experimental

Ultrapure water (Millipore Milli-Q 50 system) and A.R. reagents were used for preparation of all solutions in this work. Stock solution of carrier-free ^{234}Th in 1 M HClO_4 was prepared by separation of ^{234}Th from $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Benes 2005). Purification, characterization and preparation of stock solutions (500 mg/L) of Aldrich humic acid were described in detail previously (Mizera et al. 2003).

Experimental solutions were prepared by mixing stock solution of ^{234}Th with water and stock solutions of NaOH or NH_4OH , NaHCO_3 and humic acid so as to obtain the desired pH and composition of the solution. Other concentrations of thorium than “carrier-free” ($\ll 10^{-7}$ M) were obtained by addition of ^{232}Th . The ionic strength of the solutions was maintained close to 0.01 mol/L. The solutions were used for experiments 24 hours after their preparation. Before the use, pH of each solution was measured and, if necessary, readjusted.

The apparatus and procedure for free-liquid electrophoresis used in this work were described in detail earlier (Benes and Majer 1980). The electrophoretic cell consisted of three parts made of plastic tubings connected with two three-way Teflon stopcocks. The central part of the cell was filled with working solution labelled with ^{234}Th , the side arms contained a working solution of the same pH and composition except for the label. The electrophoretic experiments were carried out at a constant current (around 1 mA, with potential difference at the electrodes 230–240 V) at 22 ± 3 °C, mostly for 60 min. The electrophoretic mobilities of thorium towards anode ($-u$) and cathode ($+u$) were calculated from the distribution of activity (^{234}Th) between the side arms and central part of the cell, while adsorption on the walls of the cell was taken into account.

All activity measurements were made by liquid scintillation counting in glass vials using Triathler Multilaber Tester and Rotiszint eco plus scintillation cocktail. Specific conductivity of the solutions was determined with a conductometer OK 102/1 equipped with a bell electrode OK-9023 (Radelkis, Budapest), pH was measured with combined glass electrode and Orion 525A pH meter. Further experimental details can be found elsewhere (Benes 2005).

Results and discussion

Electrophoretic mobilities presented in this paper are the mean values obtained by two to six experiments carried out with one (two experiments) or more thorium solutions. Their accuracy depends on the concentration of thorium used and on the adsorption of thorium in the electrophoretic cell. Possible errors in measurement of mobilities by this method were discussed in detail recently (Mizera et al. 2003, Benes 2005). Variation of the mobilities given in Table 1 is characterized by attached error, representing span of the data measured (for two experiments) or standard deviation of the mean (for more experiments).

Table 1 contains the mobilities determined in solutions of pH 2-4, where no polynuclear hydrolysed species or precipitate of thorium oxide/hydroxide are formed at $\leq 10^{-5}$ M thorium concentration (Neck and Kim 2001). The data represent the mean mobility $+u$ or $-u$ of all thorium species present in solution:

$$+(-)u = \sum +(-)u_i \cdot \delta_i \quad (1)$$

Here u_i and δ_i are the mobility and abundance of species i , respectively.

The data obtained in the absence of humic acid characterize the mobility of dissolved inorganic thorium species. As can be seen such species migrate predominantly to cathode. Their mobility towards anode is small and, with the exception of a few results (only for carrier-free ^{234}Th), it may be within a background mobility caused by experimental errors ($0 \pm 0.30 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$, Benes 2005). The positive mobility decreases with increasing pH and with decreasing concentration of thorium, mainly due to the progressive hydrolysis of thorium and formation of pseudocolloids (at $\leq 10^{-6}$ M Th concentration) by adsorption of $\text{Th}(\text{OH})_n^{(4-n)+}$ cations ($n = 0 - 3$) on colloidal impurities ever present in solution. Existence of pseudocolloids can explain the negative mobilities found and the dependence of $+u$ on the concentration of thorium: abundance of pseudocolloids is known to decrease with increasing metal concentration and their predominantly negative charge can be reversed by adsorption of polyvalent ions (Benes and Majer 1980).

Addition of humic acid brings about decrease in $+u$ and increase in $-u$ of thorium that depend on the concentration of humic acid and thorium. The changes are due to the formation of negatively charged or neutral ThHA complexes (no indication of positively charged complexes has been obtained) and can be used for calculation of the abundance and mobility of the complexes. If no other forms of thorium than $\text{Th}(\text{OH})_n^{(4-n)+}$ ($n = 0 - 4$) and ThHA are present, abundance of ThHA can be calculated as

$$\% \text{ThHA} = 100 \delta_{\text{ThHA}} = 100 (1 - +u / +u_{\text{Th}(\text{OH})}) \quad (2)$$

where $+u_{\text{Th(OH)}}^n$ is the mean mobility of $\text{Th(OH)}_n^{(4-n)+}$ measured under the same conditions (ionic strength and pH). It has been shown recently that $+u_{\text{Th(OH)}}^n$ can be well represented by the $+u$ values determined for 10^{-5} M Th in the absence of humic acid (Benes 2005, the bold figures in Table 1). Other data of Table 1 are not suitable for this purpose as they are affected by the presence of pseudocolloids, whose ratio to the dissolved inorganic thorium species can change upon the addition of humic acid.

Table 1. Electrophoretic mobility of thorium (in $10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$) in solutions of 0.01M ($\text{HClO}_4 + \text{NaClO}_4$) as a function of pH and initial concentration of thorium [Th] and Aldrich humic acid [HA].

Mobility	[Th], M ^a	[HA], mg/l	pH 2	pH 3	pH 4
$+u$	c.f.	0	0.59±0.15	0.69±0.28	0.36±0.22
$+u$	c.f.	0.1	0.19±0.07	0.23±0.16	0.11±0.10
$+u$	c.f.	1.0	0.14±0.07	0.17±0.08	0.10±0.04
$+u$	c.f.	10	0.12±0.05	0.12±0.07	0.09±0.03
$+u$	1×10^{-7}	0	2.52±0.20	0.69±0.07	0.39±0.01
$+u$	1×10^{-7}	0.1	2.08±0.42	0.28±0.17	0.19±0.05
$+u$	1×10^{-7}	1.0	0.36±0.09	0.30±0.13	0.19±0.07
$+u$	1×10^{-7}	10	0.29±0.13	0.14±0.07	0.13±0.01
$+u$	1×10^{-6}	0	4.19±0.01	1.62±0.22	0.86±0.04
$+u$	1×10^{-6}	10	0.10±0.15	0.10±0.04	0.07±0.06
$+u$	1×10^{-5}	0	4.52±0.07	3.93±0.27	2.57±0.05
$+u$	1×10^{-5}	10	2.05±0.08	0.42±0.02	0.07±0.03
$-u$	c.f.	0	0.42±0.23	0.58±0.13	0.53±0.09
$-u$	c.f.	0.1	0.54±0.13	1.65±0.27	1.58±0.20
$-u$	c.f.	1.0	1.61±0.33	1.96±0.17	2.12±0.17
$-u$	c.f.	10	1.98±0.30	3.00±0.23	2.95±0.20
$-u$	1×10^{-7}	0	0.15±0.12	0.29±0.03	0.15±0.05
$-u$	1×10^{-7}	0.1	0.21±0.13	1.25±0.08	2.04±0.09
$-u$	1×10^{-7}	1.0	1.25±0.10	2.25±0.15	2.21±0.18
$-u$	1×10^{-7}	10	1.78±0.27	2.98±0.08	2.80±0.19
$-u$	1×10^{-6}	0	0.11±0.03	0.05±0.05	0.16±0.07
$-u$	1×10^{-6}	10	1.25±0.26	1.77±0.04	2.64±0.13
$-u$	1×10^{-5}	0	0.13±0.13	0.17±0.05	0.25±0.02
$-u$	1×10^{-5}	10	0.47±0.12	0.49±0.07	0.66±0.31

^a c.f. denotes that carrier free ^{234}Th was used. Total thorium concentration was probably lower than 10^{-9} M in this case.

Results of the calculation are shown in Table 2 and represent means of values $\%ThHA$ obtained by combination of all measured values of $+u$ and $+u_{Th(OH)}$ for the given conditions. Limits attached are the ranges of variability of the values. The data clearly indicate that thorium is extensively complexed even at very low concentrations of humic acid and low pH values. The abundance $\%ThHA$ little depends on pH and $[HA]$ except for conditions when the concentration of thorium approaches saturation of the complexing capacity of humic acid present in solution. Practically complete complexation is observed at 10 mg/L HA for 10^{-6} M Th and also at pH 4 for 10^{-5} M Th. $\%ThHA$ values for the lower thorium concentrations are lower. This can be explained by a higher formation of pseudocolloids or, more probably, by error in determination of $+u$ (Benes 2005). Most of the mobilities $+u$ used in the calculation of $\%ThHA$ lay within the possible background range ($0 - 0.30 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$).

Of special interest is the saturation of complexing capacity of humic acid with thorium, indicated by the data in Table 2 for $10^{-7}(10^{-5})$ M Th and 0.1(10) mg/L HA. The general complexation capacity of humic acid can be expressed using concentration of humic acid ($[HA]$, in mg/L), its proton exchange capacity (PEC, in mol/kg) and the degree of dissociation of complexing (here carboxyl) sites of the acid (α), determined by acidobasic titration of the acid:

$$CC_{HA} = 10^{-6} [HA] \cdot \text{PEC} \cdot \alpha \quad (3)$$

In Table 3, complexing capacities calculated using Eq. (3) and data on PEC and α taken from Mizera et al. (2003) are compared with the concentrations of ThHA, calculated from $[Th]$ and $\%ThHA$ values given in Table 2. As can be seen, concentrations of ThHA formed in the solution exceed complexation capacities of humic acid for bonding of monovalent cations, represented by the concentration of available dissociated sites (COO^-) of the acid. The effect increases with decreasing pH. Considering that thorium cations participating in the complexation under studied conditions carry higher charge than 1 (up to 4+), the exceeding of CC_{HA} is still more pronounced and means that either the complexation proceeds at least partially by displacement of H^+ from non-dissociated COOH groups of humic acid or positively charged ThHA complexes are formed. The latter possibility is not supported by the data on the negative mobility of ThHA complexes (see below).

Assuming that no other negatively charged form of thorium is present in solution the mean mobility of ThHA complexes is equal to

$$-u_{ThHA} = -u / \delta_{ThHA} \quad (4)$$

Mobilities calculated from Eq. (4) and data taken from Tables 1 and 2 are shown in Table 4, together with the ranges of their variability calculated from the corresponding variabilities of the values of $-u$ and $\%ThHA$ used. No background mobilities ($-u$ found in absence of HA) were subtracted in the calculation.

Data in Table 4 show the tendency of $-u_{ThHA}$ to increase with pH and to decrease with increasing $[Th]/[HA]$ ratio. The first effect is due to the increase in dissociation of COOH groups of humic acid with increasing pH and was not found

in solutions of 10^{-5} M thorium, where precipitation of thorium humate was observed at all pH values. The effect of $[\text{Th}]/[\text{HA}]$ ratio on u_{ThHA} in $10^{-7} - 10^{-6}$ M Th solutions can be at least partially explained by the neutralization of negative charge of humic acid molecules with thorium cations bound in ThHA complex. Detailed analysis of the effects is in progress.

At pH values larger than 4, electrophoretic mobilities were determined only for carrier-free ^{234}Th , in order to avoid precipitation of thorium hydroxide (Neck and Kim 2001). The effects of pH, concentration of humic acid and addition of 0.001 M NaHCO_3 were studied. Results are shown in Fig.1, the error bars represent the maximum probable error ($\pm 0.30 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$).

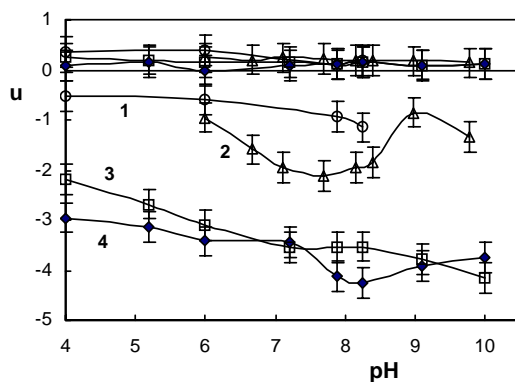


Fig. 1. Electrophoretic mobility of carrier-free ^{234}Th (in $10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$) as a function of pH and composition of solution: **1** – 0.01 M NaClO_4 + NaOH or NH_4OH , **2** – as in **1** + 0.001 M NaHCO_3 , **3** – as in **1** + 1 mg/L humic acid, **4** – as in **1** + 10 mg/L humic acid.

Table 2. Abundances of ThHA complexes (%ThHA) calculated using Eq.(2) and data of Table 1 as a function of pH and initial concentration of thorium $[\text{Th}]$ and Aldrich humic acid $[\text{HA}]$.

$[\text{Th}]$, M ^a	$[\text{HA}]$, mg/L	pH 2	pH 3	pH 4
c.f.	0.1	95.6±0.3	93.8±4.5	95.6±4.0
c.f.	1.0	96.8±1.6	95.5±2.3	96.1±1.6
c.f.	10.0	97.3±1.2	96.8±2.0	96.6±1.4
1×10^{-7}	0.1	69.4±4.2	92.4±5.0	92.4±1.9
1×10^{-7}	1.0	92.0±2.1	92.1±3.9	91.8±3.6
1×10^{-7}	10.0	93.6±3.0	96.1±2.1	94.9±0.1
1×10^{-6}	10.0	99.4±0.6	97.4±1.2	97.2±2.4
1×10^{-5}	10.0	54.6±2.5	89.4±1.1	97.3±1.2

^a c.f. denotes that carrier free ^{234}Th was used.

It can be seen that thorium migrates at $\text{pH} > 4$ predominantly to anode, its positive mobility is generally within background values. The negative mobility in the absence of added carbonates and humic acid is due to formation of pseudocolloids and/or carbonate complexes (absorption of CO_2 from the air). Addition of carbonates brings about increase of the mobility in the range of pH 6-8.5 where $\text{Th}(\text{OH})_3\text{CO}_3^-$ and $\text{Th}(\text{OH})_2(\text{CO}_3)_2^{2-}$ ions are formed (Altmaier et al. 2005). The high negative migration in solutions containing humic acid reflects predominance of negatively charged humates, whose mobility increases with pH up to about pH 8. This increase is caused by the increasing dissociation of COOH groups of the humic acid (up to pH 6, Mizera et al. 2003) and decreasing neutralization of negative charge of humic acid as the average positive charge of thorium hydroxocomplexes decreases with pH (up to pH 8, Neck and Kim 2001). The differences between the mobility at different concentrations of humic acid are due either to different abundance of the humic complexes or to different neutralization of the charge.

The difference between the mobility of thorium in solutions containing carbonates and humic acid can be used for determination of proportion of carbonate and humate complexes of thorium in waters containing both the ligands.

Preliminary experiments have shown that humate complexes predominate at pH 8-9 and ≥ 1 mg/L Aldrich humic acid even in solutions 0.001 M in HCO_3^- . Further study of thorium complexation with free-liquid electrophoresis is in progress.

Table 3. Comparison of complexation capacities CC_{HA} and $[\text{ThHA}]$ concentrations (both in mol/L) in solutions of 0.01M ($\text{HClO}_4 + \text{NaClO}_4$) containing 10^{-7} M Th + 0.1 mg/L HA or 10^{-5} M Th + 10 mg/L HA.

Compared values	pH 2	pH 3	pH 4
$[\text{ThHA}] \times 10^7$	0.694	0.924	0.924
$[\text{ThHA}] \times 10^5$	0.546	0.894	0.973
$CC_{\text{HA}} \times 10^7$ or 10^5	0.14	0.84	2.17

Table 4. Electrophoretic mobilities of ThHA complexes (μ_{ThHA} , in $10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$) in solutions of 0.01M ($\text{HClO}_4 + \text{NaClO}_4$) calculated using Eq.(4) and data of Tables 1 and 2 as a function of pH and initial concentration of thorium $[\text{Th}]$ and Aldrich humic acid $[\text{HA}]$.

$[\text{Th}]$, M ^a	$[\text{HA}]$, mg/l	pH 2	pH 3	pH 4
c.f.	0.1	0.57±0.15	1.78±0.37	1.66±0.27
c.f.	1.0	1.67±0.37	2.06±0.23	2.21±0.22
c.f.	10.0	2.04±0.33	3.11±0.30	3.06±0.26
1×10^{-7}	0.1	0.31±0.20	1.36±0.16	2.21±0.14
1×10^{-7}	1.0	1.36±0.14	2.45±0.27	2.42±0.29
1×10^{-7}	10.0	1.91±0.35	3.11±0.16	2.96±0.22
1×10^{-6}	10.0	1.26±0.27	1.83±0.07	2.72±0.20
1×10^{-5}	10.0	0.87±0.26	0.55±0.08	0.69±0.34

^a c.f. denotes that carrier free ^{234}Th was used.

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References

- Altmaier M, Neck V, Mueller R, Fanghaenel Th (2005) Solubility of $\text{ThO}_2 \cdot x\text{H}_2\text{O}$ (am) in carbonate solution and the formation of ternary Th(IV) hydroxide-carbonate complexes. *Radiochim. Acta* 93: 83-92
- Benes P, Majer V (1980) *Trace Chemistry of Aqueous Solutions*. Elsevier, Amsterdam, 43,110
- Benes P (2005) Use of free-liquid electrophoresis for analysis of thorium complexation with humic acids. In: Buckau G (Ed) *Humic Substances in Performance Assessment of Nuclear Waste Disposal: Actinide and Iodine Migration in the Far-Field*. Report FZKA 7070, Research Center Karlsruhe, 125-141
- Kim JI, Marquardt CM (1999) Chemical reaction of Np(V) with humic colloids in groundwater: influence of purification on the complexation behaviour. *Radiochim Acta* 87: 105-108
- Miekeley N, Kuechler IL (1987) Interactions between thorium and humic compounds in surface waters. *Inorg Chim Acta* 140: 315-319
- Mizera J, Benes P, Masnerova G (2003) Electrophoretic determination of the degree of Eu complexation by humic acid: analysis and assessment of experimental error. In: Buckau G (Ed) *Humic Substances in Performance Assessment of Nuclear Waste Disposal: Actinide and Iodine Migration in the Far-Field*. Report FZKA 6800, Research Center Karlsruhe, 191-202
- Neck V, Kim JI (2001) Solubility and hydrolysis of tetravalent actinides. *Radiochim. Acta* 89: 1-16
- Reiller P, Moulin V, Casanova F, Dautel Ch (2003) On the study of Th(IV)-humic acid interactions by competition sorption studies with silica and determination of global interaction constants. *Radiochim Acta* 91: 513-524
- Reiller P (2005) Prognosticating the humic complexation for redox sensitive actinides through analogy, using the charge neutralization model. *Radiochim. Acta* 93: 43-55
- Wahlgren MA, Orlandini KA (1982) Comparison of the geochemical behaviour of plutonium, thorium and uranium in selected North American lakes. In: *Environmental Migration of Long-Lived Radionuclides*, IAEA Vienna, 757-774
- Zeh P, Kim JI, Buckau G (1995) Aquatic colloids composed of humic substances. In: *Binding Models Concerning Natural Organic Substances in Performance Assessment*. Proceedings of NEA Workshop, OECD NEA, 81-90