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Stability Constants of Acetylacetonate Complexes of Tetravalent Berkelium

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Logarithms of the overall stability constants (β_1, β_2, β_3 and β_4) of acetylacetonate complexes of berkelium(IV) in aqueous 1 M NH_4ClO_4 at 25 °C are equal to 9.3, 18.3, 27.3 and 33.4, respectively, as determined by solvent extraction.

One of the most important features of actinide chemistry, especially in their tetravalent state, is their hard acid property.[1] As hard acids, these cations favour interactions with hard bases (such as oxygen or fluoride atoms) as opposed to soft bases (*e.g.* nitrogen, sulfur or phosphorous donors). This means that bonding with ligands can be accurately described as electrostatic interaction[2] with covalency playing a quite minor role.[3]

Complexes with β-diketonates ($R_1COCH_2COR_2$) are known for most elements in the periodic table, including actinides.[4] The majority of these complexes are poorly soluble in aqueous solutions, but easily dissolve in organic solvents commonly applied for solvent extraction. As a result, β-diketonates are amongst the most popular organic reagents used for extractive separation and preconcentration of metal ions in analytical chemistry and radiochemistry.[5]

The analysis of the existing literature data shows that stability constants for acetylacetonate complexes of plutonium(IV) are significantly greater than those of other tetravalent actinides and of transition metals.[4] In order to verify the aforementioned conclusion we have attempted to determine the stability constants for the respective complexes of berkelium(IV) – the only tetravalent actinide cation stable to water for which such data have not yet been determined.

The other reason for our interest in the stability constant of tetrakis(acetylacetonato)berkelium(IV) relates to studies on the outer-sphere hydration[6] of coordinatively saturated β-diketonates of tetravalent metals, carried out at the Institute of Nuclear Chemistry and Technology in Warsaw.

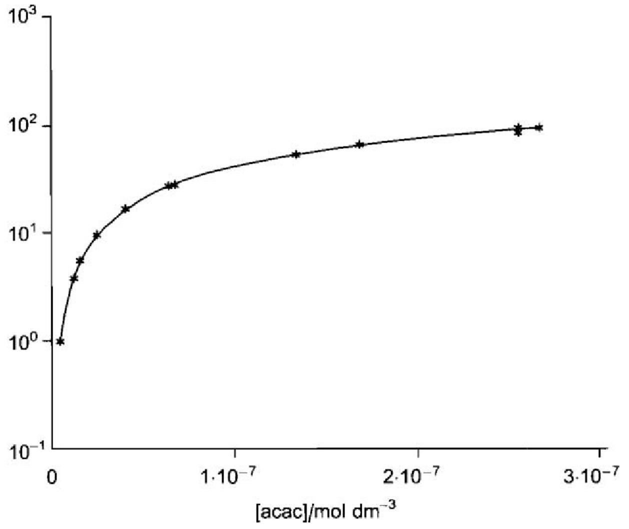

Fig. 1 Distribution ratio (*D*) of tracer berkelium(IV) between 1.0 M $NH_4(H)ClO_4$ and benzene containing 0.3 M $[Hacac]_{i,org}$ as a function of $[acac^-]$. The curve has been calculated using the experimentally obtained constants β_n and P_4.

Recent data obtained for β-diketonates of trivalent metals of the first transition series indicate a strong effect of the central metal ion on the strengths of the hydrogen bonding between the donor oxygen atoms in coordinated ligands and water molecules.[7]

The distribution of Hacac and Bk(acac)$_4$ between organic and aqueous phases can be considered as one of the most effective methods for the study of complex formation between berkelium(IV) and acetylacetonate (acac$^-$) ions in aqueous solutions.

In aqueous solutions acetylacetone exists predominantly in the enolic form (MeCOH=CHCOMe) which dissociates to form acetylacetonate anions (MeCO$^-$=CHCOMe). Under the experimental conditions[†] only M(acac)$_n^{(4-n)+}$ species have been formed by thorium(IV),[10] uranium(IV),[11] neptunium(IV)[12] and plutonium(IV).[13] Because the coordination number of tetravalent actinides is, as a rule, equal to 8 we assume that $0 \leqslant n \leqslant 4$. Due to low experimental pH values, we neglect any hydrolysis process of berkelium(IV), which could result in the formation of mixed complexes Bk(OH)$_x$(acac)$_n^{(4-n-x)+}$.

Distribution of the uncharged Bk(acac)$_4$ complex between benzene and the aqueous phase is described by the Nernst equation:

$$P_4 = \frac{[\mathrm{Bk(acac)_4}]_{\mathrm{org}}}{[\mathrm{Bk(acac)_4}]_{\mathrm{aq}}} \qquad (1)$$

where P_4 is the partition constant, and brackets denote the molar concentration of the chelate in both phases.

Equilibrium of the overall extraction process can be expressed using the distribution ratio, equation 2:

where β_n denotes the overall stability constant for the formation of the nth complex Bk(acac)$_n^{(4-n)+}$: β_n = [Bk(acac)$_n^{(4-n)+}$]/([Bk^{4+}][acac$^-$]^n).

For equal volumes of aqueous and organic phases, the free ligand concentration can be calculated using the following relation:

$$[\mathrm{acac}^-] = \frac{K_\mathrm{a}[\mathrm{Hacac}]_{\mathrm{i.org}}}{[\mathrm{H}^+](1 + \mathrm{D}_{\mathrm{Hacac}} + K_\mathrm{a}[\mathrm{H}^+]^{-1})} \qquad (3)$$

In the above relation, K_a denotes the dissociation constant of acetylacetone, D$_{\mathrm{Hacac}}$ its partition constant (equal to 10^{-9} and 4.4, respectively[4]) while [Hacac]$_{\mathrm{i.org}}$ refers to the initial concentration of acetylacetone in the organic phase.

Table 1 Logarithms of the overall consecutive stability constants (β_n) for berkelium(IV) acetylacetonates in 1 M NH$_4$ClO$_4$ aqueous solution in comparison with literature data for other tetravalent actinides.[4]

	logβ$_1$	logβ$_2$	logβ$_3$	logβ$_4$
Bk	9.3	8.3	7.3	3.4
Pu	10.0	9.1	7.6	3.5
Np	8.6[a]	7.2	3.9	0.2
U	9.0	7.0	3.9	9.8
Th	7.8	4.4	1.8	4.8

[a] logβ$_1$ = 9.5 [V. I. Mikhailov, *Analiticheskaya Khimiya Neptuniya* (*Analytical Chemistry of Neptunium*), Nauka, Moscow, 1971 (in Russian)].

$$D_{\mathrm{Bk}} = \frac{[\mathrm{Bk(acac)_4}]_{\mathrm{org}}}{[\mathrm{Bk}^{4+}]_{\mathrm{aq}} + [\mathrm{Bk(acac)}^{3+}]_{\mathrm{aq}} + [\mathrm{Bk(acac)}_2^{2+}]_{\mathrm{aq}} + [\mathrm{Bk(acac)}_3^{+}]_{\mathrm{aq}} + [\mathrm{Bk(acac)_4}]_{\mathrm{aq}} +} = \frac{P_4\beta_4[\mathrm{acac}^-]_{\mathrm{aq}}^4}{1 + \beta_1[\mathrm{acac}^-]_{\mathrm{aq}} + \beta_2[\mathrm{acac}^-]_{\mathrm{aq}}^2 + \beta_3[\mathrm{acac}^-]_{\mathrm{aq}}^3 + \beta_4[\mathrm{acac}^-]_{\mathrm{aq}}^4} \qquad (2)$$

Experimental data[†] for the berkelium(IV) distribution ratio, plotted *versus* the acac$^-$ concentration, are presented in Fig. 1. The partition constant of Bk(acac)$_4$ (P_4) as well as four stability constants [β_n of the species Bk(acac)$^{3+}$ to Bk(acac)$_4$] have been calculated using the least-squares minimization technique, based on the independent Powell,[14] Marquadt–Levenburg[15] or Simplex[16] algorithms, respectively. The logarithms of β_1, β_2, β_3, β_4 and P_4 are 9.35, 18.27, 27.28, 33.36 and 2.580, respectively, with correlation coefficent $r = 0.998$.

Table 1 presents a comparison of the values for the overall complex stability constants of berkelium(IV) acetylacetonates with the literature data for thorium(IV), uranium(IV), neptunium(IV) and plutonium(IV) acetylacetonates. As one can see, the values for berkelium(IV) are close to those for plutonium(IV) and greater than for thorium(IV), uranium(IV) or neptunium(IV). The observed pattern of the stability constants fits well to actinide contraction as well as to the double-double (tetrad) effect. As a consequence of successive filling of the 5f electronic subshell along the actinide series, the ionic radii of the consecutive elements decrease owing to the increased attraction of their nuclear charges on the 5f electrons in the outer shells. In the case of tetravalent actinides the ionic radii decrease from 98.4 pm for Th^{4+} to 87 pm for Bk^{4+}.[17] Since the actinide cations form predominantly electrostatic bonds in aqueous solutions, we can observe that the stability constants of the acetylacetonate complexes reproduce variations of the reciprocals of the tetravalent actinide ionic radii. A small decrease detected for the berkelium(IV) stability constants with respect to those for the plutonium(IV) ones can be attributed to an extra stabilization of the berkelium(IV) aqua-ion, characterized by the half-filled 5f electron subshell.[18]

[†] *Reagents*: Acetylacetone (Fluka), denoted as Hacac, was purified using standard methods.[8] Benzene and n-heptane (Reachim, USSR, standard), potassium bromate and hydroxylamine hydrochloride (Reachim, both of pure grade) were used without further purification. Nitric acid, perchloric acid and aqueous ammonia solutions of the desired concentrations were prepared from especially pure grade concentrated HNO$_3$, HClO$_4$ and NH$_3$, respectively. Di(2-ethylhexyl) phosphoric acid, HDEHP (Fluka, practical) was used for preparative purposes without additional purification.

Experimental: Commercially available ^{249}Bk isotope was purified from its daughter isotope ^{249}Cf based on the ability of berkelium to be readily oxidized to the tetravalent state. After KBrO$_3$ oxidation in nitric acid solution, berkelium(IV) was selectively extracted by 0.25 M HDEHP in *n*-heptane. Finally, ^{249}Bk was stripped into the aqueous phase as a trivalent cation using the NH$_2$OH·HCl reduction process.[9] The absence of γ-active impurities was verified by γ-spectrometry with a semiconductor Ge(Li)-detector, while that of α-active impurities was verified from the ratio of α- and β-measurements using a methane proportional counter with 2π-geometry (*i.e.* on the Protoka installation).[9]

For the solvent extraction experiments a radiotracer technique was applied. Total metal concentration was of the order of 10^{-7} M. Microlitre samples of tetravalent berkelium in amounts sufficient to establish its concentration, prepared in 1 M nitric acid solution containing 0.2 M KBrO$_3$ as an oxidizing agent, were placed into three separate glass vessels immersed in a thermostated water-bath. It has already been established that an excess amount of KBrO$_3$ in relation to berkelium(IV) ions acts as a "valence adjuster" for at least several hours.[9] The temperature was 25 ± 0.1 °C. Aliquots (2 ml) of aqueous (1 M NH$_4$ClO$_4$) and organic phase (*ca.* 0.3 M acetylacetone in benzene) were added. Various pH values, generating various values of the concentration of free acetylacetonate anion ([acac$^-$]), were obtained by adding microlitre amounts of concentrated HClO$_4$. The vessels were shaken for 10 min. The phases were then separated by standing and the samples withrawn were analysed for ^{249}Bk content. The latter results were related to the ^{249}Bk content in the initial aqueous phase.

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