

Aqueous Chemistry of Protactinium(IV). I. Stability Constants for Pa(IV) – Acetylacetonate Complexes

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Stability and distribution constants for the tetravalent protactinium acetylacetonate complexes MAA^+ and $M(AA)_2$ ($M^{2+} = Pa(OH)_2^{2+}$ or PaO^{2+} , HAA = acetylacetonate) were obtained from the liquid-liquid distribution of Pa(IV) between HAA in C_6H_6 and in 1 M (Na,H)ClO₄. The constants for 25°C were calculated as $\log \beta_1 = 6.1$, $\log \beta_2 = 13.15 \pm 0.13$ and $\log \lambda_2$ ($[M(AA)_2]_{org}/[M(AA)_2]_{aq}$) = 2.07 ± 0.10 . For the extraction reaction ($M^{2+} + 2HAA(org) \rightleftharpoons M(AA)_2(org) + 2H^+$) $\log K_D = -4.13 \pm 0.05$, $\Delta H^\circ = 30 \pm 2$ kJ mol⁻¹ and $\Delta S^\circ = 22 \pm 8$ J mol⁻¹ K⁻¹ were calculated.

In making a systematic study of acetylacetonate complexes of tetravalent actinides,^{1,2} information on the Pa(IV)-acetylacetonate system was needed. Only a few stability constants for chelate complexes with Pa(IV) have been determined;^{3,4} liquid-liquid distribution of Pa(IV) has been used as a tool to study complex formation^{5,6} of non-extractable complexes, especially hydrolysis reactions. In this work the distribution of Pa(IV) between a benzene phase and water was investigated as a function of the concentrations of Pa(IV), acetylacetonate, and hydrogen ion, as well as of the temperature.

Trace concentrations of ^{234m}Pa and ²³³Pa were used to avoid polynuclear complexes. A constant ionic strength of 1 M (Na,H)ClO₄ was maintained in the aqueous phase.

EXPERIMENTAL

Chemicals. (a) ²³³Pa was obtained by neutron irradiation for 48 h of 1 g samples of ²³²Th(NO₃)₄·5H₂O, sealed in quartz ampules, in the R2-reactor (thermal flux 10¹² n s⁻¹ cm⁻²) of Aktiebolaget Atomenergi in Nyköping. Two different stock solutions were prepared

by solvent extraction. One stock solution consisted of pure acetylacetonate and another of 7 M HClO₄.

Neither the method of preparing the stock solutions nor their age affected the distribution of Pa(IV), in contrast to what has been found for Pa(V).⁷ This is probably due to the much smaller tendency of Pa(IV) to hydrolyse and polymerize. The radiochemical purity was controlled using high resolution gamma-spectroscopy.

(b) Stock solutions of ^{234m}Pa (*t*_{1/2} 6.7 h) in 0.1 M HCl were prepared by isolation of ^{234m}Pa from its parent ²³⁴Th (*t*_{1/2} 24 d) which was itself recovered, by solvent extraction, from 20 kg of old UO₂(NO₃)₂·6H₂O.

(c) The sodium perchlorate solutions were made by neutralization of recrystallized Na₂CO₃ (Merck) with concentrated HClO₄ (Merck).

(d) Acetylacetonate was purified as recommended by Rydberg.⁸ Chromium perchlorate was prepared by dissolving chromium metal (Koch Light) in concentrated HClO₄ until neutralization.

Fluid amalgamated zinc, 2 % by weight of Zn in Hg (Merck), was prepared according to Ref. 9. The amalgam was shaken with water three times before use. Doubly-distilled water and reagents of *p.a.* quality were used throughout.

Analysis. (a) A Ge(Li)-detector (Canberra Ind.) was used for the gamma-spectroscopy: It had an efficiency of 13 % and a resolution of 3.7 keV (full width at half maximum) at 1.332 MeV. The detector was connected to a 1024-channel analyzer (Hewlett Packard). The distribution measurements, however, were made with an ordinary NaI(Tl)-detector. About 2000 disintegrations were measured from the least active phase, which was twice as active as the background. As the total measured activity from both phases was around 200 000 counts the radiometric accuracy of the logarithm of the distribution ratio was ± 0.01 or better.

(b) Hydrogen ion concentration measurements were made with a modified glass calomel

combination electrode GK 2303 C (Radiometer) with 1 M NaClO₄ replacing the saturated KCl.¹⁰

(c) The acetylacetonone concentration was checked by spectrophotometric determination of the absorbance at 490 nm¹¹ of the red Fe(III)-acetylacetonate and was found to agree, within the accuracy ($\pm 2\%$) of the method, with the calculated.

All experiments were carried out in 1 M (Na,H)ClO₄ with a hydrogen ion concentration in the range 10⁻¹ to 10⁻⁹ M. The electrode combination was calibrated by measurements in 1 M (Na,H)ClO₄ solutions of well known $pH = -\log [H^+]$. Calibration was carried out before and after each experiment, and the hydrogen ion concentration estimated using the relation

$$E = E^\circ + RTF^{-1} \ln 10 \log [H^+] + \psi[H^+]$$

The constants E° and ψ were found to be unaffected by contact of the aqueous phase with the benzene phase. The accuracy of the pH -measurements was ± 0.01 pH -units, or better.

Reduction by Cr(II). Exactly 15 ml of 1 M (Na,H)ClO₄, pH 1–2, was brought into contact with about 4 ml Zn(Hg) in an atmosphere of nitrogen in a small closed glass titration vessel equipped with a magnetic stirrer. About 10–70 μ l of 1.92 M Cr(ClO₄)₃ was added to make the solution 10⁻²–10⁻³ M in Cr³⁺. Complete reduction to blue Cr²⁺ took place in about 30 min, which agrees with other investigations.¹² The pH was increased with 1 M NaOH when required. About 10 μ l of the stock solution of ²³³Pa in acetylacetonone and 15 ml of the benzene acetylacetonone phase was then added. The nitrogen contained less than 10 ppm of oxygen, which did not affect the system.

The extraction system was equilibrated by stirring vigorously for 5 to 10 min and then allowing some minutes for settling. The EMF and the temperature were then measured. Equal samples of about 1.3 ml were taken from both phases with disposable glass pipettes with the aid of a reproducible syringe (± 0.005 ml). The pipettes containing the samples were crushed in 20 ml glass tubes for gamma counting. A check was made to see that the sum of the activities of the two phases was the same for all the points of a particular experiment. It proved to be better to successively increase the hydrogen ion concentration through an experimental run, rather than lower it, since the addition of NaOH produces stable chromium(III)-acetylacetonone complexes,¹³ which are extracted from the aqueous phase. Stable chromium(III)-acetylacetonate was always formed at pH -values higher than 3, making it impossible to reduce protactinium.

All extraction experiments were carried out in a water bath, thermostatically controlled to $\pm 0.1^\circ\text{C}$. The distribution equilibria of Pa(IV) were established within 5 min and the con-

centrations of ²³³Pa were calculated from the gamma intensities relative to a ²³⁷Np-²³³Pa standard.

Electrolytic reduction. Equal volumes (15 ml) of (0.1 HClO₄, 0.9 NaClO₄) and a solution of acetylacetonone in benzene, plus 1–3 drops of ²³³Pa stock solution in 7 M HClO₄, were electrolyzed in the glass vessel. The anode compartment consisted of a glass tube, with an almost tight glass frit separating the platinum anode from the bulk solution. The anode compartment was filled with 1 M NaClO₄ and the current was held constant around 20 mA, giving a voltage of 10–25 V. The electrolysis continued until all hydrogen ions were removed as hydrogen gas, and until all protactinium had been reduced at the mercury cathode, which reduction was complete at $pH \geq 7$. The continued reduction of protactinium was followed by changes in the distribution factor D_{Pa} , a constant value being reached after 1–10 h depending on the composition of the two phase system. When the initial concentration of acetylacetonone in the organic phase was lowered from 2.5 M to 0.5 M, the time required to reach the maximum distribution λ_2 increases from about 1 to 10 h of electrolysis; this indicates a competition between hydrolyzation and complex formation with acetylacetonone.

After completing the reduction, the pH was lowered with 1 M HClO₄ and new equilibria were established within 40 min. As to the rest, the experimental procedures were similar to those described for reduction with chromous ions.

EXTRACTION WITH ACETYLACETONE

The distribution ($D = [Pa(IV)]_{org}/[Pa(IV)]_{aq}$) of tetravalent protactinium as a function of the hydrogen ion concentration is shown in Fig. 1. The initial concentration of acetylacetonone in the benzene phase was 0.1–2.5 M, and the hydrogen ion concentration in the aqueous phase 1 M (Na,H)ClO₄ was varied between 10⁻¹ and 10⁻⁹ M. The uncertainties in the plotted values are indicated by the size of the dots in the figures. The extracted protactinium complex was deduced to be mononuclear, as the distribution of protactinium was the same in the concentration range 0.3×10^{-14} to 1.3×10^{-10} M. The distribution experiments with the lowest protactinium concentrations were investigated using the isotope ^{234m}Pa in aqueous phases 0.14–0.5 M (Na,H)Cl. The distribution of Pa(IV) was very little affected by the substitution of a chloride medium for the perchlorate media (see also Fig. 1 for ²³³Pa – 1 M (Na,H)Cl) or by the addition of less than 10⁻³ M sulphate.

In order to evaluate the extraction mechanism, the logarithm of the distribution of Pa(IV) was plotted as a function of the aqueous acetylacetonone anion concentration $[AA^-]$ in the aqueous phase; see Fig. 2. The values

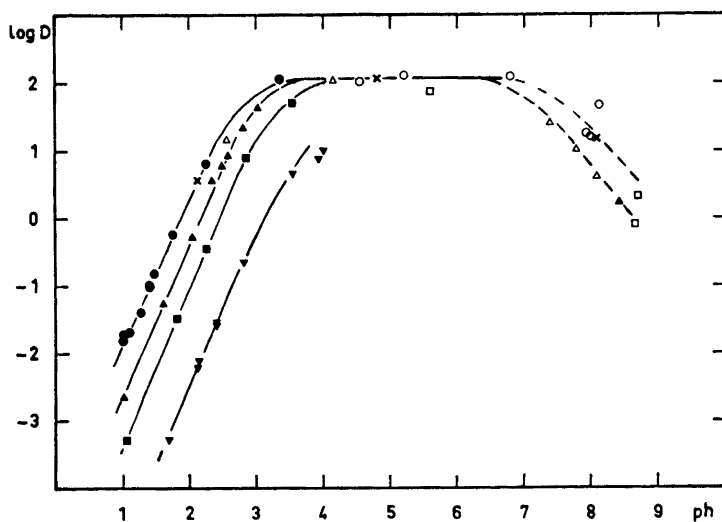


Fig. 1. Distribution of Pa(IV) between benzene and 1 M (Na,H)ClO₄, at 25°C, as a function of pH and at different initial acetylacetone concentrations in the organic phase, [HAA]_{org}^{init}. Unfilled symbols denote electrolytic reduction and filled symbols denote reduction with Cr³⁺. ●, ○, ×, 2.5 M HAA (× denote electrolysis in 1 M NaCl); ▲, △, 1.0 M HAA; ■, □, 0.5 M HAA; ▼, 0.1 M HAA.

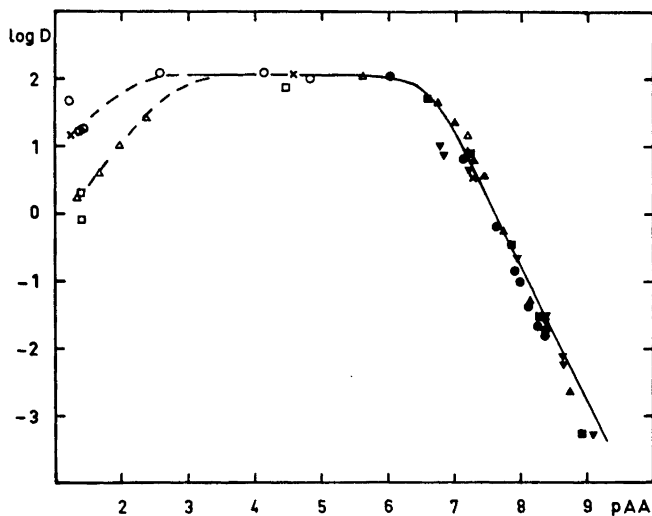


Fig. 2. Distribution of Pa(IV) between benzene and 1 M (Na,H)ClO₄, at 25°C, as a function of pAA and for different concentrations of acetylacetone in the organic phase. The same symbols as in Fig. 1 are used. The solid curve is calculated from estimated stability constants.

pAA = $-\log [AA^-]$ were calculated for equal phase volumes:

$$pAA = pK_a - pH + \log (K_d + 1 + K_a[H^+]^{-1}) - \log [HAA]_{org}^{init}$$

The following constants were used: $pK_a = 0.3027 - 0.01228T^{\circ}C$ ¹⁴ and $K_d = 4.80 \pm 0.02$ (20–40°C),¹⁵ $pH \leq 2$. The values, K_d , for the distribution constant for acetylacetone for pH-values less than 2 were estimated from

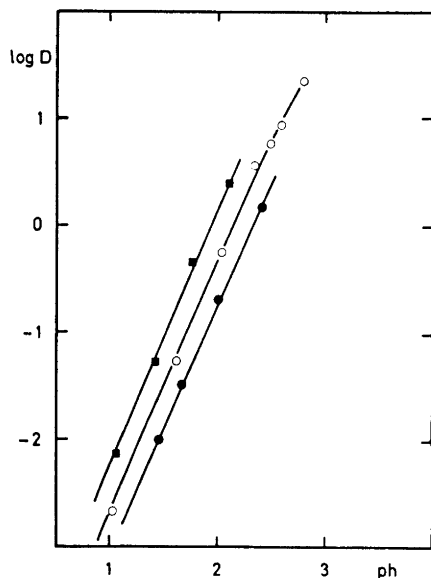


Fig. 3. Distribution of Pa(IV) between benzene and 1 M (Na,H)ClO₄, as a function of pH at different temperatures, for a 1 M initial concentration of acetylacetone in the organic phase. ■, 48.7 ± 0.1°C; O, 25.0 ± 0.1°C; ●, 3.1 ± 0.1°C.

a figure in Ref. 15 – the corrections were small.

The temperature dependence was investigated at various pH-values but at constant acetylacetone concentration ([HAA_{org}^{init} = 1 M] in the temperature interval 3–48°C, see Fig. 3.

RESULTS AND DISCUSSION

According to the general theory¹⁶ for evaluating the composition of the composite metal complex $M_m A_n(OH)_p(HA)_r(org)_s(H_2O)_t \dots$ in a liquid-liquid distribution system one concludes, from the relationship between the functions $\log D = f(pH)$ and $\log D = f(pAA)$, that the appropriate type of Pa(IV) acetylacetone complex is MA_n . The limiting slope $\delta \log D / \delta \log pAA$ as pAA is increased is equal to -2 , implying $n=2$ for the extracted species. The species of Pa(IV) formed in the aqueous phase are then M^{2+} , MAA^+ and uncharged $M(AA)_2$, the latter being distributed between the benzene phase and the perchlorate media, $\lambda_2 = [M(AA)_2]_{org} / [M(AA)_2]$.

The decrease from the plateau value λ_2 at higher pH may be explained by the formation of hydrolyzed species, and possibly also

negatively charged complexes like $M(AA)_3^-$.

From the linearity of the extraction of Pa(IV) for $pH \leq 3$ one can write the extraction mechanism as $M^{2+} + 2HAA(org) \rightleftharpoons M(AA)_2(org) + 2H^+$. The equilibrium constant has been calculated to be $\log K_D = -4.13 \pm 0.05$. The enthalpy and entropy changes have been calculated from the temperature dependence shown in Fig. 3.

$$\Delta H^\circ_{K_D}(25^\circ\text{C}) = 30 \pm 2 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{K_D} = 22 \pm 8 \text{ J mol}^{-1} \text{ K}^{-1}$$

The constants $\beta_1([MAA][M^{2+}]^{-1}[AA^-]^{-1})$, $\beta_2([M(AA)_2][M^{2+}]^{-1}[AA^-]^{-2})$ and λ_2 have been calculated by treating the data with an especially designed¹⁷ least squares program for solvent extraction data (arithmetically distributed errors). However, due to the great statistical uncertainty in β_1 new calculations were performed with only the two parameters β_2 and λ_2 . Thus neglecting the formation of MAA^+ the values $\log \lambda_2 = 2.07 \pm 0.10$ and $\log \beta_2 = 13.16 \pm 0.13$ were obtained. The elimination of the MAA^+ complex from the calculations changed the S_{min}/K value¹⁷ only slightly (from 0.195 to 0.214) which indicates that the MAA^+ complex was statistically insignificant. The calculated distribution function is given by the solid line in Fig. 2. By slope analysis¹⁸ of the function $\log D = f(pA)$ the following values were obtained: $\log \lambda_2 = 2.06$, $\log \beta_1 = 6.1$ and $\log \beta_2 = 13.0$. (The errors in the logarithm of these values was estimated graphically to be ± 0.1 .) The determination of ΔH° and ΔS° for β_1 , β_2 and λ_2 needs rather accurate temperature data for the whole distribution curves which could not be obtained because of the experimental difficulties (e.g., two different reduction methods were needed to cover the whole pH range).

Pa(IV) is here shown to coordinate only two acetylacetone molecules, thus differing from the behaviour of the tetravalent actinides Th, U, Np, and Pu which form MA_4 extraction systems.^{18,19} Solid $Zr(AA)_4$ and $Hf(AA)_4$ [but not $Pa(AA)_4$] have been prepared,^{20,21} and as a consequence the liquid-liquid distribution systems of Zr(IV)^{22,23} and Hf(IV)^{23–25} with benzoylacetone and acetylacetone have been considered to be MA_4 systems. However, the distribution data reported do not exclude the hydrolyzed MA_2 system.

The doubly charged positive aqueous Pa(IV) ion has hitherto been denoted M^{2+} as its formula is not evident. Neglecting the coordination of water molecules, one may propose the formula PaO^{2+} or $Pa(OH)_2^{2+}$. The formula $Pa(OH)_2^{2+}$ is preferred by some authors.^{3,6} However, the rather large stability range of M^{2+} (over more than two *ph*-units) favours the species PaO^{2+} rather than $Pa(OH)_2^{2+}$; the latter may be regarded as an intermediary between $Pa(OH)^{2+}$ and $Pa(OH)_3^+$, neither of which was indicated to exist in this investigation. However, a species like PaO^{2+} has not been observed for Zr(IV)²⁶⁻²⁸ Hf(IV) or the actinides.

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