Aqueous Chemistry of Protactinium(IV). 2. Pa(IV) Complexes in Acetylacetone-Sulphate Media

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Stability and distribution constants for tetravalent protactinium acetylacetonate and sulphate complexes were obtained from liquid-liquid distribution measurements of Pa(IV) between acetylacetone (HAA) in C₆H₅ and 0.94 M (Na₂H)ClO₄ + 0.06 M Na₂SO₄ at 25°C. The constants \( K_{\text{ex}} = \frac{[\text{Pa}(\text{OH})(\text{AA})]_{\text{org}}}{[\text{Pa}(\text{OH})(\text{AA})]_{\text{aq}} \times [\text{SO}_4^{2-}]_{\text{aq}}} \) and \( K_D = \frac{[\text{Pa}(\text{OH})(\text{AA})]_{\text{aq}}}{[\text{Pa}(\text{OH})(\text{AA})]_{\text{org}} \times [\text{OH}^-]_{\text{aq}}} \) were calculated to be \( \log K_{\text{ex}} = 12.3 \pm 0.1 \) and \( \log K_D = 18.34 \pm 0.10 \), and \( \log K_D = 2.54 \pm 0.06 \).

The addition of sulphate to the extraction system \( \text{Pa(IV)}^- - (\text{Na}_2\text{H})\text{ClO}_4 \rightarrow \text{HAA} - \text{C}_6\text{H}_5 \) changed the extraction mechanism from \( 2\text{HAA}_{\text{org}} \rightarrow (\text{Na}_2\text{H})\text{ClO}_4 + 2\text{H}^+ \) (where \( M = \text{Pa(OH)}^{4+} \) or \( \text{PaO}^{4+} \)) to \( \text{Pa(OH)}^{4+} + 3\text{HAA}_{\text{org}} \rightarrow (\text{Pa(OH)})(\text{AA})_{\text{org}} + 3\text{H}^+ + \text{SO}_4^{2-} \). The equilibrium constant for the latter reaction was calculated to be \( \log K_D = -8.17 \pm 0.06 \) with \( \Delta H^\circ = 14 \pm 3 \text{ kJ/mol} \) and \( \Delta S^\circ = -110 \pm 11 \text{ J/(mol K)} \).

The distribution of Pa(IV) between 1 M (Na₂H)ClO₄ and benzene in the presence of acetylacetone showed that Pa(IV) is complexed and extracted as a divalent cation. In order to examine this species, assumed to be \( \text{PaO}^{4+} \) or \( \text{Pa(OH)}^{4+} \), further, the system was investigated in an aqueous sulphate medium. Mitsuiji 4 has found a 1:1 Pa(IV) - HSQ⁻ complex with sulphate in 0.5 M (Na₂H)ClO₄ at pH 0.4 - 1.1, and suggested the reaction \( \text{Pa(OH)}^{4+} + \text{HSO}_4^- \rightarrow \text{Pa(OH)}\text{SO}_4^{2-} + \text{H}_2\text{O} \). Further, the hydrolysis of Pa(IV) has been studied by a thionyltrifluoroacetone (TTA) extraction method and the results interpreted as a stepwise formation of the hydrolyzed species \( \text{Pa(OH)}^{4+} \), \( \text{Pa(OH)}^{4+} \) (or \( \text{PaO}^{4+} \)), and \( \text{Pa(OH)}^{2+} \) (or \( \text{Pa(OH)}^{4+} \)).

THEORY

The extraction of Pa(IV) from an aqueous sulphate medium into an organic solvent in the presence of acetylacetone involves complexes of the general type \( M_m\text{L}_n(\text{OH})_pB_q(\text{HL})_r(\text{Org})_s(\text{H}_2\text{O})_t \), where in our particular case \( M \) stands for Pa(IV), \( \text{HL} \) for undissociated acetylacetone, \( \text{H}_2\text{B} \) for \( \text{HSO}_4^- \), and \( \text{Org} \) for the organic medium (benzene). Following Rydberg, neglecting solvent interaction, the general complex can be written \( \text{M}(\text{HL})_m(\text{H})_n(\text{B})_q \) (where \( x = n + r \) and \( y = n + p + 2q \), as long as only mononuclear \( (m = 1) \) complexes are formed. For \( x > -y \) this complex is acidic, white for \( x < -y \) it is basic. To simplify our case further we may assume that only one complex is extracted, \( \text{M}(\text{HL})_m(\text{H})_n(\text{B})_q \). Thus the distribution of tetravalent protactinium may be written

\[
D_M = \frac{[\text{M}(\text{HL})_m(\text{H})_n(\text{B})_q]_{\text{org}}}{\sum_{x,y} [\text{M}(\text{HL})_m(\text{H})_n(\text{B})_q]_{\text{aq}}} \tag{1}
\]

where the organic phase is denoted by the index org, and the aqueous phase is not indexed. It is, of course, necessary to verify experimentally that the conditions for the formation of the species \( M(\text{HL})_m(\text{H})_n(\text{B})_q \) are fulfilled. One may decide whether or not \( m = 1 \) by varying the metal concentration (a constant \( D_M \) implies \( m = 1 \)). To investigate whether or not solvent interactions may be neglected, different solvents may be tried. We may rewrite the above equation

\[
D_M = \frac{\lambda_{\text{abc}}[\text{HL}]^x[\text{H}]^y[B]^z}{\sum_{x,y} \beta_{\text{def}}[\text{HL}]^x[\text{H}]^y[B]^z} \tag{2}
\]

(Footnote: \( g \) is used here and not \( z \), as \( z \) is used to denote \( p+i \) in Ref. 4).
where \( \lambda_{abc} \) is the distribution constant of the species \( M(HL)_a(H)_b(B)_c \) between the two phases, and \( \beta _{xy} \) is the stability constant for the formation of a particular complex. By measuring \( D_M \) as a function of each variable separately (e.g. \( D_M ([HL])_a[H], [B] \)) it should in principle be possible to determine explicitly all equilibrium constants from a sufficiently large number of experimental points. However, it is easier to approach the problem by the slope analysis technique, \( \delta \) i.e. to determine which of the coefficients \( a, b, c, x, y, \) and \( q \) have to be considered.

The slope analysis technique involves the determination of the partial derivatives of eqn. 2 at constant \((HL), [B], \) and \([H] \). If the aqueous phase is assumed to contain a complex with the average composition \( M(HL)_a(H)_b(B)_c \), then the partial derivatives are:

\[
\delta \log D_M([HL])_a[H], [B] = (a - 2b) \delta \log [HL] \quad (3a)
\]

\[
\delta \log D_M([H])_a[H], [B] = (-b - y) \delta \log [H] \quad (3b)
\]

\[
\delta \log D_M([B])_a[H], [H] = (c - q) \delta \log [B] \quad (3c)
\]

Thus slope analysis gives only the difference between the number of ligands bound to the metal atom in the organic phase and the corresponding average number for the aqueous phase. To determine the composition of the species, other information and criteria are therefore required, for example the charge on the metal atom, the fact that only uncharged species dissolve in the organic phase, and the fact that acid and basic ligands may not at the same time occur in the metal complex (such an assumption is of course not valid for very stable basic entities such as \( UO_2^{2+} \) in the complex \( UO_4AA(HAA) \)). Such criteria, which limit the number of possible species, depend on the particular chemical system.

In the absence of the second complex former \( B \), the composite complex is reduced to \( M(HL)_a(H)_b \) (or \( MLn(OH)\)) from \( (HL)_c \). From a plot of \( \delta \log D_M([HL])_a[H] \) it is rather easy to get qualitative information about the species formed. This is helpful for estimating values for the coefficients \( x \) and \( y \). This approach will also be applied in this paper.

With the coefficients in eqn. 2 known, the equilibrium constants \( \lambda_{abc} \) and \( \beta _{xy} \) may be calculated. If a large number of complexes are formed, such a calculation becomes rather complicated, particularly by graphical methods (cf. Ref. 6). We have therefore transformed eqn. 2 into a set of linear equations and solved it explicitly for the coefficients, according to Sullivan, Rydberg and Miller. This provides the coefficients with their standard deviations.

**EXPERIMENTAL**

The distribution experiments were carried out in a 50 ml glass vessel. The vessel was closed with a tight lid and an oxygen-free atmosphere was maintained with a slow flow of nitrogen. The apparatus was equipped with a magnetic stirrer and thermostated (± 0.05°C) with a stream of water through the mantle of the vessel. Equal volumes (15 ml) of (0.1 H, 0.9 Na)ClO\(_4\) and acetylacetone in benzene were added and the system was prepared for reduction, either electrolytically or with chromous ions.

The electrolytic reduction was carried out, after addition of \(^{233}\)Pa, by electrolysis between a mercury cathode and a platinum anode. The anode compartment was separated from the bulk solution by an almost tight glass frit. The electrolysis was performed for 1–10 h at 10–50 mA (10–20 V) until the \( p\text{H} \) (\( p\text{H} = -\log[H^+] \)) reached about 8.5. After complete reduction, which was obtained for \( p\text{H} \) higher than 7, 1 ml 1 M Na\(_2\)SO\(_4\) was added. The \( p\text{H} \) was then decreased with 1 M HClO\(_4\) and the system equilibrated by stirring for about 20–40 min.

For reducing Pa(V) to Pa(IV) with chromous ions, 3–6 ml liquid amalgamated zinc (2%, by weight, Zn in Hg) and 0.1 ml 1.92 M Cr(CIO\(_4\)) were added. The green Cr(III) ions were reduced to blue Cr(II) ions before addition of \(^{233}\)Pa and 0.005–2 ml 1 M Na\(_2\)SO\(_4\), because it was observed to be relatively difficult to reduce \((10^{-2}) \) M Cr(III) in the presence of sulphate. It was unessential whether the sulphate was added prior to or after the addition of the organic phase. The \( p\text{H} \) was adjusted with 1 M NaOH, 0.1 M NaOH + 0.9 M NaClO\(_4\) or 1 M (H\(_2\)NaClO\(_4\) and additional acetylacetone was added as required. Distribution equilibrium was reached within 10 min of stirring.

In order to investigate the distribution of Pa(IV) at higher sulphate concentrations, experiments were performed with aqueous phase of 0.308 M Na\(_2\)SO\(_4\) and 0.005 M Cr\(_2\)(SO\(_4\))\(_3\). These sulphate phases of unit ionic strength were reduced electrolytically at \( p\text{H} \) 2.30. In order to measure the distribution of Pa(IV), equal samples (1.31 ± 0.005 ml) were taken from each phase with disposable glass pipettes. The pipettes were crushed in 20 ml glass tubes and the activity from \(^{233}\)Pa was measured with a NaI(Tl) crystal. Only the complex 80–110 keV gamma peaks of \(^{233}\)Pa were measured; the total efficiency was calculated to be 24% using a \(^{227}\)Np – \(^{233}\)Pa standard.
The total counts measured for both phases were around 200,000. More than 2000 disintegrations were measured from the least active phase, which was at least twice as active as the background. Thus the radiometric accuracy in $D$ was better than 3%, so that the logarithm of the distribution factor $D_{Pa}$ has a radiometric spread of ±0.01. The $pH$ was calculated from the measured EMF of a glass calomel electrode pair with the KCl replaced by 1 M NaClO$_4$. The accuracy of the $pH$ measurements was ±0.01 $pH$ units. The hydrogen ion activity ($pH$) in the sulphate phases (0.308 M Na$_2$SO$_4$ + 0.005 M Cr$_2$(SO$_4$)$_3$) was measured with an ordinary glass calomel electrode combination, which was calibrated with standard $pH$ buffer solutions. The acetylacetone concentration was checked by spectrophotometric determination of the absorbance at 490 nm of the Fe(III) acetylacetone complex and was found to agree, within the accuracy (±2%) of the method, with the added concentration. One or two drops of the stock solution of $^{239}$Pa in 7 M HClO$_4$ were normally added to the system giving a protactinium concentration of $10^{-10.4±0.4}$ M. The absorption of protactinium on the glass walls of the vessel was low as long as Pa was in the tetravalent state; moreover it was found that desorbed protactinium (that had been absorbed during previous experiments) gave the same distribution values as "fresh" protactinium. This is very different from the behaviour of Pa(V) (cf., e.g. Ref. 11). About 5 equilibrium points were determined during each distribution run, after which the vessel was washed with sulphuric acid containing potassium dichromate.

EXTRACTION WITH ACETYLACETONE IN THE PRESENCE OF SULPHATE

The distribution of Pa(IV) ($D = [Pa(IV)]_{org}/[Pa(IV)]$) between 1 M (Na$_2$H)ClO$_4$ and benzene was studied as a function of the sulphate, the hydrogen ion and the acetylacetone (HAA) concentration, and of the temperature, see Figs. 1 - 5.

The protactinium was kept in its tetravalent state either by $10^{-5}$ M Cr$_2$O$_7^{2-}$ ions at $pH$ 1 - 3, or by electrolytic reduction at $pH$ 2 - 9. Reduction with Cr$_2$O$_7^{2-}$ was not possible at $pH$ higher than 3 because of the formation of extractable Cr(III) acetylacetone complexes.

The size of the dots in the figures corresponds approximately to the uncertainties in the measured values.

The distribution experiments were made at different trace concentrations of $^{239}$Pa ($10^{-10}-10^{-11}$ M). No [Pa]-dependence was found, indicating that only mononuclear protactinium complexes were formed.

The sulphate dependence was investigated at different $pH$ and acetylacetone concentrations, see Fig. 1. The concentration of free SO$_4^{2-}$ was calculated from the relations $K_B = [HSO_4^{-}][H^+]^{-1}[SO_4^{2-}]^{-1}$ and $[SO_4^{2-}] = C_B/(1 + [H^+]K_B)$ where $C_B$ is the total amount of SO$_4^{2-}$ present (as added). The dissociation of HSO$_4$ at unit ionic strength, at 25°C, depends upon the ionic medium. The stability constant $K_B$ is $10^{6.48}$ in $H_2SO_4$ media,$^{12}$ $10^{6.74}$ for mixtures$^{13}$ of NaClO$_4$, HClO$_4$ and Na$_2$SO$_4$, and $10^{6.92}$ for (0.01 H, 0.99 Na)ClO$_4$.$^{14}$ At $pH \gtrsim 1$ the amount of free $H_2SO_4$ can be neglected, and in the presence of trace concentrations of Pa the amount of SO$_4^{2-}$ complexed by Pa can also be neglected. The dominating sulphate species for $pH > 1.4$ — i.e. over almost the entire $pH$ range investigated — was SO$_4^{2-}$.

The acetylacetone dependence was in-
Fig. 2. Distribution of $^{238}$Pa(IV) as a function of initial concentration of acetylacetone in the organic phase $C_{AA}$, at 25°C, for different pH and sulphate concentrations. Unfilled symbols denote aqueous phases of $(1-x)(Na,H)ClO_4 + xNa_2SO_4$, and filled symbols denote 0.308 $Na_2SO_4 + 0.005 Cr_3(PO_4)_3$.

○ pH 2.39 $x=0.057$
□ pH 2.40 $x=0.080$
△ pH 1.00 $x=0.059$
● pH 1.36

Fig. 3. Distribution of $^{238}$Pa(IV) between benzene and 0.937 M (Na,H)ClO_4 + 0.003 M Na_2SO_4 (at 25°C) as a function of pH, at different initial acetylacetone $C_{AA}$ concentrations in the organic phase. Filled symbols denote electrolytic reduction and unfilled symbols reduction with Cr^{3+}.

$C_{AA}$

○ 2.50 M
□ 1.00 M
△ 0.50 M
● 0.39 M

Fig. 4. Distribution of $^{238}$Pa(IV) between benzene and 0.941 M (Na,H)ClO_4 + 0.059 M Na_2SO_4 (at 25°C) as a function of pAA (=-log [AA^-]). The solid curve is calculated from estimated stability constants.

$K_a$ is the acid dissociation constant, $K_d$ the distribution constant for acetylacetone and $C_{AA}$ is the initial concentration of HAA.

The following constants were used: $pK_a = 9.3027 - 0.01228T^\circC$ and $k_d = 4.80 \pm 0.02$.

The influence of the temperature on the distribution of Pa(IV) was studied by changing the temperature (3-48°C) at constant acetylacetone ($C_{AA}$=1 M), sulphate (0.06 M) and hydrogen ion (pH 2.01) concentrations, see Fig. 5. The glass electrode combination used to measure the pH was pre-calibrated in the proper temperature range. The extraction was carried out with both increasing and decreasing temperature. Some primary experimental data are collected in Table 1.

Fig. 5. Distribution of $^{233}\text{Pa(IV)}$ between 1 M acetylacone in benzene and 0.944 M (Na,H)-ClO$_4^-+0.056$ M Na$_3$SO$_4$, at pH 2.01, as a function of the temperature 3−43°C ($T = 276−321$ K).

DERIVATION OF COMPLEXES

The plots of log $D_{\text{Pa}}([\text{SO}_4^{2-}])_{[\text{HAAs}]_[\text{H}]}$ (Fig. 1), log $D_{\text{Pa}}([\text{AA}]_{[\text{H}]})_{[\text{HAAs}]_2}$ (Fig. 2), and log $D_{\text{Pa}}([\text{H}])_{[\text{HAAs}]_2}[\text{SO}_4]_2$ (Fig. 3) show that the formation of complexes of the type Pa(HAA)$_2$(H)$_3$.[SO$_4$_]$_3$ is to be expected.

In Fig. 1 the gradient of the curves $D_{\text{Pa}}([\text{SO}_4^{2-}])$ change from zero to −1 with increasing sulphate concentration. In the horizontal part $D_{\text{Pa}}$ is independent of [SO$_4^{2-}$] and thus $c = \bar{q}$, according to eqn. 3c. The simplest assumption is that both $c$ and $q$ are zero. If no Pa−SO$_4$-complexes are formed, only Pa−AA-complexes have to be considered; the plateau values should then vary with pAA as shown by Lundqvist [1] for the system Pa−HAA−H$_2$O−C$_6$H$_5$ for which the following complexes were identified: Pa(OH)$_3$+(or PaO$^+$), Pa(OH)$_2$AA$^+$ and Pa(OH)$_2$(AA)$_2$. Such dependence is in fact found.

For log [SO$_4^{2-}$] $\geq 10^{-4}$ the slopes of the curves in Fig. 1 are again constant and equal having $c = \bar{q} = -1$. The most reasonable assumption is that $c = 0$, i.e. there is no sulphate complex in the organic phase, and $\bar{q} = 1$, i.e. one sulphate ion is attached to the aqueous central atom. Another but less likely possibility is that the metal complex in the organic phase contains one sulphate, and that in the aqueous phase two.

In Fig. 2 the slope $\delta \log D_{\text{Pa}}/\delta \log C_{\text{AA}}$ is +3. Remembering that [HAA] is a linear function of $C_{\text{AA}}$ under our conditions, one finds from the


theory that $a - \bar{x} = 3$. All lines are for constant [SO$_4^{2-}$] and pH (pH $\leq 2.4$). The simplest explanation is that $\bar{x} = 0$ and $a = 3$, i.e. that under these conditions the aqueous phase contains negligible concentrations of M(HL)$_2$(H)$_3$-complexes, while in the organic phase M(HL)$_2$(H)$_{-}$-complexes dominate.

From the plot in Fig. 3 of log $D_{\text{Pa}}([\text{H}^+])$ for various (constant) values of $C_{\text{AA}}$ and $C_{\text{SO}_4}$ it is seen that at pH $\leq 3$ different curves are obtained for different $C_{\text{AA}}$ (and consequently different [HAA]), while at pH around 5−7 all lines coincide into one horizontal line (plateau). Our theory then leads us to the conclusion that at pH $\leq 2.4$, $\bar{q} = 0$ and at pH $\geq 5$, $\bar{q} = 0$. The value of $b$, which must be the same in both pH-regions, is obtained from the electrostatic neutrality criterion for the extracted complex M(HL)$_2$(H)$_{-}$. As the charge on M is 4+ one finds that $b = 4$. Thus for pH $\leq 2.4$, $\bar{q} = 1$ and for pH $\geq 5$, $\bar{q} = 4$. The conclusions arrived at so far may be summarized as in Table 2.

To reach a conclusion concerning the nature of the species dominant at pH 5−7 one may consider Fig. 4, in which log $D_{\text{Pa}}$ is plotted against pAA for various $C_{\text{AA}}$ at constant $C_{\text{B}}$. All points seem to fall on one curve, the slope of which varies from −3 to 0 (and then assumes positive values for pAA $> 3$). According to the general theory for ML$_n$(OH)$_p$(HL)$_q$-complexes, such a curve can only be obtained if $r = 0$ and $p$ is constant throughout the region (of gradient $\geq 3$ to 0). Consequently one is led to the conclusion that the organic phase contains only Pa(OH)(AA)$_2$, and the aqueous phase Pa(OH)(AA)$_2$[SO$_4$_]$_3$, where $n$ varies from 0 to +3 and $v$ has the values 0 or +1.

The only complexes required to interpret the experimental results are thus Pa(OH)[SO$_4$]$_3$ and Pa(OH)AA$_2$ but it is reasonable to assume that the intermediate complexes Pa(OH)(SO$_4$)AA, Pa(OH)AA$_2$ and Pa(OH)AA$_3$ are also formed. (Though the mixed sulphate and acetylacone complex is expected to be weak and might therefore be neglected immediately, provision for its existence is made in the calculations below.)

The decrease in log $D_{\text{Pa}}$ at pH $> 7$ (Fig. 3) and at pAA $< 3$ (Fig. 4) indicates hydrolysis or formation of Pa(OH)(AA)$_2$ in the aqueous phase, but the data are not conclusive.
Table 1. Experimental data for the distribution of \(^{133}\text{Pa}(\text{IV})\) between acetylacetone in benzene and 0.94 M (NaH)\(\text{ClO}_4\) + 0.06 M Na\(_2\)SO\(_4\) at 25.0 ± 0.1°C. About 2000 disintegrations were measured from the least active phase, which was at least twice as active as the background. The total measured activity from both phases was around 200 000 disintegrations. Remarks: C = reduction with Cr\(^{3+}\); E = electrolytic reduction, \(C_{AA}\) = initial concentration of HAA in organic phase, \(C_B\) = total concentration of sulphate and \(p\AA = -\log [\text{AA}^\text{-}]\).

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Table 2. Summary of conclusions.

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<td>(b = 4) (Fig. 3)</td>
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CALCULATION OF EQUILIBRIUM CONSTANTS

The sulphate extraction system was found to consist of the protactinium complexes $\text{Pa(OH)}_2\text{SO}_4^{+}$, $\text{Pa(OH)}_2\text{SO}_4\text{AA}$ and $\text{Pa(OH)}_2\text{(AA)}_{2-n}$, $0 \leq n \leq 3$. If the formation of the acetylacetonate complexes $(\text{Pa(OH)}_2\text{SO}_4^{+} + \text{AA}^-) \rightleftharpoons \text{Pa(OH)}_2\text{SO}_4\text{AA}$ and $(\text{Pa(OH)}_2\text{SO}_4^{+} + n\text{AA}^-) \rightleftharpoons \text{Pa(OH)}_2\text{(AA)}_{2-n}\text{SO}_4^{2-}$; $0 \leq n \leq 3$) is described by the formation constants $\beta_1$ and $\beta_n'$ respectively, then the dependence of $D_{\text{Pa}}$ upon the variable $[\text{AA}^-]$, for $p\text{AA} > 3$, can be written:

$$D_{\text{Pa}}^{-1} = \frac{\beta_1'}{\lambda_2\beta_2'} + \frac{(\beta_1' + \beta_n'[\text{SO}_4^2]) [\text{AA}^-]^{-2}}{\lambda_2\beta_2'} + \frac{\beta_0'[\text{AA}^-]^{-1}}{\lambda_2\beta_3}$$

The coefficients in this equation were calculated with a least-squares program specially designed for solvent extraction data. However, due to the unacceptably large statistical uncertainties in $(\beta_1' + \beta_n'[\text{SO}_4^2])$ and $\beta_n'$ these constants were set equal to zero and calculations were performed with only the two parameters $\beta_1'$ and $\lambda_2$.

When the formation of $\text{Pa(OH)}_2\text{AA}^{2+}$ and $\text{Pa(OH)}_2\text{(AA)}_{2-n}$ was thus excluded, the values of $\log\lambda_2 = 2.54 \pm 0.06$ and $\log \beta_1' = 18.34 \pm 0.10$ were obtained. The exclusion of $\text{Pa(OH)}_2\text{AA}^{2+}$ and $\text{Pa(OH)}_2\text{(AA)}_{2-n}$ from the calculations changed the $S_{\text{min}}/K$ value only slightly (from 0.142 to 0.175) which indicates that those complexes were statistically insignificant. By slope analysis of the distribution function the following values were obtained: $\log \lambda_2 = 2.6$, $\log \beta_1' = 12.3$, and $\log \beta_2' = 18.4$. (The error in the logarithm of these values was estimated graphically to be $\pm 0.1$.)

The distribution of Pa(IV), under conditions where the concentrations of the acetylacetone complexes $\text{Pa(OH)}_2\text{(AA)}_{2-n}$ may be neglected in comparison with $\text{Pa(OH)}_2\text{SO}_4^{+}$, can be described by the extraction reaction

$$\text{Pa(OH)}_2\text{SO}_4^{+} + 3\text{HAA(\text{org})} \rightleftharpoons \text{Pa(OH)}_2\text{(AA)}_3(\text{org}) + 3\text{H}^+$$

The validity of this equilibrium is demonstrated by the linearity of $\log D_{\text{Pa}}$ with $[\text{SO}_4^{2-}]$ (slope $-1$), with $p\text{K}$ (slope $+3$) and with $[\text{HAA}]_{\text{org}}$ (slope $+3$) for $p\text{K} < 2.4$ and $[\text{Na}_2\text{SO}_4] > 0.05$ M (see Figs. 1, 3 and 2). The equilibrium constant $K_D$ has been calculated to be $\log K_D = -8.17 \pm 0.06$ at $25^\circ$C (0.94 M $\text{Na}_2\text{HClO}_4 + 0.06$ M $\text{Na}_2\text{SO}_4$). The enthalpy and entropy changes were found from the temperature dependence (see Fig. 5) to be $\Delta H^\circ = 14 \pm 3$ kJ/mol and $\Delta S^\circ = -110 \pm 11$ J/(mol K).

DISCUSSION

The extraction mechanism for the system $\text{Pa(IV)} - (\text{Na}_2\text{HClO}_4 - \text{HAA}$ was found to change when sulphate was added. There are good reasons for believing that this change is not associated with a change in the valency of Pa, i.e. that complete reduction is obtained even in the presence of sulphate. Firstly, it has been shown that for other extraction systems complete reduction of Pa(V) to Pa(IV) is achieved in the presence of $\text{Cr}^{3+} \geq 10^{-4}$ M (both in the presence and absence of sulphate). Secondly, as the sulphate complex with Pa(IV) is stronger than the corresponding complex with Pa(V), it ought to be easier to reduce Pa(V) in the presence of sulphate. Thirdly, the distribution of Pa(V) should not be expected to be described by the simple relation $D = f(p\text{AA})$, as the Pa(V) - HAA system was found to be much more complicated.

The change in the extraction mechanism from $\text{M}^{2+} + 2\text{HAA(\text{org})} \rightleftharpoons \text{M(\text{AA})_2(\text{org})} + 2\text{H}^+$, where $\text{M}^{2+}$ is PaO$^{2+}$ or Pa(OH)$^{2+}$, to $\text{Pa(OH)}_2\text{SO}_4^{+} + 3\text{HAA(\text{org})} \rightleftharpoons \text{Pa(OH)}_2\text{(AA)}_3(\text{org}) + 3\text{SO}_4^{2-} + 3\text{H}^+$ may be due to the dehydrolyzation of Pa(IV) with sulphate according to the reaction $\text{Pa(OH)}_2\text{SO}_4^{+} + \text{HSO}_4^- \rightleftharpoons \text{Pa(OH)}_2\text{SO}_4^{2+} + \text{H}_2\text{O}$ (or $\text{PaO}^{2+} + \text{HSO}_4^- \rightleftharpoons \text{Pa(OH)}_2\text{SO}_4^{2+}$). This would make it possible for an acetylacetone to replace the sulphate without rehydrolyzation of the central atom. Such an irreversible mechanism is proposed because Pa(OH)(AA)$_3$ is not formed in absence of sulphate. Consequently, we have not attempted to calculate the formation constant for Pa(OH)SO$_4^{2+}$.

The value of the distribution coefficient, $\lambda_3 = \log ([\text{M(\text{AA})}_2(\text{org})]/[\text{M(\text{AA})}_3]) = 10^{2.14 \pm 0.04}$, lies as expected between the distribution coefficient for $\text{M(\text{AA})}_2$, $\lambda_2 = 10^{2.67 \pm 0.10}$ (Ref. 1) and the theoretical value for $\text{M(\text{AA})}_3$, $\lambda_3 = 10^{4.65 \pm 0.05}$.

Finally, the present study did not indicate any further hydrolysis of Pa(IV) in the pH range 2.4-5.0.
range 1 to around 6 which agrees with the investigation in absence\(^1\) of sulphate.

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REFERENCES


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