Stability Constants for Protactinium(V)-Acetylacetone Complexes

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The stability (K) and distribution (Λ) constants for the complexes formed between Pa(V) and acetylacetone (HAA) have been calculated from the results of solvent extraction experiments. The following species were found; PaO^{3+}, PaO_2^+ (log $K_{02}=1.05\pm0.11$), $PaO(AA)^{2+}$ (log $K_{11}=1.00\pm0.17$), $PaO_2(AA)$ (log $K_{13}=-2.10\pm0.15$, log $\Lambda_{13}=0.02\pm0.12$), $PaO_2(AA)_2^-$ (log $K_{24}=-7.77\pm0.16$), $PaO(AA)_3$ (log $K_{33}=-0.38\pm0.11$, log $\Lambda_{33}=-0.06\pm0.30$), $PaO(AA)_3\cdot2HAA$ (log $K_{53}\Lambda_{53}=0.73\pm0.18$).

The results of solvent extraction experiments with Pa(V) and acetylacetone have been given in two earlier papers.[1,2] At that time no stability constants could be given because of computational difficulties. This paper describes how these difficulties were solved and gives the stability constants for the most probable species.

Pa(V) forms with acetylacetone (HAA) mixed mononuclear complexes of the type $M(HAA)_x H_{-y}$.[2,3] The distribution (D) of the metal (M) between an organic solvent (xylene) and water can be expressed as follows,[3]

$$D=\frac{\sum\limits_{x=0}^{X} K_{xN}\,\Lambda_{xN}[HAA]^x[H]^{-N}}{\sum\limits_{x=0}^{X}\sum\limits_{y=0}^{Y}K_{xy}[HAA]^x[H]^{-y}} \qquad (1)$$

where all charges have been omitted for simplicity.

Fig. 1 shows the dependence of the measured D-values on the hydrogen ion concentration [H] and acetylacetone concentration [HAA] in the aqueous phase. The standard deviations in the measurements, calculated from the uncertainties in the measured count rates, [HAA] and emf values, corresponds roughly to the size of the points in Fig. 1.
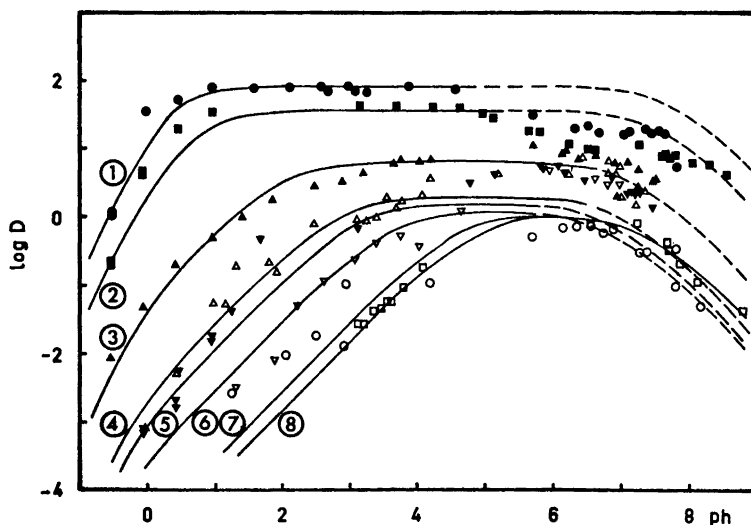
Fig. 1. The extraction of Pa(V) with acetylacetone as a function of ph at different acetyl-acetone concentrations (μ=3, H,NaClO$_4$).[2] The curves are computed from the equilibrium constants given in Table 2. The numbers in circles near the curves give the following connection between the full-drawn curves, the measured points and the acetyl-acetone concentration in the aqueous phase.

1 ● [HAA]=2.31—2.48 M,	2 ■ [HAA]=1.61—1.64 M,
3 ▲ [HAA]=0.61—0.65 M,	4 △ [HAA]=0.30—0.35 M,
5 ▼ [HAA]=0.24—0.25 M,	6 ▽ [HAA]=0.16 M,
7 ○ [HAA]=0.031—0.035 M,	8 □ [HAA]=0.016—0.019 M

GRAPHICAL ANALYSIS

In order to use eqn. 1 for the calculation of the constants K_{xy} and Λ_{xN}, the maximum values of x and y (X and Y) must be determined. In the most acid region a limiting slope of 3 is observed for the highest acetylacetone concentrations in Fig. 1, while for the lowest [HAA] a slope of 1 is obtained. These facts indicate [3] that the metal ion has a charge of at least +3 at low ph, and probably undergoes hydrolysis at higher ph to a species with charge +1. This is consistent with the assumption that Pa(V) exists as hydrated ions of PaO^{3+} and PaO$_2$$^+$ (or PaO(OH)$_2$$^+$); *cf., e.g.*, Ref. 4.

Fig. 2 shows the dependence of D on [HAA] for different ph values (ph is used to denote $-$log [H]). The change in organic solvent between the higher curves is not expected to influence the solubility and the distribution constant of the extracted complexes since k_d for HAA is constant in this concentration range. As can be seen from the figure, the slope changes from 5 at ph 0 to 1 at higher ph and low [HAA] or 2 at higher ph and high [HAA]. The figures indicate the number of acetylacetone molecules attached to each protactinium atom. Furthermore, the slope of 2 in the [HAA]-dependence in addition to the occurrence of the plateaus in Fig. 1 indicate that two of the acetylacetone molecules attached to Pa are undissociated. This corresponds
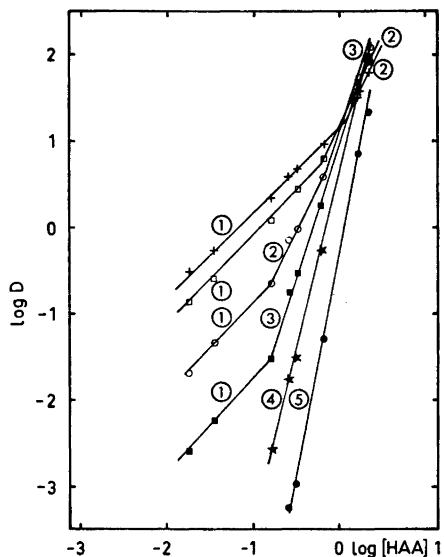
Fig. 2. The dependence of log D on log [HAA] at different values of ph. The numbers in the figure are the slopes of the lines. ● ph=0, ★ ph=1, ■ ph=2, ○ ph=3, □ ph=4, + ph=5.

to the extraction of a species $PaO(AA)_3 \cdot 2HAA$ at the highest acetylacetone concentrations used. It can also be concluded that $PaO(AA)_3 \cdot 2HAA$ never exists in significant amounts in the aqueous phase, otherwise a slope of less than 2 would occur in the [HAA]-dependence at the two highest acetylacetone concentrations. This is an important observation as it shows (see below) that it
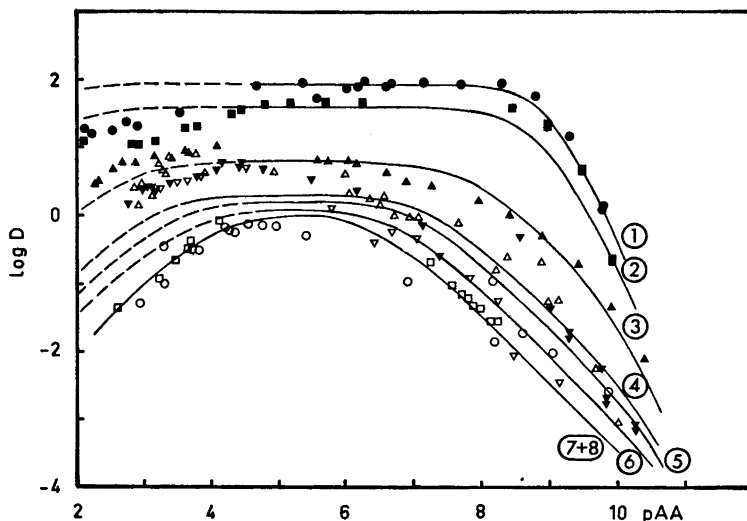

Fig. 3. The extraction of Pa(V) with acetylacetone as a function of pAA at different acetylacetone concentrations. The symbols used are the same as in Fig. 1.

is almost impossible to calculate the stability constant for $PaO(AA)_3 \cdot 2HAA$ from the experiments.

Fig. 3 shows log D as a function of pAA (*i.e.* $-\log$ [AA]) at the different [HAA] used. The formation of mixed complexes is evident as many of the curves do not coincide. At the lower acetylacetone concentrations (and higher ph), however, the measurements cluster around a single curve. This indicates the formation and extraction of the complex PaO_2AA. The slope 1 occurring at high pAA for this single curve suggests the formation of the negatively charged complex $PaO_2(AA)_2^-$.

Table 1. Species probably present in the Pa(V)-HAA-xylene-3 M NaClO$_4$ system as indicated by a graphical evaluation (x and y refer to eqn. 1). The extractable species are marked with an asterisk.

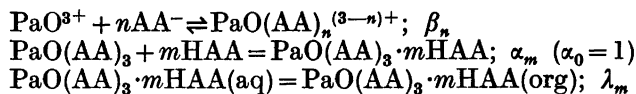| x \ y	0	1	2	3	4
0	PaO^{3+}	$PaO(OH)^{2+}$	PaO_2^+		
1		$PaO(AA)^{2+}$		$PaO_2(AA)$ *	
2			$PaO(AA)_2^+$		$PaO_2(AA)_2^-$
3				$PaO(AA)_3$ *	
4				$PaO(AA)_3 \cdot HAA$ *	
5				$PaO(AA)_3 \cdot 2HAA$ *	

The result of the graphical analysis is summarized in Table 1 which shows the different species expected. The scatter in the measurements makes a complete graphical evaluation of the constants in eqn. 1 dubious as this would depend heavily on "best" curves drawn through the measured points. The complexity of the problem makes the graphical solution very sensitive to quite small errors in a set of "best" curves. For this reason the final calculations were made numerically using the method of least squares and a small digital computer (Honeywell DDP-516).

NUMERICAL ANALYSIS

The numerical calculation of the constants in eqn. 1 was performed in six steps.

Step 1. It was assumed that only the complexes $PaO(AA)^{2+}$, $PaO(AA)_2^+$, $PaO(AA)_3$, $PaO(AA)_3 \cdot HAA$, and $PaO(AA)_3 \cdot 2HAA$ had to be considered below ph 5 for the curve in Fig. 1 with [HAA] $\simeq 2.48$. As the acetylacetone concentration is almost constant the last three complexes can be considered as a

single complex in the calculations. For this curve the following reactions can be assumed

$$PaO^{3+} + nAA^- \rightleftharpoons PaO(AA)_n^{(3-n)+}; \quad \beta_n$$
$$PaO(AA)_3 + mHAA = PaO(AA)_3 \cdot mHAA; \quad \alpha_m \quad (\alpha_0 = 1)$$
$$PaO(AA)_3 \cdot mHAA(aq) = PaO(AA)_3 \cdot mHAA(org); \quad \lambda_m$$

For constant [HAA], D can be expressed as follows

$$D = \frac{\lambda' \beta_3 \ [AA^-]^3}{\sum\limits_{n=0}^{3} \beta_n' \ [AA^-]^n} \tag{2}$$

where

$$\beta_n' = \beta_n \text{ for } n \neq 3 \tag{3}$$

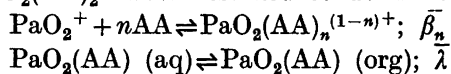$$\beta_3' = \beta_3 \ (1 + \alpha_1[HAA] + \alpha_2[HAA]^2) \tag{4}$$

$$\lambda' = \lambda_0 + \lambda_1\alpha_1[HAA] + \lambda_2\alpha_2[HAA]^2 \tag{5}$$

β_n', β_3 and λ' were first computed by applying a direct method of least squares [5] to eqn. 2. The value of β_2' thus obtained was negative. Hence it was concluded that the complex $PaO(AA)_2^+$ was either formed only in insignificant amounts or that the accuracy of the data was insufficient for a calculation of β_2'. β_2' was then omitted and the calculation repeated using an iterative method of least squares; cf., e.g., Ref. 6.

The curve with $[HAA] \simeq 1.6$ was then treated in the same way. The λ' values obtained differed, of course, for the two curves but the β_1' and β_3' values were almost identical in the two cases. This shows that the [HAA]-dependent terms can be neglected in eqn. 4 but not in eqn. 5, i.e. $PaO(AA)_3 \cdot HAA$ and/or $PaO(AA)_3 \cdot 2HAA$ are present in considerable amounts in the organic phase but only in negligible amounts in the aqueous phase. The conclusion is in accordance with the graphical evidence given above.

Step 2. In Figs. 1 and 3 the two uppermost curves are almost parallel. Assuming that the third curve also exhibits a plateau, eqn. 5 was fitted to the three λ' values. It was then found that the second term ($\lambda_1\alpha_1$) was negative. This term was therefore omitted and λ_0 and $\lambda_2\alpha_2$ estimated from the two uppermost curves. This result is an indication that the complex $PaO(AA)_3 \cdot HAA$ is only present in small amounts in the organic phase.

Step 3. For the three lowest curves in Fig. 1 the complexes $PaO_2(AA)$ and $PaO_2(AA)_2^-$ were assumed to dominate. Their formation can be written as

$$PaO_2^+ + nAA \rightleftharpoons PaO_2(AA)_n^{(1-n)+}; \quad \bar{\beta}_n$$
$$PaO_2(AA) \ (aq) \rightleftharpoons PaO_2(AA) \ (org); \quad \bar{\lambda}$$

The D value for these curves can then be expressed as

$$D = \frac{\bar{\lambda}\bar{\beta}_1[AA^-]}{\sum\limits_{n=0}^{2} \bar{\beta}_n \ [AA^-]^n} \tag{6}$$

From this equation $\bar{\beta}_1$, $\bar{\beta}_2$, and λ were computed by a direct least squares method.

Step 4. In the calculations described above, the system was treated as two independent parts. In order to explain all curves with one theory, eqn. 1, the intermediate results (values of β', α, λ, $\bar{\beta}$, and $\bar{\lambda}$) were expressed in terms of K_{xy} and Λ_{xN}. The result is given in Table 2. As can be seen in the table, one more constant (K_{02}) remains to be determined.

Table 2. First approximations and final values for the equilibrium constants.

Complex	x	y	First approximation		Final value	
			$\log K_{xy}$	$\log \Lambda_{xy}$	$\log K_{xy}$	$\log \Lambda_{xy}$
PaO_2^+	0	2	?	—	1.05 ± 0.11	
$PaO(AA)^{2+}$	1	1	-0.24	—	1.00 ± 0.17	
$PaO_2(AA)$	1	3	$\log K_{02} - 2.95$	-0.04	-2.10 ± 0.15	0.02 ± 0.12
$PaO_2(AA)_2^-$	2	4	$\log K_{02} - 8.51$		-7.77 ± 0.16	
$PaO(AA)_3$	3	3	1.26	1.09	-0.38 ± 0.11	-0.06 ± 0.30
$PaO(AA) \cdot 2HAA$	5	3	$\log (K_{53}\Lambda_{53}) = -0.18$		$\log (K_{53}\Lambda_{53}) = 0.73 \pm 0.18$	

Step 5. An estimate of K_{02} was obtained from a point on the third curve from the top (Fig. 1) at $ph \simeq 0$ ($K_{02} \simeq 6.9$), where comparable amounts of PaO^{3+} and PaO_2^+ can be expected to exist.

Step 6. The set of constants obtained in this way gave a set of distribution curves with all the important features of the curves in Fig. 1. However, the fit between these curves and the experimental points was not as good as desired. To obtain a better fit the constants were adjusted by an iterative method of least squares. When the complexes $PaO(OH)^{2+}$, $PaO(AA)_2^+$, and $PaO(AA)_3 \cdot HAA$ were introduced into this calculation their stability constants turned out to be zero or slightly negative. The result is given in Table 2 and the curves calculated from these constants are shown in Figs. 1 and 2. The error limits on the constants given in Table 2 were estimated from the error square sum according to the method described by Sillén.[7]

RESULTS AND DISCUSSION

There is one region in Fig. 1 where the computed curves and the measured points deviate considerably, namely at $ph \geq 4$ and $[HAA] > 0.035$ M. In this region a second plateau is observed for the highest acetylacetone concentrations. Careful comparison of the γ-spectra of the organic and aqueous phases excluded the possibility that the second plateau was caused by a radioactive impurity. There are, however, several other possible explanations for this phenomenon, *e.g.* formation and extraction of solvated complexes such as $PaO_2(AA) \cdot 2HAA$, extraction of species containing perchlorate or of polymeric species. The last explanation is, however, less likely than the other as it has been shown that the D-values in this region are independent of the metal concentration. This would only occur in the last case if the same polymeric

species dominated both the organic and aqueous phases over a large concentration range.

The most probable complexes in Table 2 can of course contain more water molecules than given by the formula. In the complex $PaO(AA)_3 \cdot 2HAA$, protactinium has an apparent coordination number of 9, which is unusually high. The coordination of two undissociated molecules is also observed for the TTA-complexes of Pa(V).[8]

From the value of K_{02} in Table 2 the equilibrium constant, $K_{2,OH}$ for the reaction

$$PaO^{3+} + 2OH^- \rightleftharpoons PaO_2^+ + H_2O$$
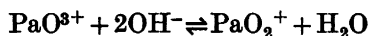
can be computed. The value obtained is $K_{2,OH} = 10^{29.4}$. Equal amounts of PaO^{3+} and PaO_2^+ should thus exist in aqueous solutions at $ph \sim 0.5$.

The intermediate complexes $PaO(OH)^{2+}$, $PaO(AA)_2^+$, and $PaO(AA)_3 \cdot HAA$ are not necessary for an explanation of the distribution curves. It is not possible, however, to draw the conclusion that these complexes do not form at all. It can only be stated that they never influence the experiments to any notable extent.

The combination of a graphical slope analysis, the division of the experiments into several regions, the numerical treatment of each sub-problem separately, and the availability of a small digital computer, where the course of the calculations could be followed by a graphical display and changes in the programs introduced when desired, turned out to be the most effective approach for solving the problem. It allowed a rapid testing of the different hypotheses for the complex formation and extraction of Pa.

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