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The Chemistry of Protactinium. VI. A Study of the Sulfato-Complex of Pa(IV) by Means of TTA-Benzene Extraction

Toshikazu MITSUJI

The Research Institute for Iron, Steel and Other Metals, Tohoku University, Katahira-cho, Sendai

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The behavior of Pa(IV) during extraction with TTA was investigated in perchlorate, chloride, and sulfate solutions (pH 0.4—1.1). In perchlorate and chloride solutions, the extraction equilibrium may be written as:

$$\mathrm{Pa(OH)_2^{2+} + 4HT \rightleftharpoons PaT_4 + 2H_2O + 2H^+}$$

On the other hand, the extraction by TTA from the sulfate solution may be described as:

$$\mathrm{Pa(SO_4)(OH)^+ + 4HT \rightleftharpoons PaT_4 + HSO_4^- + H_2O + 2H^+}$$

Therefore, the formation of the sulfato-complex of Pa(IV) is considered to occur as follows:

$$\mathrm{Pa(OH)_2^{2+} + HSO_4^- \rightleftharpoons Pa(SO_4)(OH)^+ + H_2O}$$

The equilibrium constant for the above reaction has been determined to be 320 at the ionic strength of 0.50 (temperature: 10±0.5°C).

Guillaumont investigated the distribution of Pa(IV) between the perchlorate solution with the ionic strength of 3 and the TTA-benzene solution, and reported that $\mathrm{Pa^{4+}}$ gradually hydrolyzed to $\mathrm{Pa(OH)_3^+}$ over the pH range from −0.5 to 3.0.[1] The same author also studied chloro-, sulfato-, and fluoro-complexes in aqueous solutions and calculated their stability constants at the ionic strength of 3.[2] In these papers, however, the experimental data were not reported in detail.

Two points have chiefly prevented the investigators from studying the behavior of Pa(IV) by using the ^{233}Pa tracer. One is the difficult reduction of Pa(V) in microquantities, and the other is the lack of a method to identify Pa(IV) in microquantities. In the foregoing paper, however, the present author showed that the ^{233}Pa(V) tracer was readily reduced by means of a liquid zinc amalgam in the presence of more than 10^{-4} M of Cr(III) and proposed that the co-precipitation with thorium fluoride gave an excellent method identifing of Pa(IV) in microquantities.[3]

The present author has also investigated the absorption spectra of Pa(IV) and inferred that the sulfato-complexes of Pa(IV) exist even in a dilute sulfuric acid solution, but that Pa(IV) is then reluctant to form chloro-complexes.[4] In this study, the sulfato-complex of Pa(IV) was investigated in detail by means of TTA-benzene extraction, after confirming the valency state of protactinium by the thorium fluoride co-precipitation method.

Experimental

Reagents. ^{231}Pa and ^{233}Pa were prepared by the method reported by Suzuki and Inoue.[5] All the reagents used were of the highest purity. Water was purified by distillation, followed by ion exchange treatment. Benzene was purified by distillation.

Apparatus. A reduction apparatus described earlier[4] was used for both reduction and extraction. The solvent extraction was carried out on a Iwaki universal mechanical shaker, Model V-S. The radioactivity was measured by means of a Kobe Kogyo well-type scintillation counter.

Procedure. The experimental procedures were as follows, unless otherwise noted. Pa(V) was reduced by means of a liquid zinc amalgam in the presence of 10^{-2} M Cr(III), as has been described in a previous report.[4] After the liquid zinc amalgam has been removed from the cell, the solvent extraction was carried out on a mechanical shaker for 25 min. The initial volumes of both the organic and the aqueous phases were 5.0 m*l*. The organic phase was pre-equilibrated by contact with its opposite. After the two phases had completely separated, an aliquot of each phase was transferred into a polyethylene test tube and its γ-radioactivity counted. The distribution ratio (D) was calculated by the following equation:

$$D=\frac{\gamma\text{-activity per m}l\text{ of the organic phase}}{\gamma\text{-activity per m}l\text{ of the aqeous phase}}$$

The concentration of protactinium was 10^{-7} M, and the ionic strength was kept constant at 0.50 throughout this experiment. The hydrogen ion concentration of

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[1] R. Guillaumont, *Bull. Soc. Chim. France,* **1965**, 1416.

[2] R. Guillaumont, *ibid.,* **1965**, 4739.

[3] T. Mitsuji, This Bulletin, submitted.

[4] T. Mitsuji. *ibid.,* in press.

[5] S. Suzuki and Y. Inoue, *ibid.,* **39**, 490 (1966).

the aqueous phase in equilibrium was determined by titration with the standard sodium hydroxide solution.

Results

The Confirmation of the Valency State of Protactinium. The protactinium which had been extracted into the benzene phase was back-extracted into the aqueous phase and then subjected to the thorium fluoride method described in a foregoing paper.[3)] More than 95% of protactinium was always co-precipitated with thorium fluoride. This means that protactinium remains tetravalent during solvent extraction.

Solvent Extraction from Perchlorate and Chloride Solutions. The TTA extraction of Pa(IV) was first carried out in a perchlorate solution as a non-complexing solvent. The relationship between the TTA concentration and the distribution ratio was examined in 0.37 M perchloric acid. As is shown in Fig. 1, the log-log plot of the distribution ratio and the TTA concentration shows a good linearity, with a slope of 4.

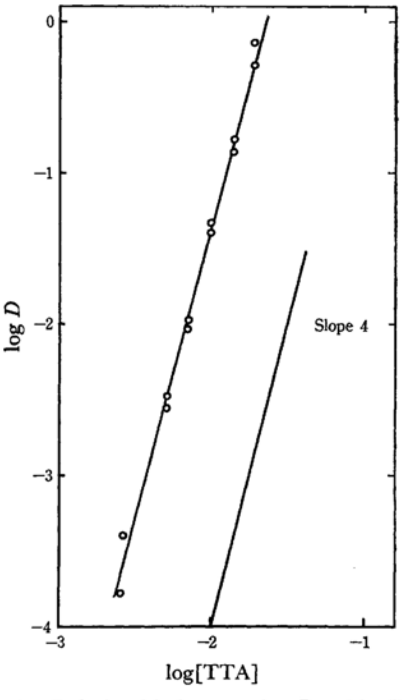

Fig. 1. Relationship between log D and log[TTA], 0.37 M $HClO_4$.

The effect of the hydrogen ion concentration on the extraction was examined by using a 10^{-2} M TTA-benzene solution. As Fig. 2 shows, the relationship between log D and $-\log[H^+]$ is linear, with a slope of 2, over the $-\log[H^+]$ range from 0.4 to 1.1.

The same experiments were also carried out in a chloride solution. The acid dependency of the distribution ratio was found to be second-power, as Fig. 3 shows.

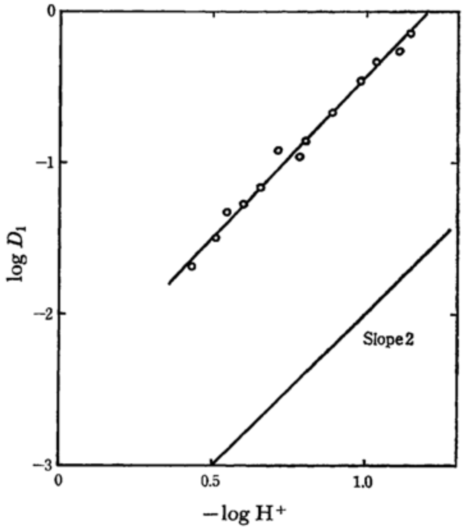

Fig. 2. Dependence of $\log D_1$ on $-\log[H^+]$ in the extraction from perchlorate solution.

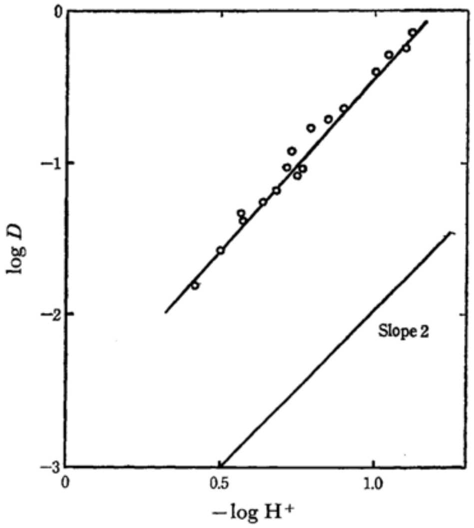

Fig. 3. Dependence of log D on $-\log[H^+]$ in the extraction from chloride solution.

Solvent Extraction from Sulfate Solution. To confirm the existence of sulfato-complexes of Pa(IV), solvent extraction was performed in a sulfate solution. The relationship between the TTA concentration and the distribution ratio was examined in 0.24 M sulfuric acid. The plot of the logarithm of the distribution ratio against the logarithm of the TTA concentration shows a linear relationship, with a slope of 4 (Fig. 4).

The relation of log D *versus* $-\log[H^+]$ was also investigated at a TTA concentration of 10^{-2} M. Figure 5 shows the linear relationship between them, with a slope of 2.

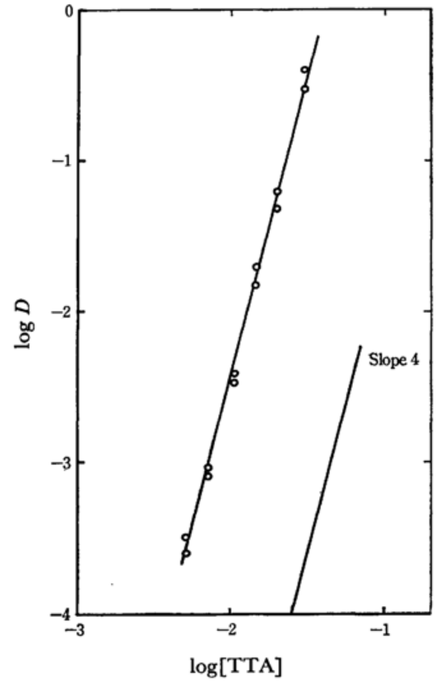

Fig. 4. Relationship between log D and log[TTA], 0.24 M H_2SO_4.

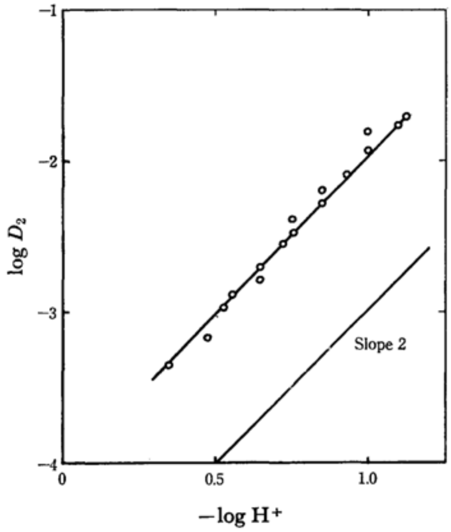

Fig. 5. Dependence of log D_2 on −log [H^+] in the extraction from sulfate solution.

Discussion

If the species extractable into the organic phase are considered to be non-charged, the general equation for the TTA extraction of Pa(IV) from the perchlorate solution can be written as follows:

$$\mathrm{Pa(OH)}_m{}^{(4-m)+} + 4\mathrm{HT} \rightleftharpoons \mathrm{PaT_4} + m\mathrm{H_2O} + (4-m)\mathrm{H^+} \qquad (1)$$

where HT represents the TTA molecule and T, the enolate ion of TTA.

If the activity coefficients of all the species are assumed to be constant, the equilibrium constant, k_1, can be defined as:

$$k_1 = \frac{[\mathrm{PaT_4}][\mathrm{H_2O}]^m[\mathrm{H^+}]^{(4-m)}}{[\mathrm{Pa(OH)}_m{}^{(4-m)+}][\mathrm{HT}]^4} \qquad (2)$$

where square brackets are used to represent the concentration of the relevant species.

Supposing only one kind of protactinium species exists in the aqueous solution, the distribution ratio can be defined as follows:

$$D_1 = \frac{[\mathrm{PaT_4}]}{[\mathrm{Pa(OH)}_m{}^{(4-m)+}]} \qquad (3)$$

As the solvent extraction was performed at a constant temperature and with a constant TTA concentration, both k_1 and HT are constant. Under these conditions, the following equation is obtained by substituting Eq. (2) into Eq. (3) and taking the logarithm:

$$\log D_1 = -(4-m)\log[\mathrm{H^+}] + \text{const.} \qquad (4)$$

As may be seen in Fig. 2, the slope of the log-D_1−log [H^+] plot is minus 2; that is, $(4-m)$ is equal to 2. Therefore, the protactinium species in the perchlorate solution may be in the form of $\mathrm{Pa(OH)_2{}^{2+}}$ over the −log [H^+] range studied; one can then describe the extraction reaction as:

$$\mathrm{Pa(OH)_2{}^{2+}} + 4\mathrm{HT} \rightleftharpoons \mathrm{PaT_4} + 2\mathrm{H_2O} + 2\mathrm{H^+} \qquad (1')$$

This finding is in agreement with the finding of Guillaumont.1)

On the other hand, the D-values in the extraction from the chloride solution were almost equal to the corresponding D-values in the extraction from the perchlorate solution. Therefore, Pa(IV) is probably reluctant to form chloro-complexes in dilute hydrochloric acid and may be predominantly in the form of $\mathrm{Pa(OH)_2{}^{2+}}$ in the acidity range studied. This finding is in good agreement with the finding of the absorption spectroscopy undertaken by the present author.3)

The general equation for the TTA extraction of Pa(IV) from a sulfate solution can be expressed as:

$$\mathrm{Pa(SO_4)}_n\mathrm{(OH)}_m{}^{(4-2n-m)+} + 4\mathrm{HT} \rightleftharpoons \mathrm{PaT_4} + n\mathrm{HSO_4^-} + m\mathrm{H_2O} + (4-m-n)\mathrm{H^+} \qquad (5)$$

The extraction constant k_2 equals:

$$\frac{[\mathrm{PaT_4}][\mathrm{HSO_4^-}]^n[\mathrm{H_2O}]^m[\mathrm{H^+}]^{(4-m-n)}}{[\mathrm{Pa(SO_4)}_n\mathrm{(OH)}_m{}^{(4-2n-m)+}][\mathrm{HT}]^4} \qquad (6)$$

On the assumption that only one kind of protactinium species is predominant in dilute sulfuric acid, the distribution ratio can be expressed as:

$$D_2 = \frac{[\mathrm{PaT_4}]}{[\mathrm{Pa(SO_4)}_n\mathrm{(OH)}_m{}^{(4-2n-m)+}]} \qquad (7)$$

By substituting Eq. (6) into Eq. (7), and by taking the logarithm, the following equation is obtained, provided both k_2 and HT are constant:

$$\log D_2 = -n\log[\mathrm{HSO_4^-}] - (4-m-n)\log[\mathrm{H^+}] + \mathrm{cost.} \quad (8)$$

Let us now consider the dissociation of H_2SO_4. As H_2SO_4 is a strong acid, it is completely dissociated to HSO_4^- or SO_4^{2-} in a dilute aqueous solution.

$$\mathrm{HSO_4^-} \rightleftharpoons \mathrm{SO_4^{2-}} + \mathrm{H^+} \quad (9)$$

$$K = \frac{[\mathrm{SO_4^{2-}}][\mathrm{H^+}]}{[\mathrm{HSO_4^-}]} \quad (10)$$

As pK is equal to 2.0,[6] Eq. (10) may be rewritten as follows:

$$\log\frac{[\mathrm{HSO_4^-}]}{[\mathrm{SO_4^{2-}}]} = 2 + \log[\mathrm{H^+}] \quad (11)$$

When $-\log[\mathrm{H^+}]$ is varied from 0.5 to 1.0, the ratio of $[\mathrm{HSO_4^-}]$ to $[\mathrm{SO_4^{2-}}]$ changes from about 32 to 10. Therefore, all the sulfuric acid is considered to be present as HSO_4^- over the entire $-\log[\mathrm{H^+}]$ range studied. This, in turn, results in a constant concentration of HSO_4^-, regardless of the acidity. Hence, Eq. 8 may be rewritten as follows:

$$\log D_2 = -(4-m-n)\log[\mathrm{H^+}] + \mathrm{const.} \quad (8')$$

The coefficient of the first term of this equation, $-(4-m-n)$, should be 2, as is shown in Fig. 5; that is, $m+n=2$. Therefore, the possible protactinium species in a sulfuric acid solution are:

1) $m=0,\ n=2,$ $\mathrm{Pa(SO_4)_2}$
2) $m=1,\ n=1,$ $\mathrm{Pa(SO_4)(OH)^+}$
3) $m=2,\ n=0,$ $\mathrm{Pa(OH)_2^{2+}}$

It is unlikely that no change species such as $\mathrm{Pa(SO_4)_2}$ is extracted into the benzene phase by TTA. It is also clear from Fig. 5 and Fig. 2 that the sulfato-complex of Pa(IV) exists. Therefore, the most probable ionic species may be considered to be $\mathrm{Pa(SO_4)(OH)^+}$; Eq. (5) then becomes:

$$\mathrm{Pa(SO_4)(OH)^+} + 4\mathrm{HT} \rightleftharpoons \mathrm{PaT_4} + \mathrm{HSO_4^-} + \mathrm{H_2O} + 2\mathrm{H^+} \quad (5')$$

The formation of the sulfato-complex of Pa(IV) can be expressed as:

$$\mathrm{Pa(OH)_2^{2+}} + \mathrm{HSO_4^-} \rightleftharpoons \mathrm{Pa(SO_4)(OH)^+} + \mathrm{H_2O} \quad (12)$$

In the above equation, the equilibrium constant, k_3, may be defined as:

$$k_3 = \frac{[\mathrm{Pa(SO_4)(OH)^+}][\mathrm{H_2O}]}{[\mathrm{Pa(OH)_2^{2+}}][\mathrm{HSO_4^-}]} \quad (13)$$

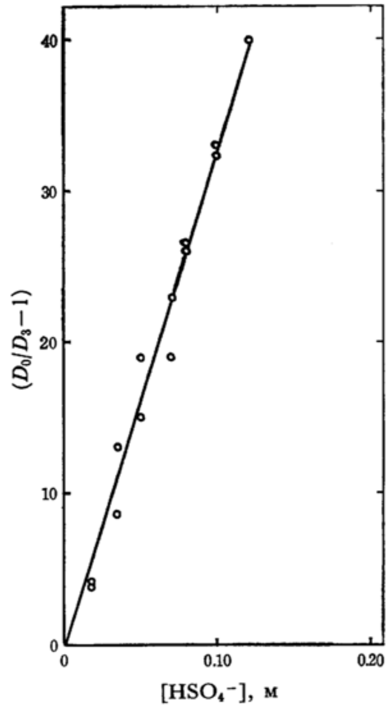

Fig. 6. Relationship between (D_0/D_3-1) and $[\mathrm{HSO_4^-}]$ at pH of 0.50.

Since the extracted species from both the perchlorate solution and the sulfate solution is $\mathrm{PaT_4}$, and since the protactinium species in the perchlorate solution and the sulfate solution are $\mathrm{Pa(OH)_2^{2+}}$ and $\mathrm{Pa(SO_4)(OH)^+}$ at a pH value of 0.5, the distribution ratio in various mixtures of perchlorate solutions and sulfate solutions at a constant pH can be defined as:

$$D_3 = \frac{[\mathrm{PaT_4}]}{[\mathrm{Pa(OH)_2^{2+}}] + [\mathrm{Pa(SO_4)(OH)^+}]} \quad (14)$$

By substituting Eq. (13) into Eq. (14) and by rearranging, the following equation is introduced:

$$D_0/D_3 - 1 = k_3[\mathrm{HSO_4^-}] \quad (15)$$

where D_0 represents the distribution ratio in the absence of the complexing anion, HSO_4^-. The relationship between (D_0/D_3-1) and $[\mathrm{HSO_4^-}]$ was examined at the pH value of 0.50 and at 10°C. As is shown in Fig. 6, the plot of (D_0/D_3-1) *versus* the concentration of sulfate ions has a straight line, with a slope of 320. This supports finding that $\mathrm{Pa(SO_4)(OH)^+}$ exists; the equilibrium constant, k_3, was determined to be 320 from the slope of the straight line.

Summary

1) The TTA extraction behavior of Pa(IV) was investigated in perchloric, hydrochloric, and sulfuric acid solutions (pH 0.4—1.1).

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[6] G. Charlot, "L'analyse qualitative et les reactions en solution," Masson et Cie, Parris (1957).

2) $Pa(OH)_2^{2+}$ was the most probable ionic species in the perchlorate solution, and the extraction reaction was considered tobe:

$$Pa(OH)_2^{2+} + 4HT \leftrightarrows PaT_4 + 2H_2O + 2H^+$$

3) Pa(IV) was reluctant to form the chlorocomplexes and was considered to be in the form of $Pa(OH)_2^{2+}$ in the dilute hydrochloric acid solution.

4) $Pa(SO_4)(OH)^+$ was the most probable ionic species in the sulfuric acid solution. The extraction reaction into the benzene phase was considered to proceed as follows:

$$Pa(SO_4)(OH)^+ + 4HT \rightleftharpoons PaT_4 + HSO_4^- + H_2O + 2H^+$$

5) In the sulfuric acid solution used as a complexing agent, the following complexing reaction was considered to take place:

$$Pa(OH)_2^{2+} + HSO_4^- \rightleftharpoons Pa(SO_4)(OH)^+ + H_2O$$

and its equilibrium constant was determined to be 320 at the ionic strength of 0.50 (temperature 10±0.5°C).

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