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The Chemistry of Protactinium. III. A Study of the Sulfate Complex of Protactinium(V) by the Solvent Extraction Technique Using TTA as the Chelating Agent

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The behavior of pentavalent protactinium in sulfuric acid solutions was investigated by paper electrophoresis and by the TTA-benzene extraction method. From the results of this investigation, it is recognized that the $Pa(OH)_2(SO_4)^+$ ion exists predominantly in dilute sulfuric acid solutions (pH 0.4—2.2), and that the complexing reaction of pentavalent protactinium by the sulfate ion may proceed as;

$$Pa(OH)_4^+ + 2H^+ + SO_4^{2-} \rightleftharpoons Pa(OH)_2(SO_4)^+ + 2H_2O.$$

The stability constant of $Pa(OH)_2(SO_4)^+$ was also determined by the solvent extraction method to be 6.4 at an ionic strength of 1.38.

It is well known that protactinium does not exist in the form of ionic or molecular monomeric species, even in a moderately acidic solution of ordinary inorganic acids, except hydrofluoric and sulfuric acids, which are known to give a stable solution. Many papers have reported on the behavior of pentavalent protactinium in perchloric,[1-5] hydrochloric,[6-9] and nitric acid solutions.[10] However, comparatively little data have been reported on the behavior of protactinium in a sulfuric acid solution, which is a good solvent of pentavalent protactinium.

Takagi *et al.*[11] studied the hydrolytic behavior of the protactinium ion in a sulfuric acid solution by the centrifugal method and observed that protactinium at a concentration of 10^{-6} M was stable

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against a hydrolysis for at least two weeks in a 0.2—0.5 M sulfuric acid solution, while at a tracer concentration of protactinium (10^{-11} M) the hydrolysis took place in a 0.015—0.5 M sulfuric acid solution.

Brown *et al.*[12] studied the behavior of protactinium in a sulfuric acid solution by the spectrophotometric method, coupled with the ion exchange and solvent extraction methods. It was concluded that an ionic species with the charge of -1 exists in an equilibrium with a cationic species in the 0.1—0.5 M acidity range, while at higher acidities a further complexing reaction takes place to produce a species of -3.

However, no detailed investigations have been reported on the cationic species in the sulfuric acid solution.

In this paper, the existence of the cationic species in the dilute sulfuric acid solution (pH 0.4—2.2) will be shown by means of paper electrophoresis, and then the nature of the cationic species will be investigated by the solvent extraction technique, using thenoyl trifluoroacetone (TTA) as the chelating agent. The stability constant of the sulfate complex of protactinium will also be determined by the solvent extraction method.

TTA is a valuable chelating agent for the solvent extraction of many metal ions, and it has often been used to determine the equilibrium constants of several metal complexes.[13-18] With a similar purpose in mind, TTA was chosen in this investigation.

Experimental

Reagents and Apparatus. The protactinium-231 isotope used as the carrier was purchased from the Radiochemical Center, Amersham, England, as protactinium pentoxide. The protactinium-233 isotope used as the tracer was prepared by the irradiation of throium dioxide in the pneumatic tube of the atomic pile JRR-2 (total flux 6.4×10^{13}) of the Japan Atomic Energy Research Institute. Pa-233 was separated from the target thorium dioxide by means of the anion exchange method, coupled with TBP-xylene extraction. Its radiochemical purity was certified by γ-ray spectrometry. Benzene was purified by distillation; doubly-distilled water was used throughout the solvent extraction. The other chemicals, such as thenoyl trifluoroacetone, sodium sulfate, sodium perchlorate and perchloric acid, were of the highest purity.

A Kobe Kogyo 100-channel pulse-height analyzer, Model AN-100, was used for the measurement of the γ-ray spectra. A Toa Denpa Kogyo pH-meter, Model HM-5A, was used for the pH measurements. A Toyo Kagaku paper electrophoresis apparatus, Model PE-2, was used for the paper electrophoresis. The paper used for the electrophoresis was Toyo filter paper No. 50 (2 cm × 40 cm).

Procedures. ^{231}Pa and ^{233}Pa were dissolved in a 0.1 M hydrofluoric acid solution and were stored in a polyethylene vessel. After 0.5 m*l* of a 0.3 M aluminum sulfate solution had been added to an aliquot of these stock solutions, solvent extraction was immediately carried out in a thermostat at 17 ± 1°C. 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. The concentration of protactinium in the aqueous phase was normally less than 10^{-6} M and the ionic strength was maintained at 1.38 with sodium perchlorate and sodium sulfate. Both phases were shaken at least 20 min with a mechanical shaker throughout the extraction experiment. One mililiter of the solution was then pipetted out from both phases and transferred into a polyethylene tube. The γ-radioactivity was measured with a well-type scintillation counter, and the apparent distribution ratio, D, was calculated by means of the usual method.

$$D = \frac{\gamma\text{-activity per 1 m}l\text{ of the org. phase}}{\gamma\text{-activity per 1 m}l\text{ of the aq. phase}}$$

The protactinium solution was spotted on the filter paper in the paper electrophoresis apparatus with a microsyringe. An electronically-stabilized D. C. potential of 700 V was applied through platinum electrodes. The potential gradient on the paper strip was 20 V/cm. After electrophoresis for the definite time, the paper was at once dried in an air-bath. The paper strip was then cut in lengths of 0.5 cm, and the γ-activity was measured in the well-type scintillation counter. A blank experiment, without the electrical potential being on, showed that protactinium diffused to a maximum of 2 cm on either side of the original line.

Results

Preliminary Experiments. The preliminary experiments were carried out on the equilibrium of solvent extraction and on the masking of fluoride ions by the aluminum sulfate. The results, shown in Fig. 1, indicate that the equilibrium of the solvent extraction was reached in about 10 min. Protactinium forms a stable anionic complex in a hydrofluoric acid solution and cannot be extracted by TTA into the benzene layer. The masking of the fluoride ions was, therefore, examined with a 0.3 M aluminum sulfate solution. The relation of the logarithm of the apparent distribution ratio to the amount of aluminum ions added is shown in Fig. 2. The aluminum-to-fluoride molar ratio of 3.0 is a satisfactory condition for the masking.

The Relation between the Apparent Distribution Ratio and the TTA Concentration. The influence of the TTA concentration on the apparent distribution ratio was investigated by

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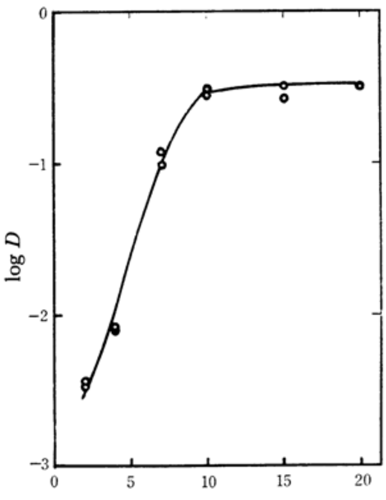

Fig. 1. The effect of the shaken time for TTA extractions.

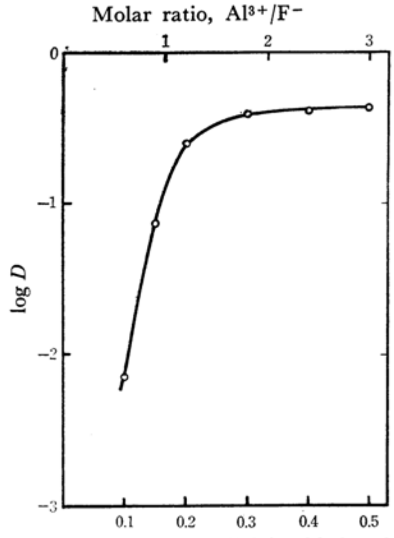

Fig. 2. The masking of fluoride ion by the aluminum sulfate.

using the constant acidity of the solution. The logarithm of the apparent distribution ratio was plotted as a function of the logarithm of the TTA activity in the benzene phase, as is shown in Fig. 3. The activity of TTA in the benzene phase at equilibrium was calculated from its initial concentration by the following equations[19];

$$\frac{(\mathrm{HT})_i}{(\mathrm{HT})_f} = 1.02 + 10^{-8}/\mathrm{H}^+ \qquad (1)$$

$$f_{\mathrm{HT}} = 1 - 0.25(\mathrm{HT})_f^{0.48}$$

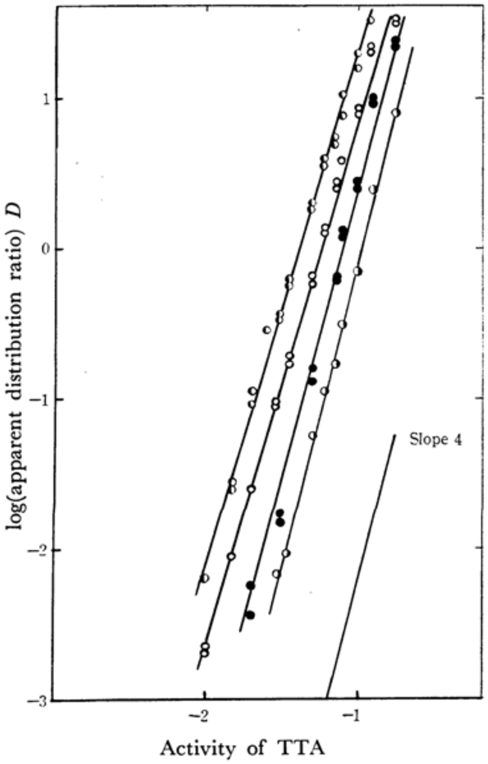

Fig. 3. Dependency of protactinium extractions on TTA concentration at 17°C.

◐=0.05 N, ○=0.10 N, ●=0.19 N, ◑=0.38 N sulfuric acids.

where f_{HT} is the activity coefficient of TTA in benzene, $(\mathrm{HT})_f$, the final concentration in benzene when equilibrated with an equal volume of an aqueous phase, and $(\mathrm{HT})_i$, the initial concentration. It is clear that the log-log plot of the apparent distribution ratio and the activity of TTA shows a good linearity, with a slope of 4 over a wide range of the TTA concentration.

The Relation between the Apparent Distribution Ratio and the pH Value in a Constant-ionic-strength Medium. The effect of the pH of the aqueous phase was studied at the constant ionic strength of 1.38 by using various mixtures of sulfuric acid and sodium sulfate. Benzene solutions of 0.05 M and 0.1 M TTA were used for the extraction. As is shown in Fig. 4, the relation between the apparent distribution ratio and the pH shows a good linearity, with a slope of +1 over the pH range from 0.4 to 2.2. The same experiment was also carried out in a perchloric acid solution by using various mixtures of perchloric acid and sodium perchlorate. Figure 5 shows that the plots of log D *versus* pH have a good linearity, with a slope of +1 over the pH range from 0.4 to 2.2. Therefore, the ionic species having a +1 charge exist predominantly in both the sulfuric acid solution and in the perchloric acid solution.

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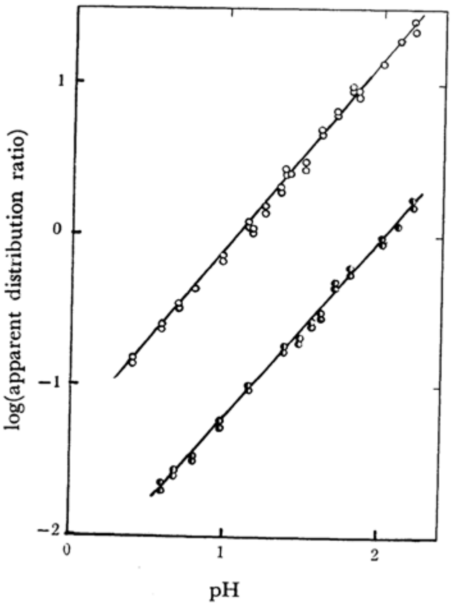

Fig. 4. Dependency of protactinium extractions on pH at 17°C for H_2SO_4 aqueous phase into TTA organic phase.

○=0.1 M TTA, ◐=0.05 M TTA

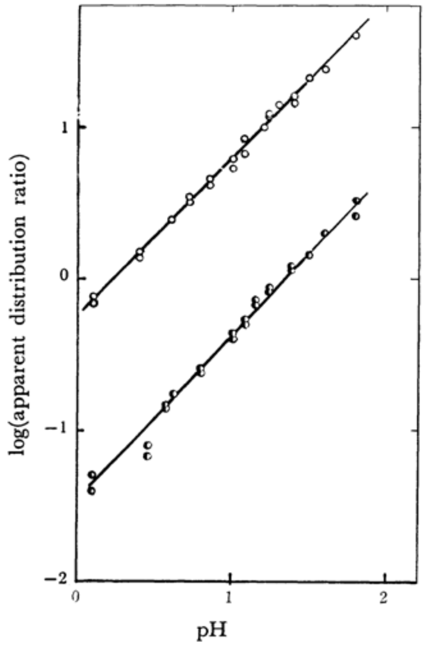

Fig. 5. Dependency of protactinium extractions on pH at 17°C for $HClO_4$ aqueous phase into TTA orgenic phase.

○=0.1 M TTA, ◐=0.05 M TTA

Paper Electrophoresis. In order to confirm the charge of extractable ionic species in the solution, the paper electrophoresis was carried out. The results, shown in Figs. 6 and 7, indicate that the ionic species in a hydrofluoric acid solution are anionic, while the extractable species in a sulfuric acid solution are cationic. The presence of anionic species in the dilute sulfuric acid solution was not detected by this method.

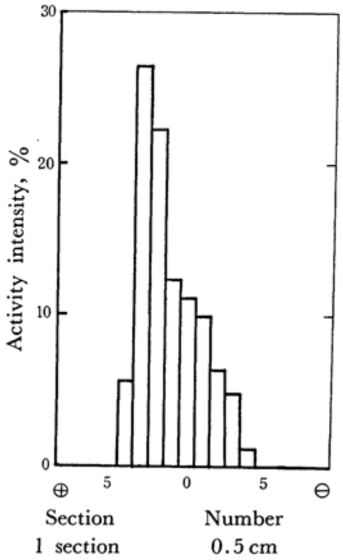

Fig. 6. Paper electrophoresis of protactinium ions in 0.1 M HF solution.

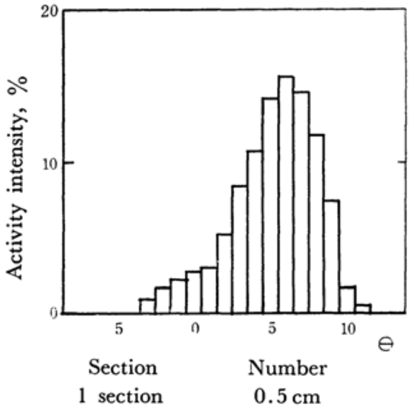

Fig. 7. Paper electrophoresis of protactinium ions in 0.2 M H_2SO_4 solution.

The Stability Constant of the Protactinium Sulfate Complex. The stability constant of the sulfate complex was determined by the solvent extraction method at an ionic strength of 1.38. The ionic strength in the aqueous phase was maintained constant by the use of perchlorate ions, which are assumed to have a negligible effect on complexing. The benzene solution of 0.1 M TTA was used for the extraction. The concentration of the sulfate ions was changed from 0.04 to 0.38 M at pH 0.50. No extraction was carried out in a more concentrated range of sulfate ions, because no suitable sulfate salt was available. The plot of $(D_0/D-1)$ *versus* the sulfate ion concentration, as is shown in Fig. 8, shows a straight line up to a 0.38 M sulfate ion concentration at pH 0.50. This result indicates that such higher complexes as $Pa(SO_4)_2{}^+$ were not present in this concentrated range. In this experiment, the straight line has a slope of 6.4, which represents the k_1 value for $Pa(OH)_2(SO_4)^+$.

Discussion

The equation for the extraction of a metal ion, M, with an n^+ charge, can be simply written as;

$$(M^{n+})_a + (nHT)_o = (MT_n)_o + (nH^+)_a \quad (3)$$

where the subscripts *a* and *o* refer to the aqueous and the organic phase respectively, and where HT stands for TTA and T for the enolate ion of TTA. The apparent distribution ratio, *D*, is written by definition as follows;

$$D = (MT_n)_o / (M^{n+})_a \quad (4)$$

If the temperature and the concentration of TTA are constant in the extraction, the following equation may be obtained from Eqs. (3) and (4);

$$\log D = n\,\mathrm{pH} + \mathrm{const.} \quad (5)$$

According to the above equation, the dependency of protactinium extraction upon pH was investigated. As may be seen in Fig. 4, the extraction of Pa(V) was found to have a first-power dependency upon the pH of the equilibrated aqueous phase. The existence of a cationic ion was confirmed by the paper electrophoresis method. Therefore, the possible ionic species may be assumed to be $Pa(OH)_4{}^+$, $Pa(OH)_2(SO_4)^+$ and $Pa(SO_4)_2{}^+$. Metal ions complexed successively with the anion of a strong acid were also considered. If *D* and D_0 represent the apparent distribution ratio in the presence and in the absence of complexing anion in the aqueous phase at a constant TTA concentration and at constant pH, the following equation can be obtained, as has been done by earlier workers[14];

$$D_0/D - 1 = k_1(X^-) + k_1k_2(X^-)^2 + \cdots \quad (6)$$

where X^- represents the complexing anion, and where k_1 and k_2 are successive stability constants. As the plot of $(D_0/D-1)$ *versus* the sulfate ion concentration shows a straight line in Fig. 8, it may be considered that only a first complexing reaction takes place up to the sulfate ion concentration of 0.38 M. Consequently, it may be concluded that $Pa(OH)_2(SO_4)^+$ is the most likely ionic species in dilute sulfuric acid solutions. The dependency of the protactinium extraction upon pH was also investigated in a perchloric acid solution as a non-complexing solvent. The slope of a straight line is equal to +1 in Fig. 5, so $Pa(OH)_4{}^+$ was assumed to exist predominantly in the perchloric acid solution. As the $SO_4{}^{2-}$ sulfate ion exists predominantly at pH 0.4—2.2, the following complexing reaction may proceed by means of the sulfate ion;

$$Pa(OH)_4{}^+ + SO_4{}^{2-} + 2H^+ \rightleftarrows Pa(OH)_2(SO_4)^+ + 2H_2O$$

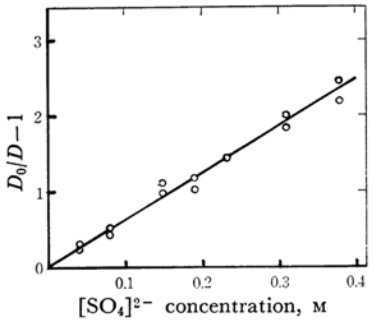

Fig. 8. Variation of $\left(\frac{K_d{}'}{K_d}-1\right)$ as a function of various ion concentrations with 1.38 M ionic strength, pH=0.5 and 0.1 M TTA.

Brown *et al.*[12] reported on the anionic species in the sulfuric acid solution. However, we could not detect the anion species by paper electrophoresis in a dilute sulfuric acid solution (pH 0.4—2.2). As the relationship between $(D_0/D-1)$ and the sulfate ion concentration is linear in Fig. 8, it seems that only the first complex is formed and the that slope of the straight line is equal to the stability constant of the first complex formation. Thus, the stability constant of $Pa(OH)_2(SO_4)^+$ was determined from Fig. 8, to be 6.4. Few papers have reported on the stability constant of protactinium complexes. Hardy *et al.*[10] studied the fluoro-complex of thorium and protactinium and inferred a K_1 value of the order of 10_4 for protactinium. As compared with this value, that of 6.4 for $Pa(OH)_2(SO_4)$ is very small. It is reasonable to consider that the protactinium is not very stable in the sulfuric acid solution as compared with its stability in the hydrofluoric acid solution. On the other hand, from the results shown in Fig. 3, the plots of log *D* *versus* the log of TTA activity show straight lines with a slope of +4, so it may be considered that the species extracted into the benzene phase have the form of $Pa(OH)_4T$. Thus, the reaction of the TTA extraction in the sulfuric acid solution may be considered to proceed as follows;

$$Pa(OH)_2(SO_4)^+ + 4HT \rightleftarrows Pa(OH)T_4 + H_2O + SO_4{}^{2-} + 3H^+$$

Summary

The behavior of pentavalent protactinium was investigated in a dilute sulfuric acid solution (pH 0.4—2.2) by paper electrophoresis and by

the TTA-benzene extraction method. It has been concluded that;

1) $Pa(OH)_2(SO_4)^+$ is the most likely species in the dilute sulfuric acid solution (pH 0.4—2.2);

2) In the sulfuric acid solution used as a complexing agent, the follwing complexing reaction takes place;

$$Pa(OH)_4^+ + 2H^+ + SO_4^{2-} \rightleftarrows Pa(OH)_2(SO_4)^+ + 2H_2O$$

3) The stability constant of $Pa(OH)_2(SO_4)^+$ was determined to be 6.4 at an ionic strength of 1.38 (temparature 17±1°C), and

4) The extraction reaction into the benzene phase is considered to proceed as follows;

$$Pa(OH)_2(SO_4)^+ + 4HT \rightleftarrows Pa(OH)T_4 + H_2O + SO_4^{2-} + 3H^+$$

Part of the expenses for this investigation have been defrayed by a grant-in-aid by the Ministry of Education.