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The Chemistry of Protactinium. VIII. Synergistic Effect of Di-isobutyl Carbinol on the Pa(V)-TTA-Benzene Solvent Extraction System

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For the purpose of understanding the behavior of protactinium in a perchloric acid solution toward TTA-benzene extraction, the effect of di-isobutyl carbinol (DIBC) on the extraction was studied. A marked synergism was observed. As a result of a detailed investigation of such things as the effects of the TTA concentration, of the DIBC concentration, and of the acidity, the unified mechanism of TTA-benzene and TTA-DIBC-benzene extraction is considered to be a series of successive reactions, (1) through (4), with an increase in the DIBC concentration:

$$PaO_m(OH)_n^{5-2m-n} + 4HT = Pa(OH)_2T_3(HT) + (m+n-2)H_2O + (5-2m-n)H^+$$
$$Pa(OH)_2T_3(HT) \rightarrow PaOT_3(HT) \text{ (slow, irreversible)} \quad (1)$$

$$PaO_m(OH)_n^{5-2m-n} + 4HT + B = Pa(OH)_2T_3(HT)B + (m+n-2)H_2O + (5-2m-n)H^+$$
$$Pa(OH)_2T_3(HT)B \rightarrow PaOT_3(HT)B \text{ (slow, irreversible)} \quad (2)$$

$$PaO_m(OH)_n^{5-2m-n} + 3HT + B = Pa(OH)_2T_3B + (m+n-2)H_2O + (5-2m-n)H^+$$
$$Pa(OH)_2T_3B \rightarrow PaOT_3B \text{ (slow, irreversible)} \quad (3)$$

$$PaO_m(OH)_n^{5-2m-n} + 3HT + 2B = Pa(OH)_2T_3B_2 + (m+n-2)H_2O + (5-2m-n)H^+$$
$$Pa(OH)_2T_3B_2 \rightarrow PaOT_3B_2 \text{ (slow, irreversible)} \quad (4)$$

The slow, irreversible reaction in each step indicates the irreversible formation of unstrippable species in the organic phase with aging. The absorption spectral measurements gave results consistent with this conclusion.

It was stated earlier[1)] that when the protactinium concentration was lower than 10^{-6}M and the perchloric acid concentration was 0.3—2.0M, the reaction of TTA extraction of protactinium from a perchloric acid solution proceeded as:

$$PaO_m(OH)_n^{5-2m-n} + 4HT = Pa(OH)T_4 + (m+n-1)H_2O + (5-2m-n)H^+ \quad (1)$$

where $2m+n$ is 3 and 4, or as:

[1)] S. Suzuki and Y. Inoue, This Bulletin, **39**, 1705 (1966).

$$PaO_m(OH)_nT^{4-2m-n} + 4HT = PaT_5 + (m+n)H_2O + (4-2m-n)H^+ \quad (2)$$

where $2m+n$ is 2 and 3.

We have been unable to distinguish between the two reactions from the experimental evidence. Reaction (1) may, however, be considered to be more probable than reaction (2) because of the very low solubility of TTA in the aqueous phase. In any case, protactinium(V) in a perchloric acid solution is present as species which have +2 and +1 charges. $Pa(OH)T_4$, which is used in Eq. (1) to represent the extracted species, is not the only form which it is possible to deduce from the experimental results. In general, the addition compounds of HT should be taken into account. Thus the extracted form may generally be written as $PaO_p(OH)_q T_{5-2p-q}(HT)_d$, where $2p+q-d$ is unity. That is, $PaOT_3(HT)$ or $Pa(OH)_2T_3(HT)$, $PaO(OH)T_2(HT)_2$ or $Pa(OH)_3T_2(HT)_2$ and $Pa(OH)_4T(HT)_3$, $PaO_2T(HT)_3$ or $PaO(OH)_2T(HT)_3$, $\cdots$ are possible as well as $Pa(OH)T_4$, depending on the d value, which cannot be determined by a simple TTA extraction experiment. In the above investigation, discussion has been restricted to the qualitative aspect because the reproducibility of the experimental data is not good enough to provide quantitative information. One of the reasons for this irreproducibility has been considered to be the complex behavior of TTA extraction, which depends greatly on the method of preparing the perchloric acid solution of protactinium. In order to elucidate the complex behavior more clearly, an elaborate investigation was carried out. Definite differences in the extraction behavior were observed among four kinds of the solutions which were prepared by different methods. Moreover, it was shown that a stripping equilibrium was established only when a freshly-prepared protactinium solution in TTA-benzene was used. Unstrippable species are formed when the Pa-TTA-benzene stands for a long period.[2]

The investigation of a synergistic effect is one of the means to determine the d values mentioned above. Guillaumont[3] studied the synergistic effect of TBP on the extraction of protactinium by TTA-benzene. The mechanism of the effect was understood by the following reaction:

$$Pa(OH)_3T_2(HT)_2 + 2TBP = Pa(OH)_3T_2(TBP)_2 + 2HT \quad (3)$$

and the extraction mechanism of protactinium by TTA was:

$$Pa(OH)_3^{2+} + 4HT = Pa(OH)_3T_2(HT)_2 + 2H^+ \quad (4)$$

As a result of the investigation of the synergism by n-amyl alcohol in the TTA extraction system, Kolarich and his co-workers[4] concluded that the extracted species was $PaOT_3(HT)$.

In the present investigation, the effect of di-isobutyl carbinol (DIBC) on the TTA-benzene extraction of protactinium has been examined; a marked synergism was observed. The consideration of the mechanism of the synergistic effect enables us to determine the d value and to make a hypothesis concerning the reasons for the irreversible change of the protactinium species in the TTA-benzene solution.

Experimental

Reagents and Apparatus. ^{231}Pa *and* ^{233}Pa. Stock solutions of these isotopes in hydrochloric acid and hydrofluoric acid mixtures were prepared by a method reported previously.[5] The concentration of protactinium in the ^{231}Pa solution was determined by gravimetry as protactinium pentoxide. The benzene was purified by distillation, and doubly-distilled water was used throughout this experiment. The acidity of the solution was determined by titration with a standard sodium hydroxide solution. The highest-purity-grade lithium perchlorate was used for the adjustment of the ionic strength, and the concentration of its solution was determined gravimetrically as lithium sulfate. The other chemicals, such as thenoyl trifluoroacetone, perchloric acid and di-isobutyl carbinol, were also all of the highest purity.

For the solvent-extraction procedure, an Iwaki universal mechanical shaker, Model V-S, was used. A Kôbe Kôgyo Model PS-400 well-type scintillation probe coupled with a Kôbe Kôgyo Model SA-400 scaler was used for the γ-ray measurement. For the measurement of the absorption spectra, a Hitachi Model EPS-3 recording spectrophotometer with a 1 cm photometric cell was used.

Procedure. All the experiments were carried out at room temperature. Ordinary separatory funnels made of glass were used for the solvent extraction. To eliminate distortions of the experimental results arising from adsorption on glass, the walls of the funnels were preliminarily saturated with protactinium by shaking the test solution for a time sufficient for adsorption equilibrium to be reached. Care was taken to ascertain the material balance in each experiment, and each value given was the average of the results of at least two determinations. For all solvent extractions except with Fomin's method,[2,6] 5 m*l* portions of the aqueous and of the organic phase were used; after the separation of the two phases, a 2 m*l* aliquot of each phase was taken into a polyethylene test tube and counted for γ radioactivity. The distribution ratio was calculated by means of the usual relationship:

$$D = \frac{\gamma \text{ activity per 1 m}l\text{ of the organic phase}}{\gamma \text{ activity per 1 m}l\text{ of the aqueous phase}}$$

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[2] S. Suzuki and Y. Inoue, This Bulletin, **42**, 1916 (1969).

[3] R. Guillaumont, *Bull. Soc. Chim. France*, **1965** (1) 132.

[4] R. T. Kolarich, V. Y. Ryan and R. P. Schuman, *J. Inorg. Nucl. Chem.*, **29**, 783 (1967).

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

[6] V. V. Fomin, E. P. Maiorova, M. I. Krapivin and V. G. Yudina, *Zh. Neorg. Khimiya*, **3**, 2113 (1958).

Forward Extraction. The protactinium solution in 1M perchloric acid for the forward extraction experiments was prepared as follows.

Aliquots of ^{231}Pa and of ^{233}Pa stock solutions (a total of 5 m*l*) and a small amount of hydrofluoric acid were transferred into a platinum dish and evaporated almost to dryness, initially on a hot plate and finally on a water bath. The residue was dissolved in 5M perchloric acid with slight heating and diluted to make the protactinium concentration 10^{-7}M.

Backward Extraction. A protactinium solution in the organic solvent for the backward extraction was prepared by the following procedure.

Aliquots of ^{231}Pa and of ^{233}Pa stock solutions were transferred into a platinum dish and heated to dryness on a hot plate. The residue was dissolved in 0.64 m*l* of 1.17M hydrofluoric acid, and then 0.99 m*l* of 5.05M perchloric acid and 1.7 m*l* of a 1.33M aluminum perchlorate solution were added, in this order. The resulting solution was diluted to 50 m*l* with distilled water. This solution was then placed in contact with 200 m*l* of a DIBC-TTA-benzene solution of a suitable composition for 20 min. The concentration of protactinium in the TTA-DIBC-benzene solution thus prepared was 0.99×10^{-7}M.

Absorption Spectra. A ^{231}Pa solution containing 6.17×10^{-6} Mole was transferred into a platinum dish and heated to dryness on a water bath. The residue was dissolved in 0.96 m*l* of 1.17M hydrofluoric acid, and then 0.53 m*l* of 4.71N sulfuric acid and distilled water were added to make 25 m*l*. This solution was then transferred into a separatory funnel containing 25 m*l* of a 0.5M TTA-benzene solution and 25 m*l* of a 0.136M aluminum perchlorate solution. Then the separatory funnel was shaken with a mechanical shaker for 15 min. The organic phase was withdrawn from the funnel and an aliquot of the solution was diluted with DIBC-benzene of a suitable concentration. This solution was used for the absorption spectral measurement. The protactinium concentration was about 2.5×10^{-5}M.

Results

The Effect of Contact Time in the Forward Extraction. The effect of the contact time on the distribution ratio of protactinium in 1M perchloric acid was investigated as a function of the DIBC concentration, as is shown in Figs. 1a and 1b. When the DIBC concentration is lower than 0.1% (the concentration of DIBC is represented by volume%), the distribution ratio reaches constant after about 10 min of contact, whereas the extraction rate becomes slower with an increase in the concentration of DIBC. Longer than an hour's contact is necessary for the extractant 1% in DIBC to reach a constant distribution ratio.

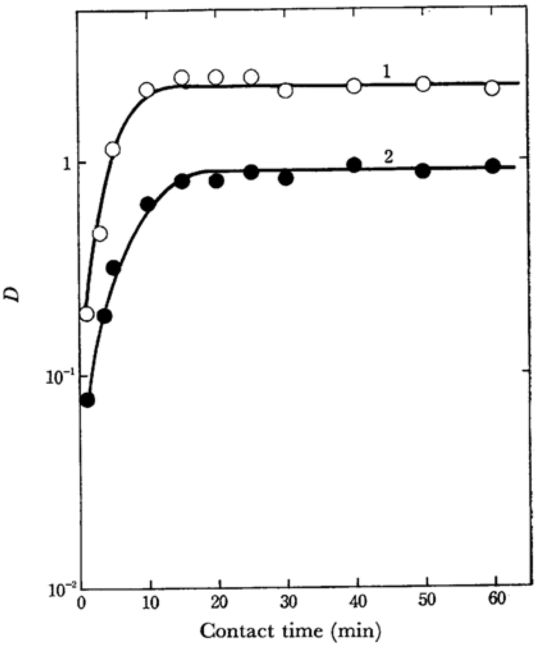

Fig. 1a. The effect of contact time on the extraction of Pa. I.
Aq. phase: 10^{-7}M Pa in 1M $HClO_4$
Org. phase: 1, 0.1% DIBC, 0.032M TTA
2, 0.4% DIBC, 0.0136M TTA

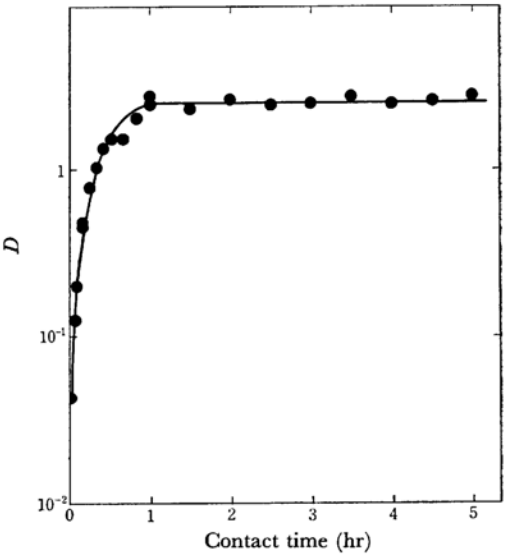

Fig. 1b. The effect of contact time on the extraction of Pa. II.
Aq. phase: 10^{-7}M Pa in 1M $HClO_4$
Org. phase: 1% DIBC, 0.0096M TTA

The Effect of Aging on the Distribution Ratio in the Forward Extraction. The effect of aging time on the distribution ratio was investigated for the forward extraction of protactinium in a 1M perchloric acid solution by both 2×10^{-2}M TTA-0.07%DIBC and 5×10^{-2}MTTA-0.02%DIBC in benzene solutions. Curves similar to that of No. 1 in Fig. 3 of the 7th report of this series$^{2)}$ were obtained; that is, the distribution ratio remains constant for about a week after the preparation of the sample, and then it begins to decrease. This constant value coincides with one obtained from the backward distribution of the fresh protactinium solution in TTA-DIBC-benzene. The conditions used in the preparation of the protactinium solution are as suitable as those used for No. 1 in a previous report.[2] The reason why the No. 1 preparation method has not been used is that in it the control of the acidity is very difficult.

The Relation between the Distribution Ratio and the TTA Concentration. The influence of the TTA concentration on the distribution ratio was investigated for a 1M solution in perchloric acid at various DIBC concentrations. The logarithm of the distribution ratio was plotted as a function of the logarithm of the TTA activity in the benzene phase, as is shown in Fig. 2. Provided the nature of TTA is not affected by the presence of DIBC at such low concentrations as 1%, the activity of TTA in the benzene phase at equilibrium can be calculated from its initial concentration by the following equations:

$$\frac{(\mathrm{HT})_\mathrm{I}}{(\mathrm{HT})_\mathrm{B}} = 1.02 + 10^{-8}/(\mathrm{H}^+)^{7)} \qquad (5)$$

$$f_{\mathrm{HT}} = 1 - 0.25(\mathrm{HT})_\mathrm{B}^{0.48\ 8)} \qquad (6)$$

where f_{HT} is the activity coefficient of TTA in benzene; $(\mathrm{HT})_\mathrm{B}$, the final concentration in benzene when equilibrated with an equal volume of an aqueous phase, and $(\mathrm{HT})_\mathrm{I}$, the initial concentration. It is clear from Fig. 2 that the log-log plot of the distribution ratio and the activity of TTA shows a good linearity, with varying slopes, depending on the DIBC concentration, over a wide range of TTA concentrations. As Table 1 shows, the slope is about 4 when the DIBC concentration is lower than 0.0003% and decreases with an increase in the DIBC concentration from 0.0003% upwards.

The Relation between the Distribution Ratio and the DIBC Concentration. The effect of the DIBC concentration on the distribution ratio was examined in 1M perchloric acid solution, with the TTA concentration kept constant. The logarithm of the distribution ratio was plotted as a function of the logarithm of the DIBC concentration in the benzene phase, as is shown in Fig. 3. Though the protactinium in the 1M perchloric acid solution was not extracted at all, even by pure DIBC, the distribution ratio increases remarkably upon the addition of a small amount of DIBC; that is, synergism is observed. The linear relationship does not hold between the log of the distribution ratio and that of the DIBC concentration, but the curves asymptotically approach straight lines with an increase in the DIBC concentration. When the concentrations of TTA were 0.02M, 0.05M, and 0.1M, the slopes of the curves approached 1.0, 1.4 and 1.8 respectively.

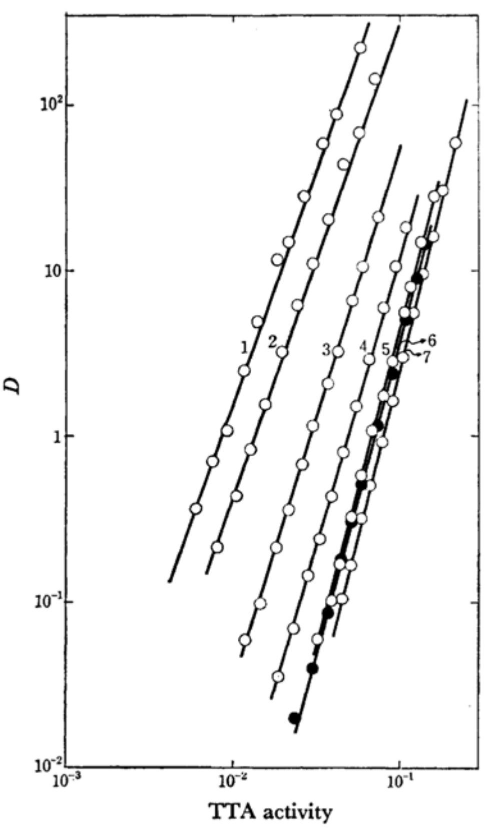

Fig. 2. Dependence of distribution ratio on TTA activity.
$\mathrm{HClO_4}$ concn.: 1M, Pa concn.: 10^{-7}M
DIBC concn.: 1, 1%; 2, 0.4%; 3, 0.1%; 4, 0.02%
5, 0.005%; 6 0.001%; 7, 0.0003%

TABLE 1. THE EFFECT OF DIBC CONCN. ON SLOPE

DIBC conc. (%)	Ratio of two species		Slope	
	T4	T3	Calcd	Exp.
0.0	100.0	0.0		4.00
0.0003				4.03
0.001	73.2	26.8	3.73	3.70
0.005				3.73
0.01	52.7	47.3	3.53	
0.02				3.61
0.1	29.9	70.1	3.30	3.27
0.4	13.8	86.2	3.14	3.02
1.0				2.85

The Relation between the Distribution Ratio and the Hydrogen-ion Concentration. The effect of acidity was studied by the backward extraction technique at a constant ionic strength of 1.967 by using various mixtures of perchloric acid and lithium perchlorate. Up to a hydrogen

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7) A. M. Poskanzer and B. M. Foreman, *J. Inorg. Nucl. Chem.*, **16**, 323 (1961).

8) E. L. King and W. H. Reas, *J. Am. Chem. Soc.*, **73**, 1804 (1951).

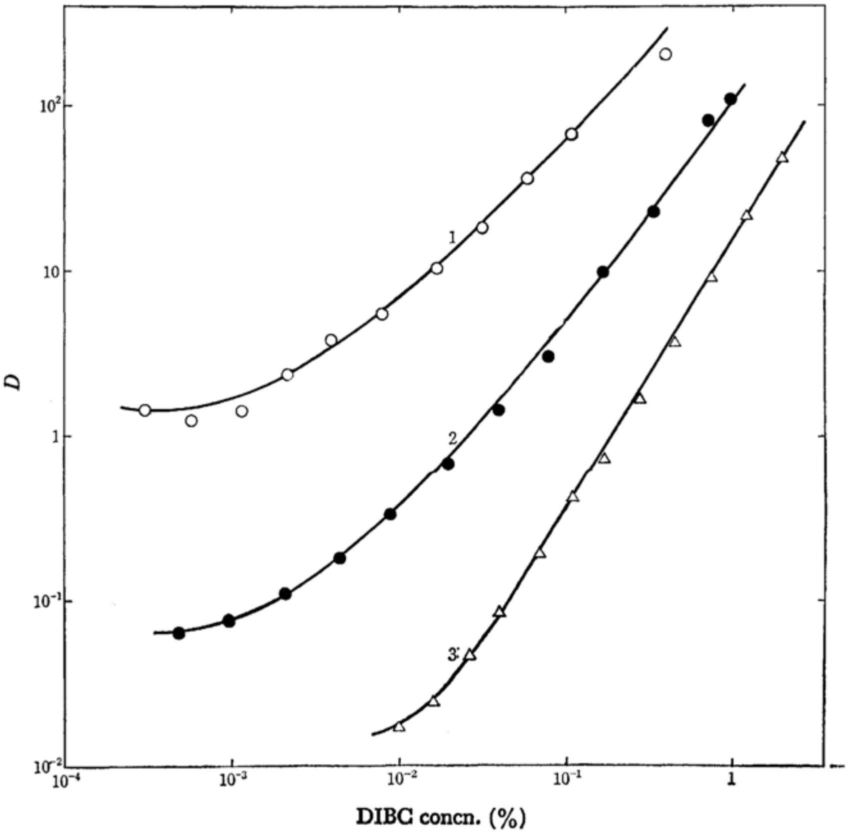

Fig. 3. Dependence of distribution ratio on DIBC concentration.
HClO$_4$ concn.: 1M, Pa concn.: 10^{-7}M
TTA concn.: 1, 0.1M; 2, 0.05M; 3, 0.02M

ion concentration of 1.5M, the log-log plots of the distribution ratio and the hydrogen ion concentration show a linear relationship with a slope of -1.7, except in the case of No. 5, as is clearly shown in Fig. 4. In the case of Curve 5, with TTA and DIBC concentrations of 0.1M and 0.0004% respectively, an exact linearity does not hold.

The Effect of Contact Time in the Backward Extraction. The effect of the contact time on the backward extraction carried out by using a freshly-prepared protactinium solution in 0.05M TTA and 0.02% DIBC-benzene was investigated; the results are shown in Fig. 5. The stripping solution was 1.0M perchloric acid. It is apparent from the figure that about an hour's contact is necessary to get a constant distribution ratio.

The Effect of Time of Standing of a Protactinium Solution in TTA-DIBC-Benzene on the Distribution Ratio. A protactinium solution in TTA-DIBC-benzene was stored in a brown bottle in the dark, and the change in the distribution ratio during the standing was followed. The protactinium in a 0.05M TTA-0.02% DIBC-benzene solution was stripped by 1M perchloric acid for 1.5 hr. It is apparent from Fig. 6 that, at first, the distribution ratio remained constant for about several hours and then gradually increased, finally reaching a constant 5 days after the preparation. The curve was analyzed by Fomin's method. As is shown in Fig. 7, the *P* value (the percentage of unstrippable species which are not in rapid equilibrium with the strippable species) observed for a fresh Pa-TTA-DIBC solution was only a few percent. It increases remarkably with the standing, however, and reaches a constant value of about 40% after 10 days of standing. The distribution ratio of strippable species does not change with standing, so that the increase in distribution ratio can be explained on the basis of the formation of unstrippable species alone.

Absorption Spectra of Protactinium in TTA-DIBC-Benzene Solution. The absorption spectra of protactinium in the TTA-DIBC-benzene mixture were measured from 340 to 650 mμ in relation to the DIBC concentration, as is shown in Fig. 8. The concentrations of protactinium and of TTA are *ca.* 2.5×10^{-5}M and 0.05M respectively. It is observed that, in the absence of DIBC, an absorption maximum appears at 408 mμ; it shifts to a shorter wavelength with an increase in the DIBC

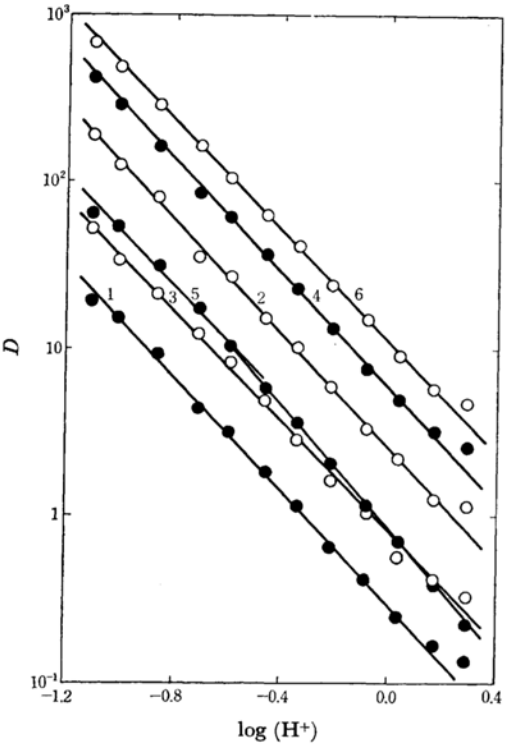

Fig. 4. Dependence of distribution ratio on hydrogen ion concentration.

Ionic strength: 1.967, Pa concn.: 10^{-7}M
Org. phase: 1, 0.02M TTA, 0.1% DIBC
2, 0.02M TTA, 0.4% DIBC
3, 0.05M TTA, 0.02% DIBC
4, 0.05M TTA, 0.1% DIBC
5, 0.1M TTA, 0.0004% DIBC
6, 0.1M TTA, 0.02% DIBC

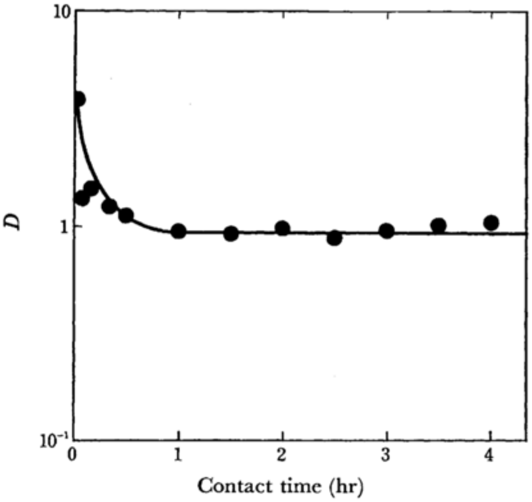

Fig. 5. The effect of contact time on the stripping of Pa.

Aq. phase: 1M $HClO_4$
Org. phase: 10^{-7}M Pa, 0.05M TTA, 0.02% DIBC

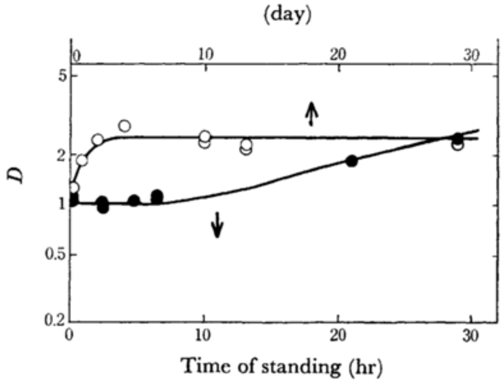

Fig. 6. The effect of time of standing on the stripping of Pa.

Aq. phase: 1M $HClO_4$
Org. phase: 10^{-7}M Pa, 0.05M TTA, 0.02% DIBC

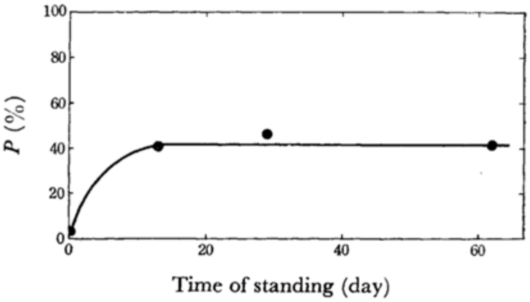

Fig. 7. P as a function of time of standing.

Aq. phase: 1M $HClO_4$
Org. phase: 10^{-7}M Pa, 0.05M TTA, 0.02% DIBC

concentration, reaching 403 mμ when the DIBC concentration becomes higher than 1%. The absorbance also decreased with the DIBC concentration. The change in the absorption spectra with the DIBC concentration is negligible when the DIBC concentration is higher than 1%.

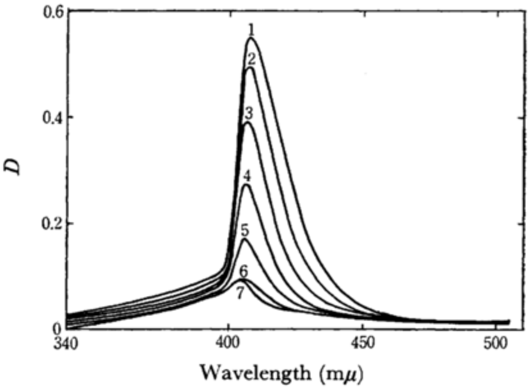

Fig. 8. Absorption spectra.

TTA concn.: 0.05M, Pa concn.: *ca.* 2.5×10^{-5}M
DIBC concn.: 1, 0%; 2, 0.001%; 3, 0.01%;
4, 0.1%; 5, 0.4%; 6, 1.0%; 7, 10.0%

Discussion

If the species extractable into the organic phase are considered to have no charge, the general equation for the TTA-DIBC extraction reaction can be written as:

$$\begin{aligned}&\mathrm{PaO}_m(\mathrm{OH})_n^{5-2m-n}(\mathrm{aq.}) + (5-q-2p+d)\mathrm{HT}(\mathrm{org.}) \\ &\qquad + b\mathrm{B}(\mathrm{org.}) \\ &= \mathrm{PaO}_p(\mathrm{OH})_q(\mathrm{HT})_d\mathrm{T}_{5-2p-q}\mathrm{B}_b(\mathrm{org.}) \\ &+ (m+n-p-q)\mathrm{H_2O} + (5-2m-n)\mathrm{H}^+(\mathrm{aq.}) \qquad (5)\end{aligned}$$

where HT, T^-, and B are used to denote the TTA molecule, the dissociated TTA anion, and the di-isobutyl carbinol molecule respectively. The equilibrium constant of this reaction can then be defined as:

$$K_{m,n,p,q,d} = \frac{[\mathrm{PaO}_p(\mathrm{OH})_q(\mathrm{HT})_d\mathrm{T}_{5-2p-q}\mathrm{B}_b][\mathrm{H_2O}]^{m+n-p-q}[\mathrm{H}^+]^{5-2m-n}}{[\mathrm{PaO}_m(\mathrm{OH})_n^{5-2m-n}][\mathrm{HT}]^{5-q-2p+d}[\mathrm{B}]^b} \qquad (6)$$

where brackets have been used to represent the activities of the enclosed species. (The designation of the phase in which each species exists has been omitted in order to simplify the writing of the equation.) A distribution ratio expressed in terms of activities is defined as the sum of the activities of the protactinium species in the benzene phase divided by the sum of the activities of the protactinium species in the aqueous phase:

$$K_d = \frac{\sum\limits_{p,q,d,b} [\mathrm{PaO}_p(\mathrm{OH})_q(\mathrm{HT})_d\mathrm{T}_{5-2p-q}\mathrm{B}_b]}{\sum\limits_{m,n} [\mathrm{PaO}_m(\mathrm{OH})_n^{5-2m-n}]} \qquad (7)$$

If the activity coefficients of TTA and DIBC are independent of the concentrations of DIBC and TTA respectively, one can derive the following relationships by the same procedure as was used before:[1)]

$$\frac{\partial \ln K_d}{\partial \ln [\mathrm{HT}]} = 5 - \sum(2p+q-d)f_{p,q,d,b} \qquad (8)$$

$$\frac{\partial \ln K_d}{\partial \ln [\mathrm{H}^+]} = -\sum(5-2m-n)f'_{m,n} \qquad (9)$$

$$\frac{\partial \ln K_d}{\partial \ln [\mathrm{B}]} = \sum b f_{q,p,d,b} \qquad (10)$$

where $f_{p,q,d,b}$ is the fraction of the total activity of the protactinium species in the benzene phase contributed by the $\mathrm{PaO}_p(\mathrm{OH})_q(\mathrm{HT})_d\mathrm{T}_{5-2p-q}\mathrm{B}_b$ species, and $f'_{m,n}$ is that in the aqueous phase contributed by the $\mathrm{PaO}_m(\mathrm{OH})_n^{5-2m-n}$ species.

Hence,

$$\sum_{p,q,d,b} f_{q,p,d,b} = 1 \qquad (11)$$

$$\sum_{m,n} f'_{m,n} = 1 \qquad (12)$$

If the activity coefficients of the protactinium species and of the hydrogen ion are assumed to be constant over the entire range of acidity when the ionic strength of a solution is kept constant, the distribution ratio (D) obtained empirically can be replaced by the thermodynamic distribution ratio (K_d) expressed in terms of activity; no appreciable error should be introduced by this assumption. As is clearly shown in Fig. 4, a linear relationship with a slope of -1.7 holds between the logarithm of the distribution ratio and the logarithm of the hydrogen-ion concentration.

Therefore,

$$-5 + \sum(2m+n)f'_{m,n} = -1.7 \qquad (13)$$

$$\sum(2m+n)f'_{m,n} = 3.3 \qquad (14)$$

Therefore, in agreement with the results of the TTA extraction,[1)] the protactinium in a perchloric acid solution may be found in the forms of $\mathrm{Pa(OH)}_3^{+2}$ or $\mathrm{PaO(OH)}^{+2}$ and of $\mathrm{Pa(OH)}_4^+$, $\mathrm{PaO(OH)}_2^+$, or PaO_2^+.

If the activity coefficients of the protactinium species are assumed to be constant, irrespective of the TTA concentration, the distribution ratio (D) obtained empirically can be replaced by the thermodynamic distribution ratio (K_d) in terms of activity; no appreciable error should be introduced by this assumption.

If DIBC is absent,

$$5 - \sum(q+2p-d)f_{p,q,d,b} = 4$$

$$\sum(q+2p-d)f_{p,q,d,b} = 1 \qquad (15)$$

When DIBC is added, the slope of the log-log plot of the distribution ratio and the TTA activity in the organic phase changes from 4 to 3, depending on the DIBC concentration.

Thus,

$$3 \leqq 5 - \sum(q+2p-d)f_{p,q,d,b} \leqq 4$$

that is,

$$2 \geqq \sum(q+2p-d)f_{p,q,d,b} \geqq 1 \qquad (16)$$

holds. In this experiment, we can not determine the d value. Depending on the postulated d value, one can obtain the following relationships:

When

$$d = 0 \qquad 2 \geqq \sum(q+2p)f_{p,q,0,b} \geqq 1 \qquad (17)$$

$$d = 1 \qquad 3 \geqq \sum(q+2p)f_{p,q,1,b} \geqq 2 \qquad (18)$$

$$d = 2 \qquad 4 \geqq \sum(q+2p)f_{p,q,2,b} \geqq 3 \qquad (19)$$

$$d = 3 \qquad \sum(q+2p)f_{p,q,3,b} = 4 \qquad (20)$$

In Eq. (20), the value of $\sum(q+2p)f_{p,q,3,b}$ over 4 is impossible because an improbable assumption must be made concerning the degree of hydrolysis, which is higher in the organic phase than in the aqueous phase. For the same reason, a d value of over 3 is impossible.

Next, in Eq. (10), if the activity coefficients of the protactinium species are assumed to be constant over the entire range of DIBC concentration, the

TABLE 2. POSSIBLE FORMS OF EXTRACTED SPECIES

No.	DIBC concn.			
	Low	Intermediate		High
1	Pa(OH)T_4	Pa(OH)T_4B		
2	Pa$(OH)_2T_3$(HT) PaOT_3(HT)	Pa$(OH)_2T_3$(HT)B PaOT_3(HT)B	Pa$(OH)_2T_3$B PaOT_3B	Pa$(OH)_2T_3B_2$ PaOT_3B_2
3	Pa$(OH)_3T_2(HT)_2$ PaO(OH)$T_2(HT)_2$	Pa$(OH)_3T_2(HT)_2$B PaO(OH)$T_2(HT)_2$B	Pa$(OH)_3T_2$(HT)B PaO(OH)T_2(HT)B	Pa$(OH)_3T_2$(HT)B_2 PaO(OH)T_2(HT)B_2
4	Pa$(OH)_4$T$(HT)_3$ PaO$(OH)_2$T$(HT)_3$ PaO_2T$(HT)_3$	Pa$(OH)_4$T$(HT)_3$B PaO$(OH)_2$T$(HT)_3$B PaO_2T$(HT)_3$B	Pa$(OH)_4$T$(HT)_2$B PaO$(OH)_2$T$(HT)_2$B PaO_2T$(HT)_2$B	Pa$(OH)_4$T$(HT)_2B_2$ PaO$(OH)_2$T$(HT)_2B_2$ PaO_2T$(HT)_2B_2$

distribution ratio (D) obtained empirically can be replaced by the thermodynamic distribution ratio (K_d) expressed in terms of activity. As is clear from Fig. 3, the relation:

$$0 \leqq \sum bf_{p,q,d,b} < 2 \tag{21}$$

holds. When the DIBC concentration is very low, the distribution ratio is independent of the DIBC concentration, whereas the dependence of the distribution ratio on the TTA concentration is of the power of 4. When the concentration of DIBC is extremely high as compared with the concentration of TTA, the slope of the log-log plot of the distribution ratio and the DIBC concentration is 1.8. At such a high concentration of DIBC, it is clear from Fig. 3 that the TTA dependence on the distribution ratio is of the power of 3. From the above considerations, the possibilities for the species extracted into the organic phase in relation to the concentration of DIBC may be summarized as is shown in Table 2.

The degree of the hydrolysis of the extracted protactinium species may not increase with an increase in the DIBC concentration, for synergism is observed in spite of the decrease in the TTA dependence with an increase in the DIBC concentration. Nor does it decrease, for it is difficult for the less basic DIBC to replace the more basic hydroxy anion. This implies that the change in the extracted species with an increase in the DIBC concentration occurs from the left to the right of the same row in Table 2. These considerations naturally obviate the possibility of the first row. The series of reactions described in the third row was also not warranted, for the following reasons. In this case, two molecules of TTA are assumed to be combined loosely with the chelate. If this is the case, the TTA dependency of 2 should be easily attained with an increase in the DIBC concentration. This is, however, contrary to observation. The same argument is applicable in the case of the series of reactions in the last row. Accordingly, the most probable species extracted into the organic phase are those listed on the second row.

On the second row, two series of the extracted species are possible, depending on p or q, but their values cannot be determined from the experimental results. If one compares the species containing Pa$(OH)_2^{3+}$ and PaO^{3+}, the former is considered to be more hydrophilic than the latter. On the other hand, it is known that, in a benzene solution saturated with water, 11% of TTA is present as the hydrate and that, in a benzene solution which has been neither dried nor equilibrated with water, there is present 3% hydrate. The rate of conversion of the enole form to ketohydrate is very slow, taking 2 or 3 days to reach equilibrium.[9] As the two phases were in contact for only thirty minutes in the preparation of the protactinium solution in TTA-DIBC-benzene, the equilibrium between the enole and ketohydrate forms is not attained. Therefore, the benzene solution has the potentiality of absorbing water. For this reason or for another, if one considers that the forms composed of Pa$(OH)_2^{3+}$, which will participate in the extraction equilibrium, undergo dehydration to form that composed of PaO^{3+}, the irreversible formation of unstrippable species in the organic phase with the time of standing can be well understood. The same is applicable to the interpretation of the similar findings in the TTA extraction reported in the previous report.[2] The difference in the amount of irreversible species formed during a long period of standing between the TTA and the TTA-DIBC extractions (80% and 40% respectively) is attributable to the difference in the TTA concentration used. This irreversible change in the extraction behavior cannot be attributed to the polymerization of the extracted TTA chelate, nor to the decomposition of the chelate by some such means as thermal or radiation decomposition, as has been pointed out previously.[2] These arguments do not violate the validity of the hypothesis mentioned above.

The continuous change in the slope of the log-log plot of the distribution ratio and the TTA acitivity

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9) E. L. King and W. H. Reas, *J. Am. Chem. Soc.*, **73**, 1806 (1951).

with the change in the DIBC concentration can be understood if we consider the extracted species to be a mixture of forms containing four TTA and three TTA, the mixing ratio continuously changing with the concentration of DIBC. In the study of the synergism of the UO_2^{2+} -TTA extraction system by TBP, Healy and his co-workers[10,11] showed that the absorption spectra of $UO_2(TTA)_2$ and $UO_2(TTA)_2TBP$ are essentially the same. In view of this fact, it can naturally be assumed that the solvation of DIBC to the protactinium TTA chelate does not affect the absorption spectrum of protactinium in the organic phase; that is, the spectra depend only on the number of TTA present in the extracted species. If we consider Curve No. 1 in Fig. 8 to be the spectrum of the protactinium species containing four molecules of TTA, and Curve No. 7 to be that of the species containing three molecules of TTA, as the spectrum does not change with an increase in the DIBC concentration above 1%, the intermediate curves can be constructed by an appropriate combination of the two curves, No. 1 and No. 7. Therefore, we can estimate the mixing ratio of the species containing three and four molecules of TTA from the absorption spectra. This calculation was done by the method of successive approximation, as is shown in the second and third columns of Table 1. From these values, the slope of the log-log plot of the distribution ratio and the TTA activity can be estimated. The results of the calculation, listed in the fourth column of Table 1, agree well with the empirical value presented in the same table.

In conclusion, one can say in summary that reactions (22) through (25) proceed in this order with the increase in the DIBC concentration:

$$\begin{aligned}&PaO_m(OH)_n^{5-2m-n} + 4HT\\&\quad = Pa(OH)_2T_3(HT) + (m+n-2)H_2O\\&\qquad + (5-2m-n)H^+\\&\quad Pa(OH)_2T_3(HT) \rightarrow PaOT_3(HT)\\&\qquad \text{(slow, irresversible)}\end{aligned} \tag{22}$$

$$\begin{aligned}&PaO_m(OH)_n^{5-2m-n} + 4HT + B\\&\quad = Pa(OH)_2T_3(HT)B + (m+n-2)H_2O\\&\qquad + (5-2m-n)H^+\\&\quad Pa(OH)_2T_3(HT)B \rightarrow PaOT_3(HT)B\\&\qquad \text{(slow, irreversible)}\end{aligned} \tag{23}$$

$$\begin{aligned}&PaO_m(OH)_n^{5-2m-n} + 3HT + B\\&\quad = Pa(OH)_2T_3B + (m+n-2)H_2O\\&\qquad + (5-2m-n)H^+\\&\quad Pa(OH)_2T_3B \rightarrow PaOT_3B\\&\qquad \text{(slow, irreversible)}\end{aligned} \tag{24}$$

$$\begin{aligned}&PaO_m(OH)_n^{5-2m-n} + 3HT + 2B\\&\quad = Pa(OH)_2T_3B_2 + (m+n-2)H_2O\\&\qquad + (5-2m-n)H^+\\&\quad Pa(OH)_2T_3B_2 \rightarrow PaOT_3B_2\\&\qquad \text{(slow, irreversible)}\end{aligned} \tag{25}$$

where $2m+n=3$ and 4.

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10) T. V. Healy and J. R. Ferraro, *J. Inorg. Nucl. Chem.*, **24**, 1449 (1962).

11) T. V. Healy, D. F. Peppard and G. W. Mason, *ibid.*, **24**, 1429 (1962).