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The Chemistry of Protactinium. II. The Behavior of Pentavalent Protactinium in a Perchloric Acid Solution

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Studies of the chemical behavior of protactinium(V) were carried out with the TTA-benzene extraction method, the ion exchange method and the filtration method. When the protactinium concentration is less than 10^{-6} M and the perchloric acid concentration is 0.3—2.0 N, the reaction of TTA extraction may proceed as:

$$\mathrm{PaO}_m(\mathrm{OH})_n{}^{5-2m-n} + 4\mathrm{HT} \rightleftarrows \mathrm{Pa(OH)T_4} + (m+n-1)\mathrm{H_2O} + (5-2m-n)\mathrm{H}^+$$

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

$$\mathrm{PaO}_m(\mathrm{OH})_n\mathrm{T}^{4-2m-n} + 4\mathrm{HT} \rightleftarrows \mathrm{PaT_5} + (m+n)\mathrm{H_2O} + (4-2m-n)\mathrm{H}^+$$

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

The cation exchange experiment gives results consistent with this conclusion. On the other hand, when the concentration of protactinium is higher than 10^{-6} M, the above relation does not hold, even in the 5 N perchloric acid solution, because protactinium forms the aggregates to a great extent. This has been confirmed by the filtration experiment.

It has been stated earlier that the results of investigations of the aqueous chemistry of protactinium are not always acceptable,[1] because the instability of the aqueous solution has resulted in some confusion on published works. This is true in investigations of the chemical behavior of pentavalent protactinium even in a perchloric acid solution, which is considered to be the most fundamental of the various aqueous systems. For example, Welch[2] assumed the existence of protactinyl ion in this medium from its behavior towards cation exchange resin, but Elson[3] concluded that, in weakly acid solutions, protactinium would be found in such hydrolyzed forms as $Pa_2(OH)_9{}^+$ and $Pa_2O_2(OH)_5{}^+$; in solutions of moderate acidity, in the form of PaO^{3+} or $Pa(OH)_2{}^{3+}$; and in a strong acid solution, perhaps in the hydrated form of Pa^{5+}. On the other hand, Bouiséres and his co-workers[4] assumed, from their TTA-benzene extraction experiments, that, in 0.9—3 M perchloric acid solutions, this element would be found in the form of $Pa(OH)_3{}^{2+}$ or $Pa(OH)_2A^{2+}$ (where A is the anion of TTA), and in $1.5\times10^{-3}-2\times10^{-5}$ M perchloric acid solutions, in the form of $Pa(OH)_2A_2{}^+$ or $PaO(OH)_2{}^+$. As to the stability of pentavalent protactinium, Guillaumont and his co-workers[5] reported that a weak absorption peak at 210 mμ which appeared in 2.4—11.8 M perchloric acid solutions containing about 10^{-5} M pentavalent protactinium disappeared in eight to ten days. Thus, the conclusions differ with the authors. For this reason, it is necessary to investigate more fully the chemical properties of pentavalent protactinium in a perchloric acid solution.

Thenoyl trifluoroacetone (TTA), as compared with the other organic complexing reagents, has a comparatively high acid dissociation constant; therefore, it is applicable even when the acidity of a solution is high. This is the reason why the TTA extraction method is frequently used for the separation of protactinium[6-11] as well as for fundamental research.

The purpose of this investigation is to elucidate the nature of pentavalent protactinium in a perchloric acid solution by the TTA-benzene extraction method, coupled with the ion exchange and filtration methods.

Experiments

Reagents and Apparatus.—*^{233}Pa and ^{231}Pa.*—Stock solutions of these isotopes were prepared by the methods reported previously.[1] Aliquots of these solutions 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 then dissolved by heating it with concentrated perchloric acid, and again evaporated to dryness. This was cooled and diluted to the desired concentration with respect to protactinium with a perchloric acid solution of a suitable concentration.

Ion Exchange Resins.—Dowex-50×8 and Dowex-1×8, 200—400 mesh, were used for the cation and anion exchange experiments respectively. Before use, they were converted to the desired forms (Dowex-50 to the H^+ form; Dowex-1 to the $ClO_4{}^-$ form), washed with distilled water, and dried in air.

Benzene was purified by distillation, and doubly-distilled water was used throughout this experiment. The other chemicals, such as thenoyl trifluoroacetone and perchloric acid, were of the highest-purity grade.

For the solvent extraction procedure, a Hiranuma-Seiki magnemixer, Model MMC-8, was used. All the vessels and radiation measurement instruments were those described in the foregoing report.[1]

Procedures.—Each value given was the average of the results of at least two determinations; care was taken to ascertain the material balance in each case.

TTA Extraction.—Ten milliliters of a perchloric acid solution of protactinium which had been adjusted to the desired condition and 10 ml. of a benzene solution of TTA in the desired concentration were mixed for 30 min. with a magnemixer in a thermostat at 30°C. After the two phases had completely separated, an aliquot of each phase was taken out and counted for γ radioactivity; the apparent distribution coefficient was calculated by means of the usual relationship:

$$K_d{}'=\frac{\dfrac{\text{Radioactivity in the org. phase}}{\text{Vol. of the org. phase (ml.)}}}{\dfrac{\text{Radioactivity in the aq. phase}}{\text{Vol. of the aq. phase (ml.)}}}$$

Ion Exchange.—The apparent distribution coefficient

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

[2] G. A. Welch, *Nature,* **172**, 458 (1953).

[3] R. E. Elson, "The Chemistry of Protactinium," The Actinide Elements, Ed. by G. T. Seaborg and J. J. Katz, McGraw-Hill Book Co., New York (1954), p. 103.

[4] G. Bouissières, M. C. Ferradini, M. Garcon, G. Guillaumont, M. Hussonois, R. Muxart, H. Pezerat, D. Robertson and T. Stchouzkoy, U. S. A. E. C., TID-4500, 160 (1963).

[5] R. Guillaumont, R. Muxart, G. Bouissières and M. Haissinsky, *Compt. rend.,* **248**, 3298 (1959).

[6] F. L. Moore, *Anal. Chem.,* **27**, 70 (1955).

[7] D. Brown, A. J. Smith and R. G. Wilkins, *J. Chem. Soc.,* **1959**, 1463.

[8] E. S. Pal'shin and B. F. Myasoedov, *J. Anal. Chem. U. S. S. R.,* **18**, 651 (1963).

[9] J. Fudge and J. L. Wood, *Analyst,* **81**, 417 (1956).

[10] B. F. Myasoedov and R. Mukhart, *J. Anal. Chem., U. S. S. R.,* **17**, 343 (1962).

[11] W. W. Meinke, U. S. A. E. C., AECD-2738 and AECD-2750 (1949).

was determined by equilibrating 500 mg. of air-dried ion exchange resin with 20 ml. of a 10^{-8} M protactinium solution under the desired condition for 2 days with intermittent shaking. Then the slurry was centrifuged in order to accelerate the complete separation of the two phases. In centrifugation, care was taken not to exceed 2000 r. p. m. because such a high speed is in danger of producing the sedimentation of some protactinium. An aliquot of the supernatant liquid was taken for the measurement of the γ radioactivity. The apparent distribution coefficient was calculated from the following equation:

$$K_d' = \frac{\dfrac{\text{Radioactivity in resin}}{\text{Amount of resin (g.)}}}{\dfrac{\text{Radioactivity in soln.}}{\text{Vol. of soln. (ml.)}}}$$

The radioactivity in the resin after equilibration was estimated from the difference between the total activity and the final activity present in the solutions.

Filtration.—Toyo-Roshi No. 5C filter paper (fine filter for quantitative use) and a membrane filter (supplied by Membrane-Filter-Gesellschaft, Göttingen), with diameters of 26 mm. and 30 mm. respectively, were used in this investigation. Filtration was performed under suction with a glass filtration apparatus with a perforated filter disk, the diameter of which was 18 mm. One or two milliliters of a sample solution was filtered, and then the filter paper was washed with 4 or 3 ml. of distilled water respectively. The filtrate and washings were then put together in the same polyethylene test tube. The radioactivities of its contents and of the filter paper were measured under the same geometrical conditions. The percentage of protactinium retained on the filter paper was then calculated from these values.

Results

TTA-benzene Extraction.—*The Relation between the Apparent Distribution Coefficient and the TTA Concentration.*—The influence of the TTA concentration on the apparent distribution coefficient was investigated by means of the constant acidity of the solution. The concentrations of protactinium used were 10^{-7} M and 10^{-10} M. The logarithm of the apparent distribution coefficient was plotted as a function of the logarithm of the TTA activity in the benzene phase, as is shown in Fig. 1.

The activity of TTA in the benzene phase at equilibrium was calculated from its initial concentration by the following equations:

$$\frac{(\mathrm{HT})_\mathrm{I}}{(\mathrm{HT})_\mathrm{B}} = 1.02 + 10^{-8}/\mathrm{H}^+ \qquad (1)^{12)}$$

$$f_\mathrm{HT} = 1 - 0.25(\mathrm{HT})_\mathrm{B}^{0.48} \qquad (2)^{13)}$$

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. 1 that, in the case of a directly-prepared solution, the log-log plot of the apparent distribution coefficient and the activity of TTA shows a good linearity, with a slope of about 4 over a wide range of reagent concentration, except in the case of an extremely low acidity, where exact linearity does not hold. The difference between solutions containing protactinium concentrations of 10^{-7} M and 10^{-10} M is not obvious. Furthermore, even when the solution is left to stand for a long time, these relationships do not change beyond the range of experimental error.

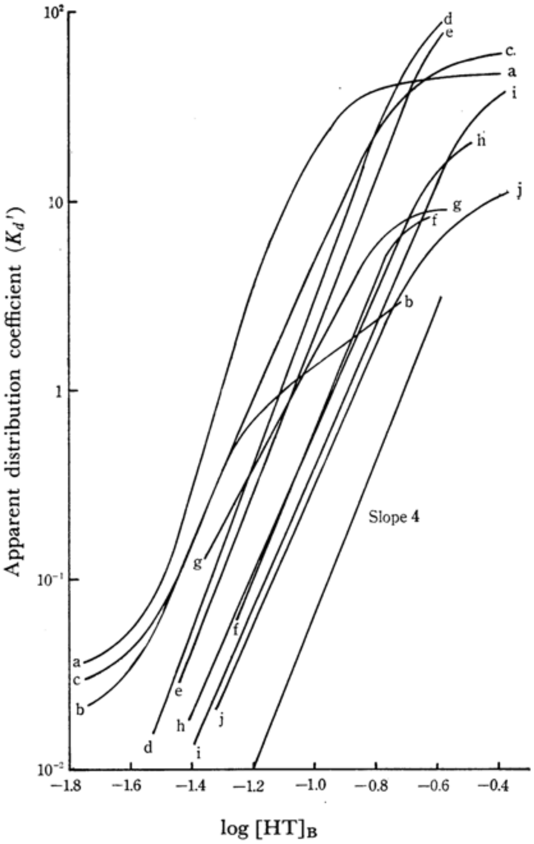

Fig. 1. Dependence of distribution coefficient on TTA activity.

a : 0.13 N $HClO_4$, 10^{-7} M Pa
b : 0.29 N $HClO_4$, 10^{-7} M Pa diluted from 10^{-5} M Pa solution in 5 N $HClO_4$
c : 0.37 N $HClO_4$, 10^{-10} M Pa
d : 0.40 N $HClO_4$, 10^{-7} M Pa
e : 0.58 N $HClO_4$, 10^{-7} M Pa
f : 1.00 N $HClO_4$, 10^{-7} M Pa
g : 0.53 N $HClO_4$, 10^{-7} M Pa diluted from 10^{-5} M Pa solution in 5 N $HClO_4$
h : 4.85 N $HClO_4$, 10^{-7} M Pa
i : 2.06 N $HClO_4$, 10^{-7} M Pa
j : 2.06 N $HClO_4$, 10^{-10} M Pa

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

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

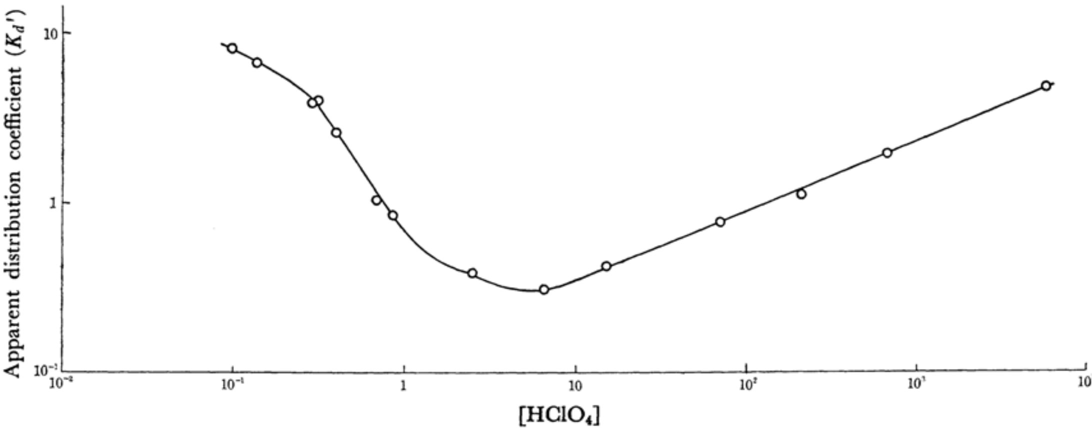

Fig. 2. Dependence of distribution coefficient of TTA extraction on perchloric acid activity.

On the contrary, when a sample solution is prepared indirectly from a 10^{-5} M stock solution, the range bearing a linear relation is narrower and the slope of the straight line is smaller than in the former case, decreasing as the aging time increases.

The Relation between the Apparent Distribution Coefficient and the Perchloric Acid Concentration.—Experiments were performed on the effect of perchloric acid concentration on the extraction of a 10^{-7} M solution of protactinium with 0.12 M TTA. The results are shown in Fig. 2. The activity of perchloric acid was calculated from the activity coefficient obtained by Robinson and Stokes.[14] As is shown in Fig. 2, the apparent distribution coefficient decreases with an increase in the concentration of perchloric acid, reaching a minimum at about 3 N acid, and then it increases with an increase in the acidity. In the range of acidity from 0.4 N to 1 N, the plot of the logarithm of the apparent distribution coefficient against the logarithm of the activity of perchloric acid shows a linear relationship with a slope of -1.45, whereas above 4 N it shows a straight line with a slope of 0.41.

The Relation between the Apparent Distribution Coefficient and the Hydrogen Ion Concentration in a Constant Ionic Srength Medium.—The effect of the acidity of the aqueous phase was studied at a constant ionic strength (2.03) by using various mixtures of perchloric acid and lithium perchlorate. Benzene solution of 0.07 M and 0.12 M TTA were used for the extraction. As is shown in Fig. 3, curves with a maximum were thus obtained, the position of the maximum differing with the difference in the TTA concentration used; with 0.12 M TTA the maximum is at 0.3 M acidity, while with 0.07 M TTA, it is at 0.1 M acidity. In a higher acidity range than the acidity that corresponds to the maximum point, the log-log plot of the apparent distribution coefficient and the hydrogen ion concentration shows a linear relationship with a slope of -1.6. This observation is different from that of Bouissieres and his co-workers[4], who obtained a slope of -2.0 in the acidity range higher than 1 N.

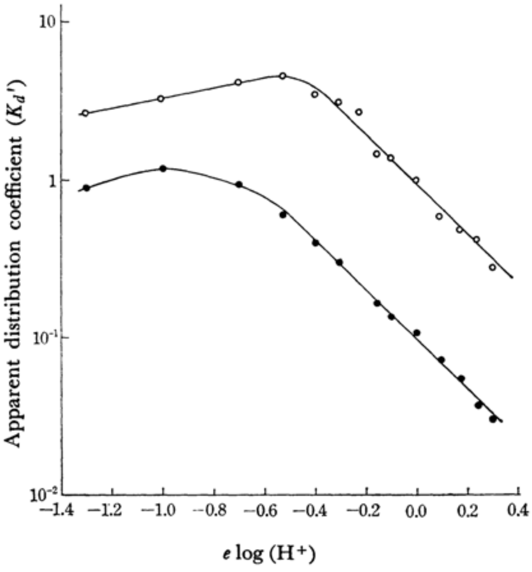

Fig. 3. Dependence of distribution coefficient of TTA extraction on hydrogen ion concentration in constant ionic strength medium.
Ionic strength, 2.03; Pa, 10^{-7} M; —○— 0.12 M TTA; —●— 0.07 M TTA.

The Variation in the Apparent Distribution Coefficient with the Concentration of Protactinium.—The relation between the apparent distribution coefficient and the protactinium concentration, from carrier-free to 10^{-6} M, was investigated at the constant acidities of 0.47, 1.0 and 5.0 N. The concentrations of TTA solution were 0.06, 0.10 and 0.12 M respectively. The results are shown in Fig. 4. Although at an acidity of 0.47 N the apparent distribution coefficient of carrier-free ^{233}Pa solutions is higher than that

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[14] R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).

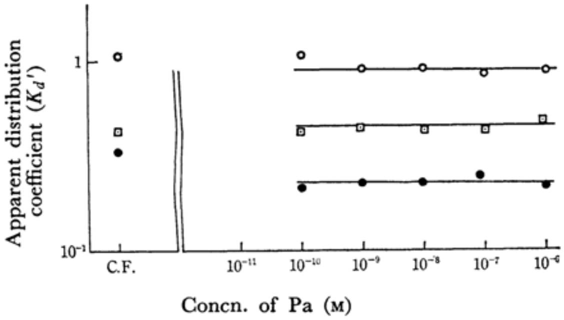

Fig. 4. Dependence of distribution coefficient of TTA extraction on protactinium concentration.

—●— 0.47 N $HClO_4$, 0.06 M TTA
—○— 1.0 N $HClO_4$, 0.12 M TTA
—⊡— 5.00 N $HClO_4$, 0.10 M TTA

of a more concentrated solution, this may be attributed to the ill reproducibility of the experiment in a trace concentration; therefore, it is considered that the apparent distribution coefficient is virtually constant in the concentration range below 10^{-6} M.

The Effect of Aging of the Solution on the Apparent Distribution Coefficient.—The relation between the apparent distribution coefficient and the aging time after the preparation of 10^{-7} M solutions of protactinium in various concentrations of perchloric acid was examined at a TTA concentration of 0.12 M. The results are presented in Fig. 5a. When the concentration of perchloric acid is low, the apparent distribution coefficient changes somewhat, but above an acidity of 0.6 N it does not change, at least not for 90 days. Then the solutions, 10^{-7} M in protactinium, were prepared just before use by the dilution of a 10^{-5} M solution which had an acidity of 5.165 N and which had been aged for a definite time. This was then extracted with a 0.12 M TTA-benzene solution in order to obtain the apparent distribution coefficients. The relations between the aging time and the distribution coefficients are shown in Fig. 5b. In contrast with the former case, the apparent distribution coefficient decreases appreciably with the time of standing.

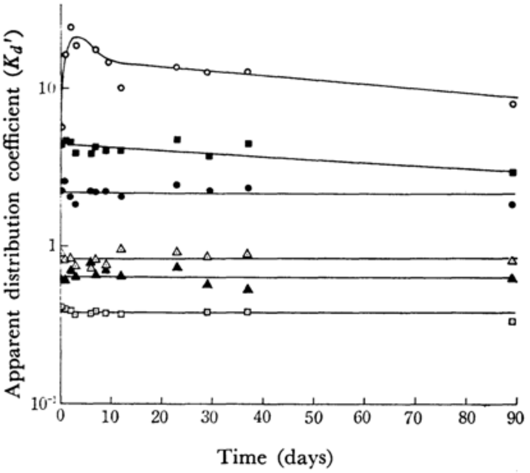

Fig. 5a. The effect of time of standing on the TTA extraction of Pa.
Pa, 10^{-7}M; TTA, 0.12M; —○— 0.087 N $HClO_4$; —■— 0.39 N $HClO_4$; —●— 0.58 N $HClO_4$; —△— 1.10 N $HClO_4$; —⊡— 2.05 N $HClO_4$; —▲— 4.91 N $HClO_4$.

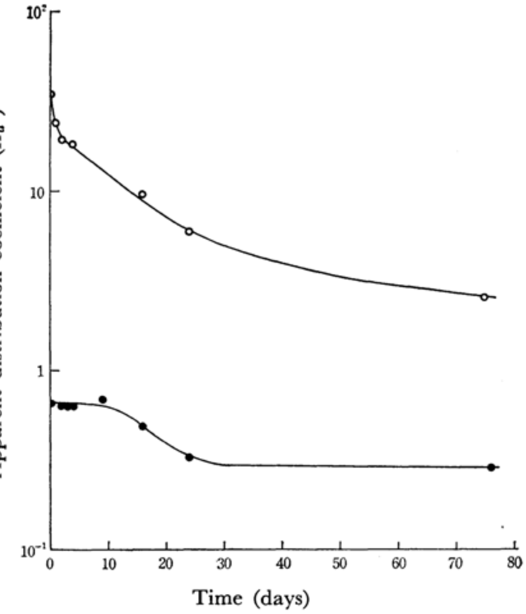

Fig. 5b. The effect of time of standing on the TTA extraction of Pa.
Pa, 10^{-7} M diluted from 10^{-5} M Pa solution of 5.62 N perchloric acid concentration; TTA, 0.12 M; —○— 0.056 N $HClO_4$; —●— 4.86 N $HClO_4$.

Ion Exchange.—The apparent distribution coefficient of protactinium was determined for cation and anion exchange resins at various concentrations of perchloric acid. As is shown in Fig. 6, protactinium is adsorbed on cation exchange resin to a considerable extent, and the distribution coefficient decreases with an increase in the concentration of perchloric acid, reaching a minimum at about 3 N; then it increases with an increase in the acidity. In the ranges from 0.4 M to 1.0 N and over 3 N, plots of the logarithm of the apparent distribution coefficient against the logarithm of the activity of perchloric acid show linear relationships, with slope of −1.5 and 0.5 respectively. As to anion exchange, the apparent distribution coefficient is lower by one order than in the case of cation exchange over the entire range of acidity, but the relation between the apparent distribution coefficient and the acidity is similar to that in cation exchange.

In order to examine the adaptability of the mass action law to cation exchange, the distribution of

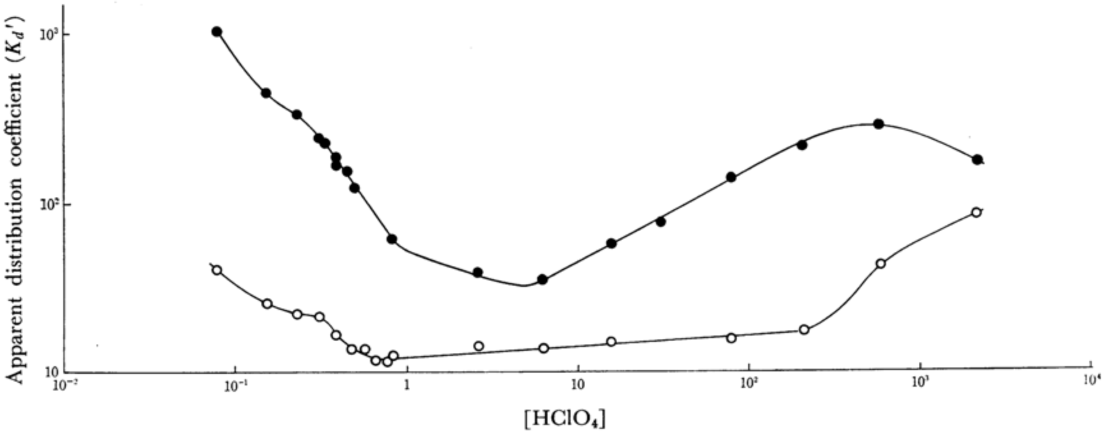

Fig. 6. Dependence of distribution coefficient of ion exchange on perchloric acid activity.
—●— Cation exchange; —○— Anion exchange

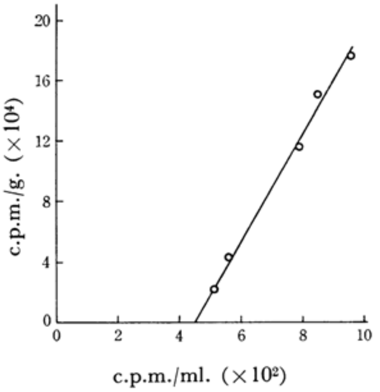

Fig. 7a. Determination of the proportion of protactinium which is not adsorbed on cation exchange resin.
Pa, 10^{-8} M; $HClO_4$, 0.50 N

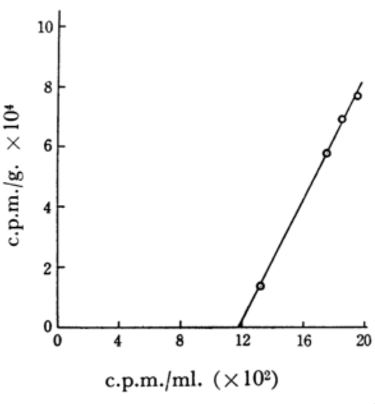

Fig. 7b. Determination of the proportion of protactinium which is not adsorbed on cation exchange resin.
Pa, 10^{-8} M; $HClO_4$, 3.10 N

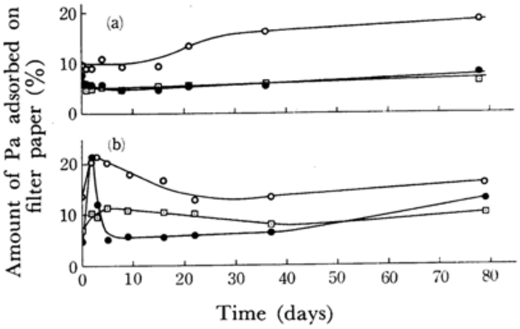

Fig. 8a. Filtration of protactinium-solution.
Pa, 10^{-7} M; —●— 0.25 N $HClO_4$;
—⊡— 2.0 N $HClO_4$; —○— 5.61 N $HClO_4$

Fig. 8b. Filtration of protactinium solution.
Pa, Carrier-free ^{233}Pa; —●— 0.36 N $HClO_4$;
—⊡— 2.05 N $HClO_4$; —○— 5.00 N $HClO_4$.

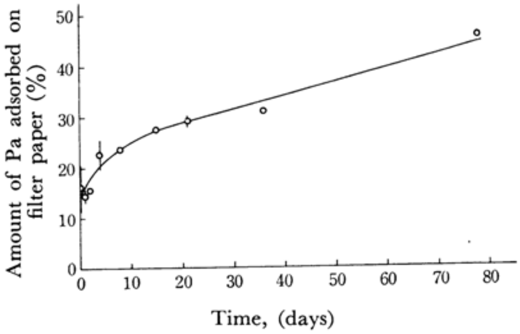

Fig. 8c. Filtration of protactinium solution.
Pa, 8.41×10^{-6} M; $HClO_4$, 5.45 N

protactinium between two phases was measured, with varying ratios between the aqueous phase volume and the amount of resin. The concentration of protactinium in the resin phase was plotted as an ordinate against the concentration of protactinium in the aqueous phase as abscissa, as is shown in Fig. 7. Experiments were undertaken at the acidities of 0.5 N and 3.10 N. In both cases, linear relationships were observed which did not surpass the original.

Filtration.—*By Filter Paper.*—The effect of acidity on the removal of protactinium from a perchloric acid solution by filtration through filter paper is shown in Table I. In this case, 2 ml. of a sample solution was used. Furthermore, the effects of aging at various acidities and at various protactinium concentrations are presented in Fig. 8. The removal of protactinium decreases with an increase in the acidity, reaching a minimum at about 0.3 M; then it increases with an increase in the acidity. In the cases of carrier-free and 10^{-1} M solutions, the difference between the two cases is not obvious and virtually no effect of aging is recognized except for the drastic initial changes in carrier-free solutions. In contrast with this, in the case of a 10^{-1} M solution the removal is increased with the lapse of aging time, attaining a value of 45 per cent after 80 days.

TABLE I. THE REMOVAL OF PROTACTINIUM FROM PERCHLORIC ACID SOLUTION BY FILTER PAPER

$HClO_4$ concn. N	Pa concn. M	% removal of Pa
0.072	C.F.	12.6
0.144	C.F.	5.52
0.216	C.F.	3.95
0.361	C.F.	4.79
2.05	C.F.	6.83
5.00	C.F.	13.5
0.248	10^{-7}	7.70
2.01	10^{-7}	5.90
5.61	10^{-7}	9.68
5.45	8.41×10^{-6}	16.3

TABLE II. THE EFFECT OF PORE SIZE ON THE REMOVAL OF PROTACTINIUM FROM PERCHLORIC ACID SOLUTION BY FILTRATION

Pa concn. M	$HClO_4$ concn. N	Filter	Pore size, mμ		% removal of Pa
			Max.	Mean	
10^{-5}	4.65	Paper*			11.1
10^{-5}	4.65	Membrane**	300	200	9.98
10^{-5}	4.65	Membrane	275	175	10.3
10^{-5}	4.65	Membrane	250	150	20.0
10^{-5}	4.65	Membrane	<100		37.9
10^{-6}	4.90	Paper			5.88
10^{-6}	4.90	Membrane	250	150	11.7
10^{-6}	4.90	Membrane	<100		18.3
10^{-7}	4.07	Paper			7.16
10^{-7}	4.07	Membrane	250	150	9.71
10^{-7}	4.07	Membrane	<100		12.1
10^{-8}	5.46	Paper			9.38
10^{-8}	5.46	Membrane	250	150	11.6
10^{-8}	5.46	Membrane	<100		19.4
10^{-9}	4.97	Paper			10.3
10^{-9}	4.97	Membrane	250	150	15.9
10^{-9}	4.97	Membrane	<100		21.0
C.F.***	4.80	Paper			12.2
C.F.	4.80	Membrane	<100		9.84

* Paper is the abbreviation of Toyo-roshi No. filter paper.

** Membrane is the abbreviation of membrane filter supplied from Membrane-Filter-Gesellschaft, Göttingen.

*** C.F. is the carrier-free ^{233}Pa solution.

By a Membrane Filter.—The percentage of the removal of protactinium by membrane filters with various pore sizes was determined at a perchloric acid concentration of 5 N. In this experiment, 1 ml. of a sample solution was used. As is apparent in Table II, the percentage of removal increases with the decrease in pore size; this effect is especially noticeable when the protactinium concentration is 10^{-5} M.

Discussion

If the species extractable into the organic phase are considered not to have any charge, the general equation for the TTA extraction reaction can be written by modifying Connick and McVey's treatment[15] as:

$$\begin{aligned}&\mathrm{PaO}_m(\mathrm{OH})_n\mathrm{T}_r{}^{5-2m-n-r}(\mathrm{aq.}) + (5-2p-q-r)\\&\quad\times \mathrm{HT}(\mathrm{org.}) = \mathrm{PaO}_p(\mathrm{OH})_q\mathrm{T}_{5-2p-q}(\mathrm{org.})\\&\quad+(m+n-p-q)\mathrm{H_2O}(\mathrm{org.})\\&\quad+(5-2m-n-r)\mathrm{H}^+(\mathrm{aq.})\end{aligned}\tag{3}$$

where HT represents the TTA molecule and T^-, the dissociated TTA anion. The equilibrium constants can then be defined as:

$$K_{m,n,p,q,r} = \frac{[\mathrm{PaO}_p(\mathrm{OH})_q\mathrm{T}_{5-2p-q}][\mathrm{H_2O}]^{m+n-p-q}\times[\mathrm{H}^+]^{5-2m-n-r}}{[\mathrm{PaO}_m(\mathrm{OH})_n\mathrm{T}_r{}^{5-2m-n-r}]\times[\mathrm{HT}]^{5-2p-q-r}}\tag{4}$$

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 coefficient expressed in terms of activities is defined as the sum of the activities of protactinium species in the benzene phase divided by the sum of the activities of protactinium species in the aqueous phase;

$$K_d = \frac{\sum_{p,q}[\mathrm{PaO}_p(\mathrm{OH})_q\mathrm{T}_{5-2p-q}]}{\sum_{m,n,r}[\mathrm{PaO}_m(\mathrm{OH})_n\mathrm{T}_r{}^{5-2m-n-r}]}\tag{5}$$

From Eq. 4, we obtain:

$$[\mathrm{PaO}_m(\mathrm{OH})_n\mathrm{T}_r{}^{5-2m-n-r}] = \frac{[\mathrm{PaO}_p(\mathrm{OH})_q\mathrm{T}_{5-2p-q}][\mathrm{H_2O}]^{m+n-p-q}\times[\mathrm{H}^+]^{5-2n-n-r}}{\mathrm{K}_{m,n,p,q,r}[\mathrm{HT}]^{5-2p-q-r}}\tag{6}$$

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[15] R. E. Connick and W. H. McVey, *J. Am. Chem. Soc.*, **71**, 3182 (1949).

Since this equation holds for any set of values of p and q, we shall, for the sake of simplicity, choose $p=q=0$.

$$[\mathrm{PaO}_m(\mathrm{OH})_n\mathrm{T}_r{}^{5-2m-n-r}] = \frac{[\mathrm{PaT}_5][\mathrm{H_2O}]^{m+n}[\mathrm{H}^+]^{5-2m-n-r}}{\mathrm{K}_{m,n,o,o,r}[\mathrm{HT}]^{5-r}} \tag{7}$$

From Eqs. 6 and 7, we obtain:

$$[\mathrm{PaO}_p(\mathrm{OH})_q\mathrm{T}_{5-2p-q}] = \frac{\mathrm{K}_{m,n,p,q,r}[\mathrm{PaT}_5][\mathrm{H_2O}]^{p+q}}{\mathrm{K}_{m,n,o,o,r}[\mathrm{HT}]^{2p+q}} \tag{8}$$

Since Eq. 8 holds for any set of values of m, n and r, we shall choose these values to be zero.

$$[\mathrm{PaO}_p(\mathrm{OH})_q\mathrm{T}_{5-2p-q}] = \frac{\mathrm{K}_{o,o,p,q,o}[\mathrm{PaT}_5][\mathrm{H_2O}]^{p+q}}{\mathrm{K}_{o,o,o,o,o}[\mathrm{HT}]^{2p+q}} \tag{9}$$

By substituting Eqs. 7 and 9 into Eq. 5, we obtain:

$$K_d = \frac{\displaystyle\sum_{p,q}\frac{\mathrm{K}_{o,o,p,q,o}[\mathrm{H_2O}]^{p+q}}{\mathrm{K}_{o,o,o,o,o}[\mathrm{HT}]^{2p+q}}}{\displaystyle\sum_{m,n,r}\frac{[\mathrm{H_2O}]^{m+n}[\mathrm{H}^+]^{5-2m-n-r}}{\mathrm{K}_{m,n,o,o,r}[\mathrm{HT}]^{5-r}}} \tag{10}$$

By taking the logarithm, we obtain:

$$\ln K_d = \ln\sum_{p,q}\frac{\mathrm{K}_{o,o,p,q,o}[\mathrm{H_2O}]^{p+q}}{\mathrm{K}_{o,o,o,o,o}[\mathrm{HT}]^{2p+q}} - \ln\sum_{m,n,r}\frac{[\mathrm{H_2O}]^{m+n}[\mathrm{H}^+]^{5-2m-n-r}}{\mathrm{K}_{m,n,o,o,r}[\mathrm{HT}]^{5-r}} \tag{11}$$

By taking the partial derivative of the logarithm of K_d with respect to the logarithm of the activity of HT and by substituting Eqs. 7 and 9, we obtain:

$$\begin{aligned}\frac{\partial \ln K_d}{\partial \ln [\mathrm{HT}]} &= \frac{-\sum_{p,q}(2p+q)[\mathrm{PaO}_p(\mathrm{OH})_q\mathrm{T}_{5-2p-q}]}{\sum_{p,q}[\mathrm{PaO}_p(\mathrm{OH})_q\mathrm{T}_{5-2p-q}]} + \frac{\sum_{m,n,r}(5-r)[\mathrm{PaO}_m(\mathrm{OH})_n\mathrm{T}_r{}^{5-2m-n-r}}{\sum_{m,n,r}[\mathrm{PaO}_m(\mathrm{OH})_n\mathrm{T}_r{}^{5-2m-n-r}]}\\ &= 5 - \sum_{p,q}(2p+q)f_{p,q} - \sum_{m,n,r} rf_{m,n,r}\end{aligned} \tag{12}$$

where $f_{p,q}$ is the fraction of the total activity of the benzene phase contributed by the PaO_p-$(\mathrm{OH})_q\mathrm{Y}_{5-2p-q}$ species, and where $f_{m,n,r}$ is that of the aqueous phase contributed by the PaO_m-$(\mathrm{OH})_n\mathrm{T}_r{}^{5-2m-n-r}$ species.

Hence:

$$\sum_{p,q} f_{p,q} = 1 \quad \text{and} \quad \sum_{m,n,r} f_{m,n,r} = 1 \tag{13}$$

Furthermore, as at least one molecule of TTA is co-ordinated to one atom of protactinium in the organic phase

$$2p + q \leqq 4 \tag{14}$$

holds.

If the activity coefficients of protactinium species are assumed to be constant, irrespective of the TTA concentration, the apparent distribution coefficient obtained empirically can be replaced for the thermodynamic distribution coefficient, K_d, expressed in terms of activity; no appreciable error should be introduced by this assumption. The curves in Fig. 1 show straight lines, with a slope of 4, in the range of TTA concentration, so that $\sum_{p,q}(2r+q)\cdot f_{p,q}+\sum_{m,n,r} rf_{m,n,r}$ should be unity. Suppose r is unity; that is, the average number of TTA molecules attached to protactinium in the aqueous phase is one; species extracted into the benzene phase should, then, have the PaT_5 form. If we can neglect the species having a TTA molecule in a perchloric acid solution, the $2p+q=1$ relation holds, so the average number of TTA attached to protactinium in the organic phase becomes 4 and then $\mathrm{Pa(OH)T}_5$ predominates. It is clear that $r\geqq 2$ is impossible. The decrease in the slope in the higher concentration range of TTA can be explained by the increase in the average numbers of TTA attached to protactinium in the aqueous phase, and that in the range of lower concentration of TTA, by the decrease in the average number of TTA attached to protactinium in the benzene phase.

Taking the partial derivative of the logarithm of K_d with respect to the logarithm of the activity of hydrogen ion and by substituting Eq. 7, we can get:

$$\begin{aligned}\frac{\partial \ln K_d}{\partial \ln [\mathrm{H}^+]} &= -\frac{\sum_{m,n,r}(5-2m-n-r)\mathrm{PaO}_m(\mathrm{OH})_n \times \mathrm{T}_r{}^{5-2m-n-r}}{\sum_{m,n,r}\mathrm{PaO}_m(\mathrm{OH})_n\mathrm{T}_r{}^{5-2m-n-r}}\\ &= -5 + \sum_{m,n,r}(2m+n+r)f_{m,n,r}\end{aligned} \tag{15}$$

If the activity coefficients of protactinium species and of hydrogen ion are assumed to be constant over the entire range of acidity when the ionic strength of a solution is held constant, the apparent distribution coefficient (K_d') obtained empirically can be replaced by the thermodynamic distribution coefficient(K_d) expressed in terms of activity; no appreciable error should be introduced by this assumption. As is clear from Fig. 3, the linear relationship with a slope of -1.6 holds between the logarithm of the apparent distribution coefficient and the logarithm of the hydrogen ion concentration with acidities of over 0.3 N and 0.1 N when the TTA concentrations are 0.12 M and 0.07 M respectively. Therefore,

$$-5+\sum_{m,n,r}(2m+n+r)f_{m,n,r} = -1.6 \tag{16}$$

When $r=0$,

$$\sum_{m,n,o}(2m+n)f_{m,n,o} = 3.4 \tag{16'}$$

Therefore, protactinium in a perchloric acid solution may be found in the forms $Pa(OH)_3^{2+}$ or $PaO(OH)^{2+}$ and $Pa(OH)_4^+$, $PaO(OH)_2^+$ or PaO_2^+. When $r=1$,

$$\sum_{m,n,1}(2m+n+1)f_{m,n,1} = 3.4 \qquad (16'')$$

Species in perchloric acid may be in the forms $Pa(OH)_2T^{2+}$ or $PaOT^{2+}$ and $Pa(OH)_3T^+$ or $PaO(OH)T^+$.

From the above considerations, one can represent the reaction mechanism as:

$$PaO_m(OH)_n^{5-2m-n} + 4HT \rightleftarrows Pa(OH)T_4 + (m+n-1)H_2O + (5-2m-n)H^+ \qquad (17)$$

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

$$PaO_m(OH)_nT^{4-2m-n} + 4HT \rightleftarrows PaT_5 + (m+n)H_2O + (4-2m-n)H^+ \qquad (18)$$

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

The reason for the phenomenon that the lower the perchloric acid concentration, the more remarkable the decrease in the slope of the curves in Fig. 1 at higher TTA concentrations, may be considered to be as follows. The solubility of TTA in the aqueous phase increases with the decrease in acidity, as is clear from Eq. 1, and the lower the acidity, the more easily TTA is dissociable. Therefore, TTA can form a complex with protactinium more easily in an aqueous solution with a low acidity. Similarly, in a weakly acidic solution, a high concentration of TTA facilitates the formation of anionic species, so that the maximum of the curves in Fig. 3 appears in the higher acidity region when the concentration of TTA is high. The curve in Fig. 2, the dependence of the apparent distribution coefficient on the perchloric acid concentration at a TTA concentration of 0.12 M, shows a straight line in the 0.3—1.0 N acidity range, with a slope of -1.5; this agrees with that in Fig. 3. The curve of an acidity below 0.3 N, however, is completely different from the results of Fig. 3. With an acidity of above 3 N, the apparent distribution coefficient increases with the increase in acidity, but this can not be understood in terms of the above-mentioned considerations, because the assumptions made in the preceding discussion are not applicable. In other words, the activity coefficients of protactinium species may change with the ionic strength; if so, in Eq. 15 the apparent distribution coefficient should not be used instead of the true distribution coefficient (K_d). Furthermore, it should be pointed out that, in performing the differentiation leading to Eq. 15, it was necessary that the activity of water remain constant, but this assumption may not hold in a case of a remarkable change in ionic strength.

For cation exchange reaction, we can write the general equation as:

$$PaO_m(OH)_n^{5-2m-n} + (5-2p-q)HR \rightleftarrows PaO_p(OH_qR_{5-2p-q} + (m+n-p-q)H_2O + (5-2m-n)H^+ \qquad (19)$$

where HR represents cation exchange resin. The equilibrium constant for this reaction can be defined as:

$$K_{m,n,p,q} = \frac{[PaO_p(OH)_qR_{5-2p-q}][H_2O]^{m+n-p-q} \times [H^+]^{5-2m-n}}{[PaO_m(OH)_n^{5-2m-n}][HR]^{5-2p-q}} \qquad (20)$$

and the distribution coefficient, as:

$$K_d = \frac{\sum_{p,q}[Pa(OH)_qR_{5-2p-q}]}{\sum_{m,n}[PaO_m(OH)_n^{5-2m-n}]} \qquad (21)$$

Proceeding as before gives:

$$\frac{\partial \ln K_d}{\partial \ln [H^+]} = -5 + \sum_{m,n}(2m+n)f_{m,n} \qquad (22)$$

This equation is in the same form as (16''), so that the similarity between curves in Fig. 2 and Fig. 6 is not surprising. The difference between these curves may be due mainly to the following two reasons: first, the difference in the dependency of the activity coefficient on the perchloric acid concentration between the benzene phase and the resin phase, and second, the presence of non-adsorbable species on ion exchange resin.

Although no meaningful difference was observed between 10^{-7} M and 10^{-10} M protactinium solutions, a great difference in the stability of the solutions was observed between 10^{-5} M and 10^{-7} M solutions. This is probably due to the ease with which the 10^{-5} M solution polymerizes. It is interesting to note that this concentration is just below the limit of the solubility of protactinium in a 5 N perchloric acid solution.[6]

To clarify this point, the effect of the protactinium concentration on the distribution coefficient for extraction was examined. It is apparent from Fig. 4, with a protactinium concentration of below 10^{-6} M, that the apparent distribution coefficient for TTA extraction is almost constant, regardless of the protactinium concentration, so this phenomenon may be characteristic of concentrated solutions such as 10^{-5} M. This is confirmed by the results of filtration experiments; that is, the amount uptaken on the filter from the solution of 10^{-5} M is extremely large. Above all, the results obtained by using a membrane filter may be an indication of the presence of colloidal aggregates of protactinium species. Furthermore, the remarkable dependence on the aging time encountered in the filtration of a 10^{-5} M solution through filter paper is consistent with the observation on the solvent extraction experiments.

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16) R. Thompson, U. S. A. E. C., AECD-1897 (1948).

Even when the concentration of protactinium is lower than 10^{-6} M, a membrane filter with smaller pores removes radioactivity more effectively than one with larger pores. This is an indication of the presence of a small amount of colloidal aggregates. This assumption is also supported by the following consideration.

We suppose that one or more species, which are nonadsorbable on cation exchange resin and which do not reach equilibrium rapidly with adsorbable species, would be present in a solution and that the fraction of such species may be expressed by a. Under identical experimental conditions, one can assume that the activity coefficients of protactinium species are constant; therefore, the protactinium concentration, namely, the radioactivity in unit volume, might be proportional to the activity of protactinium species. For this reason, the radioactivity of protactinium, instead of its activity, will be used in the following discussion for the sake of simplicity. The distribution coefficient of the species adsorbable on the cation exchange resin can be defined as:

$$K_d = \frac{A_r/M}{A_{aq}/V} \tag{23}$$

where M represents the amount of cation exchange resin per gram; V, the volume of solution in ml. and A_r and A_{aq}, the radioactivity in each phase respectively. Let A, A'_r and A'_{aq} be the total radioactivity and the radioactivities in the resin phase and in the aqueous phase at equilibrium respectively; we can then write:

$$A'_r = A_r \tag{24}$$

$$A'_{aq} = A_{aq} - aA \tag{25}$$

By combining Eqs. 23, 24 and 25, we can get:

$$\frac{K_d}{V}(A'_{aq} - aA) = \frac{A'_r}{M} \tag{26}$$

From Eq. 26 we then obtain:

$$S_r = K_d S_{aq} - \frac{aA}{V} K_d \tag{27}$$

where:

$$A'_{aq}/V = S_{aq} \qquad A'_r/M = S_r \tag{28}$$

Equation 27 represents the relationship between S_{aq} and S_r to be linear and the slope to be K_d, namely, the distribution coefficient of the adsorbable species. If we represent the intercept of abscissa as $(S_{aq})_0$,

$$a = \frac{(S_{aq})_0}{A/V} \tag{29}$$

The ratio of the value of the intercept of abscissa to the initial activity in the unit volume of solution gives the fraction of nonadsorbable species. For a solution containing only adsorbable species in rapid equilibrium, we may obtain a straight line which passes through the point of origin. Figures 7a and b give the plot for solutions of about 10^{-8} M protactinium in 0.50 N and in 3.10 N perchloric acid respectively. These figures indicate that approximately 17% and 44% of nonadsorbable protactinium species are present in these media respectively. These results are compatible with the observations of the filtration experiment. No such phenomenon, however, can be observed in the solvent extraction. This difference between solvent extraction and ion exchange can be explained by the existence of a dynamic equilibrium in the solvent extraction, which in turn destroys the colloidal aggregates to some degree by means of the strong complexing action of TTA. This offers one reason for the small difference in behavior towards solvent extraction and cation exchange. The similarity between the effects of cation and anion exchange resins on the perchloric acid concentration seems curious, but in anion exchange experiments no such simple relation as Eq. 27 could be obtained and, therefore, further investigation is needed in order to illustrate the mechanism of anion exchange.

Summary

The chemical behavior of pentavalent protactinium in perchloric acid solutions has been investigated by TTA-benzene extraction, ion exchange and filtration methods. When the protactinium concentration is less than 10^{-6} M, the log-log plot of the apparent distribution coefficient and the activity of TTA in the benzene phase gives a straight line with a slope of 4, while the plot of the apparent distribution coefficient and the acidity in a constant ionic strength medium shows a linear relationship with a slope of -1.6 over the 0.3—2.0 N range of acidity. This relationship does not change with the aging of the solution.

Thus, under these conditions, the reaction of TTA extraction may proceed as:

$$\mathrm{PaO}_m(\mathrm{OH})_n{}^{5-2m-n} + 4\mathrm{HT} \rightleftarrows \mathrm{Pa(OH)T}_4 + (m+n-1)\mathrm{H_2O} + (5-2m-n)\mathrm{H}^+$$

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

$$\mathrm{PaO}_m(\mathrm{OH})_n\mathrm{T}^{4-2m-n} + 4\mathrm{HT} \rightleftarrows \mathrm{PaT}_5 + (m+n)\mathrm{H_2O} + (4-2m-n)\mathrm{H}^+$$

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

The cation exchange experiments give consistent results, leading to these conclusions. Contrary to this, when the concentration of protactinium is higher than 10^{-6} M, this relation does not hold and the apparent distribution coefficient decreases with the increase in aging time, even in a 5 N perchloric acid solution; therefore, it is considered that protactinium forms colloidal aggregates to a greater extent. This is also confirmed by the

filtration experiment; that is, the effect of the pore size of the filter and that of the aging time on the removal of protactinium from a solution by filtration are noticeable, especially when the concentration of protactinium is higher than 10^{-6} M. The behavior towards anion exchange resin can not be explained, however, and so further experiments are needed.

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