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The Chemistry of Protactinium. IX. A Study of the Solvent Extraction of Protactinium(V) from a Perchloric Acid Solution Using Di(2-ethylhexyl)phosphoric Acid as the Extractant

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Studies of the chemical behavior of protactinium(V) in a perchloric acid solution were carried out by the HDEHP-benzene extraction method. When the protactinium concentration was lower than 10^{-7} M, the extraction reaction was considered to proceed as:

$$\mathrm{PaO(OH)^{2+}_{aq.}} + 3\mathrm{(HA)_{2\,org.}} = \mathrm{PaO}_p\mathrm{(OH)}_q\mathrm{A}_{5-2p-q}\mathrm{(HA)}_{2p+q+1\,\mathrm{org.}} + 2\mathrm{H^+_{aq.}} + (2-p-q)\mathrm{H_2O_{aq.}}$$

where $p=1$, $q=0$ or 1, and $p=2$, $q=0$

and

$$\mathrm{Pa(OH)_3{}^{2+}_{aq.}} + 3\mathrm{(HA)_{2\,org.}} = \mathrm{PaO}_p\mathrm{(OH)}_q\mathrm{A}_{5-2p-q}\mathrm{(HA)}_{2p+q+1\,\mathrm{org.}} + 2\mathrm{H^+_{aq.}} + (3-p-q)\mathrm{H_2O_{aq.}}$$

where $p=0$, q=0, 1, 2, or 3; p=1, $q=0$ or 1 and $p=2$, $q=0$.

It has been said that the aqueous solution of protactinium(V) is unstable because of its strong tendency to hydrolyze and to precipitate, even in a relatively strong acid solution. This tendency is especially noticeable in a perchloric acid solution, which is considered to be the most fundamental of the aqueous systems. Although many investigations have been carried out into the chemistry of protactinium(V) in a perchloric acid solution, the species present in this medium are far from having been established.

Suzuki and Inoue[1] reported that protactinium(V) in a perchloric acid solution existed in the forms of PaO-

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

$(OH)^{2+}$ or $Pa(OH)_3{}^{2+}$ and $PaO^+{}_2$, $PaO(OH)_2{}^+$ or $Pa(OH)_4{}^+$ when the concentration of protactinium(V) was lower than 10^{-6}M and the acidity was 0.3—2.0 M; they reached these conclutions by means of an investigation by the TTA-benzene extraction method, by the ion-exchange adsorption method, and by a filtration method using several kinds of filter paper and of membrane filter. They also observed that the distribution ratio (D) of protactinium (V) in the TTA-benzene extraction varied with the method of the preparation of the perchloric acid solution of protactinium, and pointed out that this fact was one of the reasons for the disagreement among the results obtained by various authers. This implies the necessity for a suitable choice of the experimental conditions if the thermodynamic treatment is to be made possible. Even when precautions were taken, the experimental error was too high for quantitative knowledge to be obtained.

Recently, solvent extraction studies using acidic organophosphoric esters have been successful. Among these esters di(2-ethylhexyl)phosphoric acid(HDEHP) is known to be effective for the separation of the lanthanides and of the actinides, particularly of the transplutonium elements, by means of extraction chromatography.[2–6] The acidic organophosphoric esters have greater acid dissociation constants than TTA.[7,8] HDEHP is considered to extract cations by a cation-exchange mechanism and thus is expected to have a selectivity in the solvent extraction according to the charge of the cation. Therefore, for a complete understanding of the chemical behavior of protactinium in the perchloric acid solution, it is worthwile to make a solvent-extraction study by using HDEHP as an extractant, for it has different characteristics than TTA.

Akatsu[9] pointed out, in her paper on the chemistry of neptunium, that protactinium(V) had a greater distribution ratio than neptunium(V) in a HDEHP-perchloric acid extraction system. She also emphasized the difference in the acid dependency of the distribution ratio between protactinium(V) and neptunium(V); *i.e.*, protactinium(V) showed an inversely second-power dependency, while neptunium(V) showed an inversely proportional dependency. However she did not say anything about the extraction mechanism of protactinium(V) nor the abnormal behavior of protactinium(V) in the perchloric acid solution pointed out by Suzuki and Inoue in their TTA-extraction studies. If her results indicate a special stability of the Pa(V)-HDEHP extraction system, we can except that remarkable progress in Pa(V)-solution chemistry can be attained by HDEHP-extraction study.

In this investigation, the author studied the HDEHP-extraction in order to clarify the chemical species of protactinium(V) in a perchloric acid solution.

Experimental

Reagents and Apparatus. *^{231}Pa and ^{233}Pa*: ^{231}Pa which had been obtained from The Radio-chemical Centre (Amersham, England) was purified by a method reported previously.[10] The radiochemical purity was certified by α-ray and γ-ray spectroscopy. The concentration of protactinium in the ^{231}Pa solution was determined by absolute α-ray counting and by gravimetry, using protactinium pentoxide as the weighing form. These two results agreed well within the limits of experimental error, so we can say that there was no contamination by non-radioactive impurities.

^{233}Pa was prepared by the method of Suzuki and Inoue.[10]

HDEHP and Other Reagents: Commercially-available HDEHP was purified by the method reported by Peppard *et al.*[11] In order to determine the purity of HDEHP, about a 0.1 N HDEHP-10% alcohol-benzene solution was titrated by a 0.1 N NaOH standard solution. The purity was at least 99.8%. Benzene was used as a diluent of HDEHP, which is dimeric in this solvent.[11] The benzene was purified by extracting thiophene by concentrated sulfuric acid, followed by distillation. The other reagents used in this experiment were of the highest purity.

Glass Apparatus: All of the glass apparatus, including pipettes, beakers, separatory funnels and flask, used in this experiment was preliminarily saturated with protactinium by being brought in contact with the perchloric acid solution of protactinium for a time sufficient for the saturation of the adsorption to be reached. The material balance held well under this treatment, except otherwise noted.

Procedures. *The Preparation of the Pa-perchloric Acid Solutions*: Appropriate amounts of the ^{231}Pa-stock solution and the ^{233}Pa-stock solution were placed in a platinum dish and evaporated to dryness. The residue was dissolved in concentrated perchloric acid. The solution was then diluted to 10^{-7}M with respect to protactinium with perchloric acid of a suitable concentration. In order to regulate the ionic strength (μ) of the solution, the lithium perchlorate solution, which has the same acidity as the Pa-perchloric acid solution under investigation, was added.

The Determination of the Distribution Ratio: Ten milliliters of a Pa-perchloric acid solution and 10 ml of a HDEHP-benzene solution were mixed in a separatory funnel for 15 min. After the two phases had completely separated, an aliquot of each phase was taken into a polyethylene test tube and the γ-radioactivity of ^{233}Pa was counted by means of a $1{}^{1}/_{2}''$ welltype NaI(Tl) scintillation counter. The distribution ratio was calculated by means of the usual relationship:

$$D = \frac{\gamma\text{-radioactivity per ml of the organic phase}}{\gamma\text{-radioactivity per ml of the aqueous phase}}$$

As a result of the preliminary experiment, it was established that the distribution ratio did not change even when the Pa-perchloric acid solution was left to stand for 1—7 days after its preparation. Thereafter, the distribution ratio gradually varied with time. This change reflects the change in the composition of the Pa-species in the perchloric acid solution. In this experiment, the solutions which were allowed to stand

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[2] J. W. Winchester, *J. Chromatogr.*, **10**, 502 (1963).

[3] R. J. Sochacka and S. Siekierski, *ibid.*, **16**, 376 (1964).

[4] S. Siekierski and R. J. Sochacka, *ibid.*, **16**, 385 (1964).

[5] E. P. Hotwitz, C. A. A. Bloomquist, and D. J. Henderson, *J. Inorg. Nucl. Chem.*, **31**, 1149 (1969).

[6] E. P. Horwitz, C. A. A. Bloomquist, D. J. Henderson, and D. E. Nelson, *ibid.*, **31**, 3255 (1969).

[7] D. F. Peppard, D. W. Mason, and C. M. Anderjasich, *ibid.*, **27**, 697 (1965).

[8] E. H. Cook and R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **74**, 6103 (1952).

[9] E. Akatsu, **JAERI 1099** (1965).

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

[11] D. F. Peppard, J. R. Ferraro, and G. W. Mason, *J. Inorg. Nucl. Chem.*, **7**, 231 (1958).

for 1—4 days were used, unless otherwise noted. Thus, the error in the distribution ratio was minimized to about 10% when the distribution ratio was nearly 1.0.

It was found that a 10 min shaking was sufficient to get a constant distribution ratio. The equilibrium in the aqueous phase which is established in a 10 min shaking, is called "rapid equilibrium" in the rest of this report.

The distribution ratio obtained from the backward extraction varied markedly with respect to the standing time of the Pa-HDEHP-benzene solution and did not show a constant value in any interval of the standing time. The distribution ratio obtained from the backward extraction was generally higher than that obtained from the forward extraction.

Thus, in this investigation one can not, contrary to expectations, make a quantitative discussion of the thermodynamic equilibrium of the protactinium in a perchloric acid solution but can merely get the extraction behavior of Pa-species which are in rapid equilibrium with the extractable species.

Results

The Relation between the Distribution Ratio and the Acidity. The influence of the acidity on the distribution ratio was investigated by means of the constant ionic strength of the aqueous phase, as is shown in Fig. 1.

One of the important results concerns the different acid dependency between the solutions with the inonic strengths of 2.5 and 1.5. In the former case, the log-log plot of D and the acidity shows a linear relation, with a slope of −2, if the acidity is higher than 0.7 M. In the latter case, however, the slope is about −1.2. When the acidity of the aqueous phase was very low, the material balance did not hold well because protactinium was adsorbed on the wall of the glass separatory funnel in every experiment, even though the vessels had first been saturated with protactinium from a perchloric acid solution of moderate acidity. This tendency was prominent at acidities lower than 0.5 M when the ionic strength was 2.5. When the ionic strength was 1.5, this tendency was even more pronounced, and, in addition, inextractable species were found. The percentage fraction of the total protactinium contributed by the inextractable species was greater than 30% when the acidity was between 0.15 M and 0.3 M. Therefore, Fomin's method was applied in order to obtain the true distribution ratio (D_t) of the extractable species.[12] The results are shown in Fig. 2. The maximum standard deviation of D_t amounted to about 50%. This large error seems to be caused by two independent factors: one is the scattering of data caused by the adsorption of protactinium on the wall of separatory funnel, and the other is the limitation in the application of the Fomin method. In spite of this difficulty, one can read from Fig. 2 that the log-log plot of D_t and the acidity shows a linear relation, with a slope of −2, similar to the case of the inoic strength of 2.5.

The Relation between the Distribution Ratio and the HDEHP Concentration. The relation between the distribution ratio and the HDEHP concentration was

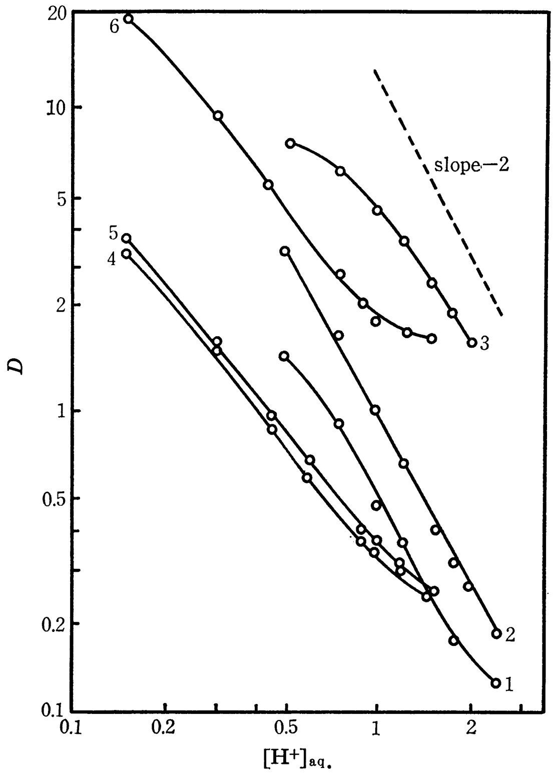

Fig. 1. The relation between the distribution ratio and the acidity.

1, $\mu=2.5$, $[(HA)_2]_{org.}=5\times10^{-2}$M, Standnig time is 10 hr
2, $\mu=2.5$, $[(HA)_2]_{org.}=5\times10^{-3}$M, Standing time is 3 days
3, $\mu=2.5$, $[(HA)_2]_{org.}=1\times10^{-2}$M, Standing time is 3 days
4, $\mu=1.5$, $[(HA)_2]_{org.}=5\times10^{-3}$M, Standing time is 1 day
5, $\mu=1.5$, $[(HA)_2]_{org.}=5\times10^{-3}$M, Standing time is 5 days
6, $\mu=1.5$, $[(HA)_2]_{org.}=1\times10^{-2}$M, Standing time is 5 days

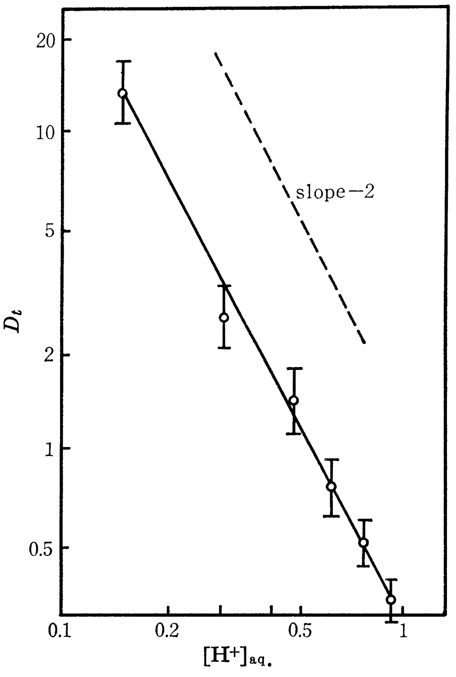

Fig. 2. The relation between the true distribution ratio obtained by the Fomin's method and the acidity.
$[(HA)_2]_{org.}=5\times10^{-3}$M, $\mu=1.5$

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[12] V. V. Fomin, E. P. Mairova, M. I. Krapivin, and V. G. Yudina, *Zh. Neorg. Khim.*, **3**, 2113 (1958).

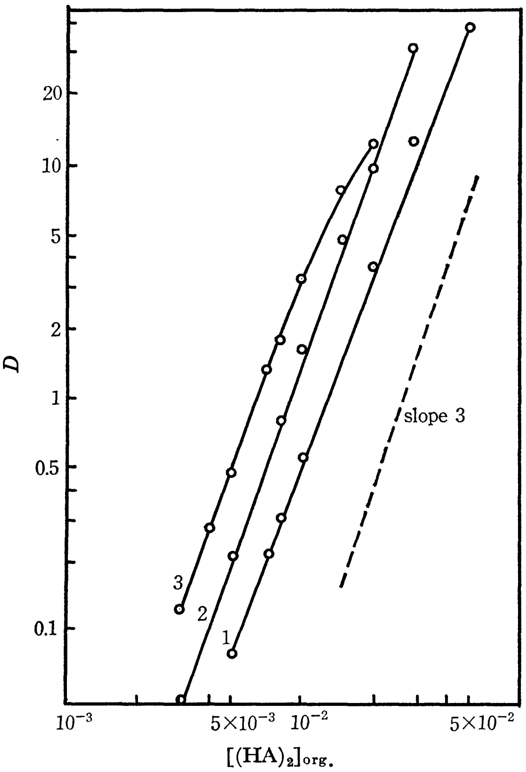

Fig. 3. The relation between the distribution ratio and the HDEHP concentration.
1, 2.32M $HClO_4$, 2, 1. 16M $HClO_4$, 3, 0. 58M $HClO_4$

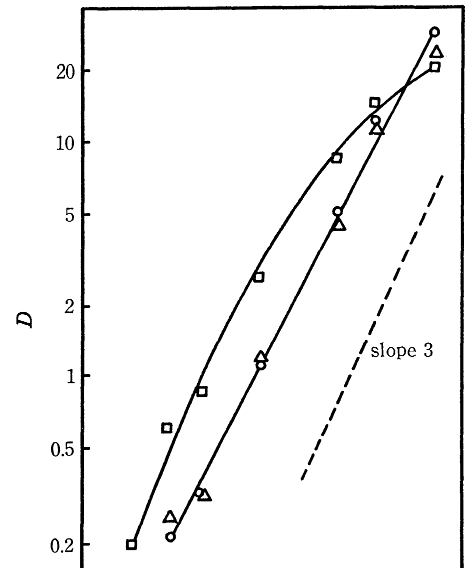

Fig. 4. The relation between the distribution ratio and the HDEHP concentration. The acidity of the aqueous phase was kept constant but the ionic strength was changed.
○ $\mu=1.3$, *i. e.* no lithium perchlorate in the aqueous phase
△ $\mu=2.5$, □ $\mu=4.8$

also investigated; the results are shown in Figs. 3 and 4. Figure 3 was obtained from the solution without lithium perchlorate, and Fig. 4 was obtained from the solution of a constant acidity, but at various ionic strengths. The dotted line indicates the slope of +3. It is clear from these figures that the log-log plot of D and the concentration of the dimeric HDEHP shows a linear relation, with a slope of about 3.

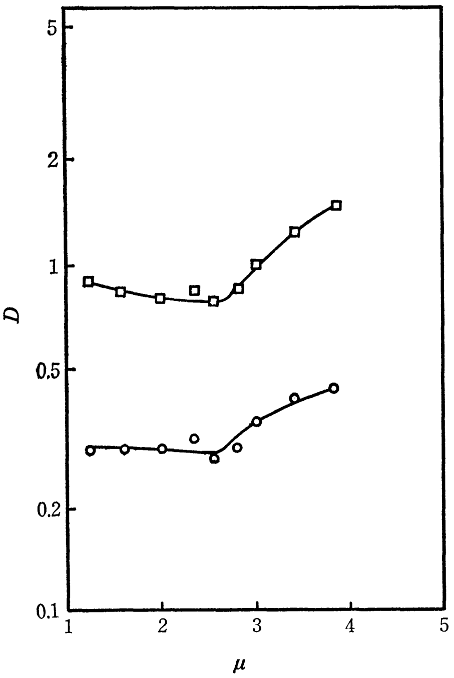

Fig. 5. The change of the distribution ratio by the change of the ionic strength of the aqueous phase.
○ org. phase, 5×10^{-3}M $(HA)_2$
□ org. phase, 7.5×10^{-3}M $(HA)_2$

The Relation between the Distribution Ratio and the Ionic Strength. The relation between the distribution ratio and the ionic strength is shown in Fig. 5. In this experiment the acidity was kept constant (1.3 M). When the ionic strength is not higher than 2.5, the distribution ratio does not vary when the ionic strength does. On the other hand, when the ionic strength is higher than 2.5, the distribution ratio increases with an increase in the ionic strength. This observation is consistent with the results shown in Fig. 4, where the values of the distribution ratio and its dependency on the HDEHP concentration are shown to be the same in the solutions having ionic strengths of both 1.5 and 2.5, but in the case of an ionic strength of 4.8 the values of the distribution ratio become larger and the linearity between the logarithm of the distribution ratio and the logarithm of the HDEHP concentration becomes poor.

Discussion

It is obvious from Figs. 1 through 4 that the distribution ratio is proportional to the cube of the HDEHP concentration and inversely proportional to the square of the acidity. If the species extractable into the organic phase are considered to have no charge, the general equation for the HDEHP extraction reaction can be written as:

$$\begin{aligned}&\mathrm{PaO}_m(\mathrm{OH})_{n\,\mathrm{aq.}}^{5-2m-n} + k(\mathrm{HA})_{2\,\mathrm{org.}}\\ &\quad = \mathrm{PaO}_p(\mathrm{OH})_q\mathrm{A}_{5-2p-q}(\mathrm{HA})_{2k+2p+q-5\,\mathrm{org.}}\\ &\quad + (5-2m-n)\mathrm{H}^+_{\mathrm{aq.}} + (m+n-p-q)\mathrm{H_2O}_{\mathrm{aq.}} \qquad (1)\end{aligned}$$

where HA, $(HA)_2$, and A^- represent the HDEHP molecule, the dimeric HDEHP, and the dissociated HDEHP anion respectively. The distribution ratio is defined by the following relation (if one omits the designation of the phase for the sake of simplicity):

$$D = \frac{\sum\limits_{p,q,k}[PaO_p(OH)_qA_{5-2p-q}(HA)_{2k+2p+q-5}]}{\sum\limits_{m,n}[PaO_m(OH)_n{}^{5-2m-n}]} \tag{2}$$

where brackets show the activity of the enclosed species. The equilibrium constant is defined by the following relation:

$$K_{m,n,p,q,k} = \frac{[PaO_p(OH)_qA_{5-2p-q}(HA)_{2k+2p+q-5}][H^+]^{5-2m-n}[H_2O]^{m+n-p-q}}{[PaO_m(OH)_n{}^{5-2m-n}][(HA)_2]^k} \tag{3}$$

By taking the partial derivative of the logarithm of the distribution ratio with respect to the logarithm of $[(HA)_2]$ and of $[H^+]$, we obtain:

$$\frac{\partial \ln D}{\partial \ln [(HA)_2]} = \sum_{p,q,k} kf_{p,q,k} \tag{4}$$

and

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

where $f_{p,q,k}$ is the fraction of the total activity of protactinium in the organic phase contributed by the $PaO_p(OH)_qA_{5-2p-q}(HA)_{2k+2p+q-5}$ species and where $f_{m,n}$ is that of the aquous phase contributed by the $PaO_m(OH)_n$ species.

If the activity coefficients of any species are assumed to be constant over the entire range of the conditions in a series of experiments, Eqs. (4) and (5) are valid when the activities are replaced by the concentrations. The conditions applied in this experiment can be considered to satisfy this assumption. Thus, according to the results of this experiment, $\partial \ln D/\partial \ln [(HA_2)]$ should be 3 and $\partial \ln D/\partial \ln [H^+]$, -2. Thus we obtain:

$$\sum_{p,q,k} kf_{p,q,k} = 3 \tag{6}$$

and

$$\sum_{m,n} (2m+n)f_{m,n} = 3 \tag{7}$$

If one excludes the fortuitous agreement between the slope obtained empirically and the values calculated from the left-hand sides of Eqs. (6) and (7) by considering the complex combination of many species, Eqs. (8) and (9) are obtained from Eqs. (6) and (7):

$$k = 3 \tag{8}$$

$$2m + n = 3 \tag{9}$$

Therefore, the species of protactinium in the perchloric acid solution are considered to be $PaO(OH)^{2+}$ or $Pa(OH)_3{}^{2+}$. The existence of such species as $Pa(OH)_4{}^+$, $PaO(OH)_2{}^+$ or $PaO_2{}^+$, which were observed by the TTA-extraction, is negligible.

We can make some assumptions which seem reasonable considering the nature of the strong Pa-O bond and the large acid-dissociation constant of HDEHP. The former tells us that p is equal to or larger than m, while the latter tells us that q is queal to or less than n, as long as the molecular form of HDEHP is present in the extracted species. Furthermore, the degree of hydrolysis can not proceed by the complex formation, *i.e.*, $p+q \leq m+n$.

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

$$\begin{aligned} &PaO(OH)^{2+}{}_{aq.} + 3(HA)_{2\,org.} \\ &\quad = PaO_p(OH)_qA_{5-2p-q}(HA)_{2p+q+1\,org.} + 2H^+{}_{aq.} \\ &\quad + (2-p-q)H_2O_{aq.} \end{aligned} \tag{10}$$

where $p=1$, $q=0$ or 1 and $p=2$, $q=0$, and:

$$\begin{aligned} &Pa(OH)_3{}^{2+}{}_{aq.} + 3(HA)_{2\,org.} \\ &\quad = PaO_p(OH)_qA_{5-2p-q}(HA)_{2p+q+1\,org.} + 2H^+{}_{aq.} \\ &\quad + (3-p-q)H_2O_{aq.} \end{aligned} \tag{11}$$

where $p=0$, $q=0$, 1, 2, or 3; $p=1$, $q=0$ or 1, and $p=2$, $q=0$.

In Fig. 1, the absolute value of the slope of log-log plot of D and the acidity is lower than 2 and the presence of the charge of $+1$ and $+2$ was expected when the ionic strength was 1.5. However, this is the effect of the existence of the inextractable species, as is quite clear from the results shown in Fig. 2. This conclusion seems at first sight to be contradictory to the results reported by Suzuki and Inoue,[1)] but it can at least qualitatively be explained by the following consideration. In the TTA-benzene extraction, the inextractable species were not observed [1,13)] but unadsorbable species were observed in the cation exchange study.[1)] Essentially, the reaction of the HDEHP-extraction reaction is considered to be a cation-exchange reaction; therefore, the existence of the inextractable species is not so surprising. Figure 2 shows the results obtained by the Fomin method, in which the contribution from the inextractable species can be omitted. This shows the prominent species, which is in rapid equilibrium with the extraction, to have a charge of $+2$. Thus, no contributions from such species as $PaO(OH_2)^+$, $Pa(OH)^+{}_4$, and $PaO_2{}^+$ were observed, though the existence of these species had been concluded in the TTA-extraction. Therefore, the inextractable species may be $PaO(OH)^+{}_2$, $Pa(OH)^+{}_4$, or $PaO^+{}_2$ if we do not take the presence of the polymer into account.

Thus far we have considered the monomeric species only, but it is natural also to consider the inextractable species to be some polymeric species whose charge per atom of Pa is lower than 1. Further study is necessary to make a correct choice out of two possibilities mentioned above. At any rate, the presence of the TTA anion will play an important role in the establishment of the equilibrium between the extractable and the inextractable species.

Another interesting fact is shown in Fig. 1. Although the extraction conditions of the curves 1 and 2 were identical except for the standing time, the values of the distribution ratio were not the same. This difference can be explained by the difference in the standing time; *i.e.*, the equilibrium in the aqueous phase has not yet been established in the curve 1 while it has nearly been

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13) R. T. Kolarich, V. A. Ryan, and R. P. Schuman, *J. Inorg, Nucl. Chem.*, **29**, 783 (1967).

established in the curve 2. On the other hand, when the ionic strength is 1.5, the difference in the distribution ratio is not observed between the curves 4 and 5, which were obtained under identical extaction conditions except for the standing time. These observations are consistent with the results of the preliminary experiment and show that the choice of the length of the standing time; *i.e.*, 1—4 days, is proper. However, their distribution ratios in the low acidity range are not identical with the extrapolated values of the curve 1 nor of the curve 2, although the HDEHP concentration is identical; *i.e.*, 5×10^{-3} M. Then the correction by the Fomin method was made, as is shown in Fig. 2, and the corrected distribution ratio was compared with the curves 1 and 2. Even by this procedure, the difference was still pronounced. In order to investigate this difference in more detail, the dependency of the distribution ratio on the perchloric acid concentration was examined by using a 5×10^{-3} M HDEHP-benzene solution. The results were compared with the results obtained by the use of the Fomin method (Fig. 2) and with the curve 2 in Fig. 1 (*cf.* Fig. 6).

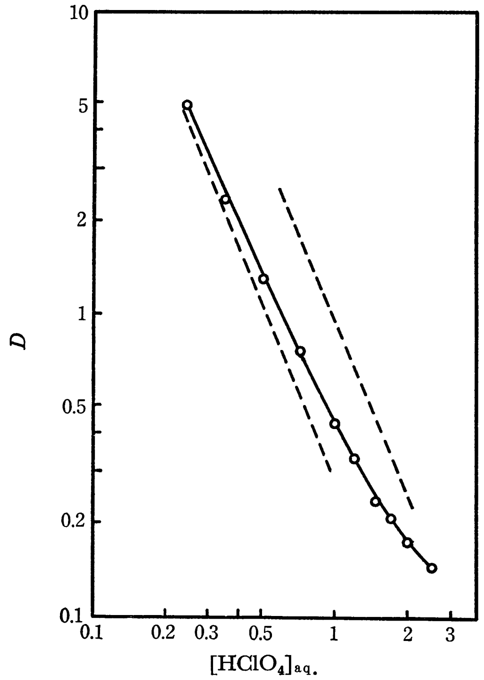

Fig. 6. The relation between the distribution ratio and the perchloric acid concentration. The upper dotted line indicates the curve 2 in Fig. 1 and the lower one, curve in Fig. 2.

In this figure the upper dotted line corresponds to the curve 2 of Fig. 1 and the lower one, to the curve shown in Fig. 2. The values of the distribution ratio obtained by extraction from the pure perchloric acid solution are distributed between the two dotted lines. The slope of the curve obtained by plotting the logarithm of the distribution ratio *vs.* the logarithm of the perchloric acid concentration asymptotically approaches −2 with a decrease in the acid concentration. This tendency is not so unusual in the adsorption on the cation-exchange resin. The most significant difference in the physical properties of the solution is the activity of water; in this case, the activity is higher when the ionic strength is 1.5. The transformation to the inextractable species and the adsorption on the glass vessel seem to occur upon the addition of lithium perchlorate to the perchloric acid solution of protactinium. However, as has been outlined above, their contribution to the distribution ratio is negligible when the acidity is 1.3 M or higher.

Therefore, the gradual approach of the slope to −2 seems to be explainable by the gradual increase in the activity of water. If there exists this equilibrium;

$$PaO(OH)^{2+} + H_2O = Pa(OH)_3{}^{2+} \qquad (12)$$

between the extractable species, the $Pa(OH)_3{}^{2+}$ must be more stable than $PaO(OH)^{2+}$ at lower acid concentrations or in media of lower ionic strengths, where the activity of water is lower. Thus, the dependency of the distribution ratio on the inoic strength can be explained by the change in $f_{1,1}$ and $f_{0,1}$ in Eq. (7). In order to confirm this assumption, it is necessary to investigate directly the dependency of the distribution ratio on the activity of water.

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