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Abstract

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THE STATE OF PROTACTINIUM IN NITRIC ACID SOLUTIONS

The process of breeding nuclear fuel in a power breeder reactor according to the scheme:

$$ {}_{90}\mathrm{Th}^{232}(n,\gamma)_{90}\mathrm{Th}^{233} \xrightarrow[\text{23.3 min.}]{\beta^-} {}_{91}\mathrm{Pa}^{233} \xrightarrow[\text{27.4 days}]{\beta^-} {}_{92}\mathrm{U}^{233} $$

is associated with the separation of protactinium from thorium, uranium, and fission products. Separation of these elements is often carried out in nitric acid media ($^{1-4}$). The effectiveness of separation methods is influenced by the state of protactinium in solution. In a number of studies an attempt has been made to evaluate qualitatively the state of trace amounts of protactinium (10^{12}—10^{13} mol/l) in nitric acid solutions ($^{5-8}$). There are no data in the literature on the stability of nitrate complexes of protactinium, apart from the stepwise formation constants $\mathrm{Pa(NO_3)_6}^{1-}$, $K = 0.141$, and $\mathrm{Pa(NO_3)_7}^{2-}$, $K = 1.09$ (^{9}).

To determine the state of protactinium in nitric acid solutions and to estimate the stability of the compounds formed, we studied the extraction of protactinium by solutions of tributyl phosphate in benzene.

The isotopes used in the work were: Pa^{233}, obtained from neutron-irradiated thorium nitrate, and Pa^{231}, isolated from uranium-production wastes (^{10}). Tributyl phosphate (TBP) was subjected to soda purification followed by vacuum distillation.

A study of the kinetics of the extraction of protactinium by tributyl phosphate, carried out on two types of protactinium-233 solutions—the first freshly prepared and the second "old," stored for 4 months—showed that in freshly prepared solutions 1—12 *M* in nitric acid, equilibrium is established in less than 1 hour, whereas in the "old" solutions it is not reached even within 100 hours. The continuous increase of the distribution coefficients with time may be due to two causes: 1) the presence in the nitric acid solution of both extractable and nonextractable by tributyl phosphate forms of protactinium, between which

Figure 1

Figure 1: Figure 1

equilibrium is established slowly; 2) decomposition of TBP during prolonged contact with nitric acid, leading to the formation of acidic butyl phosphates—powerful extractants of protactinium (^{11}).

To exclude the latter supposition, experiments were set up on the extraction of protactinium by tributyl phosphate that had been preliminarily contacted with nitric acid. It turned out that even prolonged stirring (up to 100 hours) of the extractant with the acid does not lead to a noticeable increase in the extraction ability of tributyl phosphate. Consequently, in the case of "old" solutions, the gradual increase of the distribution coefficient with time is caused by the slow establishment of equilibrium between extractable and nonextractable forms of protactinium, and not by the decomposition of tributyl phosphate. The slow attainment of equilibrium indicates the polymeric or colloidal character of the nonextractable forms.

In order to determine the region of existence of monomeric forms of protactinium, the dependence of the distribution coefficient on the concentration of the element was studied. The experiments were carried out with freshly prepared solutions of Pa^{233} and Pa^{231}. The values of the distribution coefficients were calculated from re-extraction data. With 2-hour contact of the phases, the distribution coefficient retains a constant value in the concentration range of protactinium from 10^{-12} to 10^{-7} M for 1 M nitric acid, and up to 10^{-5} M in the case of 3 M nitric acid. In the light of the ideas developed in (^{12}), this indicates the absence, under these conditions, of processes leading to poly-

polymerization of protactinium both in the aqueous and in the organic phases. However, relatively concentrated solutions containing only monomeric forms of protactinium can exist only for a short time. Figure 1 gives data on the kinetics of the process of forward and back extraction of a $10^{-5}M$ solution of protactinium in $3M$ acid, stored after preparation for more than a day.

Fig. 1. Dependence of the distribution coefficient on the phase-contact time during extraction of a $10^{-5}M$ solution of Pa^{231} in $3M$ HNO_3 with a 25% solution of TBP.
1 —forward extraction, 2 —back extraction

In forward extraction no appreciable increase in the distribution coefficient is observed with an increase in the phase-contact time up to 20 h, which still does not indicate the absence in the solution of nonextractable polymeric forms. The distribution coefficient for back extraction exceeds the distribution coefficient for forward extraction and, after prolonged contact of the phases (more than 8 h), begins to decrease, approaching the value obtained for forward extraction. This is probably associated with the polymerization process of the monomeric forms of protactinium present in the aqueous phase at the initial moment of

Figure 2

Figure 2: Figure 2

re-extraction, leading to the formation of nonextractable forms of the element.

The calculation of the percentage content of nonextractable forms by the methods of Fomin (^{13}) and Martin (^{8}) was carried out for a $10^{-10}M$ solution of protactinium in $7.6M$ HNO_3, stored for about four months. Both methods gave coincident results (44 and 42%). In a freshly prepared solution, the content of protactinium in the nonextractable form, calculated by Fomin's method, proved to be $\sim 3\%$.

The nature of these forms was not specially investigated; however, it may be assumed that in ultradilute solutions (10^{-12}—$10^{-10}M$) the nonextractable forms are pseudocolloids, while in the case of sufficiently concentrated solutions ($10^{-5}M$) the formation of true colloids is not excluded. Since the processes leading to the appearance of nonextractable forms are poorly reproducible and difficult to control, in studying the complex formation of protactinium in nitric-acid media we used distribution coefficients obtained from re-extraction data.

Fig. 2. Dependence of the distribution coefficient on the concentration of hydrogen ions

The dependence of the distribution coefficient on the concentration of TBP, hydrogen ions, and nitrate ions was determined at a constant ionic strength of the aqueous phase equal to 5. The initial and equilibrium concentrations of the components of the system were calculated taking into account their interaction, leading to the formation in the organic phase of the complexes $HNO_3 \cdot TBP$, $(HNO_3)_2 \cdot TBP$, with equilibrium constants $2.2 \cdot 10^{-1}$ and $2 \cdot 10^{-3}$ (^{14,15}), and the complex $HClO_4 \cdot TBP$ with equilibrium constant $6.0 \cdot 10^{-2}$, calculated from the data of work (^{16}). In the calculations we also took into account the change in phase volumes (ΔV), which was found experimentally in preliminary experiments. The correctness of the calculations was checked by titrating the aqueous phase with $0.1M$ alkali solution.

The value of the tangent of the angle of inclination of the straight line expressing the dependence $\lg K_p = f(\lg[\mathrm{TBP}]_{\mathrm{free}})$ proved close to 2, which indicates the formation by protactinium of a disolvate with TBP. The dependence $\lg K_p = f(\lg[\mathrm{H}^+])$

is close to quadratic in the region of hydrogen-ion concentrations 3-6 M (Fig. 2). As the acidity of the solution decreases, a change in this dependence is observed in the direction of a decrease in the tangent of the angle of inclination, which indicates an increase in the degree of hydrolysis of protactinium or a change in the extraction mechanism. The dependence $\lg K_p = f(\lg[\mathrm{NO}_3^-])$ is presented in Table 1.

On the basis of the data given, several equations for the extraction reaction may be proposed, each of which formally satisfies the experimental results to an equal degree:

$$\mathrm{Pa(OH)_4^+ + 2H^+ + 3NO_3^- + 2TBF \rightleftarrows Pa(OH)_2(NO_3)_3 \cdot 2TBF + 2H_2O} \qquad \text{(A)}$$

$$\mathrm{Pa(OH)_3^{2+} + 2H^+ + 4NO_3^- + 2TBF \rightleftarrows Pa(OH)(NO_3)_4 \cdot 2TBF + 2H_2O} \qquad \text{(B)}$$

$$\mathrm{Pa(OH)_2^{3+} + 2H^+ + 5NO_3^- + 2TBF \rightleftarrows Pa(NO_3)_5 \cdot 2TBF + 2H_2O} \qquad \text{(V)}$$

$$\mathrm{Pa^{5+} + 2H^+ + 7NO_3^- + 2TBF \rightleftarrows H_2Pa(NO_3)_7 \cdot 2TBF + 2H_2O} \qquad \text{(G)}$$

Table 1

Dependence of the distribution coefficient on the concentration of NO_3^- ions

HNO_3, M	$HClO_4$, M	TBF, M	H^+ (from analysis), M	ΔV*	Initial HNO_3, M	Initial $HClO_4$, M	Initial TBF, M	K_p
5.0	0.0	0.3	5.15	0.40	6.56	0.00	2.20	12.6 ± 0.6
4.5	0.5	0.3	5.02	0.37	5.91	0.51	2.04	12.1 ± 0.7
4.0	1.0	0.3	5.04	0.32	5.26	1.03	1.88	12.8 ± 1.2
3.5	1.5	0.3	4.90	0.31	4.59	1.55	1.73	11.7 ± 0.6
3.0	2.0	0.3	4.90	0.30	3.93	2.07	1.59	9.91 ± 0.16
2.5	2.5	0.3	4.97	0.26	3.22	2.61	1.44	10.0 ± 1.1
2.0	3.0	0.3	4.92	0.22	2.63	3.15	1.30	9.21 ± 0.42
1.5	3.5	0.3	4.80	0.21	1.97	3.63	1.16	8.28 ± 0.90

HNO_3, M	$HClO_4$, M	TBF, M	H^+ (from analysis), M	ΔV*	Initial HNO_3, M	Initial $HClO_4$, M	Initial TBF, M	K_p
1.0	4.0	0.3	4.85	0.20	1.31	4.31	1.03	7.45 ± 0.61
0.75	4.25	0.3	4.85	0.18	0.98	4.49	0.99	7.14 ± 0.46
0.5	4.5	0.3	4.90	0.17	0.66	4.77	0.90	4.34 ± 0.30
0.4	4.6	0.3	4.92	0.16	0.53	4.88	0.87	4.58 ± 0.26
0.0	5.0	0.3	4.93	0.15	0.00	5.31	0.77	0.41 ± 0.01

* Initial phase volumes, 5 ml each.

The most probable extraction, in our opinion, is that according to mechanism (V), since in this case the unhydrolyzed complex $Pa(NO_3)_5 \cdot 2TBF$ is extracted into the organic phase, similarly to the complexes of zirconium, thorium, uranium, and others. Extraction of hydrolyzed complexes by such an extractant as TBF is less probable. Extraction of protactinium according to mechanism (G) is not excluded, but it presupposes the participation of the unhydrolyzed ion Pa^{5+}, the existence of which in aqueous solutions is open to doubt ([17,18]).

Fig. 3. Dependence of the function $\bar{n}/[NO_3^-]$ on $[NO_3^-]$. *a*—experimental values; *b*—values found from equation (5).

Proceeding from the extraction mechanism according to equation (V), the stability constants of the nitrate complexes of Pa were calculated ([13]).

The equilibrium constant of reaction (V), expressed through concentrations,

$$K = \frac{[Pa(NO_3)_5 \cdot 2TBF]}{[Pa(OH)_2^{3+}]\,[H^+]^2\,[NO_3^-]^5\,[TBF]^2}, \qquad (1)$$

and the distribution coefficient are related by the ratio:

$$K_p = \frac{c_0}{c_b} = \frac{[Pa(NO_3)_5 \cdot 2TBF]}{c_b} =$$

Fig. 4. Ratio between individual forms of protactinium in the system HNO_3–$HClO_4$ at μ=5. 1–$Pa(OH)_3{}^{3+}$, 2–$Pa(OH)_2(NO_3)^{2+}$, 3–$Pa(OH)_2(NO_3)_2{}^{1+}$, 4–$Pa(OH)_2(NO_3)_3{}^{0}$, 5–$Pa(OH)_2(NO_3)_4{}^{1-}$

Figure 3: Fig. 4. Ratio between individual forms of protactinium in the system HNO_3–$HClO_4$ at μ=5. 1–$Pa(OH)_3{}^{3+}$, 2–$Pa(OH)_2(NO_3)^{2+}$, 3–$Pa(OH)_2(NO_3)_2{}^{1+}$, 4–$Pa(OH)_2(NO_3)_3{}^{0}$, 5–$Pa(OH)_2(NO_3)_4{}^{1-}$

$$= K[\mathrm{H}^+][\mathrm{NO}_3^-]^5[\mathrm{TBF}]^2\frac{[\mathrm{Pa(OH)}_2^{3+}]}{c_b}. \tag{2}$$

The total concentration of protactinium in the aqueous phase is equal to

$$c_b = [\mathrm{Pa(OH)}_2^{3+}]\left(1+\beta_j[\mathrm{NO}_3^-]^j\right), \tag{3}$$

where β_j is the stability constant of the corresponding complex ion

$$\beta_i = \frac{[\mathrm{Pa(OH)}_2(\mathrm{NO}_3)_j^{5-2-j}]}{[\mathrm{Pa(OH)}_2^{3+}]\,[\mathrm{NO}_3^-]^j}. \tag{4}$$

The stability constants of the nitrate complexes of protactinium, written according to equation (4) and calculated for solutions with ionic strength 5, proved to be equal to $\beta_1 = 17$, $\beta_2 = 127$, $\beta_3 = 540$, $\beta_4 = 1380$. The calculation of the stability constants was checked by substituting the obtained values β_1–β_4 into the expression known as the Bjerrum formation function:

$$\bar{n} = \frac{\Sigma j\beta_j[\mathrm{NO}_3^-]^j}{1+\Sigma\beta_j[\mathrm{NO}_3^-]^j}. \tag{5}$$

Fig. 4. Ratio between individual forms of protactinium in the system HNO_3–$HClO_4$ at $\mu = 5$.
1–$Pa(OH)_3^{3+}$, 2–$Pa(OH)_2(NO_3)^{2+}$, 3–$Pa(OH)_2(NO_3)_2^{1+}$, 4–$Pa(OH)_2(NO_3)_3^{0}$, 5 –$Pa(OH)_2(NO_3)_4^{1-}$

Figure 3 presents the dependence of the function $\bar{n}/[\mathrm{NO}_3^-]$ on the concentration of the complex-forming agent. It is seen from the figure that the values of this function, found on the basis of a graphical analysis of the experimental data on the dependence of the distribution coefficient on the concentration of nitrate ions, and the values calculated by equation (5) using the constants β_1–β_4, agree satisfactorily. Evidently, the concentration of the complex $Pa(OH)_2(NO_3)_5^{2-}$, if it is formed, is small.

Using the obtained values of the stability constants of the nitrate complexes of protactinium, the quantitative ratio between the individual complexes in the system HNO_3–$HClO_4$ at an ionic strength of the solution equal to 5 was calculated. It is seen from Fig. 4 that the dominant form of protactinium at $[NO_3^-] > 1\ M$ is the anion $Pa(OH)_2(NO_3)_4^{1-}$.

It is interesting to note that the predominant form of niobium in 2–6 M HCl solutions is the anion $Nb(OH)_2Cl_4^-$, the existence of which was established by the spectrophotometric method ([19]). The formation by protactinium and niobium of complexes of analogous composition once again testifies to the closeness of the chemical properties of these elements in aqueous solutions.

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Note: Figure translations are in progress. See original paper for figures.