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Studies of the Behavior of Trivalent Uranium in an Aqueous Solution. II. Absorption Spectra and Ion Exchange Behavior in Various Acid Solutions

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The absorption spectra of trivalent uranium in hydrochloric, sulfuric and perchloric acid solutions were investigated. It was found that there is a possibility of the formation of a chloro-complex from the fact that a large change in absorption spectra was observed at high concentrations of chloride ion. On the basis of the above facts, the behavior of trivalent uranium in those media toward ion exchange resin was studied. It was considered that an anionic complex of trivalent uranium begins to form at concentrations of hydrochloric acid above 7 N, which shows good agreement with results obtained on trivalent ions of plutonium, americium and curium, which are similar actinide elements. However, it was not possible to confirm the existence of a soluble carbonate complex of trivalent uranium, as in the case of trivalent plutonium or americium.

In 1927, Someya(1) first obtained trivalent uranium ion in a hydrochloric acid solution by treating hexavalent uranium with liquid zinc amalgam. Since then, few papers have been reported on its chemical behavior in aqueous solution except for absorption spectra in hydrochloric and perchloric acid solutions(2,3) That is, it was thought that studies on the aqueous chemistry of trivalent uranium would be difficult because trivalent uranium is very unstable and oxidizes rapidly in aqueous solution. One of the authors(4) studied the reduction of hexavalent uranium to the trivalent state and found that reduction with liquid zinc amalgam in hydrochloric, sulfuric and perchloric acid solutions is simple in operation, and gives a high yield within a short period of time and with good reproducibility; almost complete reduction is possible, particularly in 0.5 N hydrochloric acid solution. Next, the stability of trivalent uranium in these acidic solutions was investigated; it was found that trivalent uranium is fairly stable in all hydrochloric, sulfuric and perchloric acid solutions at low acid concentrations in the absence of atmospheric oxygen, but that it becomes unstable as the acid concentration increases. These observations are contrary to the previously-accepted view.(5-10) On the basis of

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1) K. Someya, *Z. Anorg. Allgem. Chem.*, **161**, 46 (1927).

2) C. K. Jörgensen, *Acta Chem. Scand.*, **10**, 1503 (1956).

3) D. C. Stewart, ANL-4812 (1952).

4) A. Satô, This Bulletin, **40**, 2107 (1967).

5) R. J. Meyer and E. Pietsch, "Gmelins Handbuch der Anorganischen Chemie," 8th Edition, System No. 55, Verlag Chemie, G.m.b.H., Berlin (1936).

6) J. J. Katz and E. Rabinowitz, "The Chemistry of Uranium," National Nuclear Energy Series, Division VIII, Volume 5, McGraw-Hill Book Co., Inc., New York (1951).

7) G. T. Seaborg, "The Actinide Series" in "Comprehensive Inorganic Chemistry," Vol. 1, ed. by M. C. Sneed, J. L. Maynard and R. C. Brasted, D. Van Nostrand Company, Inc., New York (1953), Chap. 3, p. 161.

8) H. R. Hoekstra and J. J. Katz, "The Chemistry of Uranium" in "The Actinide Elements," National Nuclear Energy Series, Division IV, Vol. 14A, ed. by G. T. Seaborg and J. J. Katz, McGraw-Hill Book Co., Inc., New York (1957), Chap. 6, p. 130.

9) J. J. Katz and G. T. Seaborg, "The Chemistry of the Actinide Elments," John Wiley & Sons, Inc., New York (1957), Chap. 5, p. 94.

the above facts, the authors plan to conduct a detailed study of the aqueous chemistry of trivalent uranium.

In this paper, the absorption spectra and ion exchange behavior of trivalent uranium in hydrochloric, sulfuric and perchloric acid solutions were investigated, and the possibility of the existence of a chloro-complex of trivalent uranium in aqueous solutions was discussed through a comparison with results obtained on trivalent ions of plutonium, americium and curium, which are similar actinide elements.

Experimental

Reagents. *Uranium-237 and Various Acid Solutions of Hexavalent Uranium.* The uranium-237 isotope used as a tracer was prepared by the method reported by Ishimori *et al.*[11] Natural uranium dioxide was irradiated for about 2 hr with 20 MeV bremsstrahlung from the linear electron accelerator of the Japan Atomic Energy Research Institute. After irradiation, uranium, containing uranium-237 isotope produced by (γ·n) reaction, was separated from the fission products by the TBP-toluene extraction method from a nitric acid solution. The organic substance in the nitric acid solution of the purified uranium was decomposed completely by repeated heating to dryness with nitric acid. The radioactive decay curve of uranium-237 in the purified uranium obtained indicated half lives of 6.5 days for γ-activity and 6.7 days for β-activity, which agreed very well with priviously reported values.[11–15] Energy measurements on the γ-rays of uranium-237 were also carried out, and sharp peaks were found at energies of 59, 163, 210, 265 and 325 keV, which were assigned to γ-rays emitted by uranium-237 in reasonable agreement with the established decay scheme.[12,13] From these observations, uranium-237 thus prepared was thought adequate for use as a tracer. The uranyl nitrate solution thus obtained was heated almost to dryness several times with hydrochloric, sulfuric or perchloric acid in order to convert the salt into each form completely. The residue was then dissolved in an appropriate quantity of hydrochloric, sulfuric or perchloric acid solution in order to prepare acid solutions of various concentrations. The concentration of uranium was determined by first reducing the hexavalent uranium to the tetravalent state in the air with liquid zinc amalgam, then by titrating the tetravalent uranium with a standard solution of 0.01 N potassium dichromate, using sodium diphenylamine sulfonate as an indicator.[16]

Ion Exchange Resins. Dowex-50X8 (100—200 mesh) and Dowex-1X4 (50—100 mesh) were used for the cation and anion exchange experiments, respectively. Before use, they were conditioned sufficiently in the usual manner, converted to the desired forms (Dowex-50 to the hydrogen form; Dowex-1 to the chloride, sulfate or perchlorate form), washed with distilled water and then dried in air.

The liquid zinc amalgam was prepared by a method reported previously.[4] All other chemicals used were of the highest-purity grade.

Apparatus. For the reduction of hexavalent uranium to the trivalent state with liquid zinc amalgam, the reduction apparatus was that described in a foregoing report.[4] A Hitachi EPS-3 recording spectrophotometer and a 1 cm quartz cell with a glass stopper were used in measuring the absorption spectrum. The γ-radioactivity was measured with a Kobe-Kogyo well-type scintillation counter and a $1\frac{3}{4}''$ ida. $\times 2''$ NaI(Tl) well-type detector coupled to a Kobe-Kogyo 100 channel pulse-height analyzer, Model AN-100.

Procedures. A plastic globe-box was used throughout and all experiments were carried out in an argon, nitrogen or carbon dioxide atmosphere in order to prevent the oxidation of trivalent uranium at room temperature, which was 20—25°C.

Trivalent Uranium Solution. An acid solution of hexavalent uranium was reduced to the trivalent state by the liquid-zinc-amalgam method described in a previous paper.[4]

Absorption Spectrum. After reduction of the hexavalent uranium to the trivalent state, the uranium solution was put into the spectrophotometer cell and stopperd in an inert gas atmosphere. The absorption spectrum of 400—1400 mμ was immediately measured with reference to an acid solution of the same concentration as the sample.

Ion Exchange. The apparent distribution coeffcient was determined by equilibrating 500 mg of air-dried ion exchange resin with 25 m*l* of a 10^{-5} M trivalent uranium solution under the desired conditions with shaking. An aliquot of the supernatant liquid was taken for the measurement of γ-radioactivity. The radioactivity in the resin after equilibration was estimated from the difference between the total activity and the final activity present in the solutions.

The apparent distribution coefficient was calculated by means of the usual relationship.

$$K_{d'}=\frac{\left(\dfrac{\text{Radioactivity of U}^{3+}\text{ in resin}}{\text{Amount of resin (g)}}\right)}{\left(\dfrac{\text{Radioactivity of U}^{3+}\text{ in solution}}{\text{Volume of solution (m}l\text{)}}\right)}$$

However, the reduction of the hexavalent uranium to the trivalent state does not proceed completely, depending on the acid and its concentration, as described in a previous paper,[4] and although slowly, the trivalent uranium in the solution which has once been reduced is oxidized to the tetravalent state. Therefore, tetravalent uranium is also contained in the sample solution. Consequently, it is necessary to correct for this. The results, given in Tables 1 and 3 mentioned later, indicate that the apparent distribution coefficient

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10) J. E. Grindler, "The Radiochemistry of Uranium," NAS-NS 3050, U. S. Atomic Energy Commission (1962).

11) E. Akatsu, T. Kuroyanagi and T. Ishimori, *Radiochimica Acta,* **2**, 1 (1963).

12) I. F. Wagner, Jr., M. S. Freedman, D. W. Engekemeir and J. R. Huizenga, *Phys. Rev.*, **89**, 502 (1953).

13) J. O. Rasmussen, F. L. Canavan and J. M. Hollander, *ibid.*, **107**, 141 (1957).

14) A. C. Wahl and G. T. Seaborg, *ibid.*, **73**, 940 (1948).

15) Y. Nishina, T. Yasaki, H. Ezoe, K. Kimura and M. Ikawa, *ibid.*, **57**, 1182 (1940).

16) T. Nakazono, *Nippon Kagaku Kwaishi (J. Chem. Soc. Japan)*, **42**, 761 (1921).

is almost constant, even when the time of standing or the amount of resin present is varied. Therefore, it is thought that cation or anion exchange resin has no effect on the re-oxidation rate of trivalent uranium in our experiments. On the other hand, it was found from our latest study to be published in the near future, that tetravalent uranium is completely extracted with 0.1 M DBP (di-*n*-buthyl phosphate)-benzene solution from a hydrochloric acid solution in an acid concentration range above 0.35 N. However, trivalent uranium can not be extracted at all under the same condition as above. Therefore, the re-oxidation rate of trivalent uranium in hydrochloric acid solutions at acid concentrations above 0.35 N can be determined by the DBP-benzene extraction method. It was also found that the concentration of uranium in the range of 10^{-3}—10^{-5} M has no effect on the re-oxidation rate of trivalent uranium as long as all atmospheric oxygen is excluded.

On the basis of the above facts, it is thought that the percentage of reduction of hexavalent uranium to the trivalent state and the quantity of trivalent uranium present after a fixed time can be calculated by knowing the kind of acid used and its concentration in the sample solution and using the results reported in the previous paper.[4] Corrections to the radioactivity in the solution can be made on the basis of these values. Namely, the radioactivity corrected through calculating the quantity of tetravalent uranium actually present in solution is the radioactivity of trivalent uranium actually present in the solution. Next, the radioactivity of trivalent uranium adsorbed in the resin should also be corrected by obtaining the apparent distribution coefficient of tetravalent uranium under the same conditions and by calculating the cocentration of tetravalent uranium in the solution by the same method as above. That is, the radioactivity corresponding to tetravalent uranium adsorbed in the resin is deducted from the apparent radioactivity of trivalent uranium adsorbed in the resin. The value thus obtained is taken as the actual radioactivity of trivalent uranium adsorbed in the resin.

Results

The Absorption Spectra of Trivalent Uranium. The absorption spectra of trivalent uranium obtained in perchloric and sulfuric acid solutions at 400—1400 mμ are shown in Fig. 1. Even when the concentration of perchloric acid is changed in the range 0.01—6 N and the concentration of sulfuric acid in the range of 0.01—10 N, there is no change in both absorption spectra and they remain completely the same. The absorption spectra are about the same as those reported by Jörgensen[2] and Stewart[3], as the positions of the main peaks are at 455, 526, 619, 639, 740, 890, 910, 980, 1075 and 1230 mμ. The 4 peaks at 526, 890, 910 and 1230 mμ are particularly characteristic, as they are strong, and when the relation between their heights and the concentration of trivalent uranium was obtained, it was found that Beer's law is obeyed. The molar extinction coefficients, E_m, at 526, 890, 910 and 1230 mμ under the above conditions were 171, 222, 226 and 175, respectively. For reference, the absorption spectra of tetravalent uranium under the same conditions are also shown in Fig. 1. Since trivalent uranium becomes unstable as the acid concentration of perchloric or sulfuric acid increases, the experiment was not carried out with higher acid concentrations than those mentioned above.

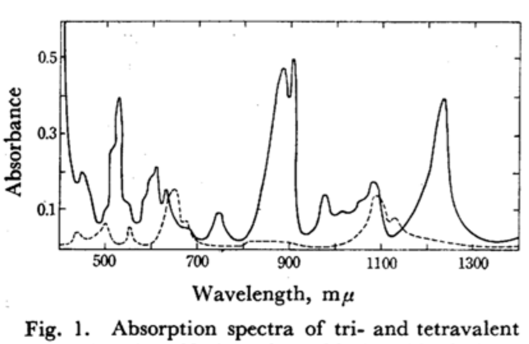

Fig. 1. Absorption spectra of tri- and tetravalent uranium in sulfuric and perchloric acid solutions.
——: U^{3+} - - -: U^{4+}
Concentration of U: 2×10^{-3} M

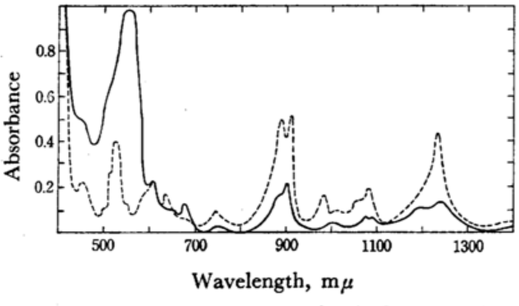

Fig. 2. Absorption spectra of trivalent uranium in hydrochloric acid solution.
——: 12 N - - -: below 6 N
Concentration of U: 2×10^{-3} M

In a hydrochloric acid solution, the absorption spectra of trivalent uranium, when the concentration is in the range 0.001—6 N, are nearly the same as those in sulfuric acid and perchloric acid solutions, as shown in Fig. 2. However, the positions of peaks at 740, 890 and 980 mμ have shifted 5 mμ to 745, 895 and 985 mμ, respectively. Furthermore, these spectra show marked changes as the hydrochloric acid concentration increases; the peak at 526 mμ shows a sudden increase in height as the acid concentration increases and at the same time, becomes broad and is shifted to 532 mμ at 11 N, and to 548 mμ at 12 N, *i. e.*, to longer wavelengths. On the other hand, the peak at 619 mμ is shifted to 618 mμ at 11 N and to 615 mμ at 12 N, to shorter wavelengths. The peak at 639 mμ does not change up to 11 N hydrochloric acid, but shows a large shift up to 654 mμ at 12 N. In order to study this phenomenon, the hydrochloric acid concentration was maintained below

6 N and the chloride ion concentration increased gradually by adding chloride salts such as lithium chloride, by which a marked change was observed in the absorption spectra similar to that indicated above. It is inferred from the above fact that trivalent uranium forms a chloro-complex in solutions of very high chloride ion concentration. Furthermore, the rate of decrease of the absorption peak at 526 mμ was obtained as a fuction of time and the stability of trivalent uranium in the various acidic solutions was also obtained, by which similar results to those reported in the previous paper4) were obtained.

Finally, in order to study the formation of a soluble carbonate complex of trivalent uranium, an experiment was carried out by adding potassium or ammonium carbonate to a trivalent uranium solution to a concentration of several % or several tens of %, and also by changing the pH. However, a dark violet, insoluble precipitate was formed under all conditions and it was not possible to confirm the presence of a soluble carbonate complex even from the absorption spectra of the supernatant liquid.

The Ion Exchange Behavior of Trivalent Uranium. *Rate of Exchange.* To evaluate the time of standing necessary for batch experiments, the rate of exchange was investigated by almost the same method as in the K_d determination. The experimental accuracy becomes poor with increase in the time of standing, because the reoxidation of trivalent uranium occurs gradually, even in the absence of atmospheric oxygen; this must be avoided as much as possible. Therefore, the change in the apparent distribution coefficient was measured for anion exchange resin in a concentrated hydrochloric acid solution which is assumed to be adsorbed most. As shown in Table 1, it was found that equilibrium is reached after approximately 45 min. An almost similar result was obtained in the experiment using cation exchange resin. From the above investigation, a standing period of 1 hr is recommended for this batch equilibrium experiment.

TABLE 1. RATE OF EXCHANGE

Time, min	Distribution coefficint*	
	Dowex-1**	Dowex-50***
10	3.0	270
20	4.5	380
30	5.9	400
45	6.6	460
60	6.8	490
90	6.7	480
120	6.9	480
180	6.8	500
300	6.4	500

* Each of the value is the mean of five experiments.
** U, 1.05×10^{-5} M; HCl, 12 N
*** U, 1.30×10^{-5} M; HCl, 0.1 N

Amount of Resin. As the trivalent uranium prepared by reduction with liquid zinc amalgam, a considerable quantity of zinc dissolves, particularly in the case of hydrochloric acid solution. As Table 2 shows, the zinc concentration in the solution after reduction is 1×10^{-2} M in a 0.5 N hydrochloric acid solution and 9×10^{-1} M in a 12 N hydrochloric acid solution. It has been known that zinc ion is adsorbed on an anion exchange resin in a hydrochloric acid solution.17) Therefore, in order to find out whether it affects the apparent distribution coefficient of trivalent uranium or not, an experiment was carried out to investigate whether the apparent distribution coefficient changes with the quantity of resin using anion exchange resin in a similar manner to that mentioned above. As seen from Table 3, the apparent distribution coefficient is almost constant in the range 0.1—5 g of resin, and there is no effect due to the liquid zinc amalgam used in the reduction. A similar experiment was carried out using cation

TABLE 2. CONCENTRATION OF ZINC IN HYDROCHLORIC ACID SOLUTION AFTER THE REDUCTION WITH LIQUID ZINC AMALGAM

Concn. of acid N	Concn. of zinc* M
0.5	1.1×10^{-2}
2.0	1.2×10^{-2}
6.0	3.7×10^{-2}
10.0	2.1×10^{-1}
12.0	8.6×10^{-1}

* Each of the value is the mean of three experiments.

TABLE 3. EFFECT OF AMOUNT OF RESIN ON THE DISTRIBUTION COEFFICIENT OF TRIVALENT URANIUM

Amount of resin g	Distribution coefficient*	
	Dowex-1**	Dowex-50***
0.10	6.6	490
0.25	6.1	460
0.50	6.8	480
1.00	6.4	490
2.00	6.5	500
3.00	6.5	470
5.00	6.7	500

* Each of the value is the mean of five experiments.
** U, 1.05×10^{-5} M; HCl, 12 N
*** U, 1.05×10^{-5} M; HCl, 0.1 N

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17) K. A. Kraus and F. Nelson, P/837, Proc. Intern. Conf. Peaceful Uses Atomic Energy, Geneva, 1955, **7**, 113 (1956).

exchange resin and it was found that, as in the case of the anion exchange resin, there is no effect. From the above results, 0.5 g of the resin is recommended for use in this experiment.

Apparent Distribution Coefficient. The apparent distribution coefficient of trivalent uranium was determined for cation and anion exchange resins at various concentrations of hydrochloric, sulfuric and perchloric acids, using 0.5 g of the resin and 1 hr of standing. However, experiments above 6 N in the case of sulfuric acid solution and above 2 N in the case of perchloric acid solution were not carried out, because trivalent uranium becomes unstable as the acid concentration increases. The apparent distribution coefficient of tetravalent uranium under exactly the same conditions is also determined for reference.

TABLE 4. DISTRIBUTION COEFFICIENT OF TRI- AND TETRAVALENT URANIUM IN HYDROCHLORIC ACID SOLUTION

Concn. of HCl N	Distribution coefficient*			
	Dowex-1		Dowex-50	
	U^{3+}	U^{4+}	U^{3+}	U^{4+}
0.01	0	0	510	3650
0.05	0	0	490	2120
0.1	0	0	480	1680
0.5	0	0	380	155
1	0	0	320	75
2	0	2.5	270	56
4	0	17	33	19
6	0	19	12	6.6
7	1.5	21	9.5	5.7
8	2.9	23	5.9	4.6
9	4.6	25	4.2	4.0
10	5.0	24	3.7	3.4
11	6.0	21	4.0	3.5
12	6.7	25	4.1	3.9

* Each of the value is the mean of six experiments.

As is clear from Table 4, in a hydrochloric acid solution trivalent uranium is adsorbed on the cation exchange resin to a considerable extent, and the apparent distribution coefficient increases with decrease in the concentration of hydrochloric acid, reaching a maximum at about 0.1 N; in the range 0.1 N to 0.01 N, the apparent distribution coefficient shows an approximately constant value of 500. In the case of tetravalent uranium, the apparent distribution coefficient increases with decrease in the concentration of hydrochloric acid, similar to trivalent uranium. However, the value is larger by nearly one order of magnitude than in the case of trivalent uranium, especially in the low acidity range. Also, the apparent distribution coefficient for the anion exchange resin is low for both trivalent and tetravalent uranium in low concentrations of hydrochloric acid, but increases gradually with increase in the concentration of hydrochloric acid. At any rate, their values are small and that for trivalent uranium is smallest.

In the case of sulfuric and perchloric acid solutions, as shown in Tables 5 and 6, trivalent uranium is not entirely adsorbed on the anion exchange resin in the range of acid concentration of the experiment. In contrast to this, a larger value than that for tetravalent uranium was obtained in the case of cation exchange resin. A very large value of the apparent distribution coefficient was indicated, particularly in a low acid solution, as it became about 7000 even at 0.1 N and is almost completely adsorbed on the cation exchange resin.

TABLE 5. DISTRIBUTION COEFFICIENT OF TRI- AND TETRAVALENT URANIUM IN SULFURIC ACID SOLUTION

Concn. of H_2SO_4 N	Distribution coefficient*			
	Dowex-1		Dowex-50	
	U^{3+}	U^{4+}	U^{3+}	U^{4+}
0.1	0	421	6600	340
0.5	0	57	320	40
1	0	18	12	18
2	0	5.2	2.9	2.2
4	0	2.0	0	1.7
6	0	1.3	0	1.4

* Each of the value is the mean of six experiments.

TABLE 6. DISTRIBUTION COEFFICIENT OF TRI- AND TETRAVALENT URANIUM IN PERCHLORIC ACID SOLUTION

Concn. of $HClO_4$ N	Distribution coefficient*			
	Dowex-1		Dowex-50	
	U^{3+}	U^{4+}	U^{3+}	U^{4+}
0.1	0	0	7000	721
0.5	0	0	4400	59
1	0	0	2000	30
2	0	0	880	13

* Each of the value is the mean of six experiments.

Discussion

On the basis of the above experimental results, complex formation of trivalent uranium in sulfuric, perchloric and hydrochloric acid solutions was compared with that of trivalent plutonium, americium or curium ion, which are relatively stable in aqueous solution, from among the same actinide elements. That is, as prevoiously described[18] for trivalent plutonium, both cationic and anionic complexes are formed in sulfate solutions, negatively charged complexes exist predominantly in concentrated sulfuric acid solutions and trivalent plutonium has a greater tendency to form sulfate complexes than trivalent americium; however, even in solutions where sulfate complexes are definitely known to exist, for example, in a 16 M sulfuric acid solution, changes in the absorption spectra of these solutions are very slight. According to experiments in sulfuric acid solutions, there is no formation of an anionic complex of trivalent uranium, at least at acid concentrations below 6 N, because the absorption spectra show almost no change and trivalent uranium ion is not adsorbed on the anion exchange resin over the entire range of acidity used.

Also, an investigation of complex formation by trivalent plutonium and americium in 1—5 M perchloric acid solution showed no appreciable changes in absorption spectra, and hardly any noticeable changes in absorption spectra of trivalent plutonium were observed at higher concentrations of perchloric acid.[19] Results concerning absorption spectra and the ion exchange behavior of trivalent uranium in a perchloric acid solution hitherto obtained indicate the absence of anionic complex formation at acid concentrations below 2 N, similar to the above results for a sulfuric acid solution.

In the literature, there are quite definite examples of the existence of chloride complexes of trivalent plutonium.[20-22] Changes in the absorption spectra of trivalent plutonium in hydrochloric acid solutions at acid concentrations right up to 4.4 M indicate the formation of complexes of trivalent plutonium with chloride ions.[20] In an ion exchange investigation, Diamond, Street and Seaborg[21] found that at high hydrochloric acid concentrations trivalent transuranium elements form complexes with chloride ions to a greater extent than lanthanides. Quantitative data on the composition and stability of complex chloride ions of Me^{3+} (where Me^{3+} is Pu^{3+}, Am^{3+} and Cm^{3+}) were obtained by Ward and Welch[22] through the ion exchange method. They established the formation of complex ions $MeCl^{2+}$, and at hydrochloric acid concentrations above 1 M, also complexes $MeCl_2^+$. Apparently, complex ions of the type $MeCl_3^0$ are also formed in more concentrated hydrochloric acid solutions, *i. e.*, in solutions with a large excess of chloride ions. In 12.6 M hydrochloric acid solution complex anions are formed, whose relative stabilities go as $Pu \gg Am > Cm$.

From the results of our study on absorption spectra and ion exchange behavior, it is thought that an anionic chloride complex of trivalent uranium begins to form at hydrochloric acid concentrations above 7 N, showing good agreement with results obtained on trivalent states of plutonium, americium and curium. However, in the case of trivalent plutonium, the stability of anionic chloride complexes increased rapidly at 12.6 N. On the other hand, from results obtained by the present authors, a sudden change occurred in the absorption spectra when the concentration of hydrochloric acid became greater than 10 N in the case of trivalent uranium, and similar to the case of trivalent plutonium, it can be expected that the stability of an anionic complex of trivalent uranium will increase suddenly above 10 N. However, according to results from the ion exchange experiment, a large change in the apparent distribution coefficient for anion exchange resin in high concentrations of hydrochloric acid solutions in the case of trivalent americium or curium was not indicated, contrary to expectation.

In general, the tendency of ions of a given element to form complexes increases with decrease in ionic radius and increase in charge, *i. e.*, with increase in the ionic potential,

$$\varphi = \frac{Z}{r},$$

where Z is the ionic charge and r the ionic radius. In accordance with this, it is to be expected that the ion U^{4+} will have a greater tendency to form complexes with acid anions than the ion U^{3+}. The results of investigating complex formation by uranium in tri- and tetravalence forms are in agreement with this. Also, by analogy with the lanthanides and from the known behavior of the transuranium elements, the relative strengths of the multichloride complex ions of trivalent plutonium, americium and curium should decrease in that order. In dilute hydrochloric acid solutions, the order of the relative strengths of the multichloride complex ions of trivalent uranium, plutonium, americium and curium was found to be identical, while in the case of concentrated hydrochloric acid solutions, the order of uranium and plutonium was reversed.

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22) M. Ward and G. A. Welch, *J. Inorg. Nucl. Chem.*, **2**, 395 (1956).

Finally, it was reported with respect to the formation of carbonate complexes that carbonate ions form soluble anionic complexes in 40% potassium carbonate solution in the case of actinide elements such as trivalent plutonium and americium. That is, it was reported that the absorption spectra of carbonate complexes of trivalent plutonium showing absorption maxima at wavelengths of 565, 600, 835 and 920 mμ were observed,[23] and the formation of anionic complexes confirmed by the study of the electromigration in carbonate solutions.[24,25] It is expected that there is a possibility of the formation of a soluble carbonate complex in the case of trivalent uranium, similar to the case of plutonium and americium, and consequently, this was studied from various points of view. However, in the case of trivalent uranium, a precipitate with a low solubility which is believed to be an insoluble carbonate always formed, and it was not possible to confirm the presence of a soluble carbonate complex from the absorption spectra of the supernatant liquid.

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