332. *The Nature and Stability of the Complex Ions formed by Ter-, Quadri-, and Sexa-valent Plutonium Ions with Ethylenediaminetetra-acetic Acid (edta). Part II.* Spectrophotometric Studies.*

By J. K. Foreman and T. D. Smith.

Absorption spectra of the ethylenediaminetetra-acetates of plutonium(III), plutonium(IV), and plutonium(VI) are presented, and the stability constants of these chelates obtained from them. Chelation of the unhydrolysed plutonium(IV) ion with ethylenediaminetetra-acetate in 1N-nitric acid has been observed.

Several attempts have been made to correlate shifts in absorption spectra which occur on chelate formation with structure, bond-type, and stability of the chelates. Martell and his co-workers [1-3] have examined the spectra of a number of edta chelates and given orders of relative stabilities [4] for a number of elements at pH values in the range 4·00—11·00; for essentially ionic chelates, the edta absorption band shifts to progressively shorter wavelengths with increasing stability of the chelates.

The absorption spectra of the edta chelates of plutonium have been recorded primarily to obtain confirmatory values for the chelate stability constants reported in Part I.* The spectra of the fully formed complexes are plotted in Figs. 1, 2, and 3 together with the spectra of the component ions.

The spectra of the 1 : 1 complexes of plutonium(III) and plutonium(IV) are markedly different from those of the unchelated ions; not only is there considerable intensification of the spectrum, but several peaks characteristic of the aqueous ions are either missing or

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* Part I, preceding paper.

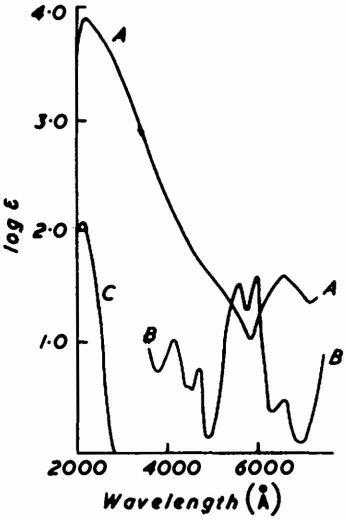
[1] Martell and Calvin, " Chemistry of the Metal Chelate Compounds," Prentice-Hall Inc., New York, 1952.

[2] Hughes and Martell, *J. Phys. Chem.*, 1953, **57**, 694.

[3] Martell and Plumb, *ibid.*, 1952, **56**, 993.

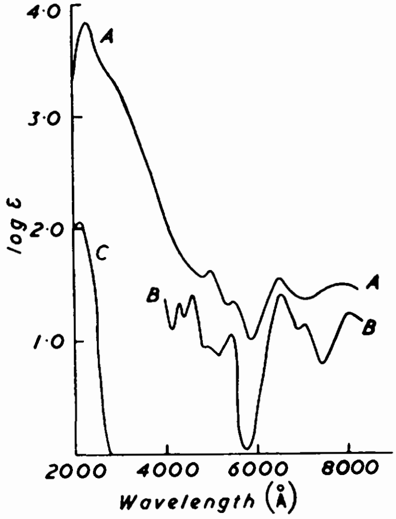
[4] Plumb, Martell, and Bersworth, *J. Phys. Colloid Chem.*, 1950, **54**, 1208.

FIG. 1.



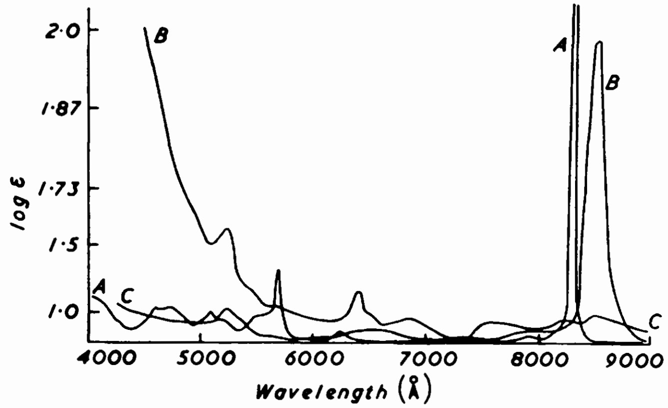
A, 1 : 1 edta chelate of plutonium(III) at pH 4·7.
B, Unchelated plutonium(III) at pH 1·0.
C, Tetrasodium salt of edta at pH 10·0.

FIG. 2.



A, 1 : 1 edta chelate of plutonium(IV) at pH 4·7.
B, Unchelated plutonium(IV) at pH 1·0.
C, Tetrasodium salt of edta at pH 10·0.

FIG. 3.



A, Unchelated plutonyl ion in 0·1N-nitric acid.
B, ,, ,, at pH 6·5.
C, 1 : 1 edta complex of plutonyl ion at pH 6·5.

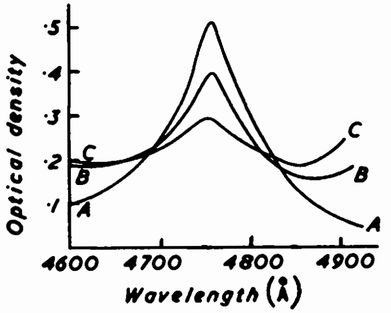


FIG. 4.

1·63 × 10^{-3}M-Plutonium(IV) in :
A, N-Nitric acid.
B, N-Nitric acid + 1·63 × 10^{-3}M-edta.
C, ,, + 3·26 × 10^{-3}M-edta.

have undergone wavelength displacement. The general intensification of the absorption spectrum accords with the findings of Moeller and his co-workers[5,6] for the edta chelate of neodymium and the acetylacetone complexes of several rare-earth elements, where the effect is attributed to enhancement of electronic $4f^n$ transitions, forbidden for the free atoms, due to the increased electric dipole arising from the strong field imposed by the chelating anions. It seems likely that a similar effect is operative in the case of plutonium(III) and plutonium(IV) since considerable evidence is now available[7] suggesting that the absorption spectra of the actinide elements arise from electronic transitions between terms of the $5f^n$ series. The spectrum of unchelated plutonium(III) in 0·1M-potassium chloride solution undergoes virtually no intensity changes between pH 1 and the pH used to record the spectrum of the fully formed complex (pH 4·7), and the entire observed intensification of absorption on addition of edta may reasonably be ascribed to the chelating effect. For plutonium(IV), results quoted in Part I indicated that at pH 4·7 a partially hydrolysed species of the Pu^{4+} ion is involved in the chelation. It is known that progressive hydrolysis of this ion results in increased absorption of radiation, particularly at wavelengths below about 4500 Å.[8] Thus, the unchelated plutonium(IV) spectrum taken at pH 1·0 is probably not a true representation of the absorption due to the species undergoing chelation, and the true intensification observed due to chelation may be less than that observed in Fig. 2, especially at the lower wavelengths. Absorbancy measurements on plutonium(IV) solutions in which hydrolysis of the ion is prevalent tend to be variable owing to contributions from scattering resulting from polymerisation and ultimate formation of colloidal species.

The spectrum of the plutonyl–edta chelate (Fig. 3) shows virtually none of the features characteristic of the plutonyl ion; in particular, the strong absorption at 8320 Å is absent and a new peak appears at 5700 Å. [The characteristic absorption of plutonium(V) also occurs at this wavelength.] In contrast with plutonium(III) and plutonium(IV), the plutonyl chelate does not exhibit the pronounced absorption in the low-wavelength visible region. The absorption due to the plutonyl ion in this region is seen to be small at pH 1 but increases markedly with increasing pH, and at pH 6·5, at which the spectrum of the fully formed complex was taken, it is very large. It is noteworthy that the spectrum of the plutonyl chelate is the same whether the formation of the chelate is approached from acid or from alkaline conditions. If the increase in absorption due to the plutonyl ion in the region 4000—5000 Å with increasing pH is attributed to the formation of ionic hydrolysis products,[9] *e.g.*, $PuO_2(OH)^+$ or $PuO_2(OH)_2$, then the absence of this strong absorption when the chelate is formed under alkaline conditions and the pH brought to 6·5 suggests that the carboxyl groups of edta can replace the hydroxyl groups of the hydrolysed plutonyl ion.

Unlike the edta chelates of plutonium(III) and plutonium(IV), that of the plutonyl ion is unstable and decomposes slowly during a period of several days. The effects observed are a gradual increase in pH (from 6·5 to 8·1 in three days, and to 9·1 in six days), the reduction of plutonium(VI) to plutonium(IV), and a gradual change in colour from the original violet-blue of the chelate to pale yellow. The main absorption spectra changes are the decrease in intensity of the characteristic peak due to the chelate at 5700 Å, and the appearance of new absorptions at 4400, 5050, and 5550 Å, and broader peaks around 6500 and 8000 Å, all increasing in intensity with time and pH. The plutonium valency states present after a given period of standing were recognised by decomposing the chelate, making the solution about 2N in nitric acid, and examining the spectrum of the resulting

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[5] Moeller and Brantley, *J. Amer. Chem. Soc.*, 1950, **72**, 5447.

[6] Moeller and Ulrich, *J. Inorg. Nuclear Chem.*, 1956, **2**, 164.

[7] "The Actinide Elements" (Ed. Seaborg and Katz), National Nuclear Energy Series IV-14A, McGraw-Hill, London, 1954, pp. 783 *et seq.*

[8] Ockenden and Welch, *J.*, 1956, 3358.

[9] "The Transuranium Elements" (Ed. Seaborg, Katz, and Manning), National Nuclear Energy Series IV-14B, Part I, McGraw-Hill, London, 1949, p. 528.

solution. After a solution of the plutonyl chelate had stood for six days, the spectrum showed clearly the presence of both plutonium(IV) (absorption peaks at 4500, 4760, 4950, 5450, 6600, 7960 Å) and plutonium(VI) (peak at 8320 Å). The mechanism of the reduction of the plutonyl chelate is not understood. Kraus and Dam [1] have observed self-reduction of plutonium(VI) at high pH, and it is possible that the presence of the electron-donating edta carbonyl groups around the plutonyl ion at pH 6·5 simulates high pH conditions of the unchelated ion.

Determination of Stability Constants.—The stability constant of the 1 : 1 chelate of plutonium(III) was determined directly by making optical-density measurements on a solution containing equimolar amounts of the component ions, and brought to pH 1·5 to produce appreciable decomposition of the chelate. The stability constant was evaluated by using measured molar absorbancies of the chelate and the uncomplexed ion and Cabell's values [10] for the ionisation constants of edta.

As indicated above, the spectra of the ions of plutonium(IV) and plutonium(VI) and of the plutonyl chelate are pH dependent. Isohydric conditions are therefore desirable for evaluating the required molar absorbancies needed to calculate the stability constants of the plutonium(IV) and plutonyl chelates, and to meet this condition the replacement method of Hughes and Martell [2] was employed, cadmium being used as the reference ion. Relative stability constants are evaluated according to

$$K = [\mathrm{Pu(IV)Y}][\mathrm{Cd}^{2+}]/[\mathrm{CdY}^{2-}][\mathrm{Pu(IV)}^{4+}]$$

where $K = K_{\mathrm{Pu(IV)Y}}/K_{\mathrm{CdY}^{2+}}$, and similarly for the plutonyl ion. Schwarzenbach's weighted value $\log K = 16{\cdot}1$ has been used for the stability constant of the cadmium chelate.[11] Table 1 lists the values obtained together with those from the ion-exchange technique. For each valency state the ion-exchange and spectrophotometric values for $\log K$ are in reasonable agreement.

Chelation of the Unhydrolysed Pu^{4+} *Ion.*—The low value for the stability constant of the plutonium(IV)–edta chelate has been attributed to the fact that the recorded value at pH 3·30 applies to a hydrolysed species of the Pu^{4+} ion. Assuming, by analogy with thorium, that an edta chelate of unhydrolysed Pu^{4+} would have $\log K = 23$ approximately, we may readily calculate that appreciable complex formation should occur in 1N-acid solutions. In 1N-acid it is considered that hydrolysis products of the Pu^{4+} ion are virtually non-existent and therefore any interaction observed between edta and plutonium(IV) must be attributed to chelation of the unhydrolysed ion, and would be the result of formation of a chelate of stability much greater than $\log K = 17{\cdot}66$ observed for the interaction at pH 3·30. Fig. 4 shows the effect of edta addition upon part of the spectrum of plutonium(IV) in 1N-nitric acid, and it is evident that chelation is occurring. It is not possible to obtain an accurate value for the stability constant of the complex since its spectrum is not known and cannot be isolated. However, it is apparent from the spectra of the edta chelates of the plutonyl ion and of uranium(IV) [12] that hydrolysis

TABLE 1.

Ion	Method	pH	log *K*
Pu(III)	Ion exchange	3·30	18·12
Pu(III)	Direct spectrophotometric	1·5	18·59
Pu(IV)	Ion exchange	3·30	17·66
Pu(IV)	Replacement spectrophotometry	3·30	17·10
Pu(VI)	Ion exchange	3·30	16·39
Pu(VI)	Replacement spectrophotometry	4·0	16·03

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[10] Cabell, Atomic Energy Research Establishment Report AERE C/R813.
[11] Schwarzenbach, *Analyst*, 1955, **80**, 713.
[12] Smith, unpublished work.

of the component cation mainly affects the absorption in the low-wavelength visible region and at higher wavelengths it is virtually unaffected. Thus, using molecular absorbancy values for the chelate of the hydrolysed plutonium(IV) ion at wavelengths of about 5000 Å and above, we can obtain a first approximation to the stability constant. By using 4900, 5600, and 5700 Å for ratios of edta to plutonium of 1 : 1, 2 : 1, and 3 : 1, mean values for log K of 24·2, 24·2, and 24·3 were obtained. Subject to the inaccuracies mentioned above, these values are clearly of the right order for the 1 : 1 chelate of a quadrivalent ion.

EXPERIMENTAL

All spectra were taken with a Hilger Uvispek spectrophotometer, both quartz and glass prisms and cells being used. Solutions of plutonium-(III), -(IV), and -(VI) were prepared as described in the previous paper and were used at concentrations of 0·7—3·0 × 10^{-2}M. Constant ionic strength of 0·1N-potassium nitrate or chloride was maintained.

TABLE 2.

Species	pH	λ (Å)	ε	Species	pH	λ (Å)	ε
Pu(IV)	3·30	5400	11·7	Cd–edta	3·30	5400	3·7
,,	,,	5500	11·4	,,	,,	5500	3·7
,,	,,	5600	11·9	,,	,,	5600	3·7
,,	,,	5700	11·9	,,	,,	5700	3·1
Pu(IV)–edta	,,	5400	51·4	PuO_2^{2+}	4·0	8600	3·9
,,	,,	5500	52·6	,,	,,	8700	0·6
,,	,,	5600	51·4	,,	,,	8800	0·3
,,	,,	5700	45·9	PuO_2^{2+}–edta	,,	8600	9·4
				,,	,,	8700	8·6
				,,	,,	8800	7·0

The stability constant of the plutonium(III) chelate was calculated from optical density measurements at 4200 Å and 5500 Å. At these wavelengths the edta ions do not contribute to the absorption. Adherence to Beer's law was established for both the chelate and the free Pu^{3+} ion.

For the replacement reactions used to determine the stability constants of the plutonium(IV) and plutonyl chelates, the wavelengths used and molar absorbancies of the relevant species are listed in Table 2. The cadmium ion has no absorption in the visible region. Replacement of plutonium(IV) at pH 3·30 fairly certainly results in the formation of colloidal species of this ion, and the data of Ockenden and Welch[8] have been used for the molar absorbancy of such species. For the plutonyl chelate pH 4·00 was chosen to yield a measurable amount of the species involved.

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