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A behavioural study of some transplutonium elements in condensed phosphate solutions

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The chemical and electrochemical behaviour of americium, curium and californium in $K_4P_2O_7$, $K_5P_3O_{10}$ and $Na_6P_6O_{18}$ solutions has been studied.

The separation and determination of transplutonium elements (TPE) based on the use of their 'unusual' oxidation states is known to be most effective. In particular, a number of selective coulometric methods for americium determination have been developed using Am^{IV} and americium can be extracted from other TPE.[1–5] Therefore, the search for new media that can hold and stabilize TPE in the highest oxidation states has gained urgency.

Condensed phosphates are formed as a result of numerous condensations of tetrahedral PO_4 groups connected either in chains (polyphosphates) or in rings (metaphosphates).[6] For the first time the use of pyrophosphate for Am^{IV} stabilization has been reported.[7] We have previously investigated in detail the electrochemical oxidation of americium in potassium pyrophosphate solution.[8] However, Am^{III} oxidation in the presence of other condensed phosphates was not studied. It is also of interest to investigate the behaviour of Cm^{III} and Cf^{III} in solutions of these complex-forming compounds. Here we investigate the electrochemical and chemical oxidation of Am^{III}, Cm^{III} and Cf^{III} in aqueous solutions of pyro-, tripoly- and hexa-metaphosphates.

Americium containing 97% ^{243}Am and 3% ^{241}Am by mass was used in the work. The curium sample had the following isotopic compositions (mass%): ^{242}Cm (0.02), ^{244}Cm (20.56), ^{245}Cm (3.66), ^{246}Cm (60.09), ^{247}Cm (5.10), ^{248}Cm (9.78). The specific activity of this mixture was 6.15×10^8 Bk mg^{-1}. ^{249}Cf was obtained from berkelium decay in which it is the daughter product resulting from β-decay of the mother isotope ^{249}Bk. Californium was separated from berkelium by berkelium oxidation to Bk^{IV} with potassium bromate in nitric acid and subsequent berkelium(IV) extraction by a 0.25 M solution of D2EHPA in heptane. The concentration of TPE ranged from 1×10^{-3} to 2×10^{-3} M. Electrolysis of the solutions and chemical oxidation were carried out in a special spectroelectrochemical cell, the design of which has been previously described.[8] Electrolysis and/or chemical oxidations were carried out simultaneously with measurement of the absorption spectra of the investigated solutions. Spectrophotometric measurements were carried out using a Shimadzu UV-160 spectrophotometer. All of the curium and californium radionuclide was used up in each separate experiment, so each experiment ended with the extraction and regeneration of the radionuclide consumed, according to the extraction technique developed earlier.[9]

The composition of investigated TPE complexes with condensed phosphates. Absorption spectra of Cm^{III} in 0.2 M HNO_3 (curve *a*) and Cf^{III} solution in 0.1 M $HClO_4$ (curve *b*) are shown in Figure 1. The Cm^{III} molar absorptivity at λ 397 nm is equal to 49.7 dm^3 mol^{-1} cm^{-1} and 10 dm^3 mol^{-1} cm^{-1} at λ 435 nm for Cf^{III} under these conditions; this coincides well with literature data.[10] Spectrophotometric titration curves of Am^{III} at λ 503 nm with potassium tripolyphosphate $K_5P_3O_{10}$ (curve *c*) and sodium hexametaphosphate $Na_6P_6O_{18}$ (curve *d*) and also spectrophotometric titration curves of Cm^{III} at λ 397 nm (curve *a*) and Cf^{III} at λ 435 nm (curve *b*) with potassium pyrophosphate $K_4P_2O_7$ are shown in Figure 2. These curves have character-

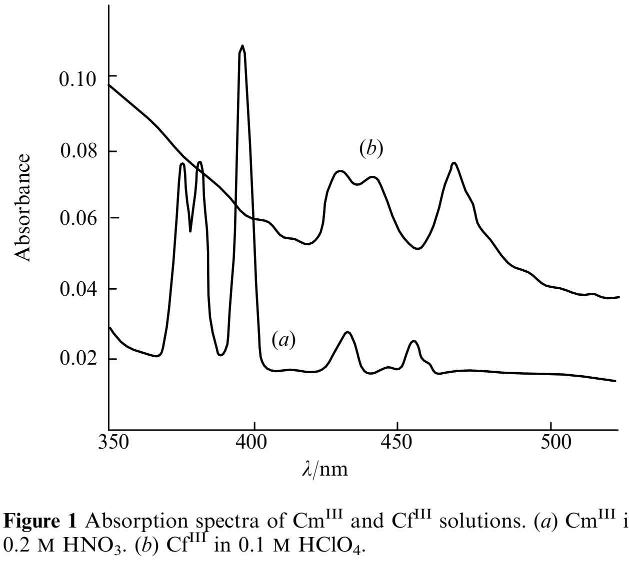

Figure 1 Absorption spectra of Cm^{III} and Cf^{III} solutions. (*a*) Cm^{III} in 0.2 M HNO_3. (*b*) Cf^{III} in 0.1 M $HClO_4$.

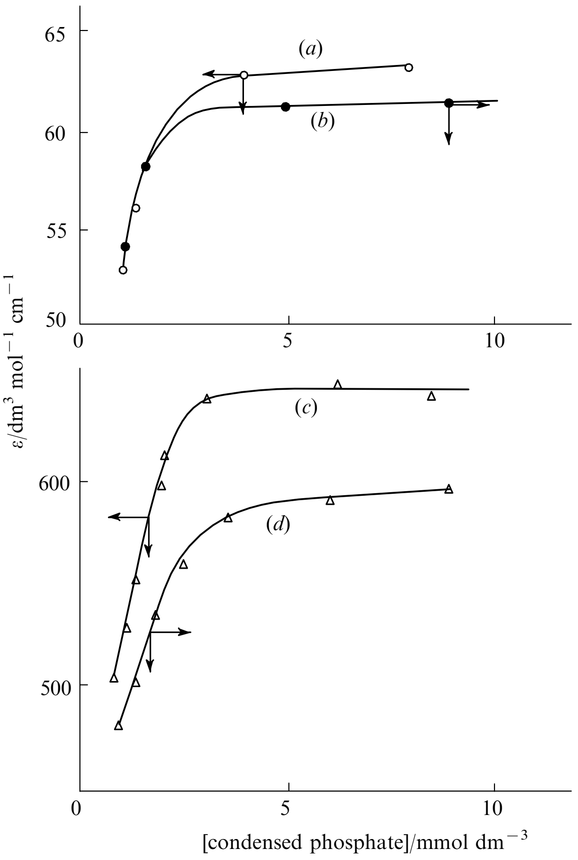

Figure 2 Spectrophotometric titration of TPE(III) solutions with condensed phosphates. [TPE] = 1×10^{-3} M. (*a*) Titration of Cm^{III} with $K_4P_2O_7$. (*b*) Titration of Cf^{III} with $K_4P_2O_7$. (*c*) Titration of Am^{III} with $Na_6P_6O_{18}$. (*d*) Titration of Am^{III} with $K_5P_3O_{10}$.

istic breaks at [condensed phosphate] : [TPE] = 2 that correspond to the formation of complexes containing two molecules of condensed phosphate per TPE atom. Moreover, white precipitates are isolated from the solution with [condensed phosphate] : [TPE] < 1. Analysis of these precipitates has shown that the TPE content in the precipitate was twice as large as the concentration of added condensed phosphate. This fact seems to bear witness to the formation of low soluble TPE compound with condensed phosphate in a 2 : 1 ratio. Increase of condensed phosphate concentration in this system to [TPE] : [condensed phosphate] = 1 : 1 results in complete dissolution of the precipitate, suggesting 1 : 1 complex formation.

Electrochemical oxidation. Similar to the carbonate solutions,[11] changes in absorption spectra do not occur during electrolysis of Cm^{III} and Cf^{III} in 0.5 M pyro- and tripolyphosphate solutions at pH 1 and 10 and at a working platinum electrode potential +1.9 V (potential values are subsequently given relative to the normal hydrogen electrode). However, the molar absorptivity of both curium and californium decreases in alkaline solutions (from 49.7 to 28 $dm^3\ mol^{-1}\ cm^{-1}$ at λ 397 nm and from 10 to 6.7 $dm^3\ mol^{-1}\ cm^{-1}$ at λ 435 nm, respectively). A decrease in molar absorptivity usually occurs for all transuranium elements when going from acidic to alkaline solutions and is attributed to the formation of hydroxy complexes.

Electrochemical oxidation of americium in tripolyphosphate occurs in a similar way to oxidation in pyrophosphate.[8] Am^{III} is completely oxidized to Am^{IV} during electrolysis of Am^{III} in 0.1–1 M solutions of potassium tripolyphosphate acidified to pH < 1 at a working platinum electrode potential +1.9 V. Am^{IV} is rather stable under these conditions and is gradually reduced to Am^{III} (2% h^{-1}).

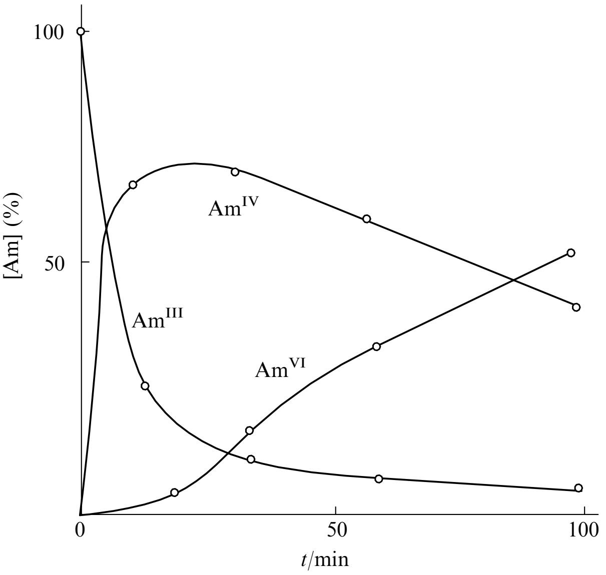

Figure 3 Kinetics and valent forms obtained from the oxidation of Am^{III} in potassium tripolyphosphate solution. [$K_5P_3O_{10}$] = 1 M.

In weakly alkaline solutions of $K_5P_3O_{10}$ (pH 7–10) Am^{III} at a working platinum electrode potential +1.9 V is oxidized to Am^{VI} which can be electrochemically reduced to Am^{V} at a working platinum electrode potential +0.8 V. In the weakly alkaline tripolyphosphate solution Am^{VI} is gradually reduced to Am^{V} (1–1.5% h^{-1}) on standing.

In weakly acidic tripolyphosphate solutions (pH 4) electrochemical oxidation of Am^{III} at a working platinum electrode potential +1.9 V results in the formation of an Am^{IV} and Am^{VI} mixture. As this takes place, for the first 10 min of electrolysis Am^{IV} is largely formed, then its concentration decreases and the Am^{VI} concentration increases (Figure 3). In solutions of pH 4 without electrodes, the Am^{IV} concentration decreases at 3% h^{-1} and the Am^{VI} concentration decreases at 0.5% h^{-1} (reduced to Am^{III}).

Formal oxidation potentials of Am^{IV}/Am^{III} and Am^{VI}/Am^{V} pairs in tripolyphosphate solutions were measured. As seen from Table 1, where the values of formal oxidation potentials of Am^{IV}/Am^{III} and Am^{VI}/Am^{V} pairs in pyrophosphate solutions obtained earlier [8] are also presented, E_f(IV)/(III) decreases regularly with increase of Am^{IV} complexation as pyro- or tripoly-phosphate ion concentration increases.

Electrochemical oxidation of Am^{III} in solutions of hexametaphosphates of alkaline metals proceeds with extreme difficulty. That is why Cm^{III} and Cf^{III} oxidation in these solutions was not carried out. The reasons for this

Table 1 Formal oxidation potentials of Am^{IV}/Am^{III} and Am^{VI}/Am^{V} pairs in pyro- and tripoly-phosphate solutions.[a]

Am^{IV}/Am^{III}			Am^{VI}/Am^{V}		
Solution composition	pH	E_f/V	Solution composition	pH	E_f/V
$H_4P_2O_7$	0.5	1.70	$(NH_4)_4P_2O_7$	8.0	1.10
$(NH_4)_4P_2O_7$	2.1	1.59	$K_5P_3O_{10}$	8.0	1.12
$K_5P_3O_{10}$	2.0	1.61	$(NH_4)_4P_2O_7$	10.0	1.06
$(NH_4)_4P_2O_7$	2.3	1.56	$K_5P_3O_{10}$	10.0	1.07
$(NH_4)_4P_2O_7$	4.0	1.41			
$K_5P_3O_{10}$	4.0	1.42			
$(NH_4)_4P_2O_7$	5.0	1.31			
$(NH_4)_4P_2O_7$	6.0	1.24			
$K_5P_3O_{10}$	6.0	1.26			

[a] [condensed phosphate] = 1 M.

Table 2 Oxidation of Am^{III} by sodium persulfate in hexametaphosphate solution.[a]

Length of solution heating/min	$[Am^{III}]$ (%)	$[Am^{IV}]$ (%)	$[Am^{VI}]$ (%)
1.5	70	28	2
2.5	30	63	7
5.0	1	20	79
10.0	0	0	100

[a] Conditions: $[Am] = 2.0\times10^{-3}$ M; $[Na_2S_2O_8] = 0.1$ M; $[Na_6P_6O_{18}] = 0.2$ M; pH = 1.5; $T = 95\,°C$.

phenomenon are yet to be explained, and are under investigation.

Chemical oxidation. 1. Oxidation by sodium persulfate. Am^{III} can be easily oxidized by persulfate ions on heating in solutions of both linear and ring condensed phosphates, Table 2. Conditions and results of the oxidation in either case do not differ appreciably. Oxidation of Cm^{III} and Cf^{III} was not observed under these conditions. As seen from Table 2, a mixture of Am^{IV} and Am^{VI} was formed in weakly acidic solutions of $Na_6P_6O_{18}$ (pH 1–3), the concentration relationship between them developing with heating time. The stability of Am^{IV} obtained is low. Its concentration in the solution decreases by 50% after 20 min and Am^{III} was formed. Am^{VI} is very stable under these conditions and is reduced to Am^{III} at the rate of 0.2% h^{-1}. The maximum yield of Am^{IV} obtained during Am^{III} oxidation by sodium persulfate did not exceed 75%, although we do not exclude the possibility that it might be increased.

Complete oxidation of Am^{III} to Am^{VI} was observed at pH 4–10. In this case heating for 2 min was sufficient to oxidize americium. The obtained Am^{VI} was very stable. For example, Am^{VI} is reduced to Am^{III} in 0.2 M solution of $Na_6P_6O_{18}$ at pH 5 at the rate of 0.05% h^{-1}.

The formation of an Am^{V} and Am^{VI} mixture is observed in pyro- and tripoly-phosphate solutions at pH 10–12. The stability of Am^{VI} decreases considerably when the solution pH increases. At pH 10–12, an instantaneous reduction of Am^{VI} to Am^{V} occurs. Am^{V} is essentially stable under these conditions.

2. Oxidation by sodium perxenate. In spite of the higher oxidation potential of sodium perxenate compared to persulfate it was not possible to oxidize curium and californium in condensed phosphate solutions. This is due to the fact that the magnitude of the complexing ability of pyro-, tripoly- and hexameta-phosphates is insufficient to achieve the oxidation potential of the M^{IV}/M^{III} couple for curium and californium required to carry out oxidation of these elements using the oxidizers involved.

Sodium perxenate $Na_4XeO_6{\cdot}8H_2O$ can be used for Am^{III} oxidation in pyro- and tripoly-phosphate solutions at pH$\ll$3 and for oxidation in potassium hexametaphosphate at pH 8–10. In all cases a five-fold excess of oxidizer in relation to Am^{III} concentration was needed to completely oxidize americium.

An Am^{IV} (20%) and Am^{VI} (80%) mixture was obtained by the oxidation of Am^{III} with sodium perxenate in pyro- and tripoly-phosphate solutions at pH 3–4. A decrease in Am^{IV} content and an increase in Am^{VI} content in this mixture occurs with increasing pH from 4 to 6. The Am^{IV} formed is not so stable and *ca.* 50% is reduced to Am^{III} after 30 min. Am^{VI} obtained under these conditions reduces to Am^{III} at less than 1% h^{-1}.

At pH 6–8 the final oxidation product was Am^{VI} which was reduced to Am^{V} at *ca.* 1% h^{-1}.

The product of Am^{III} oxidation, both in $Na_6P_6O_{18}$ and in linear phosphate solutions at pH >9, was Am^{V} which is stable under these conditions.

Such solutions of condensed phosphates are found to be convenient media for obtaining americium in various oxidation states (+4, +5, +6). Decreasing the oxidation potential of Am^{IV}/Am^{III} and Am^{VI}/Am^{V} couples in the presence of condensed phosphate ions permits facile oxidation of Am^{III} to Am^{IV}, Am^{V} and Am^{VI}, both electrochemically and chemically even in rather dilute (0.1–1 M) solutions. Since americium in these oxidation states is rather stable in condensed phosphate solutions these media are promising for developing the techniques of americium isolation and determination using its highest oxidation states. Sufficient oxidation potential shifts of M^{IV}/M^{III} pairs for curium and californium are not achieved in pyro-, tripoly- and hexametaphosphate solutions and this fact precludes oxidation of these elements to the highest oxidation states, either electrochemically or chemically.

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