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On the Stability of Nitrate and Chloride Complexes of Plutonium(IV)

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The nitrate and chloride complexes of Pu^{4+} were studied in an acid perchlorate medium of ionic strength $I = 4$ M at a temperature of 20°C, using the cation-exchanger method of Fronæus [1-3]. The calculation method was extended to systems of the type $M^{4+}-A^-$, where the central ion, the first, second and third complexes can be sorbed on the ion-exchanger. The complexity constants obtained for the nitrate system were:

$\beta_1 = 5.5 \pm 0.2$ M^{-1}; $\beta_2 = 23.5 \pm 1$ M^{-2}; $\beta_3 = 15 \pm 10$ M^{-3}

and for the chloride system:

$\beta_1 = 1.4 \pm 0.2$ M^{-1}; $\beta_2 = 1.2 \pm 0.2$ M^{-2}; $\beta_3 = 0.1 \pm 0.1$ M^{-3}.

The nitrate and chloride complexes of Pu^{4+} have previously been studied by several authors [4-8] using ion-migration, spectrophotometric, electrometric and solvent extraction methods. Most of the work is of a qualitative nature and all the quantitative measurements are confined to the spectrophotometric and electrometric methods. In the electrometric measurements the variation of the redox potential for the couple Pu(IV)/Pu(III) has been studied. To evaluate the complexity constants for Pu^{4+} it is then necessary to know the corresponding complexity constants for Pu^{3+}. As these are not known with any degree of accuracy the result has a corresponding uncertainty in the magnitude of the Pu^{4+} constants. In addition mixed complexes of Pu^{4+} and Pu^{3+} are neglected.

The ion-exchanger method seems to be a more direct and accurate way of studying these complex systems than theother methods mentioned above.

The hydrolysis [9] and disproportionation [10] reactions of Pu^{4+} must be taken into consideration for work in water solutions. By using a medium with a hydrogen-ion concentration of 4 M, the hydrolysis can be sufficiently suppressed. The disproportionation reaction

$$3\,Pu^{4+} + 2\,H_2O \rightleftharpoons 2\,Pu^{3+} + PuO_2^{2+} + 4\,H^+$$

is also strongly displaced towards left at this high acidity. The disproportionation rate of Pu^{4+} decreases with decreasing plutonium concentration and at the concentrations used here ($< 1.2 \times 10^{-5}$ M) it is entirely negligible. The high acidity and the low plutonium concentration thus removes the complications that would arise because of the presence of hydrolysis-products and oxidation states other than + 4.

THEORETICAL

The calculation of the complexity constants is made according to a method developed by Fronæus [1-3]. In the derivation it is assumed that only mononuclear complexes are formed both in the solution and in the ion-exchanger. This assumption is reasonable because of the low total metal-ion concentration ($< 1.2 \times 10^{-5}$ M) and the high acidity (4 M) of the solution.

The following symbols and equations have been used:

C'_M, C'_A = the total concentrations of metal-ion and ligand in solution before addition of the ion-exchanger.
C_M, C_A = the total concentrations of metal-ion and ligand in the solution in equilibrium with the ion exchanger.
$[M^{4+}]$, $[MA_j^{4-j}]$, $[A^-]$ = equilibrium concentrations of the different species in solution.
$[M^{4+}]_R$, $[MA_j^{4-j}]_R$ = equilibrium concentrations of the different species in the resin phase.
β_j = the complexity constant for the complex MA_j^{4-j} in solution.
v = the volume of the solution before addition of ion-exchanger.
m = the weight in grammes of dried ion-exchanger.
δ = the swelling factor of the ion-exchanger.
$X_n = \sum_{j=n}^{N} \beta_j \cdot [A^-]^{j-n}; \qquad (\beta_o = 1)$

Using these notations following equations are obtained

$$C_M = [M^{4+}](1 + \sum_{j=1}^{N} \beta_j [A]^j) \tag{1}$$

$$C_{MR} = \sum_{j=0}^{3} [MA_j^{4-j}]_R \tag{2}$$

For each of the ions $MA_j^{4-j} (j \leq 3)$ exchanging for hydrogen-ions in the resin, the following equilibrium can be written

$$MA_j^{4-j} + (4-j)\ H_R^+ \rightleftharpoons MA_{jR}^{4-j} + (4-j)\ H^+$$

Applying the law of mass action gives the expression

$$\frac{[MA_j^{4-j}]_R}{[MA_j^{4-j}]} = k_j \frac{[H^+]_R^{4-j}}{[H^+]^{4-j}} = l_j; \ (j = 0, 1, 2, 3) \tag{3}$$

where the coefficients k_j and l_j are functions of the activity coefficients in resin and solution. In this case the activity coefficients in solution are kept constant by using a medium of constant ionic strength and in the ion-exchanger by having a constant value of C_{MR} and $[H^+]_R$[1,11]. $[H^+]_R$ is constant because the load, C_{MR}, is much smaller (1.2×10^{-7} moles/g) than the total exchange capacity of the resin. The constant C_{MR} is obtained from a determination of the distribution coefficient, φ, at several different C'_M. The original articles should be consulted for further details [1-3].

The distribution of the metal-ion between resin and solution is given by

$$\varphi = \frac{C_{MR}}{C_M} = l_0 \frac{1 + l'_1[A^-] + l'_2[A^-]^2 + l'_3[A^-]^3}{X} \tag{4}$$

where $l'_j = l_j \cdot \beta_j \cdot l_0^{-1}$, $(j = 1, 2, 3)$

and $l_0 = [M^{4+}]_R/[M^{4+}] = \lim\limits_{[A^-] \to 0} \varphi$

Because of the impossibility of an accurate determination of the total metal-ion concentration in the resin phase, φ is obtained from a determination of C'_M and C_M.

Thus $v \cdot C'_M = v \cdot \delta \cdot C_M + m \cdot C_{MR}$

$$\varphi = \frac{C_{MR}}{C_M} = \frac{v}{m}\left(\frac{C'_M}{C_M} - \delta\right)$$

and because $C'_M \ll C'_A$ $\qquad [A^-] \approx C_A = C'_A/\delta$

In order to obtain the complexity constants from corresponding values of φ and $[A^-]$, three new functions φ_1, f and g are introduced.

$$\varphi_1 = \left(\frac{l_0}{\varphi} - 1\right) \cdot \frac{1}{[A^-]} \tag{6}$$

$$f = \left\{\frac{l_0}{\varphi}\left[(\beta_1 - l'_1)[A^-] - 1\right] + 1\right\} \cdot \frac{1}{[A^-]^2} \tag{7}$$

$$g = \left\{f - \beta_1 \varphi_1 + \frac{l_0}{\varphi}(\beta_2 - l'_2)\right\} \cdot \frac{1}{[A^-]} \tag{8}$$

By substitution of expression (4) in eqns. (6) and (7) the following limiting values are obtained

$$\lim_{[A^-] \to 0} \varphi_1 = \varphi_1^0 = \beta_1 - l'_1 \tag{9}$$

$$\lim_{[A^-] \to 0} f = f^\circ = \beta_1(\beta_1 - l'_1) - (\beta_2 - l'_2) \tag{10}$$

A combination of eqns. (4), (6) and (7) gives

$$f = \beta_1\varphi_1 - X_2 + (\varphi_1 \cdot [A^-] + 1)(l'_2 + l'_3 \cdot [A^-]) \tag{11}$$

In the same way eqn. (12) is obtained by a combination of eqns. (6), (9), (10) and (11).

$$\frac{\Delta f}{[A^-]} = \beta_1 \cdot \frac{\Delta\ \varphi_1}{[A^-]} + \varphi_1\,(l_2' + l_3' \cdot [A^-]) + l_3' - X_3 \tag{12}$$

where $\Delta\ f = f - f^\circ$ and $\Delta\ \varphi_1 = \varphi_1 - \varphi_1^0$

For small [A] eqn. (12) can be approximated to

$$\frac{\Delta f}{[A^-]} = \beta_1 \frac{\Delta\,\varphi_1}{[A^-]} + (\beta_1 - l_1') \cdot l_2' + l_3' - \beta_3 \tag{13}$$

β_1 can thus be obtained by plotting $\Delta f/[A^-]$ against $\Delta\ \varphi_1/[A^-]$. When β_1 is known $(\beta_2 - l_2')$ can be calculated from eqn. (10). This makes it possible to calculate the function g.

By introducing the functions φ_1, f and g eqn. (4) can be written in the alternate form

$$g = \beta_2\varphi_1 - X_3 + l_0 l_3' \varphi^{-1} \tag{14}$$

At small ligand concentrations the last term in eqn. (14) is approximately equal to l_3' and X_3 equal to β_3. Thus g is a linear function of φ_1 with the slope β_2 and the intercept $-(\beta_3 - l_3')$.

It is desirable to know the magnitude of l_2'. This can be obtained from the expression [3]

$$\frac{\beta_1^2}{\beta_2} = \frac{(l_1')^2}{l_2'} \tag{15}$$

If the term $l_3'[A^-]$ in eqn. (11) can be neglected in comparison with l_2' in a wide range of $[A^-]$ then the constants of higher complexes are obtained from corresponding values of [A] and X_3 using the approximation

$$X_3 = \beta_2\ \varphi_1 - g \tag{16}$$

which also is obtained from eqn. (14) if $l_0 l_3' \varphi^{-1}$ is neglected.

Eqn. (13) cannot always be used for graphical evaluation of β_1 because in some cases $\Delta f/[A^-]$ and $\Delta\ \varphi_1/[A^-]$ are nearly constant over the entire [A]-range investigated. In this case the quotient $\Delta f/\Delta\ \varphi_1$, can be used as a first approximation of β_1. Using this value the order of magnitude of β_2 and β_3 can be obtained from eqns. (10), (8) and (14). The approximate value of β_3 is then used for a better estimate of β_1, and so on until the β-values remain constant.

EXPERIMENTAL

A concentrated plutonium solution was prepared as before [12]. From this concentrated plutonium $-HNO_3$ solution, a stock solution of Pu(IV) was prepared by dilution with 4 M $HClO_4$. The final concentration of the stock-solution was $C_H = 4.25$ M, $C_{HNO_3} = 0.25$ M, $C_{Pu} = 0.5 \times 10^{-3}$ M.

More than 99.5 % of the total amount of plutonium was in the oxidation state + 4. Hydrochloric acid, nitric acid and perchloric acid were all of analytical grade. The ion-exchanger Dowex 50, 50—100 mesh, was converted to the hydrogen form by repeated shaking with 6 M HCl. After saturation it was washed with distilled water and finally dried for 15 h at 40°C. The ion-exchanger was then stored in a closed bottle to keep the water content of the resin constant.

The value of v/m was kept constant (4×10^{-2} l/g) in all measurements thus keeping the volume decrease of the solutions, caused by the swelling of the resin, constant. The swelling factor δ was determined by shaking 250 mg ion-exchanger with 10 ml of 4 M $HClO_4$ and 4 M HNO_3. From the change in hydrogen-ion concentration a value of $\delta = 0.99$ was obtained in both cases. The distribution coefficient, φ, was determined by shaking 5 ml of solutions of the following composition to equilibrium at 20° C.

$C_{HClO_4} = 4 - [A]$ M
C_{HNO_3} or $C_{HCl} = [A]$ M
$C_{Pu(IV)} = C'_M$ M
0.125 g Dowex 50

The time necessary for attainment of equilibrium was determined in a separate experiment. The results given in Table 1 show that equilibrium was established after 20 h. A shaking time of 40 h was nevertheless used in most of the experiments.

Table 1. Determination of φ as a function of the shaking time for $[NO_3^-] = 7, 207$ and 707 mM. $C_H = 4$ M, $T = 20°C$, $v/m = 4 \times 10^{-2}$ l/g, $C'_M = 2 \times 10^{-6}$ M

Hours	10	20	60
$[NO_3^-]$ mM	$\varphi \times 10^3$ l/g		
7	559	948	922
207	337	341	333
707	76	72	77

The plutonium concentration of the above solutions was determined by measuring the α-activity of 0.1 ml of the solution before addition of ion-exchanger and after equilibrium was attained. The analytical procedure has been described before [12]. Since the activity of the solution is proportional to the plutonium-concentration, φ can be calculated from the following expression

$$\varphi = 4 \times 10^{-2} \left(\frac{I_0}{I} - \delta\right)$$

where I_0 is the activity in cpm/0.1 ml of the solution before addition of ion-exchanger and I is the activty in the same units after equilibrium.

RESULTS

The plutonium(IV)-nitrate system

The distribution fucntion φ was determined at three different C'_M, Fig. 1. From these values φ, at a constant load, $C_{MR} = 1.2 \times 10^{-7}$ moles/g, was obtained by interpolation. Only a slight variation of φ with C_{MR} was obtained,

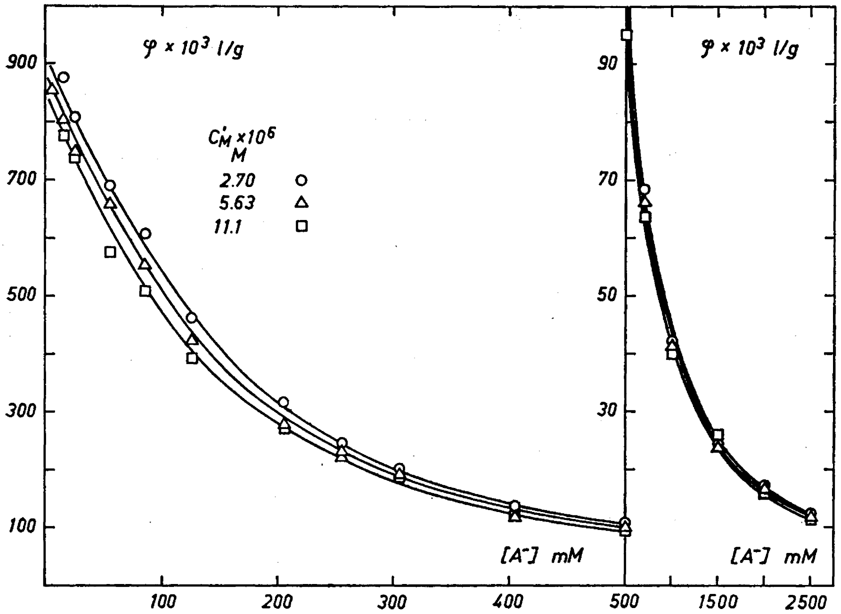

Fig. 1. φ for the nitrate complex system of plutonium(IV). The points refer to determination with different values of C_M', as indicated by the scheme given in the figure. Note that the ordinate is expanded and the abscissa contracted for $[A^-] \geq 500$ mM. $C_H = 4$ M, $v/m = 4 \times 10^{-3}$ l/g, $T = 20°C$.

Table 2. In Table 3 the values of φ_1, f, g, $\Delta f/[A^-]$ and $\Delta\varphi_1/[A^-]$, valid for $C_{MR} = 1.2 \times 10^{-7}$ moles · g^{-1}, are given. l_0, φ_1^0 and f° are determined with a fairly good accuracy by the graphical extrapolation shown in Figs. 2, 3 and 4. The values obtained are

$$l_0 = 0.92 \pm 0.02 \text{ g/l}$$
$$\varphi_1^0 = 5.3 \pm 0.2 \text{ M}^{-1}$$
$$f^\circ = 6.0 \pm 0.5 \text{ M}^{-2}$$

In Fig. 5, $\Delta f/[A^-]$ has been plotted as a function of $\Delta\varphi_1/[A^-]$. A straight line with the slope $\beta_1 = 5.5 \pm 0.2$ M^{-1} is obtained. With known values of f°, β_1 and φ_1^0 a value of $(\beta_2 — l_2') = 23 \pm 3$ M^{-2} is calculated from eqn. (10). Using this value the function g is determined. The results are given in Table 3. Fig. 6 gives a plot of g against φ_1. From the resulting straight line a value of of $\beta_2 = 23.5 \pm 1$ M^{-2} is obtained. The intercept gives a very uncertain value ofβ_3 —$l_3' = 15 \pm 10$ M^{-3}, which can be put equal to β_3 since l_0 is much greater than l_3, *i.e.* Pu^{4+} is more strongly sorbed on the ion exchanger than $Pu(NO_3)_3^+$. Another value of β_3 is obtained from eqn. (16), Table 3, which gives $\beta_3 = 11 \pm 7$ M^{-3}.

Table 2. Corresponding values of [A], C_{MR} and φ for the nitrate system taken from Fig. 1. $C_H = 4$ M, $T = 20°C$.

[A] mM	$C_{MR} \times 10^7$ moles/g	$\varphi \times 10^3$ l/g	$C_{MR} \times 10^7$ moles/g	$\varphi \times 10^3$ l/g	$C_{MR} \times 10^7$ moles/g	$\varphi \times 10^3$ l/g
5	1.03	894	2.16	864	4.25	840
15	1.03	848	2.14	820	4.23	792
25	1.03	803	2.14	779	4.22	748
55	1.02	684	2.12	657	4.17	628
85	1.01	575	2.11	553	4.14	522
125	0.99	462	2.04	422	4.05	420
205	0.96	321	1.99	298	3.88	281
255	0.93	244	1.92	235	3.76	222
305	0.89	191	1.86	188	3.62	178
405	0.84	137	1.72	129	3.34	123
505	0.79	107	1.62	101	3.12	95
705	0.68	68	1.40	66	2.73	64
1 000	0.56	43.0	1.14	41.5	2.22	40.0
1 500	0.42	25.8	0.86	24.5	1.65	23.5
2 000	0.33	17.5	0.67	17.1	1.27	16.0
2 500	0.25	12.3	0.52	12.0	1.02	11.8

Table 3. Corresponding values of [A], φ, φ_1, f, g, $\Delta f/[A^-]$, $\Delta\varphi_1/[A]$ and X_3 for the nitrate system. X_3 is calculated according to eqn. (16). $C_H = 4$ M, $T = 20°C$, $C_{MR} = 1.2 \times 10^{-7}$ moles/g.

[A] mM	$\varphi \times 10^3$ l/g	φ_1 M^{-1}	f M^{-2}	g M^{-3}	$\Delta f/[A]$ M^{-3}	$\Delta \varphi_1/[A]$ M^{-2}	X_3 M^{-3}
0	*920*	*5.3*	*6.0*				
5	884						
15	840						
25	798						
55	680	6.4	14.5	189	155	20.0	(−39)
85	570	7.2	16.0	158	118	22.4	11
125	456	8.1	20.7	178	118	22.4	12
205	310	9.6	29.9	221	117	21.0	5
255	240	11.1	36.1	248	118	22.7	13
305	190	12.6	42.8	278	120	23.9	18
405	134	14.5	54.1	326	119	22.7	15
505	103	15.7	62.6	358	112	20.6	11
705	67	18.0	77.4	416	101	18.0	7
1 000	41.5	21.2	96.5	491	91	15.9	8
1 500	24.0	24.8	118.8	576	75	13.0	8
2 000	16.5	27.4	134.2	634	64	11.1	11
2 500	11.6	31.3	155.6	724	60	10.4	12

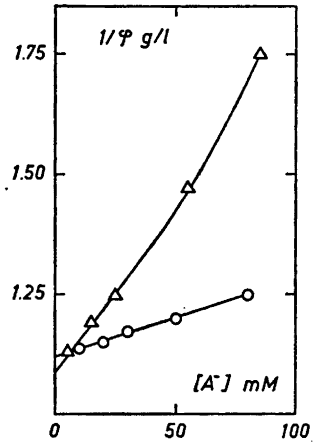

Fig. 2. $1/\varphi$ as a function of [A] for the nitrate △ and chloride O systems. C_H = 4 M, T = 20°C.

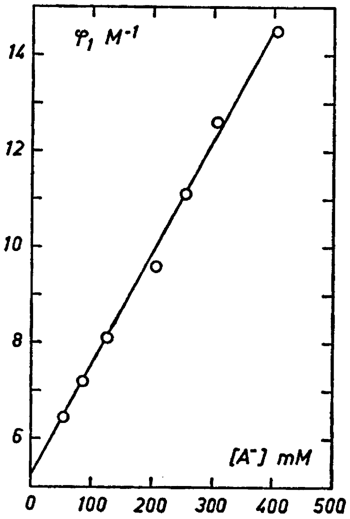

Fig. 3. φ_1 plotted against [A] for the plutonium(IV) nitrate system.

The value of $\beta_1—l'_1 = 5.3 \pm 0.2$ M^{-1} and $\beta_1 = 5.5 \pm 0.2$ M^{-1} gives an upper limit of $l'_1 = 0.6$ M^{-1}. Another estimate can be obtained from eqn. (6) which for low values of [A$^-$] can be written as

$$\varphi_1 \approx (\beta_1—l'_1) + \{\beta_2—l'_2—l'_1\ (\beta_1—l'_1)\}\ [A]$$

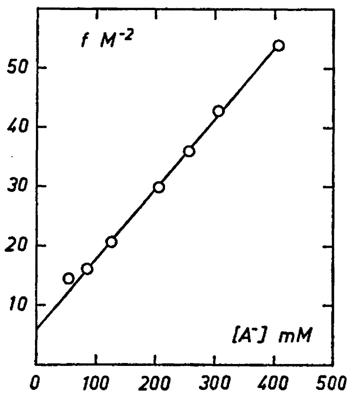

Fig. 4. The function f for the plutonium (IV) nitrate system.

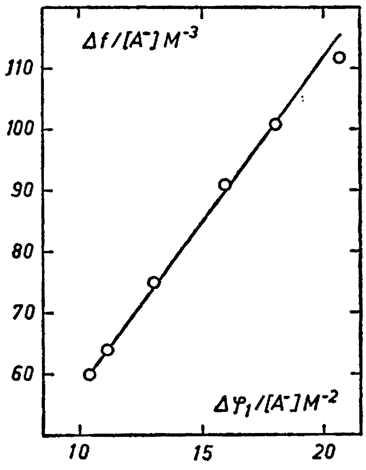

Fig. 5. Δf/[A] plotted against $\Delta\ \varphi_1$/[A] for the plutonium(IV) nitrate system.

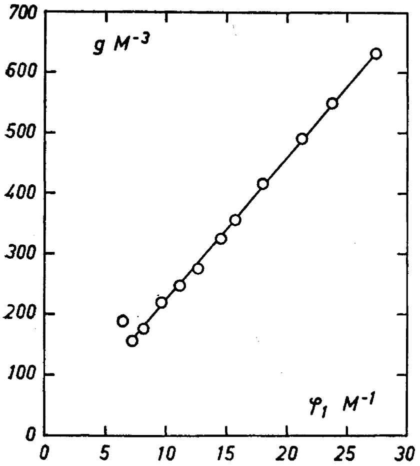

Fig. 6. g as a function of φ_1 for the plutonium(IV) nitrate system.

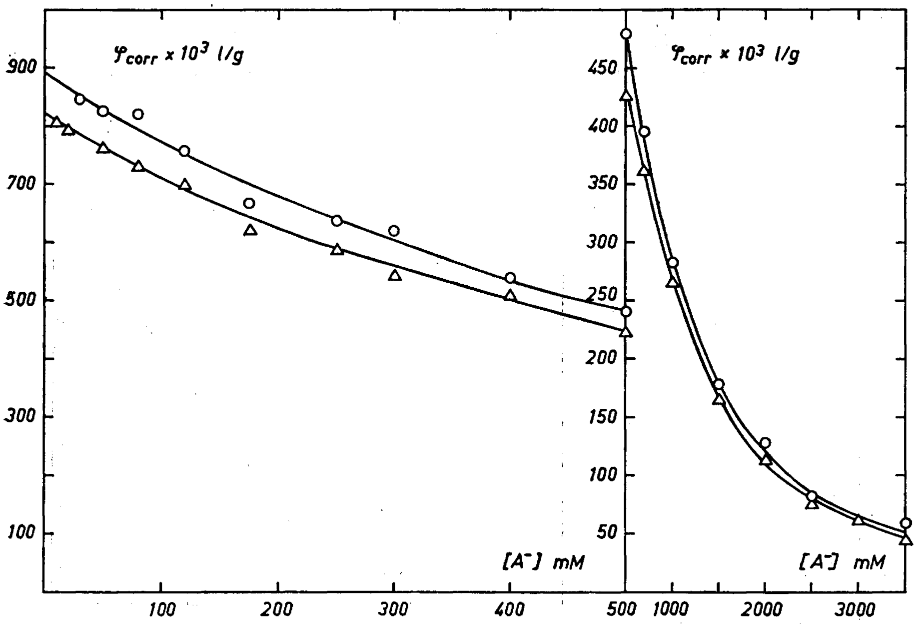

Fig. 7. φ_{corr} for the chloride complex system of plutonium(IV). Note that the ordinate is expanded and the abscissa contracted for $[\mathrm{A}^-] \geq 500$ mM. $C_{\mathrm{M}}' = 3.15 \times 10^{-6}$ M ○, $C_{\mathrm{M}}' = 6.30 \times 10^{-6}$ M △. $C_{\mathrm{H}} = 4$ M, $v/m = 4 \times 10^{-2}$ l/g, $T = 20$°C.

Table 4. Corresponding values of [A], C_{MR}, and φ_{corr} for the chloride system taken from Fig. 7. $C_H = 4$ M, $T = 20°C$.

[A] mM	$C_{MR} \times 10^7$ moles/g	$\varphi \times 10^3$ l/g	$C_{MR} \times 10^7$ moles/g	$\varphi \times 10^3$ l/g
10	1.20	878	2.40	815
20	1.20	868	2.40	803
30	1.20	855	2.40	792
50	1.20	832	2.40	772
80	1.20	800	2.40	741
120	1.20	760	2.38	700
175	1.19	708	2.37	650
250	1.19	640	2.36	587
300	1.19	602	2.35	574
400	1.18	537	2.34	497
500	1.16	480	2.31	447
700	1.15	385	2.28	365
1 000	1.10	281	2.19	268
1 500	1.03	177	2.03	165
2 000	0.96	120	1.85	111
2 500	0.84	82	1.66	78
3 000	0.79	67	1.51	60
3 500	0.72	53	1.36	47

Table 5. Corresponding values of [A], $\varphi_{corr.}$, φ_1, f, g, $\Delta f/\Delta \varphi_1$ and X_3 for the chloride system. X_3 is calculated according to eqn. (16). $C_H = 4$ M, $T = 20°C$, $C_{MR} = 1.2 \times 10^{-7}$ moles/g.

[A] mM	$\varphi_{corr} \times 10^3$ l/g	φ_1 M^{-1}	f M^{-2}	g M^{-3}	$\Delta f/\Delta \varphi_1$ M^{-1}	X_3 M^{-3}
0	*892*	*1.25*	*0.56*			
10	878					
20	868					
30	855					
50	832					
80	800					
120	760					
175	708					
250	640					
300	602	1.61	0.82	1.13	0.72	0.8
400	536	1.66	1.05	1.80	1.20	0.2
500	480	1.72	1.21	2.04	1.38	0
700	384	1.89	1.45	2.27	1.39	0
1 000	280	2.19	1.80	2.56	1.32	0.1
1 500	174	2.75	2.44	3.16	1.25	0.1
2 000	118	3.28	3.08	3.77	1.24	0.2
2 500	80	4.06	3.95	4.65	1.21	0.2
3 000	64	4.31	4.37	5.01	1.25	0.2
3 500	51	4.71	4.90	5.50	1.25	0.2

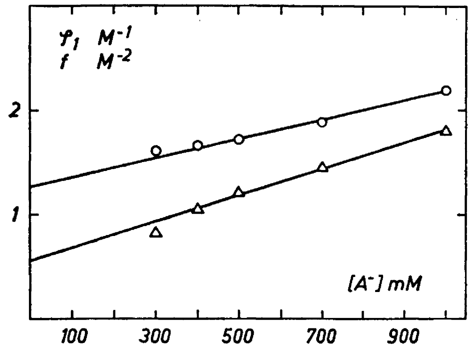

Fig. 8 φ_1 (O) and f (△) as functions of [A] for the plutonium(IV) chloride system.

i.e., φ_1 is a linear function of [A], *cf.* Fig. 3. The slope of the line gives a value of $(\beta_2—l_2')—l_1'\ (\beta_1—l_1') = 23 \pm 2\ \mathrm{M}^{-2}$ which together with the previously determined values of $\beta_2—l_2' = 23 \pm 3\ \mathrm{M}^{-2}$ and $\beta_1—l_1' = 5.3 \pm 0.2\ \mathrm{M}^{-1}$ gives $l_1' < 1\ \mathrm{M}^{-1}$. From (15) and the definion of l_j the maximum values of the coefficients l_1 and l_2 can be calculated to be $l_1 < 0.1$ l/g and $l_2 < 0.01$ l/g.

The plutonium(IV)-chloride system

φ was determined at two different C_{M}' (Fig. 7) and the interpolation to a constant load was made as before. In this case too, the variation of φ with C_{MR} was slight, Table 4. The measured φ-values must be corrected for the complex formation caused by the presence of nitrate ion in the Pu(IV) stock solution. This has been done in the following way: Because of the low nitrate ion concentration (≤ 0.010 M) in the solutions only the prescence of the first nitrate complex has to be considered.

$$\varphi = \frac{l_0\ (1 + l_1'[\mathrm{Cl}^-] + l_2' \cdot [\mathrm{Cl}^-]^2 + l_3' \cdot [\mathrm{Cl}^-]^3 + l_1'^{(\mathrm{NO_3})}[\mathrm{NO_3^-}]}{X_{\mathrm{Cl}} + \beta_1^{(\mathrm{NO_3})} \cdot [\mathrm{NO_3^-}]}$$

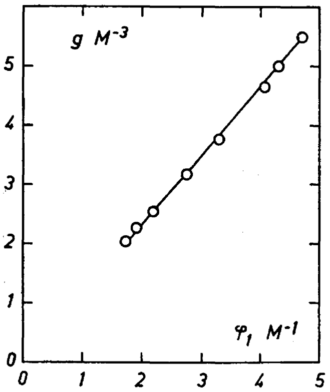

Fig. 9. g as function of φ_1 for the plutonium (IV) chloride system.

Table 6. Formation constants for nitrate and chloride complexes of Pu^{4+}.

	Reference	Medium	β_1 M^{-1}	β_2 M^{-2}	β_3 M^{-3}
NO_3^-	5	$I = 2$ M; 2 M $HClO_4$; $T = 25°C$	2.9		
	6	$I = 1$ M; 1 M $HClO_4$; $T = 25°C$	3.48		
	This work	$I = 4$ M; 4 M $[H^+]$; $T = 20°C$	5.5 ± 0.2	23.5 ± 1	15 ± 10
Cl^-	5	$I = 2$ M; 2 M HNO_3; $T = 25°C$	0.38		
	6	$I = 1$ M; 1 M $HClO_4$; $T = 25°C$	0.58		
	7	$I = 2$ M; 2 M $HClO_4$; $T = 25°C$	0.59		
	7	$I = 1$ M; 1 M $HClO_4$; $T = 25°C$	0.56		
	13	$I = 1$ M; 1 M $HClO_4$; $T = 25°C$	2.10		
	This work	$I = 4$ M; 4 M $[H^+]$ $T = 20°C$	1.4 ± 0.2	1.2 ± 0.2	0.1 ± 0.1

The term $l_1'^{(NO_3)} \cdot [NO_3^-]$ is $< 0.6 \times 0.01$ and is negligible compared with 1. In the denominator the term $\beta_1^{(NO_3)}$. $[NO_3^-]$ varies from 0.03 to 0.06 and is not negligible for small values of $[Cl^-]$ when $X_{Cl} \approx 1$. Using the above approximation φ can be expressed as

$$\varphi = \frac{l_0 \cdot (1 + l_1'[Cl^-] + l_2' \cdot [Cl^-]^2 + l_3'[Cl]^3)}{X_{Cl}} \left(1 + \frac{5.5 \times [NO_3^-]}{X_{Cl}}\right)^{-1}$$

$$i.e., \varphi_{corr} = \varphi \cdot \left(1 + \frac{5.5[NO_3^-]}{X_{Cl}}\right)$$

where φ_{corr} is the distribution coefficient that would be obtained in abscence of nitrate. φ_{corr} was calculated using approximate values of $\beta_1 = 2$ M^{-1} and $\beta_2 = 10$ M^{-2} for the evaluation of X_{Cl} in the correction term. The φ-values obtained in the following calculation were then used to get a better estimate of φ_{corr} and better values of the complexity constants. The β-values obtained using the second φ_{corr} were the same as the ones obtained in the first approximation. Corresponding values of φ_{corr}, φ_1, f, $\Delta f/\Delta\varphi_1$ and [A] are given in Table 5. The graphical determination of l_0, $\overset{0}{\varphi_1}$ and $f°$ are given in Figs. 2 and 8.

$$l_0 = 0.89 \pm 0.02 \text{ g/l} \qquad \overset{0}{\varphi_1} = 1.25 \pm 0.05 \text{ M}^{-1} \qquad f° = 0.56 \pm 0.06 \text{ M}^{-2}$$

In this case β_1 can not be determined graphically from the function $\Delta f/[A^-]$ because the values of $\Delta f/[A^-]$ and $\Delta\varphi_1/[A^-]$ are nearly constant over the entire $[A^-]$ range, Table 5. Instead β_1 is calculated from eqn. (9) using the approximate value of l_1 obtained from the nitrate system. In this way a value of $\beta_1 = 1.4 \pm 0.1$ M^{-1} is obtained. Using this value of β_1 the function g is calculated according to eqn. (8). From a plot of g as a function of φ_1, Fig. 9., β_2 is found to be 1.2 ± 0.2 M^{-2}. β_2 can also be determined from eqn. (10) if l_2' is neglected. We obtain in this case $\beta_2 = 1.2 \pm 0.2$ M^{-2}. X_3 calculated from eqn.

Table 7. The nitrate and chloride complexes of Zr^{4+}, Th^{+4} and U^{+4}.

	Metal ion	Ref.	Medium	β_1 M^{-1}	β_2 M^{-2}
NO_3^-	Zr^{4+}	14	2 M $HClO_4$ $T = 25°$	2.0	
		15	4 M $HClO_4$ $T = 20°C$	2.20	1.30
	Th^{4+}	16	2 M $HClO_4$ $T = 20°C$	6.0	13.0
		17, 18	5.97 M $NaClO_4$ $T = 25°C$	2.8	1.4
Cl^-	Zr^{4+}	14	2 M $HClO_4$ $T = 25°C$	2.0	
		15	6.54 M $HClO_4$ $T = 20°C$	8.4	21.0
	Th^{4+}	19	4 M $NaClO_4$ $T = 25°C$	1.7	0.16
		17	4 M $NaClO_4$ $T = 25°C$	1.3	0.11
	U^{4+}	20	1 M $NaClO_4$, $[H^+] = 0.6$ M $T = 20°C$	2.0	
		21	2 M $NaClO_4$ $[H^+] = 1$ M $T = 25°C$	1.8 *	
				1.2 *	1.15 *

* Alternative interpretation.

(16) gives a very approximative value of $\beta_3 = 0.1 \pm 0.1$ M^{-3}, Table 5. With this value of β_3 eqn. (13) gives, if l_3' is neglected, $\beta_1 = 1.4 \pm 0.2$ M^{-2} in good accordance with the value calculated from eqn. (9).

The distribution coefficients, l_j, show the sorption of the plutonium complexes to be very low compared with the sorption of the uncomplexed Pu^{4+}-ion.

$$l_0 = 0.9 \text{ l/g} \qquad l_1 < 0.1 \text{ l/g} \qquad l_2 < 0.01 \text{ l/g}$$

This means that the absolute decrease of φ will be so small when PuA_2^{2+} is converted into higher complexes that it is impossible to obtain the higher constants with any accuracy.

DISCUSSION

A comparison between the complexity constants obtained in this work and those obtained by other authors is given in Table 6. It is difficult to make any quantitative comparisons because of the differences in experimental conditions. No values of the higher constants have been previously reported in the literature.

It is also of interest to compare the complexity constants of Pu^{4+} with those of other four-valent ions. Values are given in the literature for nitrate and chloride complexes fo Zr^{4+}, Th^{4+} and U^{4+} but they have usually been measured under other conditions than in this work. The results are summarised in Table 7. The corresponding complexity constants of the four-valent actinide elements all have about the same magnitude. As to Zr^{4+} its chloride complexes are decidedly stronger than those of the actinides. This is to be expected on account of the smaller ionic radius of Zr^{4+} if the complex formation is governed mainly by electrostatic forces which is very likely for complexes of this type. On the other hand, the nitrate complexes of Zr^{4+} seems to be weaker than the corresponding actinide complexes. This is rather unexpected and is possibly an indication of a somewhat different type of bond in these complexes [22].

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