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Radiochimica Acta 13(1): 1-5 (1970)
Radiochim. Acta; 13: No. 1, 1-5 (1970)

Translated from the German
For Oak Ridge National Laboratory
Purchase Order No. 34B-88372
Letter Release No. 13

STS Order No. 11931

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II. NITRATE AND CHLORIDE COMPLEXES OF URANIUM, NEPTUNIUM, PLUTONIUM AND AMERICIUM

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With 1 Figure

(Received 14 October 1968)

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Summary

Stability constants of the nitrato complexes of several actinides have been determined under identical experimental conditions: U-IV, U-VI; Np-IV, Np-V, Np-VI; Pu-III, Pu-IV, Pu-VI; Am-III. The ionic strength was held constant ($\mu = 8$) by addition of $HClO_4$. A collection of known constants is given for comparison. A systematic relation between cationic radius, ionic charge and complex strength within a series of actinides of equal valency or different oxidation states of one element could not be established.

A knowledge of the stability constants of complex compounds of actinides and the ligands of inorganic acids is important particularly for analytical and technological separating processes. With the availability of a larger quantity of data, it should also be possible to draw comparative conclusions concerning the bond conditions in complex actinide ions of identical oxidation state.

In an earlier paper [1] a method was described for the calculation of stability constants from the distribution of a compound in two immiscible liquid phases. In addition to the stability constants, this method furnishes information on the extractibility of the individual elements and thus in turn provides valuable pointers on possible separating techniques.

The stability of some complexes investigated by us have been determined earlier. However, the results are contradictory and rarely refer to similar experimental conditions, so that a comparative study is not possible. In all cases, they are not thermodynamic constants, since the activities of the participating components are not known. In order to circumvent this disadvantage in part, the total ionic concentration is generally maintained constant by the addition of a salt (or acid) which does not participate in complexing so that the activity coefficients will not change significantly with a change in ligand concentration. The stability constants thus obtained admittedly are also only concentration constants and are constant and valid only for the selected conditions.

We investigated the extraction of a number of actinides of different valence under identical conditions and using the computer program described earlier, we determined the number and stability of the complexes present in the aqueous phase.

Experimental

Tri-n-octylamine (distilled at 4 torr and 204°C) dissolved in xylene (0.5 M ~ 21 vol.%) served as the extractant. An ionic strength of $\mu = 8$ was maintained in the aqueous phase by the addition of $HClO_4$. The actinides were added in traces, so that no concentration dependence of the distribution coefficients was to be expected. Standard methods which will not be described further here were used for shaking of the samples and measurement of the α-activity. Before extraction, the organic solution was treated with aqueous solutions of suitable HNO_3 and HCl concentration with formation of the amine salt. All vessels were of plastic in order to avoid losses (especially of Pu) by adsorption on the vessel wall. The experiments were performed at 20°C ± 1°C.

The presence of a single oxidation state is an important requirement for the quality of the stability constants. We therefore investigated only the complexing of actinides in such oxidation states which could be prepared quantitatively for the duration of the experiments with some certainty.

U(IV): Reduction of U(VI) with H_2(Pt sponge), stabilized with urea.

Pu(III): $\mu = 6$; reduction with Fe(II) sulfamate.

Pu(IV): Stabilized with $NaNO_2$.

Pu(VI): Oxidation by $KBrO_3$ (5 h at 95°C).

Np(IV): Reduction with Fe(II) sulfamate, stabilization with urea.

Np(V): Stabilization by $NaNO_2$ (increasing disproportionation at high acid concentrations).

Np(VI): Repeated fuming with 5 M $HClO_4$.

The values of the stability constants calculated for the individual complexes $\beta_n = (MA_n)/(M)(A)^n$ are listed in Table 1. These values allow a calculation of the so-called degree of formation x of each individual complex MA_n in the mixture of the complexes forming stepwise in the aqueous solution:

$$x_{MA_n} = \frac{(MA_n)}{(M_{tot})} = \frac{\beta_n (A)^n}{1 + \sum_{n=1}^{N} \beta_n (A)^n}$$

(A) = ligand concentration.

The degree of formation as a function of the ligand concentration is shown in Figs. 1 a-c (b = number of ligands).

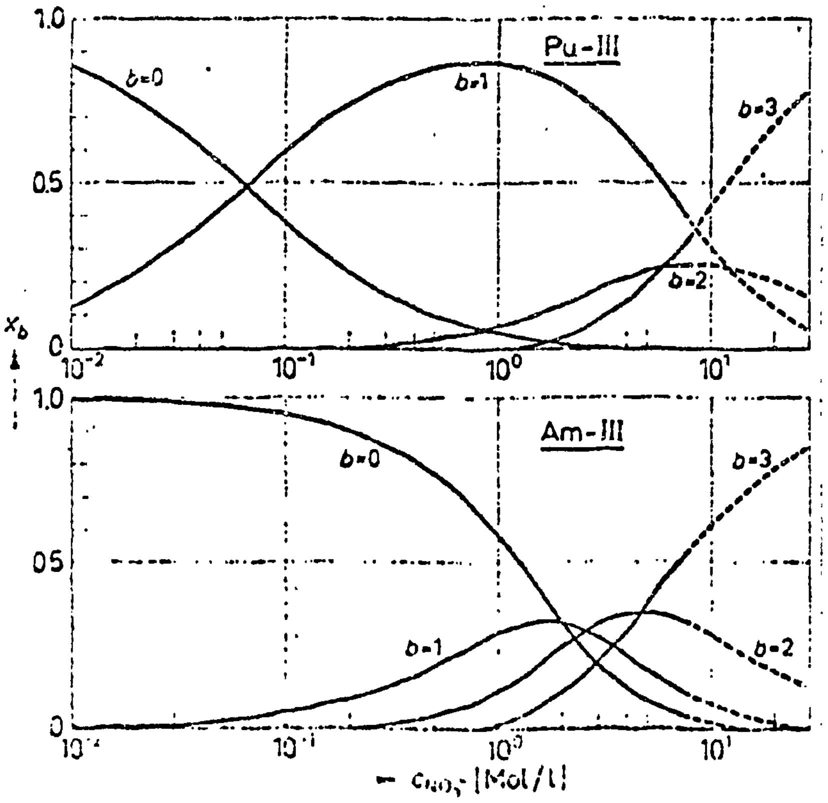

Fig. 1a.--Degree of formation of the nitrate complexes of Pu(III) and Am(III).

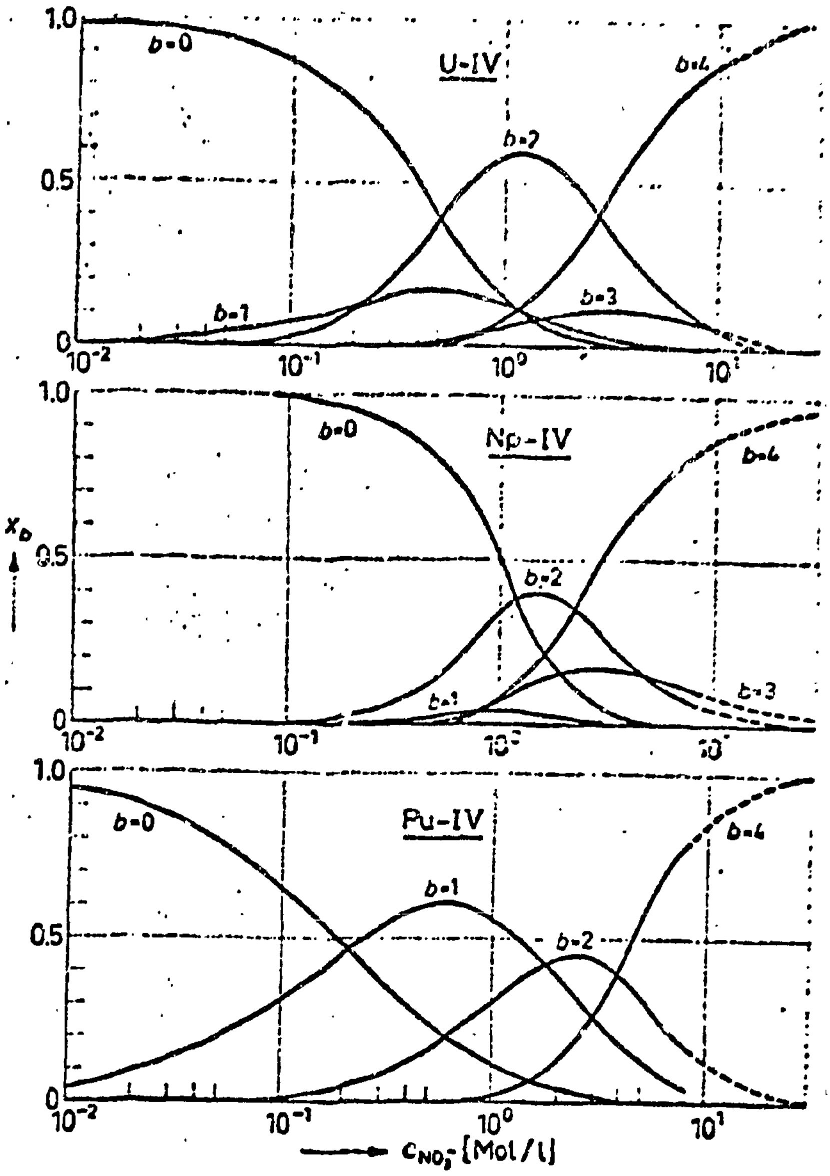

Fig. 1b.--Degree of formation of the nitrate complexes of tetravalent actinides.

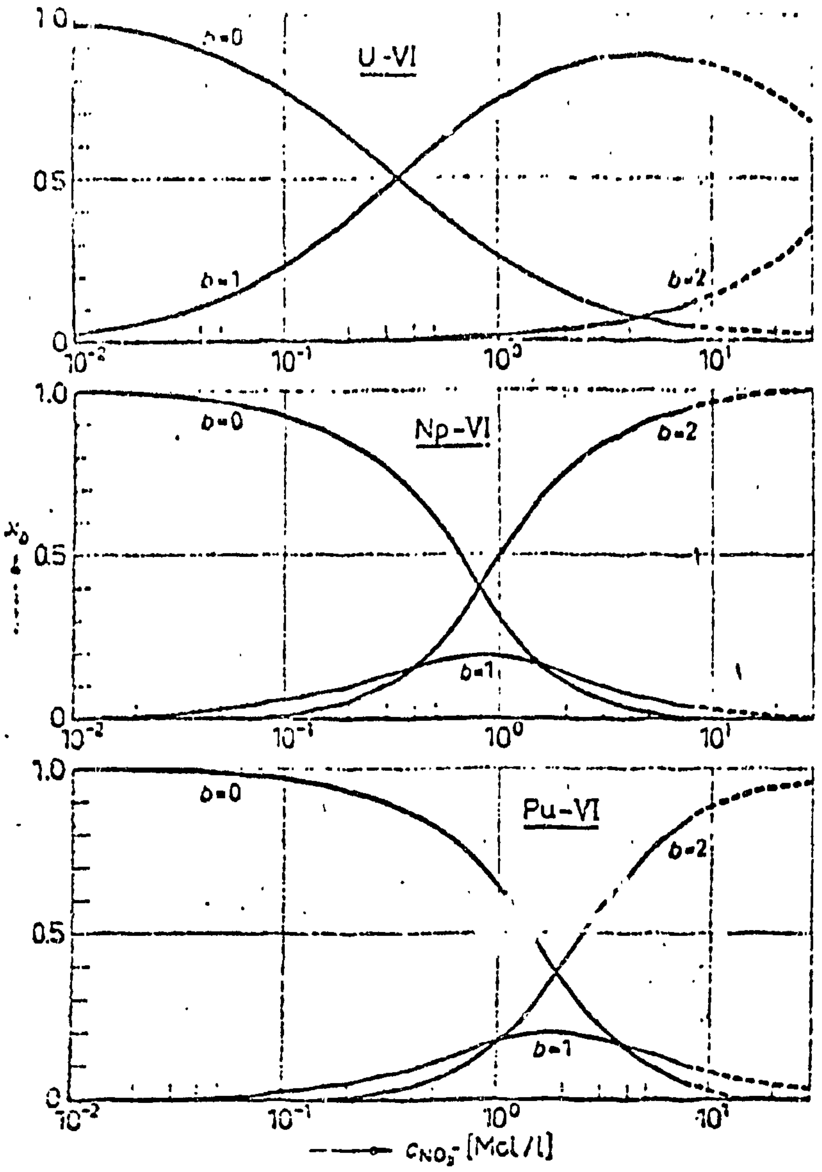

Fig. 1c.--Degree of formation of the nitrate complexes of hexavalent actinides.

Table 1.--Formation constants of the nitrate complexes of some actinides.

Formation reaction	$\beta_n = \frac{[M(NO_3)_n]^{m-n}}{[M^{m+}][NO_3^-]^n}$ U	Np	Pu	Am
$M^{3+} + NO_3^- \rightarrow [M(NO_3)]^{2+}$			15,14	0.47
$M^{3+} + 2\,NO_3^- \rightarrow [M(NO_3)_2]^+$			1,17	0.17
$M^{3+} + 3\,NO_3^- \rightarrow M(NO_3)_3$			0,19	0.04
$M^{4+} + NO_3^- \rightarrow [M(NO_3)]^{3+}$	0,84	0.03	4,88	
$M^{4+} + 2\,NO_3^- \rightarrow [M(NO_3)_2]^{2+}$	3,76	0,68	2,66	
$M^{4+} + 3\,NO_3^- \rightarrow [M(NO_3)_3]^+$	0.37	0.15	0	
$M^{4+} + 4\,NO_3^- \rightarrow M(NO_3)_4$	0,50	0.13	0.19	
$MO_2^+ + NO_3^- \rightarrow MO_2NO_3$		0.53		
$MO_2^{2+} + NO_3^- \rightarrow [MO_2(NO_3)]^+$	2.94	0.57	0.27	
$MO_2^{2+} + 2\,NO_3^- \rightarrow MO_2(NO_3)_2$	0.03	1.57	0.28	

At the start of the analysis of a complex mixture it is usually not known which complexes are formed in the metal-ligand system at all. The maximum coordination number, to the extent to which it is known, gives an indication of the maximum number of possible complexes. Thus, for example, for U(VI) in the nitrate system the following series of complexes would be conceivable with neglect of hydratation: $[UO_2NO_3]^+$, $UO_2(NO_3)_2$, $[UO_2(NO_3)_3]^-$ (max. coordination number 8); for Pu(IV): $[PuNO_3]^{3+}$ $[Pu(NO_3)_2]^{2+}$, $[Pu(NO_3)_3]^+$, $Pu(NO_3)_4$, $[Pu(NO_3)_5]^-$, $[Pu(NO_3)_6]^{2-}$ (max. coordination number probably 12).

Various authors of earlier papers assumed the existence of anionic complexes in aqueous solution at high ligand concentration. This assumption derives partly from the spectroscopic identification of such anions in organic solvents as well as from the crystallization of corresponding compounds. The maxima in the adsorption and extraction curves with the use of anionic exchangers were also interpreted by the presence of anionic complexes in the aqueous solutions or the formation of undissociated acids [e.g.

$HPu(NO_3)_5]$ [2,3,4]. Extraction curves with a maximum as a rule appear only when the ligand is used in the form of an acid (HNO_3, HCl).

The distribution curves measured by us have a continuously rising trend without a maximum. The nitrate ions are added as HNO_3 and the ionic strength ($\mu = 8$) is maintained constant by the addition of suitable quantities of $HClO_4$. The absence of a maximum in the extraction curve indicates that complex anions are not present in significant quantities in the aqueous equilibrium phase. The calculations also resulted in the presence of a negatively charged complex in only one single case.

The thermodynamic significance of the calculated stability constants depends on the validity of a number of hypotheses:

1. The central ions form no complexes with ClO_4.

2. The activity coefficient of the ligand in the aqueous phase changes only insignificantly with a change of the $HA/HClO_4$ ratio. The hydrogen ion activity in the aqueous phase is independent of the ratio $HA/HClO_4$.

3. The activity of the extractant in equilibrium with the aqueous phase is independent of the composition of the latter in the investigated range.

4. Complexing reactions other than those considered in the model [1] do not take place, particularly not the formation of polynuclear complexes, hydroxo-complexes or mixed complexes.

A closer examination of the results (Table 1) does not demonstrate any expected relationships within a series of equivalent ions of different actinides or in a comparison of the ions of different valence of a given element. In many cases the complexing tendency of an ion is correlated with the value of the so-called ionic potential = Z(charge)/r (radius). Accordingly, complexing in equivalent actinide ions should increase with increasing atomic number (decreasing ionic radius) and in different ions of an element should decrease in the sequence $M^{4+} > M^{3+} > MO_2^{2+} > MO_2^{+}$. Since the differences in ionic radii as well as ionic charge are often slight in the actinide series (MO_2^{2+} has an effective charge of the M atom > 2 because of the linear M-O configuration), an exchange of the sequence by influences of a different nature is probable: valence and structure of the ligand, mutual polarizability of the ions, steric hindrance, differences in electron configuration, hybridization of bond orbitals.

The small energy differences of the 5f and 6d electrons of U, Np, Pu, which are available for covalent bonds, in particular facilitate a change of the stability sequence of the nitrate and chloride complexes which are already comparatively weak. Our results suggest the conclusion that a consistent correlation of the complex strength with the ionic characteristics alone, such as charge and radius, is not possible in the lighter half of the actinide series.

Table 2 contains the literature data on the complex formation of actinides investigated in this study. Our values are listed once more for a comparison. In addition to the method, the ionic strength and temperature are listed as the most important experimental parameters. The often considerable discrepancies between the results of different authors are attributable first of all to the different experimental methods and the techniques of evaluation utilized. A critical analysis of the individual data is rarely possible and would go beyond the present scope.

MO_2^{++} nitrates. In the uranyl compounds, uranium has a coordination number of 8 and the nitrate groups are in a coordinate and bidentate bond in the equator plane of the linear O-U-O group. Surprisingly neutron diffraction has shown that the two nitrate groups in the compound $UO_2(NO_3)_2.6H_2O$ are not equivalent [35] even though the two water molecules located in the equator plane in addition are in trans-position. It is possible that this is the reason for the considerable difference of the stability constants found by us for $[UO_2(NO_3)]^+$ and $UO_2(NO_3)_2$. The existence of the anionic complex $[(UO_2(NO_3)_3]^-$ in organic complexes as well as some salts is known. However, in aqueous solutions the displacement of the two H_2O molecules in the trans-position by a nitrate group is evidently made more difficult and occurs only at very high nitrate concentrations:

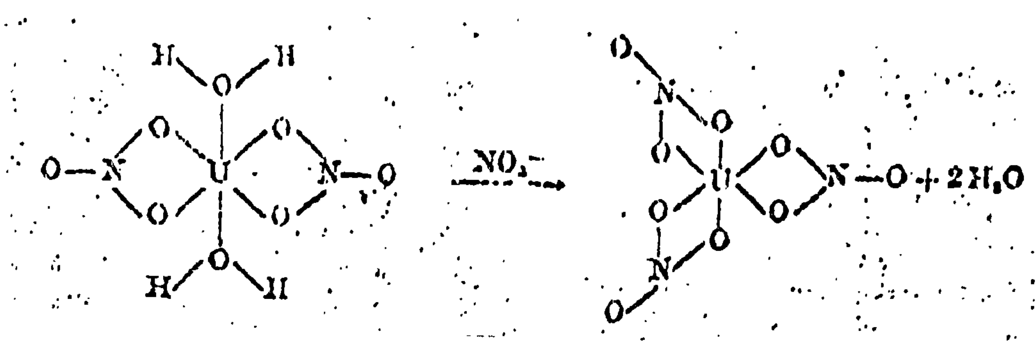

Table 2--Compilation of the stability constants of some actinide complexes.

M	β_1	β_2	β_3	β_4	Ionic strength	Temp. °C	Method	Lit.
U^{4+}	1,6	1,48	0,96	0,35	2	26,5	Sp	5
NO_3^-	1,9	2,03	1,48	0,71	3 $HClO_4$	26,5	Sp	5
	2,3	2,95	2,63	1,51	3,5	26,5	Sp	5
	1,1	0,5	0,1		1 $HClO_4$/ $LiClO_4$	20	Sp	6
	1,15	1,0	0,1		2 $HClO_4$/ $LiClO_4$	20	Sp	6
	1,6	2,0	0,1		3 $HClO_4$/ $LiClO_4$	20	Sp	6
	1,5	6,0	0,1		4 $HClO_4$/ $LiClO_4$	20	Sp	6
	0,84	3,76	0,37	0,50	8 $HClO_4$	20	E	*
UO_2^{++}	0,37				0,54	25	L	7
NO_3^-	0,20				0,82	25	L	7
	0,19				1,06	25	L	7
	0,63				0,71 $HClO_4$	25	E	8
	0,5				1 $HClO_4$	20		9
	0,04	0,04	0,32		1 $NaClO_4$ pH 3	32	KA	10
	0,32				2 $NaClO_4$ pH 3	10	E	11
	0,24				2 $NaClO_4$ pH 3	25	E	11
	0,19				2 $NaClO_4$ pH 3	40	E	11
	0,21				5,4 $NaClO_4$	25	Sp	12
	0,27				7 $NaClO_4$		Sp	12
	2,94	0,03			8 $HClO_4$	20	E	*
UO_2^{++}	1,6				0	25	Sp	14
Cl^-	2,4				var 0 korr	25	P,Sp	13
	2,42				0,54 $NaClO_4$	25	L	7
	0,89				0,82 $NaClO_4$	25	L	7
	1,40				1,06 $NaClO_4$	25	L	7
	0,79				1 $NaClO_4$	20	P	9
	0,50				$NaClO_4$	20	Sp	9
	2,0				1 $HClO_4$ $NaClO_4$	32	KA	10
	0,57				2 $NaClO_4$	10	E	11
	0,87				$NaClO_4$	25	E	11
	1,1				$NaClO_4$	40	E	11
	44				$NaClO_4$ pH 0,5	40	Sp	15
	2	0,2	0,004				E	16
	1,8				KNO_3 ges.	—3	fp	17
	0,82	0,05			8 $HClO_4$	20	E	*
Np^{4+}	2,4				1 $HClO_4$	25	E	18
NO_3^-	2,8				0,5 $HClO_4$	20	E	19
	2,2				1 $HClO_4$	20	E	19
	2,3				1,5	20	E	19
	2,0				2	20	E	19
	0,03	0,68	0,15	0,13	8 $HClO_4$	20	E	*
NpO_2^+	0,53				8 $HClO_4$	20	E	*
NO_3^-								
NpO_2^{++}	0,57	1,57			8 $HClO_4$	20	E	*
NO_3^-								
Pu^{3+}	5,8	14,3	14,4		1 $HClO_4$	20	E	20
NO_3^-	15,1	1,17	0.19		8 $HClO_4$	20	E	*
Pu^{4+}	3,48				1 $HClO_4$	25		21
NO_3^-	2,9				2 $HClO_4$		Sp	22
	5,5	23,5	15		4 $HClO_4$	20	KA	23
	5,5	2,3	1,5		4 $HClO_4$	20	KA	25
NO_3^-	9,4	27	0,41		4 $HClO_4$	25	E	26
	5,2	11.4	13	7.2	4,7 $HClO_4$		E	27
	4,7	4,5	1,5		6	25	E	24
	10	23	0,97		6	25	E	26
	4,88	2,66	0	0,19	8 $HClO_4$	20	E	*
PuO_2^{++}	72	2590			pH 2,7-3,5			28
NO_3^-	0,27	0,28			8 $HClO_4$	20	E	*
Am^{3+}	14,8				0		KA	33
Cl^-	2,25				0,2		KA	33
	1,72				0,5		KA	33
	0,9				1 $HClO_4$	26	KA	32
	1,4				1 $NaClO_4$ pH 3	26	KA	32
	0,25	0,38			$NaClO_4$ pH 3		E	32
	0,9				1 $HClO_4$	22	E	29
	0,69	0,18			4 $HClO_4$	20	KA	34
Am^{3+}								
NO_3^-	1,82				1 $HClO_4$	22	E	29
	4,0				1 NH_4ClO_4 pH 1,5	20- 25	KA	30
	1,8				1 $HClO_4$	25	E	31
	1,6				1 $NaClO_4$ pH 3	26	KA	32
	1,4	0,4			1 $HClO_4$	26	KA	32
	0,55	1,5			1 $NaClO_4$ pH 3	26	E	32
	0,47	0,17	0,04		8 $HClO_4$	20	E	*

AA : Anionic exchange
E : Extraction
KA : Cationic exchange
L : Conductivity
P : Potentiometry
Sp : Spectrophotometry
R : Reduction
fp : Melting point
var 0 korr : Ionic strength varied; was corrected to $\mu = 0$ by calculation
* : Measurements of this study

Nothing is known about the structure of the corresponding nitrate complexes of Np and Pu. However, if we assume that they have a similar hexagonal configuration, the differences in the stability constants (Table 3) must be sought primarily in the different electron configurations with corresponding hybridization possibilities (especially d^2sf^3).

Table 3.--Stability constants of nitrate complexes of hexavalent actinides ($\mu = 8$).

MO_2^{++}	$[MO_2(NO_3)]^+$		$MO_2(NO_3)_2$		$[MO_2(NO_3)_3]^-$
	β_1	K_1	β_2	K_2	β_3
U	$2,94 \pm 0,03$	2,94	$0,03 \pm 0,005$	0.01	—
Np	$0,57 \pm 0.18$	0,57	$1,57 \pm 0.32$	2.75	—
Pu	$0,27 \pm 0,02$	0,27	$0.28 \pm 0,014$	1,04	—

$$\beta_n = \prod_{i=1}^{n} K_i$$

Table 4.--Stability constants of nitrate complexes of tetravalent actinides.

M^{4+}	$[M(NO_3)]^{3+}$	$[M(NO_3)_2]^{2+}$	$[M(NO_3)_3]^+$	$M(NO_3)_4$
	β_1	β_2	β_3	β_4
U	0.84	3,76	0,37	0,50
Np	0,03	0,68	0,15	0,13
Pu	4,88	2,66	0	0,19

It is known that the energies of the 5f, 6d, 7s and 7p orbitals are of comparable magnitude particularly between uranium and americium and that the energies necessary for electron transitions are in the range of the chemical bond energies.

M^{4+}-nitrates. Little is known about the structure of the nitrates of tetravalent actinides. Thorium forms a complex anion $[Th(NO_3)_6]^{2-}$ in which Th has a coordination number of 12 and the nitrate groups are again bidentate.

The higher values of β_2 and β_4 (Table 4) compared to β_1 and β_3 (except $\beta_{1\,Pu}$) indicate the coordination of two O-atoms each of one NO_3^-. Again one can not detect a complex strength sequence $U < Np < Pu$ determined by the size and charge of the ion. The literature data also do not show such a general tendency.

The strength of the M^{3+}-complexes is surprising; however, only the values of Pu and Am are available for their comparison and for these, Pu > Am.

If we compare the stability of the nitrate complexes of the different valence states of an element, we find a good agreement of the stability sequence with the sequence of the ionic potential Z/r for Pu but not for Np (Table 5). This tendency is particularly pronounced in the highly stable EDTA complexes of Pu [36].

Table 5.--Dependence of the stability constants on the Z/r ratio.

	Radius (Å)		NO_3^-	$(EDTA)^{4-}$	NO_3^-
	Pu	Z/r	β_2(Pu)	log β_1 (Pu)	β_1 (Np)
M^{4+}	0,90	4,44	2,66	24,2	0,03
M^{3+}	1,03	2,91	1,17	18,3	—
MO_2^{2+}	0,81	2,47	0,28	16,2	0,57
MO_2^{+}	0,87	1,15	—	10,2	0,53

In general, the nitrate ion is a better complex former than the halide ions, since the NO_3^--group is coordinated in bidentate manner and displaces 2 molecules of water. In the three systems which we investigated comparatively with NO_3^- and Cl^- (U(IV), Np(V), Am(III)), this sequence is not valid in Am^{3+}, the chloride complexes of which are considerably more stable than the corresponding nitrate complexes.

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