

## The Fluoride Complexes of Neptunyl(VI)

STEN AHRLAND and LARS BRANDT

*Department of Inorganic Chemistry, University of Lund, Lund, Sweden*

The complex formation between neptunyl(VI) and fluoride ions in aqueous solution has been investigated at 21°C by means of an extraction method, involving equilibration of the neptunyl(VI) between the aqueous phase and a solution of dibutyl phosphate (DBP) in carbon tetrachloride. In order to prevent the hydrolysis of neptunyl(VI), and also in order to keep the DBP in the organic phase, as is desired, the aqueous phase must have a fairly high acidity. As ionic medium in this phase, 1 M perchloric acid has therefore been chosen. The volatility of this medium also facilitates the analytical procedure.

Within the range of concentrations investigated (neptunyl(VI)  $\leq 0.44$  mM; hydrogen fluoride  $\leq 4.51$  M), only the two complexes  $\text{NpO}_2\text{F}^+$  and  $\text{NpO}_2\text{F}_2$  are formed. Their "acid" stability constants are  $\beta_1^* = 8.6 \pm 2.1$  and  $\beta_2^* = 13 \pm 3$ , respectively. Further, the constant for the DBP extraction reaction (eqn. (1) below) is  $K = (2.0 \pm 0.1) \times 10^4$ .

Remarkably enough, the fluoride complexes of neptunyl(VI) are weaker than those of uranyl(VI).

The neptunium(VI) fluoride system of complexes in aqueous solution has not been investigated previously. At least partly, this certainly depends upon the experimental difficulties created by the strongly oxidizing properties of neptunium(VI).<sup>1</sup> Thus iron(II) is oxidized to iron(III) which prevents the use of the "ferric" method successfully applied to the fluoride system of neptunium(IV).<sup>2</sup> Even organic ion exchangers are slowly oxidized<sup>3,4</sup> so that the very general method of measurement depending upon the distribution of the metal species between the aqueous phase and a cation exchanger also seems to be unsuitable. There still remains the possibility of applying a solvent extraction method, however. After some trying, a workable extracting system has also really been found, *viz.* a solution of dibutyl phosphate, DBP, in carbon tetrachloride. This system is only very slowly oxidized by neptunium(VI), and it is moreover possible to choose the concentration of DBP so that the distribution of neptunium between the two phases can be conveniently and accurately measured. Besides DBP, tributyl phosphate, TBP, and thenoyltrifluoroacetone, TTA, have been tried as auxiliary complexing ligands in the carbon tetrachloride phase. Contrary to DBP, however, they both caused a reduction

of neptunium(VI), extensive enough to make them useless for the present purpose.

In order to make a direct comparison possible with previous measurements on the uranyl fluoride system,<sup>5</sup> the present investigation has been carried out with an ionic strength  $I = 1$  M in the aqueous phase, and at a temperature of 21°C. To facilitate the preparation of samples for  $\alpha$ -counting (*cf.* below), 1 M perchloric acid was used as an ionic medium in all series of measurement which were actually utilized for the calculation of the stability constants, and the ligand was added as hydrogen fluoride solution. It has been assumed that this qualitative change from the  $\text{Na}^+, \text{H}^+$  perchlorate medium used for the uranyl system<sup>5</sup> does not essentially detract from the validity of the comparison intended.

To be able to write a correct formula for the distribution ratio between the aqueous and organic phases, one has to know the composition of the neptunium-DBP species in the organic phase, and also whether such species possibly exist in the aqueous phase. Very probable answers to these questions can be deduced from the work of Dyrssen and Krašovec<sup>6</sup> on the uranium(VI)-DBP-chloroform system, but to confirm these, the hydrogen ion concentration in the aqueous phase has to be varied, as well as the concentration of DBP in the organic phase. It is then necessary to exchange part of the perchloric acid for sodium perchlorate which somewhat complicates the preparation of the  $\alpha$ -samples, as described below.

Even in the neptunium(VI)-DBP-carbon tetrachloride system, a slight reduction of the neptunium gradually occurs, possibly induced by products formed by the radiation of the active nuclides present, *viz.*  $^{237}_{93}\text{Np}$  and its daughter  $^{233}_{91}\text{Pa}$ . The latter is a  $\beta^-$ -emitter with  $t_{1/2} = 27$  d; it will thus rather soon reach radioactive equilibrium with its parent. The energy of its radiation is quite low compared with that of the  $\alpha$ -emitting  $^{237}_{93}\text{Np}$ , however, and the main radiochemical effect will therefore be due to the latter nuclide.

A self-reduction caused by  $\alpha$ -radiation is known to take place in solutions of plutonium(VI), containing  $^{239}_{94}\text{Pu}$  (Ref. 1, p. 325). Now the half-life of this nuclide (24 300 y) is about 100 times shorter than that of  $^{237}_{93}\text{Np}$  ( $2.2 \times 10^6$  y). Under otherwise equal conditions, the effect should thus be much less marked for solutions containing  $^{237}_{93}\text{Np}$ . This is in fact also the case. For neptunium(VI), it is after all possible to find a workable organic extracting system while plutonium(VI) is fairly rapidly reduced even in pure aqueous solutions, in spite of the fact that neptunium(VI) is *per se* the stronger oxidant.

To prevent the reduction of neptunium(VI) in the present system, a slight quantity of permanganate ion has been added to the aqueous phase (to an initial concentration of 0.2 mM). As long as permanganate is still there (which is easily discernible from its colour), no reduction of neptunium(VI) occurs, as is evident from the constancy and consistency of the distribution results presented below.

## SYMBOLS

$M = \text{NpO}_2^{2+}$ ;  $A = \text{F}^-$ ;  $\text{HA} = \text{HF}$ ;  $h = [\text{H}^+]$ ;  $\text{HB} = \text{dibutyl phosphate (DBP)}$ ;  $\text{B} = \text{anion of DBP}$ ;  $\text{H}_2\text{B}_2 = \text{dimer of DBP}$ ;

$[\ ]$ ,  $[\ ]_o = \text{equilibrium concentrations in the aqueous and the organic phases, respectively.}$

$C_M$ ,  $C_{MO} = \text{total equilibrium concentration of neptunium(VI) in the aqueous and organic phases, respectively.}$

$C_M' = \text{initial total concentration of neptunium(VI) in the aqueous phase.}$

$C_B' = \text{initial total concentration of DBP in the organic phase.}$

$C_A = \text{total concentration of fluoride in the aqueous phase.}$

$q$ ,  $q_0 = \text{the distribution ratio } C_{MO}/C_M \text{ with and without fluoride present.}$

$\beta_n^* = [\text{MA}_n]h^n/[\text{M}][\text{HA}]^n$ ;  $\beta_{nH} = \beta_n^*/h^n = [\text{MA}_n]/[\text{M}][\text{HA}]^n$

$X_H = 1 + \sum_{n=1}^N \beta_{nH}[\text{HA}]^n$ ;  $X_{1H} = (X_H - 1)/[\text{HA}] = \sum_{n=1}^N \beta_{nH}[\text{HA}]^{n-1}$

## CALCULATION OF EQUILIBRIUM CONSTANTS FROM THE MEASURED DISTRIBUTION DATA

Previous measurements of the distribution of DBP between an aqueous phase and several organic solvents indicate that if the concentration of DBP is not very low, it is almost completely dimerized in non-polar solvents like carbon tetrachloride.<sup>7,8</sup> Also in only slightly polar solvents like chloroform, the dimerization is very extensive.<sup>7-9</sup> Provided that the acidity of the aqueous phase is so high that the anion concentration  $[\text{B}]$  is of minor importance, as is the case here, the overall distribution of DBP will then be very much in favour of the organic phase. The investigation of Dyrssen and Krašovec already mentioned<sup>6</sup> has further shown that, for low concentrations of uranium(VI), the only complex formed in a DBP-chloroform phase is  $\text{UO}_2(\text{HB})_2\text{B}_2$  and that no significant amounts of uranyl-DBP-complexes exist in the aqueous phase. It may then be assumed that the extraction of neptunium(VI) into the DBP carbon tetrachloride phase takes place according to the reaction



Hence

$$K = \frac{[\text{M}(\text{HB})_2\text{B}_2]_o h^2}{[\text{M}][\text{H}_2\text{B}_2]_o^2} \quad (2)$$

If no fluoride is present, the distribution ratio  $q_0$  should then vary with  $h$  and  $[\text{H}_2\text{B}_2]_o$  according to

$$q_0 = K \frac{[\text{H}_2\text{B}_2]_o^2}{h^2} \quad (3)$$

The validity of this formula has been tested and confirmed as described below.

If fluoride is present in the aqueous phase, then  $C_M$  will be a sum

$$C_M = [\text{M}] + \sum_{n=1}^N [\text{MA}_n] = [\text{M}] X_H \quad (4)$$

while  $C_{MO}$  is still  $= [M(HB)_2B_2]_o$ , as no fluoride complexes are likely to exist in the non-polar organic phase. Thus, with eqn. (2), the following expression is obtained for the distribution ratio:

$$q = K \frac{[H_2B_2]_o^2}{h^2} \cdot \frac{1}{X_H} \quad (5)$$

Eqn. (4), and hence also eqn. (5), presumes that only mononuclear fluoride complexes are formed. Only in this case,  $q$  will be independent of  $[M]$ , and hence of  $C_M$ . The truth of the assumption made can therefore be tested by measuring  $q([HA])$  for different values of  $C_M$ .

From eqn. (5), the function  $X_H/K$  can be computed for various  $C_A$  from quantities that can be measured or calculated, *viz.* as  $[H_2B_2]_o^2/qh^2$ . Further, in the present measurements  $C_M \ll C_A$ , and therefore  $C_A \approx [HA]$ . Consequently,  $X_H/K$  will be known as a function of  $[HA]$ , and from this function the constants can be calculated according to the extrapolation method of Fronæus.<sup>10</sup>

For the calculation of  $[H_2B_2]_o$ , corrections have to be introduced for the amount of DBP present as other species in the two phases. As these are of equal volume, the following formula is valid:

$$2[H_2B_2]_o = C_B' - [HB]_o - [HB] - [B] - 4[M(HB)_2B_2]_o \quad (6)$$

The correction terms are all small, their sum never exceeding  $\approx 10\%$  of  $C_B'$ . The last one is evidently  $= 4C_{MO}$ ; the other ones have been calculated from the constants determined by Hardy and Scargill<sup>8</sup> ( $K_d$  and  $K_2$ ) and by Dyrssen<sup>9</sup> ( $K_a$ ) as follows:

$$K_a = h[B]/[HB] = 10^{-1.00}; \quad K_d = [HB]_o/[HB] = 10^{-0.91}; \\ K_2 = [H_2B_2]_o/[HB]_o^2 = 10^{5.33}$$

These constants have all been determined under conditions different from those chosen for this investigation ( $K_d$  and  $K_2$  in 1 M HNO<sub>3</sub>;  $K_a$  in 0.1 and 1 M (H<sup>+</sup>, Na<sup>+</sup>)ClO<sub>4</sub>; all at 25°C) but for the present purpose they are nevertheless certainly adequate.

## EXPERIMENTAL

*Chemicals.* The nuclide <sup>237</sup>Np was obtained from A.E.R.E., Harwell, as neptunium(IV) oxide. A stock solution of neptunium(VI) in 1 M perchloric acid was prepared as follows. The oxide ( $\approx 100$  mg) was dissolved in  $\approx 20$  ml concentrated perchloric acid, containing 50 mg sodium bromate as an extra powerful oxidant (Ref. 1, p. 31) and the solution was evaporated to dryness. To make sure that the excess of bromate was certainly destroyed, the residue was again dissolved in concentrated perchloric acid and the solution evaporated to dryness. The stock solution was then prepared by dissolving the residue in 1 M perchloric acid. Its concentration was around 20 mM, as determined by  $\alpha$ -counting in known geometry.<sup>2</sup> DBP was purified according to the procedure recommended in Ref. 7.

The other chemicals were of analytical grade and used without further purification.

*Procedure.* For equilibration, equal volumes (5 ml) of the aqueous and the organic phases were shaken at 200 cycles/min for 1 h. Under these conditions, equilibrium was attained with ample margin. The phases were then separated by centrifugation and the distribution  $q$  determined by  $\alpha$ -counting on dry and thin samples prepared from both phases.<sup>2</sup> For the main series, where both phases contained nothing but volatile material, the samples could be prepared by simple evaporation. The activities counted per min and 0.1 ml of sample have been denoted  $a$  and  $b$  for the organic and aqueous phases,

respectively. For the series performed for determining the dependence of  $q_0$  on the acidity, however, evaporation of the aqueous phase would leave a disturbing residue of solid sodium perchlorate. In these cases the following technique was therefore applied.<sup>6</sup> After equilibration, the phases were separated and the organic phase was sampled and counted as usual, its activity as before being denoted  $a$ . Of the aqueous phase, a known volume (3 ml) is equilibrated again with an equal volume of the original solution of DBP in carbon tetrachloride. The phases are separated and the organic phase sampled and counted as before. The found activity is denoted  $c$ . If the unknown activities of the two aqueous phases are denoted  $y$  and  $z$ , then  $q = a/y = c/z$  and  $z = y - c$ . Hence  $q = (a - c)/c$ .

From the sum of activities  $a + b$  and the known counting efficiency of the detector (31 %),<sup>2</sup> the initial concentration of neptunium  $C_M'$  has also been calculated for each solution extracted. As very accurate values of  $C_M'$  are not wanted for the present study, no special care has been taken to make  $C_M'$  exactly constant within a series of measurement. The actual values varied within  $\pm 10\%$  from the average values stated in Table 3.

The whole procedure up to the separation of the phases had to be performed before the permanganate added had been completely reduced. Otherwise a reduction of neptunium(VI) soon occurred, as was obvious from the erratic and much too low values of  $q$  then encountered. This behaviour is just to be expected on the formation of neptunium(V), here present as  $\text{NpO}_2^+$ , as this ion is virtually non-extractable under the present conditions.

Plastic vessels, including plastic pipettes, have been used for all handling of hydrofluoric acid solutions.

## RESULTS

*Validity of the DBP extraction formula.* If the extraction reaction occurs as postulated in eqn. (1),  $q_0$  should vary with  $h$  and  $[\text{H}_2\text{B}_2]_0$  as described by eqn. (3). This means that if  $\log q_0$  is plotted *vs.*  $\log h$  at constant  $[\text{H}_2\text{B}_2]_0$ , a

Table 1. The distribution of Np(VI) between DBP in carbon tetrachloride and 1 M  $\text{HClO}_4$ - $\text{NaClO}_4$  as a function of  $h$ .  $C_B' = 50$  mM;  $[\text{H}_2\text{B}_2]_0 = 23.2$  mM;  $C_M' = 0.22$  mM;  $[\text{HA}] = 0$ .

$h$ M	$a$	$c$	$q_0$
0.422	2257	40	55.4
0.520	2192	58	36.8
0.612	2244	78	27.7
0.712	2177	102	20.4
0.804	2154	133	15.2
0.896	2149	155	13.4
1.000	—	—	10.3

Table 2. The distribution of Np(VI) between DBP in carbon tetrachloride and 1 M  $\text{HClO}_4$  as a function of  $[\text{H}_2\text{B}_2]_0$ .  $C_M' = 0.22$  mM;  $h = 1.000$  M;  $[\text{HA}] = 0$ .

$C_B$ M	$a$	$b$	$q_0$	$[\text{H}_2\text{B}_2]_0$ M
0.1000	2183	49.7	43.9	0.0476
0.1000	2137	49.9	42.8	0.0476
0.0500	2079	201	10.3	0.0232
0.0240	1571	705	2.23	0.0107
0.0240	1518	707	2.15	0.0107

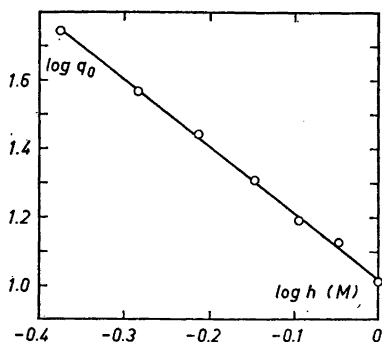


Fig. 1.  $\log q_0$  as a function of  $\log h$ . Aqueous phase 1 M  $\text{HClO}_4$ - $\text{NaClO}_4$ .  $[\text{H}_2\text{B}_2]_0 = 0.0232$  M;  $C_M' = 2.2 \times 10^{-4}$  M;  $[\text{HA}] = 0$ .

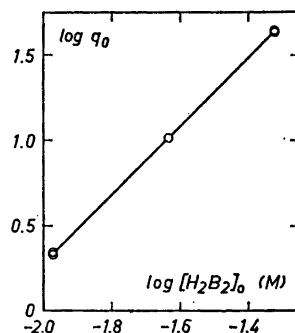


Fig. 2.  $\log q_0$  as a function of  $\log [\text{H}_2\text{B}_2]_0$ . Aqueous phase 1.000 M  $\text{HClO}_4$ ;  $C_M' = 2.2 \times 10^{-4}$  M;  $[\text{HA}] = 0$ .

straight line of a slope  $-2$  should result, while  $\log q_0$  vs.  $\log [\text{H}_2\text{B}_2]_0$  at constant  $h$  should give a straight line of a slope  $+2$ . The results of the experimental tests are given in Tables 1 and 2, and in Figs. 1 and 2  $\log q_0$  is drawn as function of  $\log h$  and  $\log [\text{H}_2\text{B}_2]_0$ , respectively. The lines have slopes of  $-2.0 \pm 0.1$  and  $2.01 \pm 0.05$ , respectively, in very good agreement with the values demanded by the postulated extraction formula. The two sets of experiments further yield (from the intercepts of the lines) very concordant values of the distribution constant, viz.  $\log K = 4.29 \pm 0.03$  from Fig. 1 and  $4.28 \pm 0.02$  from Fig. 2.

*Formation of fluoride complexes.* In the main series, an initial concentration of DBP  $C_B' = 50$  mM has been chosen for low fluoride concentrations while for higher ones  $C_B' = 100$  mM proved necessary in order to obtain well measurable values of  $q$ . In the range of  $[\text{HF}]$  between 1.15 and 1.84 M,  $q$  has been determined for both values of  $C_B'$ . The initial concentration of neptunium(VI) has been varied between 0.09 and 0.44 mM over the whole range of  $[\text{HA}]$ . The results are presented in Table 3, where the values calculated for

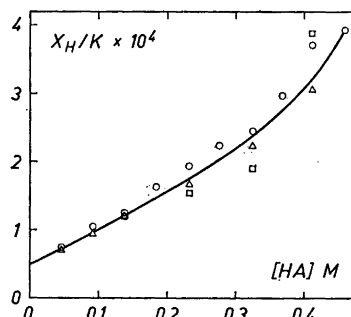


Fig. 3.  $X_H/K$  as a function of  $[\text{HA}]$ .  $C_B' = 50$  mM. Circles, squares and triangles refer to  $C_M' = 0.09, 0.22$  and  $0.44$  mM, respectively.

Table 3. Corresponding values of  $q$  and  $[HA]$  and the functions  $X_H/K$  and  $X_{1H}/K$ .

$C_B' = 50 \text{ mM}$					$C_B' = 100 \text{ mM}$				
$[HA]$ mM	$[H_2B_2]_0$ mM	$q$	$X_H/K$ $\times 10^4$	$X_{1H}/K$ $\times 10^4 \text{ M}^{-1}$	$[HA]$ mM	$[H_2B_2]_0$ mM	$q$	$X_H/K$ $\times 10^4$	$X_{1H}/K$ $\times 10^4 \text{ M}^{-1}$
$C_M' = 0.09 \text{ mM}$									
46.0	23.2	7.3	0.74	5.2	1150	47.7	1.74	13.1	11.0
92.0	23.2	5.13	1.05	6.0	1380	47.7	1.32	17.2	12.1
138.0	23.2	4.30	1.25	5.4	1840	47.7	0.83	27.3	14.6
184.0	23.3	3.34	1.63	6.1	2300	47.7	0.480	47.4	20.4
232.0	23.3	2.80	1.94	6.2	2760	47.8	0.369	61.9	22.2
276.0	23.3	2.43	2.24	6.3	3680	47.8	0.224	102	27.6
325	23.3	2.22	2.45	6.0	4510	47.8	0.120	190	42.1
368	23.3	1.83	2.97	6.7					
412	23.3	1.46	3.71	7.8					
460	23.3	1.38	3.93	7.4					
585	23.3	0.96	5.65	8.8					
690	23.4	0.71	7.8	10.5					
794	23.4	0.67	8.2	9.7					
920	23.4	0.56	9.7	10.0					
1150	23.4	0.449	12.2	10.2					
1380	23.4	0.304	18.0	12.7					
1840	23.4	0.189	29.0	15.5					
$C_M' = 0.22 \text{ mM}$									
138.0	23.0	4.45	1.19	5.0	2300	47.6	0.532	42.6	18.3
232.0	23.1	3.47	1.54	4.5	2760	47.7	0.360	63.2	22.7
325	23.1	2.81	1.90	4.3	3680	47.7	0.203	112	30.3
412	23.2	1.39	3.88	8.2	4510	47.7	0.146	156	34.4
585	23.2	1.09	4.94	7.6					
794	23.2	0.73	7.3	8.6					
$C_M' = 0.44 \text{ mM}$									
46.0	22.6	7.3	0.70	4.3	1150	47.2	1.83	12.2	10.1
92.0	22.6	5.42	0.94	4.8	1380	47.4	1.14	19.8	14.0
138.0	22.6	4.24	1.21	5.1	1840	47.4	0.69	32.4	17.3
232.0	22.7	3.11	1.66	5.0	2300	47.5	0.538	41.9	18.0
325	22.8	2.33	2.23	5.3	2760	47.6	0.348	65.1	23.4
412	22.8	1.70	3.05	6.2	3680	47.7	0.211	108	29.2
585	22.9	1.09	4.79	7.3	4510	47.7	0.150	152	33.5
794	23.0	0.73	7.2	8.5					
920	23.1	0.61	8.8	9.0					
1150	23.1	0.402	13.3	11.1					
1380	23.2	0.273	19.7	13.9					
1840	23.3	0.188	28.9	15.4					

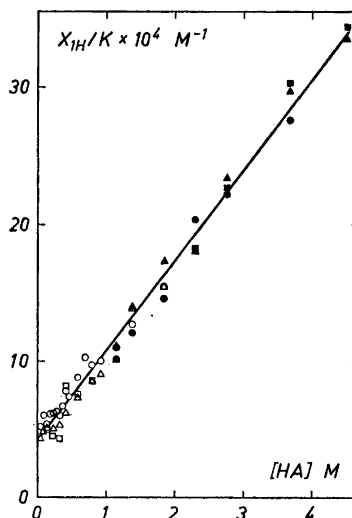


Fig. 4.  $X_{1H}/K$  as a function of  $[HA]$ . Open signs:  $C_{B'} = 50$  mM. Filled signs:  $C_{B'} = 100$  mM. Circles, squares and triangles refer to  $C_{M'} = 0.09, 0.22$  and  $0.44$  mM, respectively.

$[H_2B_{2o}]$  and  $X_H/K$  are to be found. In Fig. 3, the function  $X_H/K$  has been plotted. By extrapolation,  $(X_H/K)_0 = 1/K = (0.50 \pm 0.05) \times 10^{-4}$  is found, *i.e.*  $\log K = 4.30 \pm 0.04$ , in very good agreement with the values found previously from the fluoride free series where  $h$  and  $[H_2B_{2o}]$  were varied.

Now the function  $X_{1H}/K = (X_H/K - 1/K)/[HA]$  can be computed, with an intercept  $(X_{1H}/K)_0 = \beta_{1H}/K$  and a slope in the point of intersection  $(d(X_{1H}/K)/d[HA])_0 = \beta_{2H}/K$ . Actually, this function turns out to be linear within the whole range of  $[HA]$  investigated, Fig. 4, and the slope of the line will thus be  $\beta_{2H}/K$ . Higher complexes than the second one consequently do not exist within this range of  $[HA]$ . From Fig. 4, values of  $\beta_{1H}/K = (4.3 \pm 0.9) \times 10^{-4} M^{-1}$  and  $\beta_{2H}/K = (6.5 \pm 1.5) \times 10^{-4} M^{-2}$  are found from the intercept and slope, respectively.

Neither  $X_H/K$ , nor  $X_{1H}/K$  depend upon the value of  $C_{M'}$  chosen. At least for the low values of  $C_{M'}$  used here, only mononuclear complexes are thus formed. The function  $X_{1H}/K$  is also independent of  $C_{B'}$ , *i.e.* of  $[H_2B_{2o}]$ . As is easily derived, this means that no fluoride or mixed DBP-fluoride complexes are extracted into the organic phase, nor do DBP-complexes exist in the aqueous phase. The postulates advanced at the derivation of eqn. (5) have thus been verified.

By combination of all results, the following set of constants is obtained:

$$K = (2.0 \pm 0.1) \times 10^4; \beta_1^* = 8.6 \pm 2.1; \beta_2^* = 13 \pm 3.$$

The errors stated are maximal ones, as estimated from the graphical treatment of the data.

The values of  $\beta_1^*$  and  $\beta_2^*$  are much lower than for the corresponding uranium(VI) system, where  $\beta_1^* = 41$  and  $\beta_2^* = 108$  have been found. This is remarkable, in view of the actinoid contraction taking place from U to



Np (Ref. 1, p. 437). As the formation of the actinoid fluoride complexes certainly very much depends upon purely electrostatic interaction,<sup>11</sup> an increase of stability would rather be expected from U to Np. On the other hand, it has been observed also for many lanthanoid complexes of decidedly electrostatic character that the increase of stability by no means proceeds smoothly with decreasing ionic radius.<sup>12</sup> This has been connected with a change of the acceptor's sphere of hydration along the lanthanoid series. A similar interpretation may possibly be advanced in order to account for the sequence of complex stabilities found in the actinoid series. Further discussion of these questions will be postponed, however, until more experimental results are available.

We gratefully acknowledge the support given to this investigation by *Statens naturvetenskapliga forskningsråd* (The Swedish Natural Science Research Council) and *AB Atomenergi* (The Swedish Atomic Energy Company).

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Received July 7, 1967.