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AQUEOUS COORDINATION COMPLEXES OF NEPTUNIUM

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CONTENTS

A. INTRODUCTION

Neptunium, the first of the transuranium elements, was discovered by McMillan and Abelson [1]. The aqueous chemistry of neptunium has not received much attention until recently as compared to its neighbours uranium and plutonium although it resembles them in many of its chemical properties.

The inception of the production programme for ^{238}Pu from ^{237}Np has boosted the efforts for the recovery of neptunium from the spent reactor fuels [2]. This, coupled with the availability of larger quantities of neptunium, has probably generated a fresh interest in the study of the chemical behaviour of neptunium. The chemistry of neptunium has been recently reviewed by Keller [3] and by Burney and Harbour [4]. In the present review a comprehensive discussion of neptunium complexes in aqueous solutions is attempted since a large bulk of the data has been accumulated recently.

(i) Oxidation states

Neptunium exhibits five oxidation states (III, IV, V, VI and VII) in aqueous solutions and all of them form complexes, of varying stability, with a number of ligands. The differences in the complex forming abilities of these ions are mainly due to differences in their charge and size. The strong complexing tendencies of Np(V), Np(VI) and Np(VII) ions are revealed by the existence, in aqueous solutions, of oxycations NpO_2^+, NpO_2^{2+} and NpO_2^{3+} or oxyanion NpO_5^{3-}, respectively. These oxygenated ions have a lower charge and larger size compared to the bare ions which lower their complexing abilities relative to that of Np^{4+}. It should be remembered, however, that the actual charges on the neptunium atoms in the oxygenated ions viz. NpO_2^+, NpO_2^{2+} and NpO_2^{3+} are in fact much higher than the formal ionic charges of +1, +2 and +3 respectively and therefore such ions have a relatively high tendency toward complex ion formation [5]. Thus the complexing abilities of neptunium ions follow the order Np(IV) > Np(VI) > Np(V). There is little work on the complex formation of Np(III) presumably because this ion is highly unstable towards oxidation (E^0 for the Np(III)/Np(IV) couple in 1 M $HClO_4$ is -0.155 V [6]). On the other hand Np(VII) is a strong oxidising agent stable mainly in alkaline solutions and is fairly rapidly reduced to Np(VI) in acid solutions [7—10]. This instability of Np(VII) is the main limitation in studying its complex formation behaviour. Even Np(VI) is a moderately strong oxidising agent (E^0 for the Np(V)/Np(VI) couple, in 1 M $HClO_4$ is -1.14 V [6]) but it is possible to maintain it in the presence of stronger oxidising agents. Thus it has been possible to investigate the complexing behaviour of Np(VI) with some ligands in the presence of oxidising agents such as $K_2Cr_2O_7$ and $KMnO_4$. The exceptional stability of Np(V) in aqueous solutions as compared to U(V) and Pu(V) has enabled the study of its complex formation with several ligands.

In general while studying the complex formation of any metal ion which has more than one stable oxidation state the results obtained may be erroneous unless care is taken to ensure that the oxidation state does not change during the course of the experiment. Peppard has very much emphasised this aspect while summarising the proceedings of a solvent extraction conference [11]. This is particularly true in the case of neptunium and plutonium where several oxidation states can be formed by the conversion from one oxidation state to another due to the shift in their redox equilibria under a wide variety of experimental conditions. While studying the complex formation of Np(VI) by solvent extraction and ion exchange methods, in the absence of any holding oxidant, one has to bear in mind the possible reduction of Np(VI). Tracer concentrations of Np(VI) are reduced rapidly and quantitatively to Np(V) [12] and to some extent to Np(IV) [13] by common organic ion exchangers. Similarly Np(IV), in the absence of a holding reductant, was reported to be oxidized to Np(V) in the presence of some solvent extractants [14]. Even when holding redox reagents are present the complexing ligand itself might induce the changes in the direction of the redox equilibria and bring about the changes in the oxidation state [15,16]. However, when Np(V) is involved, it is difficult to use any redox reagent to maintain its oxidation state. Thus, maintaining the oxidation state of the ion whose complex formation studies are being investigated throughout the course of the experiments becomes a primary criterion for obtaining reliable results.

(ii) Stability constants

Several methods are available for studying the complex formation of metal ions in aqueous solutions and these methods along with their advantages and disadvantages have been described by several authors [17—19]. It is known that the complexes formed in solution are broadly classified as inner-sphere and outer-sphere depending on whether the ligand is in close proximity to the metal ion or is separated from it by one or more solvent molecules. While most methods of determining stability constants do not distinguish between the two types of complexes, spectrophotometric methods are capable of making some distinction. While changes in the visible spectrum usually detect only inner-sphere complexes changes in the UV region may reflect outer-sphere complexing [20]. The determination of the enthalpy and entropy changes accompanying complex formation also enables one to distinguish between inner and outer sphere complexing. For inner-sphere complexing, the hydration spheres of both metal ion and ligand are sufficiently disrupted and net entropy and enthalpy changes would usually be positive. On the other hand in outer-sphere complexes, the hydration spheres appear to be only partially disrupted and hence the net enthalpy and entropy changes would be negative [21].

(iii) Scope

In this review the stability constant data for the complexes of neptunium ions in different oxidation states, obtained by different methods reported in the literature until the end of 1976, are critically discussed. Thermodynamic values associated with complex formation, wherever available, are also included.

Additional evidence for complex formation in aqueous solution was sought from spectral as well as solvent extraction and ion exchange data. It should, however, be mentioned that although changes in the absorption spectra of the metal ions in the presence of complexing ligand do indicate complex formation, lack of appreciable spectral changes need not necessarily mean that complex formation is absent [22]. Extraction of the metal ion from an aqueous medium containing the ligand into neutral or anionic extractants and metal uptake from such media by organic anion exchangers also provides evidence for the existence of neutral or anionic metal complexes in solution. Here again the data should be carefully interpreted as even though extraction into the organic solvent may be taken as evidence for the complex, the lack of extraction need not mean that such a complex is absent in the solution. Such qualitative information is summarized in the Appendix.

A comparison of the stability constant values of neptunium with those of the other actinide ions, in the same oxidation state and obtained under comparable conditions, wherever available, is also made. The cation—cation complexes and mixed ligand complexes which are also formed in aqueous solutions are not included in the present review. Though many carboxylates and other organic ligands containing multifunctional groups are known to form chelates they are grouped separately for the sake of convenience.

(iv) Nomenclature

The nomenclature used by Sillen and Martell [23] is followed in the present review. Thus, for the reaction of a metal ion M with a ligand L, $ML_{n-1} + L \rightleftharpoons ML_n$, the stepwise stability constant is written as $K_n = [ML_n]/[ML_{n-1}][L]$, while the overall stability constant for the reaction, $M + nL \rightleftharpoons ML_n$, is expressed as $\beta_n = [ML_n]/[M][L]^n$. The charges on the ions are omitted for convenience. If the complex formation reaction involves a protonated ligand species with the resultant liberation of a proton the symbols $*K_n$ and $*\beta_n$ are used

$$ML_{n-1} + HL \rightleftharpoons ML_n + H^+$$

$$*K_n = [ML_n][H^+]/[ML_{n-1}][HL]$$

$$M + nHL \rightleftharpoons ML_n + nH^+; \qquad *\beta_n = [ML_n][H^+]^n/[M][HL]^n$$

B. HYDROXIDE COMPLEXES

Knowledge of hydrolysis of neptunium ions in different oxidation states is very important for all complex formation studies as the hydroxocomplexes are the most obvious products in aqueous solutions depending on the experimental conditions viz., pH, metal ion concentration and temperature. Unfortunately sufficient attention has not been paid to this problem and few data are available (Table 1). From the existing literature data on the hydrolysis of lanthanide ions Pr(III) and Nd(III) which are close in size and hence in properties to Np(III) the hydrolysis constant for Np(III) has been estimated [24] and is included in Table 1.

All the data included in Table 1 have been obtained using macroconcentra-

TABLE 1

Hydrolysis constants of neptunium ions

Ion	Method	Medium	Temp. °C	$*K_1$	Ref.
Np^{3+}	Calc.	—	—	3.7×10^{-8}	24
Np^{4+}	Spec.	2.0 M $NaClO_4$	25	5.0×10^{-3}	25
	Spec.	2.0 M $NaClO_4$	25	3.2×10^{-3}	25 [a]
	Spec.	1.0 M $NaClO_4$	25	3.26×10^{-2}	26 [b]
	Spec.	1.0 M $NaClO_4$	25	1.23×10^{-2}	26 [c]
NpO_2^+	Pot.	ClO_4^-	—	1.26×10^{-9}	27, 28
	Sol.	0	20	8.3×10^{-11}	29
NpO_2^{2+}	Sol.	0	20	4.3×10^{-4} [d]	29

[a] D_2O medium. [b] 1.0 cm path cell. [c] 0.5 cm path cell. [d] $*K_2 = 3.6 \times 10^{-6}$ and $*K_3 = 2.0 \times 10^{-10}$.

tions of neptunium, which usually leads to the formation of polynuclear species. Hence it is desirable to investigate the hydrolysis using solvent extraction or ion exchange methods which permit the use of tracer concentrations of neptunium, thereby minimizing the formation of polynuclear species. It may be noted that in the case of Pu(IV) the hydrolysis constant values obtained by potentiometric [30] and solvent extraction [31] methods differ appreciably.

(i) Neptunium(IV)

Sullivan and Hindman [25] as well as Paul [26] utilized the sharp absorption band of Np(IV) around 960 nm to follow the course of hydrolysis. The differences in the ionic strengths alone probably cannot explain the differences in the values of $*K_1$ obtained by these two groups.

Literature data on the hydrolysis of tetravalent actinides, obtained under comparable conditions, reveal that the hydrolysis constants ($*K_1$) follow the order

Th(IV) [32] < *U*(IV) [25,33] > Np(IV) < Pu(IV) [30,31,33–35]

(ii) Neptunium(V)

It can be seen from the data presented in Table 1 that the potentiometric value differs significantly from the value obtained by the solubility method. Though Np(V) was reported [36] to be hydrolyzed at pH = 6.5, hydrolysis constant data suggest that hydrolysis at this pH should be negligible. From the hydrolysis constant data for Np(V) and Pu(V) [27,28,37], Np(V) appears to be somewhat more acidic than Pu(V). Although this behaviour was not expected on the basis of their relative sizes [38], in fact this seems to be the order for inner-sphere complexes of both penta- and hexavalent actinide ions.

(iii) Neptunium(VI)

The hydrolysis of Np(VI) has been investigated potentiometrically [27,28] from which it was inferred that the average number of hydroxide ions ($\bar{n}$) per Np(VI) ion was 0.4 in the pH region 4—4.5 when the Np(VI) concentration was 10^{-3}—10^{-2} M. Apart from the hydrolysis constant values included in Table 1, Moskvin [29] has also determined the constants for the following equilibria

$$\mathrm{NpO_2(OH)^+ + NpO_2(OH)_2 \overset{k'}{\rightleftharpoons} (NpO_2)_2(OH)_3^+};\ K' = 2.9 \times 10^{-4}$$

$$\mathrm{NpO_2(OH)_2 + NpO_2(OH)_3^- \overset{k''}{\rightleftharpoons} (NpO_2)_2(OH)_5^-};\ K'' = 2.2 \times 10^{-4}$$

No spectrophotometric observations on the hydrolysis of Np(VI) have been reported. The hydrolysis of hexavalent actinides follows the order [28], U(VI) > Np(VI) > Pu(VI).

(iv) Neptunium(VII)

No quantitative data on the hydrolysis of Np(VII) have been reported in the literature although $\mathrm{NpO_2(OH)_3}$ was found [39] to be precipitated in the pH range 5—9.

C. FLUORIDE COMPLEXES

The fluoride complexing of neptunium ions has been studied extensively and the stability constant values are given in Table 2. Thermodynamic values associated with complex formation are given in Table 3.

(i) Neptunium(IV)

The absorption spectra of Np(IV), in 1.0 M perchloric acid containing different concentrations of hydrofluoric acid, have recently been obtained [49a] and are shown in Fig. 1. These spectra clearly show the effect of fluoride complexing on the absorption bands of Np(IV). These are similar to the changes observed in the case of fluoride complexing of Pu(IV) [49b].

The agreement between the various stability constant values of Np(IV) given in Table 2 is reasonably good. A comparison of the stability constants ($^*K_1$) for tetravalent actinides shows the order of complexing to be Th(IV) [42,50,51] < U(IV) [44,52] > Np(IV) ≃ Pu(IV) [43,53]. From the thermodynamic values given in Table 3 it is seen that the fluoride complexing of Np(IV) is predominantly inner-sphere type.

(ii) Neptunium(V)

The absorption spectrum of Np(V) in fluoride medium [49a] shown in Fig. 2, clearly indicates fluoride complexing of Np(V). The failure to observe

TABLE 2

Constants for the stepwise association of HF and neptunium ions. Temp. = 25° C

Ion	Method	Medium	$*K_1$	$*K_2$	Ref.
Np(IV)	Cix	4.0 M $HClO_4$	6.6×10^4	5.6×10^2	41 [a]
	Pot.	4.0 M $HClO_4$	—	4.9×10^2 [b]	41 [a]
	DNNS	2.0 M $HClO_4$	4.2×10^4	—	42
	TTA	2.0 M $HClO_4$	5.2×10^4	—	42
	TTA	2.0 M $HClO_4$	4.0×10^4	7.75×10^2	42
	TTA	2.0 M $HClO_4$	5.0×10^4	4.8×10^2	43
	DNNS	1.0 M $HClO_4$	4.0×10^4	—	44
Np(V)	DNNS	2.0 M $NaClO_4$	9.8 (K_1)	—	44a
Np(VI)	DBP	1.0 M $HClO_4$	8.6	1.5	45 [c]
	Cix	1.04 M $HClO_4$	157.0	—	46
	Cix	2.1 M $HClO_4$	130.0	—	46
	Pot.	2.0 M $NaClO_4$ ($[H^+] = 0.05$—0.1 M)	8.33	1.05	47
	Pot.	0.1 M $HClO_4$	16.0	0.92	48
	Pot.	0.2 M $HClO_4$	14.6	1.06	48
	Pot.	0.3 M $HClO_4$	13.7	1.17	48
	Pot.	0.4 M $HClO_4$	13.2	1.20	48
	Pot.	0.5 M $HClO_4$	12.9	1.07	48
	Pot.	0	25.6	1.1	48
	DNNS	2.0 M $HClO_4$	13.2	—	16

[a] Temp. = 20° C. [b] $*K_3 = 2.2 \times 10^2$ and $*K_4 \simeq 20$. [c] Temp. = 21°C.

fluoride complexing by earlier workers [47,48] can now be regarded as due to the use of high acidity in their studies which results in a low fluoride ion concentration.

TABLE 3

Thermodynamic values associated with the complexing of neptunium ions with fluoride. Temp. = 25° C

Equilibrium	Method	Medium	$-\Delta G$ (Kcal mole^{-1})	ΔH (Kcal mole^{-1})	ΔS (e.u.)	Ref.
$Np^{4+} + F^- \rightleftharpoons NpF^{3+}$	DNNS	1.0 M $HClO_4$	10.3	0.76	37.0	44
$NpO_2^{2+} + F^- \rightleftharpoons NpO_2F^+$	Pot.	2.0 M $NaClO_4$ ($[H^+] =$ 0.05—0.1 M)	5.2	—1.5	7.7	47
$NpO_2^{2+} + F^- \rightleftharpoons NpO_2F^+$	DNNS	2.0 M $HClO_4$	5.5	4.0	27.1	49
$NpO_2F^+ + F^- \rightleftharpoons NpO_2F_2$	Pot.	2.0 M $NaClO_4$ ($[H^+] =$ 0.05—0.1 M)	4.0	0.04	10.0	47

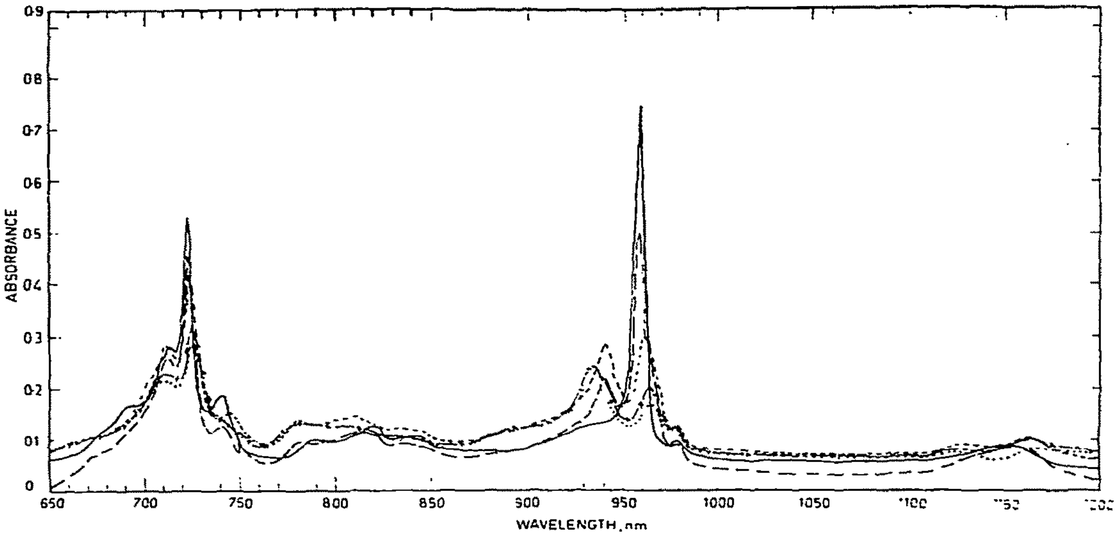

Fig. 1. Absorption spectra of Np(IV) in 1.0 M $HClO_4$ containing no HF (———), [Np(IV)] ≅ 1.74×10^{-3} M, 2.0 cm cells) and varying concentrations of HF ([Np(IV)] ≅ 8.7×10^{-4} M, 5.0 cm cells), 5.0×10^{-4} M HF (– – – –), 1.0×10^{-3} M HF (———), 5.0×10^{-3} M HF (—x—x—x—) and 1.0×10^{-2} M HF (......) [49a].

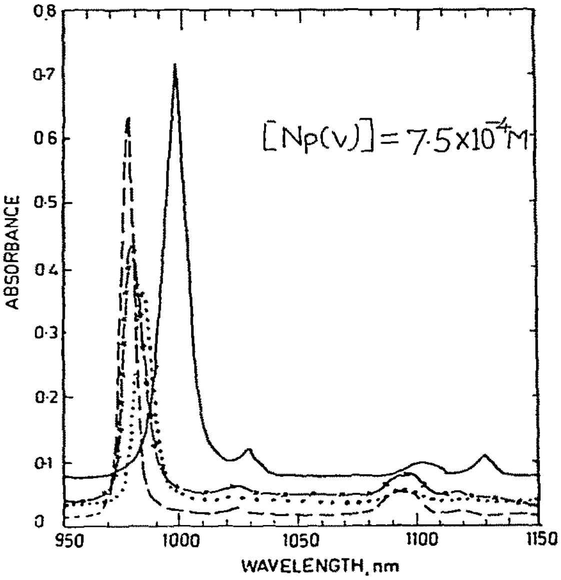

Fig. 2. Absorption spectra of Np(V) obtained using 2.0 cm cells in 6.6 M $NaClO_4$ (– – – – –), 0.05 M NaF (-x-x-x-x-x), 3.0 M Na_2SO_4 (.........) and using 1.0 cm cells in 8 M NaSCN (———) [49a].

(iii) Neptunium(VI)

From Table 2 it is seen that the values obtained by the cation-exchange method [46] are very high. It was reported that both Np(VI) and Np(V) are slowly reduced by common organic ion exchangers [12,13]. The reduction of Np(VI) to Np(IV) might probably be aided by the presence of fluoride ions which strongly complex Np(IV). In the cation exchange work [46] no holding oxidant for Np(VI) was used whereas in the subsequent work [16,45] either $KMnO_4$ or $K_2Cr_2O_7$ was used. The values for $^*K_1$ reported by various authors seem to be in reasonable agreement with each other considering the differences in ionic strengths and methods used. A comparison of the stability constants ($^*K_1$) for hexavalent actinides reveals [16] their order of stabilities to be U(VI) > Np(VI) > Pu(VI). The enthalpy values obtained for the formation of NpO_2F^+ by the potentiometric method [47] and DNNS extraction method [49] differ considerably and this may, at least partly, be attributed to the different media employed. In any case the data given in Table 3 clearly indicate that the fluoride complexing of Np(VI) is predominantly inner-sphere type.

D. CHLORIDE COMPLEXES

Chloride complexing of neptunium ions has been widely investigated and the data are summarised in Table 4.

(i) Neptunium(III)

The absorption spectrum of Np(III) has revealed [55] a new intense band at 384 nm in > 7 M lithium chloride solutions which was used for the computation of the stability constants for inner-sphere complexes (Table 4).

(ii) Neptunium(IV)

The absorption spectra of Np(IV) [49a] in perchlorate, chloride, bromide and iodide media shown in Fig. 3 clearly indicate the effect of complexing by these ligands on the Np(IV) absorption bands.

In the calculation of K_1 from the measured potentials of the Np(III)/Np(IV) couple in 1 M perchloric and 1 M hydrochloric acids it was assumed [56] that only the first complex was formed and that complexing of Np(III) is negligible. Very high values obtained by spectrophotometry [59] were attributed to the high ionic strength used. In general there is a good agreement between the values obtained by various authors using low ionic strength media. The values of β_1 reported for an ionic strength of 2.0 for Th(IV) [42,73], U(IV) [52], Np(IV) and Pu(IV) [53] lie in the range 0.9—1.4 which indicates that all these ions apparently have similar orders of complexing tendency towards chloride ions. In concentrated hydrochloric acid media, however, such a situation may not exist as is revealed by the fact that Th(IV) is neither absorbed on anion

TABLE 4

Constants for the overall association of chloride and neptunium ions. Temp. = 25° C

Ion	Method	Medium	β_1	β_2	Ref.
Np(III)	Spec.	>7.0 M LiCl	4.0×10^{-3}	1.04×10^{-3}	55
Np(IV)	Pot.	1.0 M HCl	0.5	—	56
	TTA	0.5 M $HClO_4$	1.4	—	57 [c]
	TTA	1.0 M $HClO_4$	0.92	0.58	57 [a,c]
	TTA	2.0 M $HClO_4$	1.1	0.7	57 [c]
	DNNS	2.0 M $HClO_4$	0.9	0.7	42
	TTA	4.0 M ClO_4^- ($[H^+]$ = 1.0 M)	0.8	0.8	58
	Spec.	9.0 M $HClO_4$	1.33×10^2	1.46×10^5	59
Np(V)	Cix	2.0 M $HClO_4$	0.51	—	60
	Pot.	4.0 M ClO_4^- ($[H^+]$ = 1.0 M)	0.003	0.03	58
	DNNS	2.0 M $NaClO_4$	0.38	—	44a
Np(VI)	Kin.	3.0 M $HClO_4$	0.42	—	61 [b]
	Pot.	0.3 M $HClO_4$	0.48	0.8	61
	Pot.	0.4 M $HClO_4$	0.44	0.4	61
	Pot.	0.5 M $HClO_4$	0.45	—	61
	TTA	4.0 M ClO_4^- ($[H^+]$ = 0.1 M)	0.9	—	62

[a] β_3 = 0.33. [b] Calculated from the data of Ref. 81. [c] Temp. = 20°C.

exchangers [74] nor extracted by amines [75] whereas other tetravalent actinides are well absorbed on anion exchangers [66] as well as well extracted by amines [68].

(iii) Neptunium(V)

Though Danesi et al. [58] reported the β_1 and β_2 values for the chloride complexing of Np(V) given in Table 4 they subsequently recalculated their earlier data and concluded [62] that there is no chloride complexing of Np(V). However, our recent spectrophotometric [80] as well as solvent extraction work [44a] does establish the complexing, though weak, of Np(V) by chloride.

(iv) Neptunium(VI)

The β_1 value calculated [61] may be treated as an approximate estimate as the original data [81] were obtained in connection with a kinetics study. All the values reported for β_1 appear to be in reasonable agreement with each other. A comparison of β_1 values for U(VI) [82], Np(VI) and Pu(VI) [83] indicates that they are almost the same in magnitude. Unlike the case of chloride complexing of U(VI) [82] and Pu(VI) [83] for which the stability con-

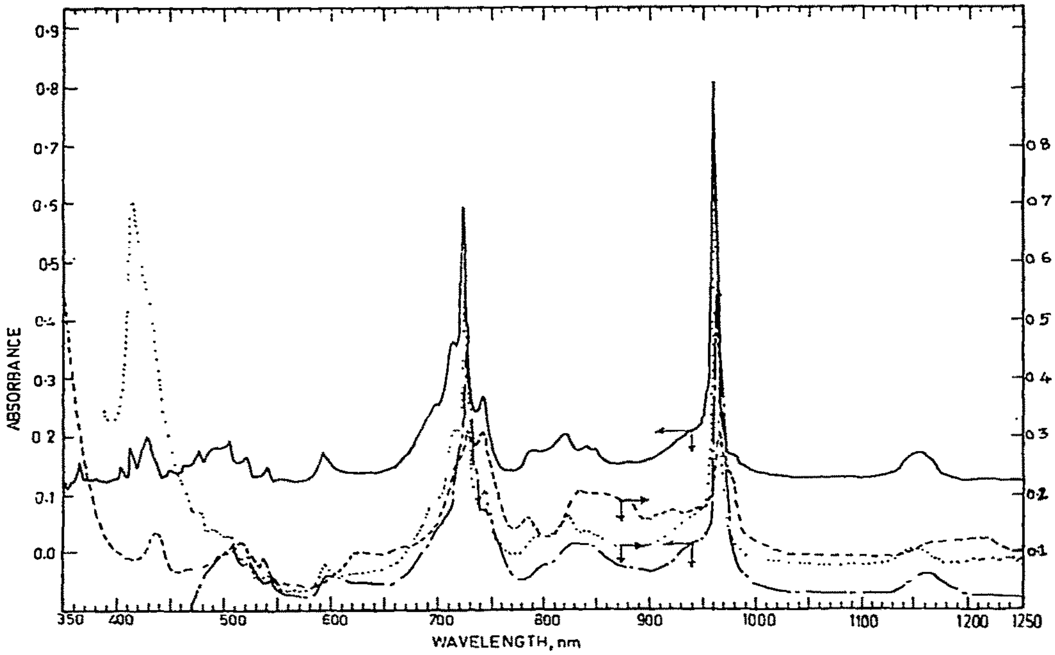

Fig. 3. Absorption spectra of Np(IV) ([Np(IV)] ≅ 1.74 × 10^{-3} M, 2.0 cm cells) in 8 M $HClO_4$ (———), 8 M HCl (– – – – –), 8 M HBr (—·——·—) and 4.6 M NaI in 1.0 M $HClO_4$ (······) [49a].

TABLE 5

Thermodynamic values associated with the chloride complexing of Np(VI) [81]. Temp. = 0°C

Equilibrium	$-\Delta G$ (Kcal mole^{-1})	ΔH (Kcal mole^{-1})	ΔS (e.u.)
$NpO_2^{2+} + Cl^- \rightleftharpoons NpO_2Cl^+$	0.25 or 0.12	−8.7 or −6.9	−32.2 or −21.0
$NpO_2Cl^+ + Cl^- \rightleftharpoons NpO_2Cl_2$	−0.95	3.5	16.0

stants increase with increasing temperature the values for Np(VI) (Table 5) decrease with increasing temperature. Thus these data need reinvestigation.

E. BROMIDE COMPLEXES

(i) Neptunium(III)

The absorption spectrum of Np(III) in bromide media shows a new intense band at 387 nm from which $\beta_1 = 4 \times 10^{-4}$ and $\beta_2 = 2.9 \times 10^{-7}$ for the formation of the inner-sphere complexes $NpBr^{2+}$ and $NpBr_2^+$, respectively, at 25° C, were calculated [55].

(ii) Neptunium(IV)

The absorption spectrum of Np(IV) in HBr medium is shown in Fig. 3 [49a]. The complexing of Np(IV) with bromide ions has been studied [85] by the HTTA extraction method which gave $\beta_1 = 0.61$ and $\beta_2 = 0.27$ in 2 M perchloric acid medium at 25°C. From a comparison of the β_1 values for the tetravalent actinides the order of complexing is seen to be Th(IV) [85] < U(IV) [86,87] > Np(IV) < Pu(IV) [85].

F. NITRATE COMPLEXES

The nitrate complexing of neptunium ions has been studied extensively and the stability constant values are given in Table 6.

(i) Neptunium(IV)

Absorption spectra of Np(IV) [97] are given in Fig. 4 which show the changes in the absorption maxima due to nitrate complexing. Changes in the absorption spectra of Np(IV) (Fig. 5) [99] were used to calculate the fraction of neptunium present as the hexanitrato complex at different nitric acid concentrations (Fig. 6).

While estimating β_1 from the potentials measured for the Np(III)/Np(IV) couple in 1 M perchloric and 1 M nitric acids it was assumed [56] that only $Np(NO_3)^{3+}$ is formed and that Np(III) is not complexed. The TBP extraction method [90] assumes that the tetranitrato complex of Np(IV) is the only extracted species. However, the reported extraction of other Np(IV) [96] as well as U(IV) [114] species into TBP makes the validity of the TBP extraction method questionable. Besides, as the organic phase composition changes appreciably due to extraction of nitric acid the activity coefficients of the organic phase would vary considerably. Thus this method of determination of stability constants is not reliable [115].

Rossotti and Rossotti [116] have discussed the limitations of the use of anion exchangers for the determination of stability constants and the same limitations are applicable to amine extraction systems. It is known that perchlorate ion is extracted [111] far more favourably into amines than nitrate ion or the nitrate complex of the metal ion. The composition and hence the activity coefficients of the amine phase would therefore change appreciably when the aqueous perchloric acid-nitric acid composition changes. With such limitations the TOA extraction method used [91] is not expected to yield reliable values of the stability constants. β-values obtained by spectrophotometry [93,94] are much higher and were attributed to the higher ionic strengths used.

TABLE 6

Constants for the overall association of nitrate and neptunium ions. Temp. = 25° C

Ion	Method	Medium	β_1	β_2	Ref.
Np(IV)	Pot.	1.0 M HNO_3	2.4	—	56
	TTA	0.5 M $HClO_4$	2.8	—	57[a]
	TTA	1.0 M $HClO_4$	2.2	1.2	57[a,b]
	TTA	2.0 M $HClO_4$	2.0	2.2	57[a]
	TTA	0	47.9	—	57[a]
	Spec.	2.0 M	1.3	—	88
	Kin.	2.0 M	1.3	—	89
	Kin.	2.0 M	2.2	1.5	89
	TTA	4.0 M ClO_4^- ($[H^+] = 1.0$ M)	0.71	0.18	58
	TBP	2.0 M $HClO_4$	6.8	20.3	90[c]
	TBP	4.0 M $HClO_4$	5.2	12.0	90[d]
	TOA	8.0 M $HClO_4$	0.03	0.68	91[a,e]
	DNNS	2.0 M $HClO_4$	1.6	4.5	92
	Spec.	9.0 M $HClO_4$	8.0	115.0	93
	Spec.	7.0 M $HClO_4$	8.0	85.0	94
Np(V)	Cix	2.0 M $HClO_4$	0.56	—	60
	TOA	8.0 M $HClO_4$	0.53	—	91
	Pot.	4.0 M ClO_4^- ($[H^+] = 1.0$ M)	0.025	0.04	58
	DNNS	2.0 M $NaClO_4$	0.28	—	44a
Np(VI)	TTA	4.0 M ClO_4^- ($[H^+] = 0.1$ M)	0.87	—	58
	Pot.	0.4 M $HClO_4$	0.105	~0.1	61
	Pot.	0.5 M $HClO_4$	0.110	~0.1	61
	Pot.	0.6 M $HClO_4$	0.130	~0.1	61
	Pot.	0.8 M $HClO_4$	0.115	~0.1	61
	TOA	8.0 M $HClO_4$	0.57	1.57	91

[a] Temp. = 20° C. [b] $\beta_3 = 0.55$. [c] $\beta_3 = 35.1$. [d] $\beta_3 = 16.8, \beta_4 = 14.5$. [e] $\beta_3 = 0.15, \beta_4 = 0.13$.

The values of β_1 reported for $\mu = 2.0$, for Th(IV) [92], U(IV) [117], Np(IV) and Pu(IV) [53] lie within the range 1—5 and do not show any clear trend.

(ii) Neptunium(V)

The β_1 value obtained by cation exchange [60] appears to be high which may perhaps be due to the partial reduction of Np(V) to Np(IV). The β_1 value obtained by TOA extraction [91] is also doubtful because of the limitations of the amine extraction method as discussed earlier. Besides, in such a high concentration of acid (8 M), Np(V) would disproportionate [125] and this would be favoured by the addition of nitric acid which complexes Np(IV) more strongly.

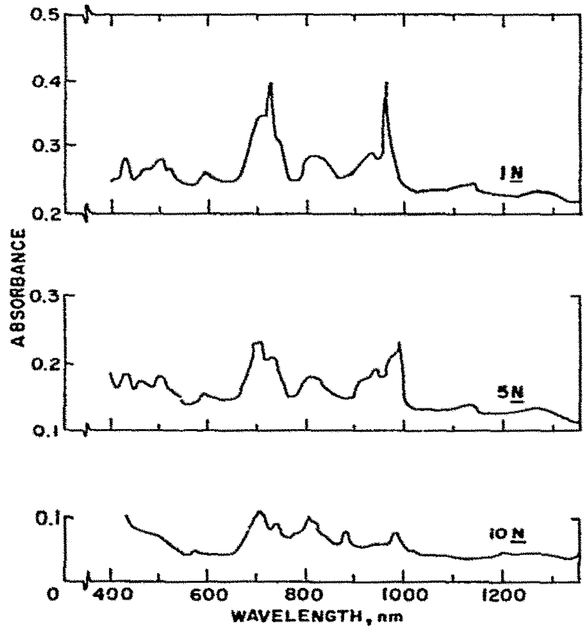

Fig. 4. Absorption spectra of Np(IV) in 1.5 and 10 M nitric acid ([Np(IV)] = 2.0×10^{-3} M 1.0 cm cells) [97].

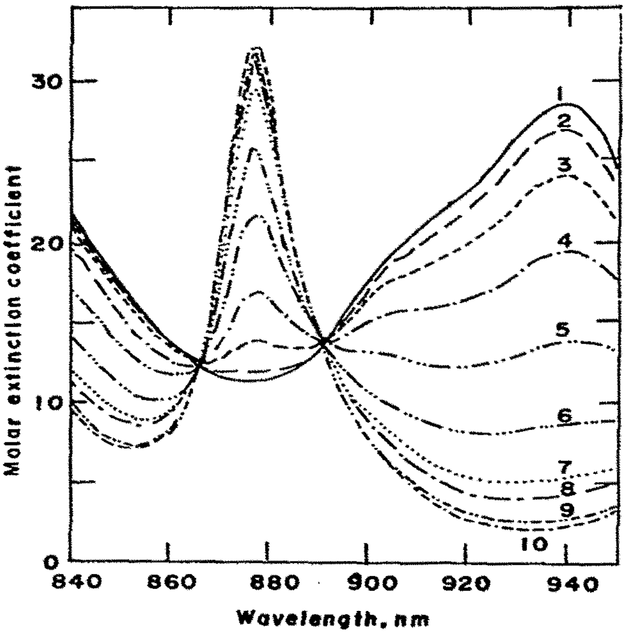

Fig. 5. Absorption spectra of Np(IV) in nitric acid in region of 877 nm peak: (1) 5.0 M HNO_3, (2) 6.0 M HNO_3, (3) 7.0 M HNO_3, (4) 8.0 M HNO_3, (5) 9.0 M HNO_3, (6) 10.0 M HNO_3, (7) 11.0 M HNO_3, (8) 12.0 M HNO_3, (9) 13.0 M HNO_3, (10) 14.0, 15.0 and 15.5 M HNO_3. Reprinted with permission from J. Phys. Chem., 64 (1960) 1375. Copyright by the American Chemical Society.

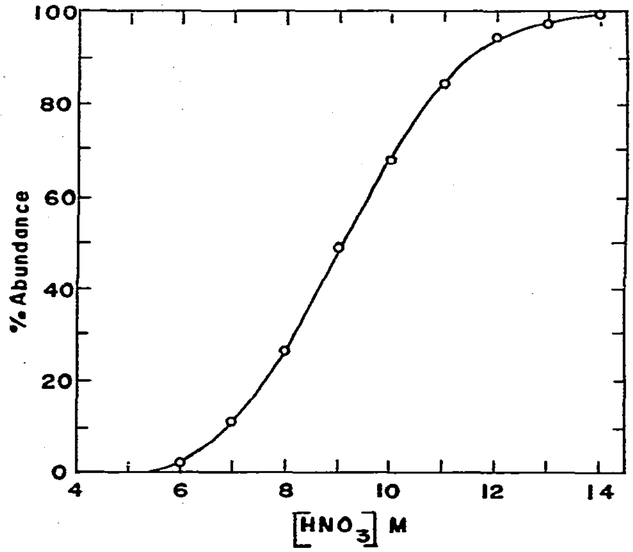

Fig. 6. Abundance of Np(IV) hexanitrato complex in HNO_3. Reprinted with permission from J. Phys. Chem., 64 (1960) 1375. Copyright by the American Chemical Society.

(iii) *Neptunium(VI)*

Absorption spectra of Np(VI) [97], at varying nitric acid concentrations, are given in Fig. 7. The changes observed [94] in the molar extinction coeffi-

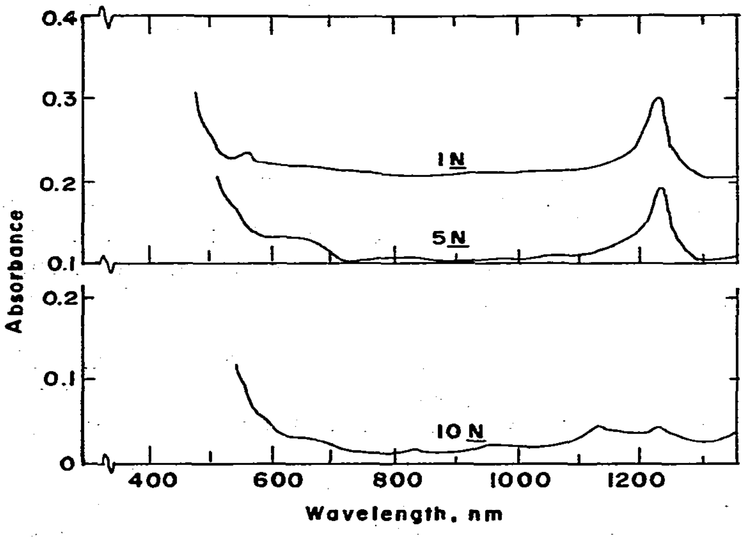

Fig. 7. Absorption spectra of Np(VI) in 1, 5 and 10 M nitric acid ([Np(IV)] = 2.0 × 10^{-3} M, 1.0 cm cells) [97].

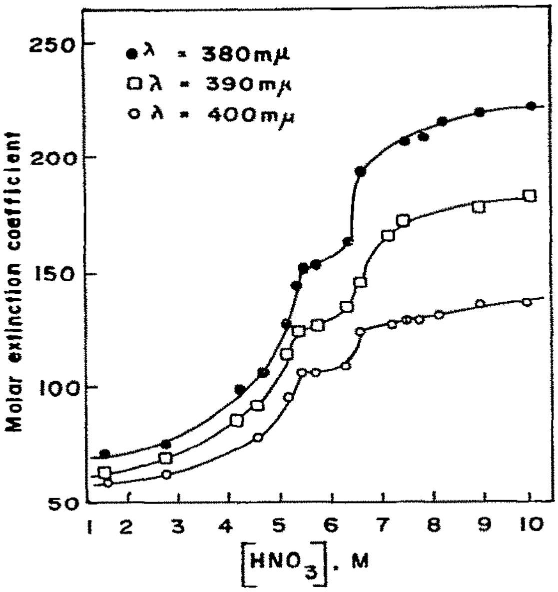

Fig. 8. Variation of molar extinction coefficient of Np(VI) with nitric acid concentration [94].

cient values of Np(VI) as a function of nitric acid concentration, are given in Fig. 8.

The TOA extraction method [91] is subject to the same limitations as mentioned under Np(IV)—nitrate complexing. The β_1 values reported for an ionic strength of 2—4, for U(VI) [82], Np(VI) and Pu(VI) [127,128] appear to be less than unity and did not show any clear trend within themselves.

G. THIOCYANATE COMPLEXES

(i) Neptunium(IV)

Stability constants of the thiocyanate complexes of Np(IV) using TTA and DNNS extraction at 25°C and in a perchlorate medium ($\mu = 2.0$, $[H^+] = 1.0$ M) [130,130a] gave the values of β_1, β_2 and β_3 respectively as 31.3, 115 and 341 by the TTA method and 30.4, 183 and 316 by the DNNS method. The thermodynamic data are given in Table 7. These data suggest that, for the first complex, there is no predominance of the outer-sphere complex as was the case with U(IV) [52]. From the available data on the thiocyanate complexing of Th(IV) [132], U(IV) [52] and Np(IV) it is clearly seen that for the tetravalent actinides the order of thiocyanate complexing is Th(IV) < U(IV) ≃ Np(IV).

(ii) Neptunium(V)

The effect of thiocyanate medium on the absorption spectrum of Np(V) can be seen from Fig. 2. It is clear that thiocyanate complexing causes con-

TABLE 7

Thermodynamic values associated with the thiocyanate complexing of Np(IV) [130a]. Temp. = 25° C; μ = 2.0 M; [H^+] = 1.0 M; Method—TTA

Equilibrium	$-\Delta G$ (Kcal $mole^{-1}$)	$-\Delta H$ (Kcal $mole^{-1}$)	ΔS (e.u.)
$Np^{4+} + SCN^- \rightleftharpoons Np(SCN)^{3+}$	2.0	1.7	1.14
$Np(SCN)^{3+} + SCN^- \rightleftharpoons Np(SCN)_2^{2+}$	0.77	0.52	0.84
$Np(SCN)_2^{2+} + SCN^- \rightleftharpoons Np(SCN)_3^+$	0.65	0.9	−0.85

siderable shift towards longer wavelength, of all the principal absorption bands of Np(V) with simultaneous increase in their intensity.

Values of β_1 = 2.1 and $\beta_2 \simeq$ 0.4 in 2.0 M $NaClO_4$ at 25°C have recently been obtained [44a] by the DNNS extraction method.

The study of thiocyanate complexing of Np(VI) may be difficult as thiocyanate ion is expected to reduce Np(VI) to Np(V).

H. SULPHATE COMPLEXES

The sulphate complexing of neptunium ions has been studied extensively (Table 8).

(i) Neptunium(IV)

Absorption spectra of Np(IV) in perchloric and sulphuric acid solutions [49a] are shown in Fig. 9.

In the earlier investigations by TTA extraction [14,134] correction due to the aqueous phase complexing of Np(IV) with TTA, though such a complexing was suggested [134], was ignored. In our recent work [43], however, the necessary corrections have been applied. The spectrophotometric value [88] appears to be high and this may probably be due to the assumption that only one complex was formed.

A comparison of the values of $^*K_1$ obtained for the sulphate complexing of Th(IV) [139], U(IV) [52], Np(IV) and Pu(IV) [53] shows the complexing trend to be Th(IV) < U(IV) $\simeq$ Np(IV) < Pu(IV).

The thermodynamic data associated with the sulphate complexing of Np(IV) are given in Table 9 from which it is seen that the complex $Np(SO_4)^{2+}$ is predominantly an inner-sphere type with a positive enthalpy change opposing complex formation and a large positive entropy change favouring complex formation as suggested by Ahrland [140].

(ii) Neptunium(V)

Absorption spectra of Np(V) in perchlorate and sulphate media included in Fig. 2 clearly establish the sulphate complexing of Np(V). Spectral changes

TABLE 8

Constants for the stepwise association of bisulphate and neptunium ions. Temp. = 25°C

Ion	Method	Medium	$^*K_1$	$^*K_2$	Ref.
Np(IV)	Spec.	2.0 M $NaClO_4$	594.0	—	88
	Pot.	3.0 M ClO_4^- ($[H^+] = 1.0$ M)	312.0	12.0	133
	Cix	4.0 M $HClO_4$	501.0	36.3	41 [a]
	TTA	2.0 M $HClO_4$	270.0	11.0	134
	TTA	2.0 M $HClO_4$	306.0	37.7	14
	TTA	2.0 M $HClO_4$	293.0	22.9	135 [b]
	TTA	2.0 M $HClO_4$	340.0	32.4	43
	DNNS	2.0 M $HClO_4$	326.0	29.8	14
Np(V)	DNNS	2.0 M $NaClO_4$	2.8 (K_1) [d]	—	44a
Np(VI)	Spec.	2.0 M $NaClO_4$	3.7	—	88
	DBP	1.0 M $HClO_4$	6.2	0.6	136 [c]
	Pot.	1.0 M $HClO_4$	13.0	—	56
	Pot.	0.1 M $HClO_4$	7.6	<0.2	48
	Pot.	0.2 M $HClO_4$	6.5	<0.2	48
	Pot.	0.3 M $HClO_4$	6.0	<0.2	48
	Pot.	0.4 M $HClO_4$	5.7	<0.2	48
	Pot.	0.5 M $HClO_4$	5.6	<0.2	48
	Pot.	0	18.9	—	48
	Pot.	2.0 M $NaClO_4$	7.14	0.17	47
	DNNS	2.0 M $HClO_4$	11.7	0.34	16

[a] Temp. = 20°C. [b] Recalculated using data from Ref. 134. [c] Temp. = 21°C. [d] $K_1 = [NpO_2SO_4^-]/[NpO_2^+][SO_4^{2-}]$.

could not be observed in the earlier study [63] as the acid medium employed limits the sulphate ion concentration.

(iii) Neptunium(VI)

The potentiometric value [56] may be taken as approximate as the formation of only one complex was assumed even in 1 N H_2SO_4 and Np(V) complexing was ignored. The spectrophotometric value [88] also suffers from the same disadvantage as the formation of only one complex was assumed which may not be true under the experimental conditions employed.

A comparison of the values of $^*K_1$ obtained for the hexavalent actinides suggests [16] the complexing order to be U(VI) < Np(VI) < Pu(VI). The thermodynamic data are given in Table 9 from which it is seen that the complex is predominantly inner-sphere.

(iv) Neptunium(VII)

Using spectrophotometry at $\mu = 1.0$ ($[H^+] = 0.03$ M and 0.1 M) and 6°C [143] $K_1 \doteq 1.1 \times 10^4$ was obtained. In view of the very high instability of Np(VII) in acid solutions further work is necessary to confirm this value.

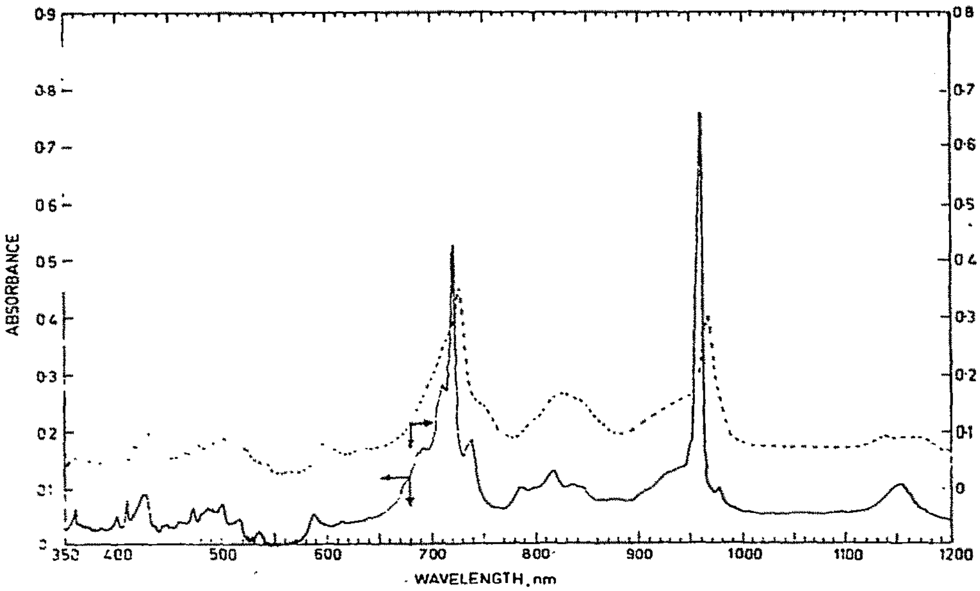

Fig. 9. Absorption spectra of Np(IV) ([Np(IV)] ≅ 1.74×10^{-3} M, 2.0 cm cells) in 1.0 M $HClO_4$ (———) and 1.0 M H_2SO_4 (– – – –) [49a].

TABLE 9

Thermodynamic values associated with the sulphate complexing of neptunium ions. $\mu = 2.0$; $[H^+] = 2.0$ M

Equilibrium	Method	$-\Delta G$ (Kcal mole^{-1})	ΔH (Kcal mole^{-1})	ΔS (e.u.)	Ref.
I [a]	TTA	4.79	4.00	30.0	134
	TTA	4.84	6.97	39.6	135 [d]
	TTA	4.86	6.74	38.9	135
	DNNS	4.90	6.83	39.3	135
II [b]	TTA	2.89	8.84	39.0	134
III [c]	Pot.	2.62	1.52	10.25	47 [e]

[a] I. $Np^{4+} + SO_4^{2-} \rightleftharpoons Np(SO_4)^{2+}$. [b] II. $Np(SO_4)^{2+} + SO_4^{2-} \rightleftharpoons Np(SO_4)_2$. [c] III. $NpO_2^{2+} + SO_4^{2-} \rightleftharpoons NpO_2(SO_4)$. [d] Recalculated using data from Ref. 134. [e] $[H^+] < 0.1$ M.

J. MISCELLANEOUS INORGANIC COMPLEXES

(a) Iodide complexes

(i) Neptunium(IV)

The absorption spectrum of Np(IV) in iodide medium [49a] is included in

Fig. 3. The iodide complexing of Np(IV) was recently studied [144] in a perchlorate—iodide medium ($\mu = 2.0$; $[H^+] = 1.0$ M) at 25°C using the TTA extraction method and the DNNS extraction method. The value of $\beta_1 = 0.8$ was obtained by the former while $\beta_1 = 1.3$ was obtained by the latter method.

(b) Iodate complexes

(i) Neptunium(IV)

The absorption spectrum of Np(IV) [49a], in iodic acid medium is shown in Fig. 10. The spectral changes suggest formation of strong iodate complexes of Np(IV).

(ii) Neptunium(V)

Using the DNNS extraction method, $\beta_1 = 2.1$ was obtained for the formation of NpO_2IO_3 in 2 M $NaClO_4$ at 25°C [44a].

(iii) Neptunium(VI)

The addition of potassium iodate to a weakly acidic solution of Np(VI) results [144] in a sharp increase in the absorption of Np(VI) in the range 370—410 nm. Using these data the stability constant of the complex $NpO_2IO_3^+$ is calculated to be $K_1 = 4.1$ at $\mu = 0.3$ and 25°C. Higher complexes were also indicated.

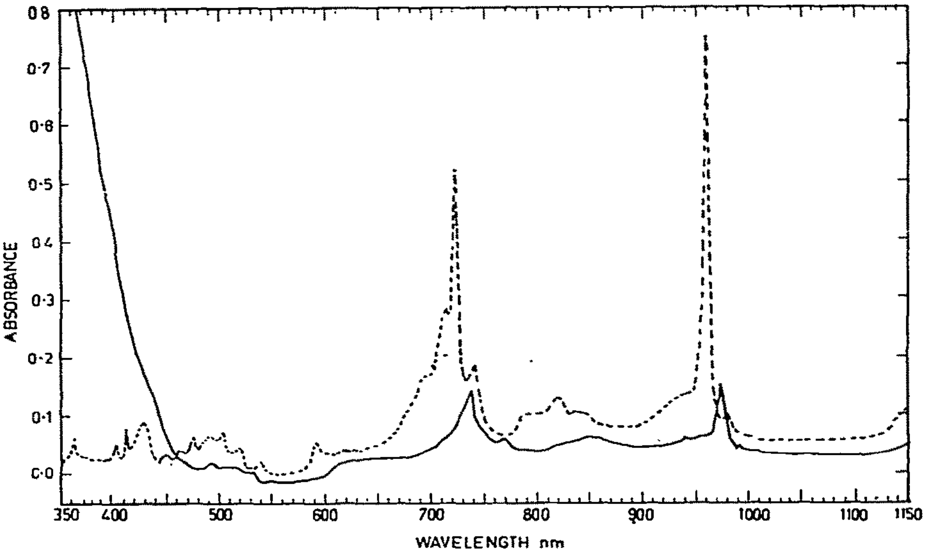

Fig. 10. Absorption spectra of Np(IV) in 1.0 $HClO_4$ ($[Np(IV)] \cong 1.74 \times 10^{-3}$ M, 2.0 cm cells) (------) and 2.0 M HIO_3 ($[Np(IV)] \cong 7.5 \times 10^{-4}$ M, 2.0 cm cells) (———) [49a].

(c) Sulphite complexes

(i) Neptunium(V)

It was shown [146] by spectrophotometry, that in neutral solutions, Np(V) forms two complexes $NpO_2SO_3^-$ and $NpO_2(SO_3)_2^{3-}$ with $K_1 = 4.0 \times 10^2$ and $K_2 = 10$ respectively at $\mu = 1.0$ and 25°C. By the cation exchange method [147] the values $K_1 = 1.41 \times 10^2$ and $K_2 = 7.1$ were obtained for the formation of the same complexes.

(d) Carbonate complexes

(i) Neptunium(IV)

The absorption spectra of Np(IV) [149] in 1.0 M hydrochloric acid and 1.0 M ammonium carbonate are shown in Fig. 11. The spectral changes are presumably due to the carbonate complexing of Np(IV). The stability constant for the formation of the complex $Np(OH)_4CO_3^{2-}$ was determined [150], using the data obtained on the solubility of Np(IV) hydroxide in ammonium carbonate solutions, to be $\beta_1 = 1.2 \times 10^{53}$. This value is quite close to that obtained [151] for the corresponding Pu(IV) complex. However, no data were available for the simple carbonate complexes of Np(IV).

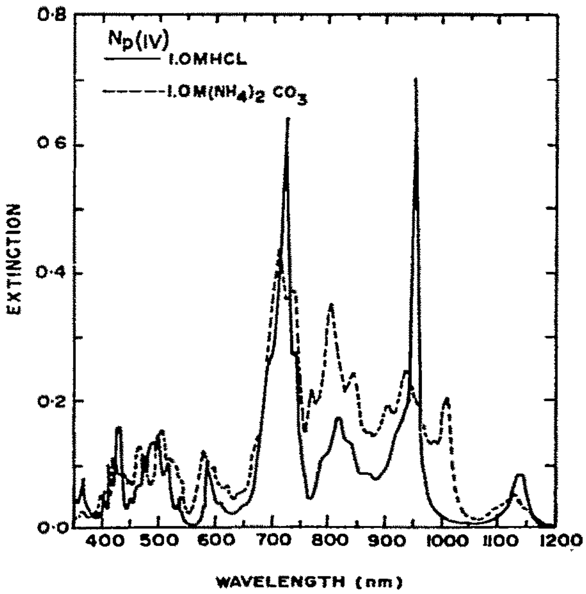

Fig. 11. Absorption spectra of Np(IV) ([Np(IV)] = 7.0×10^{-3} M, 1.0 cm cells). Reprinted with permission from J. Inorg. Nucl. Chem., 39 (1977) 315. Copyright by Pergamon Press Ltd.

(ii) Neptunium(V)

Absorption spectra of Np(V) [152] in 2.0 M sodium carbonate solution and 0.1 M hydrochloric acid shown in Fig. 12, indicate the carbonate complexing of Np(V).

Using the cation exchange method the stability constant for the formation of NpO_2HCO_3 was determined [153] to be $\beta_1 = 270$ at $\mu = 0$. From the solubility studies of the salts, ammonium neptunyl carbonate and Np(V) hydroxide, in ammonium carbonate solutions the stability constants for the formation of $NpO_2(OH)(CO_3)^{2-}$ and $NpO_2(OH)(CO_3)_2^{4-}$ were evaluated [150] to be $\beta_1 = 6.7 \times 10^4$ and $\beta_2 = 7.0 \times 10^4$ respectively.

(iii) Neptunium(VI)

Carbonate complexing of Np(VI) was studied [150] by the solubility method and stability constant values are given in Table 10.

(e) Phosphate complexes

(i) Neptunium(III)

Using data available on phosphate complexing of actinide(III) ions stability constants (at $\mu = 0$) for the complexes $Np(H_2PO_4)^{2+}$, $Np(H_2PO_4)_2^{+}$ and $Np(H_2PO_4)_3$ were estimated [154] to be 2.5×10^2, 5.4×10^3 and 4.4×10^5 (β values) respectively.

(ii) Neptunium(V)

Using the cation exchange method at 20°C and $\mu = 0.2$, the formation of

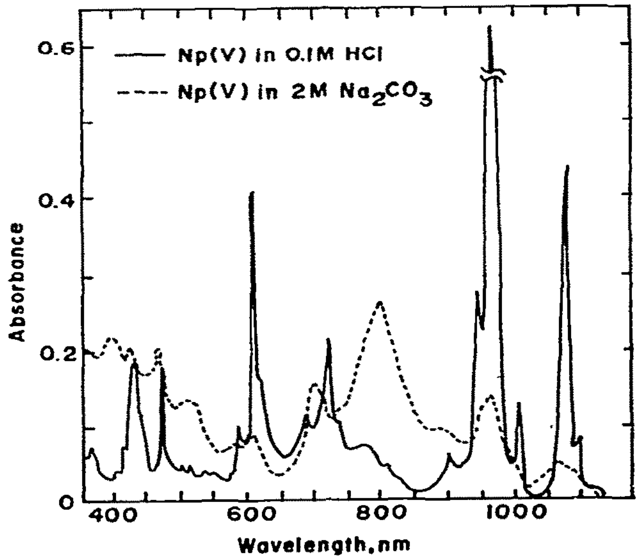

Fig. 12. Absorption spectra of Np(V) ([Np(V)] = 2.2×10^{-1} M, 1.0 cm cells) [152]. Reprinted with permission from Akademiai Kaido.

TABLE 10

Stability constants for the formation of carbonate complexes of Np(VI) [150]

Equilibrium	K
$NpO_2(OH)_2 + CO_3^{2-} \rightleftharpoons NpO_2(OH)_2CO_3^{2-}$	81.0
$NpO_2(OH)_2CO_3^{2-} + CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_2^{4-} + 2(OH)^-$	1.5×10^{-9}
$(NH_4)_2NpO_2(CO_3)_2 + (NH_4)_2CO_3 \rightleftharpoons (NH_4)_4NpO_2(CO_3)_3$	1.2×10^{-2}

the complexes $NpO_2HPO_4^-$ and $NpO_2H_2PO_4$, in the pH region 4.8—6.7 was reported [155] with the stability constant values 7.1×10^2 and 6.4 respectively. Only one complex, $NpO_2HPO_4^-$, was found to exist when the $(NH_4)_2HPO_4$ concentration was in the range 5×10^{-3} to 5×10^{-2} M. The thermodynamic stability constant value ($\mu = 0$) for the formation of $NpO_2HPO_4^-$ was calculated to be 2.4×10^3 using the Davies [156] equation.

(iii) Neptunium(VI)

The stability constants for the formation of the complexes $NpO_2(HPO_4)$ and $NpO_2(H_2PO_4)^+$ are [154] 1.5×10^7 and 50 at $\mu = 1.0$ and 1.5×10^8 and 2.14×10^2 at $\mu = 0$ respectively.

(f) Nitrite complexes

(i) Neptunium(V)

Using the DNNS extraction method, $\beta_1 = 0.9$ was obtained for the formation of NpO_2NO_2 in 2.0 M $NaClO_4$ at 25°C [44a].

K. MONOCARBOXYLATE COMPLEXES

Studies on the complexing of neptunium ions with monocarboxylate ligands have been limited and have often been obtained by one method only. Stability constant values obtained with several such ligands are given in Table 11.

(a) Acetate complexes

(i) Neptunium(IV)

The β values given in Table 11 for the acetate complexing [160] are much lower than expected when compared with the corresponding values for Pu(IV) [169] and Th(IV) [170]. In the low acid medium ($[H^+] = 0.1$ M) employed [160] Np(IV) might have been, at least partly, oxidised to Np(V) thus giving the lower values. This necessitates a reexamination of acetate complexing of Np(IV).

TABLE 11

Constants for overall association of neptunium ions with different monocarboxylate ligands. Temp. = 25°C

Ion	Ligand	Method	Medium	β_1	β_2	β_3	Ref.
Np(III)	Acetate	Calc.	0	5.9×10^2	1.1×10^5	3.8×10^6	154
	Glycolate	Calc.	0	4.0×10^3	1.4×10^6	—	154
	α-OH⁻-isobutyrate	Calc.	0	4.0×10^3	1.3×10^6	2.0×10^7	154
Np(IV)	Formate	?	0.1—0.3 M HCOONa	5.0×10^2	—	—	159
	Acetate	Cix	0.5 M NH_4Cl ($[H^+] = 0.1$ M)	4.8×10^2	5.8×10^4	3.1×10^7	160 [b]
	α-picolinate	Spec.	1.0 M ClO_4^-	3.2×10^6	—	—	26
	α-picolinic acid-N-oxide	Spec.	1.0 M ClO_4^-	2.6×10^6	—	—	26
Np(V)	Acetate	?	1.5	12.0	36.0	—	153
	Acetate	Spec.	1.5 M NH_4Cl	11.0	35.0	—	161
	Acetate	?	1.0	5.4	—	—	162
	Acetate	Spec.	2.0	7.7	16.8	—	163
	Acetate	DNNS	2.0 M $NaClO_4$	9.3	—	—	80
	Benzoate	Spec.	1.0 M ClO_4^-	6.35	1.48	—	163
	Glycolate	Cix	2.0 (pH ≃ 6.5)	40.0	—	—	147
	Glycolate	Cix	0	80.0	—	—	147
	Glycolate	Spec.	0.1 M ClO_4^-	32.4	—	—	164
	Glycolate	Spec.	1.0 M ClO_4^-	24.8	47.8	—	163
	Lactate	Cix	0.05 (pH = 4.5—6.5)	51.0	300.0	—	147
	Lactate	?	0.2	36.0	160.0	—	147
	Lactate	Spec.	0.1	56.2	—	—	164
	α-OH⁻-isobutyrate	Cix	0.05 (pH ≃ 6)	98.0	790.0	3400.0	165
	α-OH⁻-isobutyrate	Cix	0	148.0	1175.0	3390.0	165
	Salicylate	Spec.	1.0 M ClO_4^-	1.12×10^7	4.19×10^{11}	—	163
	Glycinate	Spec.	1.0 M ClO_4^-	1.84×10^4	2.0×10^5	0.65 (K_3)	163
	α-amino propionate	Spec.	1.0 M ClO_4^-	1.09×10^3	8.64×10^4	—	163
	α-amino butyrate	Spec.	1.0 M ClO_4^-	1.06×10^3	3.39×10[illegible]	—	163
Np(VI)	Acetate	Spec.	0.7 M $HClO_4$	—	6.7×10^5	8.37×10^7	161
	Acetate	Pot.	1.0 M ClO_4^-	204.0	1.7×10^4	1.0×10^6	166 [a]

TABLE 11 (continued)

Ion	Ligand	Method	Medium	β_1	β_2	β_3	Ref.
Np(VI)	Acetate	Pot.	1.0	240.0	4.0×10^4	2.5×10^6	160
	Propionate	Pot.	1.0 M ClO_4^-	2.8×10^2	2.9×10^4	3.2×10^6	167 [a]
	Glycolate	Pot.	1.0 M ClO_4^-	235.0	9.0×10^3	1.0×10^5	168 [a]
	Monochloracetate	Pot.	1.0 M ClO_4^-	21.4	126.0	605.0	167 [a]
	β-Cl^--propionate	Pot.	1.0 M ClO_4^-	75.0	2.0×10^3	4.0×10^3	167 [a]

[a] Temp. = 20°C. [b] $\beta_4 = 4.7 \times 10^9, \beta_5 = 1.0 \times 10^{12}, \beta_6 = 5.0 \times 10^{14}, \beta_7 = 2.5 \times 10^{17}, \beta_8 = 1.6 \times 10^{20}$.

(ii) Neptunium(V)

Absorption spectra of Np(V), as a function of acetate ion concentration, are shown in Fig. 13.

(iii) Neptunium(VI)

Comparison of the stabilities of the acetate complexes of Np(VI) (Table 11) with those of U(VI) [173,174] and Pu(VI) [175] reveals that the stabilities follow the order U(VI) > Np(VI) > Pu(VI).

(b) Propionate complexes

(i) Neptunium(VI)

When the β values of Np(VI) (Table 11) are compared with those of U(VI) [177] it is observed that U(VI) is more strongly complexed than Np(VI) by propionate.

(c) Glycolate complexes

(i) Neptunium(VI)

Comparing data for Np(VI), U(VI) [178] and Pu(VI) [179] reveals that the glycolate stability constants follow the order U(VI) > Np(VI) > Pu(VI).

(d) Salicylate complexes

(i) Neptunium(V)

The high β values obtained reveal a strong complexing tendency of the

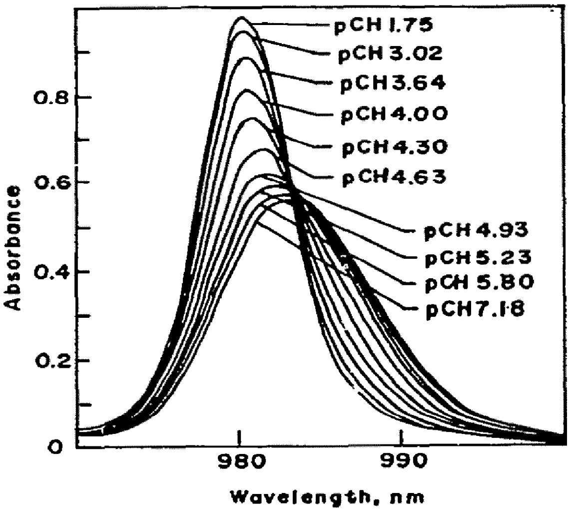

Fig. 13. Absorption spectra of Np(V) ([Np(IV)] = 2.5×10^{-3} M, 1.0 cm cells) [163].

salicylate ion and this must be due to the 2^- charge on this ligand as was reported in connection with the salicylate complexing of Pu(VI) [180].

(e) Aminocarboxylate complexes

(i) Neptunium(V)

The high β values obtained for the amino carboxylate complexing of Np(V) might be due to the formation of a 5-membered chelate ring involving coordination of Np(V) through both the nitrogen and the carboxyl oxygen as was suggested in the case of glycinate complexing of Pu(V) [181].

(f) Chlorocarboxylate complexes

(i) Neptunium(VI)

Comparison of data for Np(VI), U(VI) [174,182] and Pu(VI) [179,183] indicates that stability constants of monochloroacetate and β-chloropropionate complexes follow the order U(VI) > Np(VI) > Pu(VI).

(g) Pyridinacetate complexes

(i) Neptunium(IV)

Comparison of data for Np(IV), Th(IV) and U(IV) suggests that their complexing with α-picolinate follows the order, Th(IV) < U(IV) > Np(IV). However, with α-picolinic acid-N-oxide the order was Th(IV) < U(IV) < Np(IV). This sort of reversal in the complexing order between U(IV) and Np(IV), however, is not uncommon.

L. DICARBOXYLATE COMPLEXES

The complex formation studies on neptunium ions with dicarboxylate ligands were mostly confined to oxalate and the stability constant values are given in Table 12.

(a) Oxalate complexes

(i) Neptunium(IV)

In calculating stability constant values from solubility data obtained using HCl [184] and HNO_3 [185,186] media, chloride or nitrate complexing of Np(IV) was not taken into consideration. From the temperature dependence of stability constants obtained by the TTA extraction method thermodynamic parameters were evaluated to be $\Delta G = -12.6$ Kcal mole^{-1}, $\Delta H = -4.6$ Kcal mole^{-1} and $\Delta S = 27$ e.u., indicating thereby that the complexing is essentially inner-sphere [188b].

Comparison of the β_1 values for the oxalate complexing obtained at the same ionic strength [188] reveals that complexing follows the order Th(IV) < Np(IV) < Pu(IV).

TABLE 12

Constants for the overall association of neptunium ions with different dicarboxylate ligands

Ion	Ligand	Method	Medium	Temp. °C	β_1	β_2	β_3	β_4	Ref.
Np(IV)	Oxalate	Solubility	0.5 M HCl	19	3.5×10^8	3.2×10^{17}	1.0×10^{24}	2.5×10^{27}	184
	Oxalate	Solubility	0	19	1.26×10^{11}	2.51×10^{20}	6.31×10^{26}	6.31×10^{29}	184
	Oxalate	Solubility	0.5–1.0 M HNO_3	—	4.4×10^8	6.3×10^{16}	1.6×10^{23}	1.0×10^{27}	185, 186
	Oxalate	Solubility	1.0 M $HClO_4$	26	2.9×10^7	4.9×10^{13}	2.35×10^{19}	—	187
	Oxalate	Solubility	1.0 M $NaClO_4$ ($[H^+] = 0.5$ M)	26	2.5×10^7	4.2×10^{13}	2.9×10^{19}	—	187
	Oxalate	TTA	1.0 M $HClO_4$	26	1.54×10^8	1.63×10^{16}	—	—	187
	Oxalate	TTA	1.0 M $HClO_4$	25	1.66×10^9	4.24×10^{16}	—	—	188
	Oxalate	DNNS	1.0 M $HClO_4$	25	2.1×10^9	2.7×10^{16}	1.7×10^{23}	—	188a
	N-β-hydroxyethylimino-diacetate	Spec.	1.0 M ClO_4^-	25	9.3×10^{12}	5.3×10^{23}	—	—	26, 189
Np(V)	Oxalate	Spec.	0.5 (pH = 1–5)	25	1.96×10^3	1.15×10^7	—	—	190
	Oxalate	Cix	0.05 NH_4ClO_4	20	1.0×10^4	2.0×10^7	—	—	191
	Oxalate	Cix	0	20	2.5×10^4	2.3×10^7	—	—	191
	Oxalate	Spec.	0	25	8.5×10^3	1.15×10^7	—	—	190, 191
	Oxalate	Spec.	1.0 M ClO_4^-	25	3.5×10^4	7.22×10^7	—	—	163
	Tartrate	Cix	0.05 M NH_4ClO_4	20	2.1×10^2	2.0×10^4	1.5×10^6	—	192
	Iminodiacetate	Spec.	?	?	3.18×10^5	6.21×10^6	—	—	163
Np(VI)	Oxalate	Spec.	1.0 M $HClO_4$	20	1.0×10^6	—	—	—	193
	Oxalate	Spec.	1.0 M NH_4NO_3 ($[H^+] = 0.3$ M)	13	—	$K_2 = 1.2 \times 10^4$	—	—	193
	Oxalate	Sol.	1.0 M HNO_3	14	1.3×10^6	—	—	—	193

(ii) Neptunium(V)

The enthalpy of formation of $NpO_2(C_2O_4)^-$ was found to be 0.0 ± 0.3 kcal mole^{-1} [190] thus suggesting that the complex is predominantly entropy stabilized and hence of inner-sphere type.

(iii) Neptunium(VI)

As oxalic acid is known to reduce Np(VI) in acid solutions [194,195] the Np(VI)—oxalate β values (Table 12) may need further confirmation.

M. POLYCARBOXYLATE COMPLEXES

There are not many data on the complexing of neptunium with polycarboxylate ligands and wherever data are available the agreement within the data is not very satisfactory. It can be said that a systematic investigation of the complex formation equilibria involving neptunium ions and polycarboxylate ligands has just begun with spectrophotometric studies [26,163]. The stability constant values are given in Table 13. In addition to the values given in Table 13 values for DTPA complexing of Np(IV), $\beta' = 3.2 \times 10^{21}$ for the formation of NpHY and $\beta'' = 2.0 \times 10^{12}$ for the formation of NpH_2Y^+ were obtained [202]. Data on DTPA complexing of tetravalent actinides revealed [199,200] that the complexing order is Th(IV) < U(IV) < Np(IV) < Pu(IV).

N. CHELATE COMPLEXES

(i) Neptunium(IV)

For this ion only acetylacetone complexing has been studied [207]. For a 1.0 M sodium perchlorate medium ($\mu = 1.0$) at 25°C, the values $K_1 = 3.8 \times 10^8$, $K_2 = 4.5 \times 10^8$, $K_3 = 5.1 \times 10^6$ and $K_4 = 1.9 \times 10^6$ were reported. In this work it was found that Np(IV) was partially oxidised which necessitated applying corrections for the distribution data. Although such corrections have been applied it is, however, desirable to study this system under conditions which permit the stabilization of Np(IV). Thermodynamic data for the formation of the third and fourth complexes are given in Table 14.

The value $^*\beta_1 = 45$ for TTA complexing of Np(IV) was obtained [43] at 25°C for a 2.0 M perchloric acid medium ($\mu = 2.0$). Comparison of $^*\beta_1$ values for Th(IV) [50,73], Np(IV) and Pu(IV) [43] obtained at $\mu = 2.0$ shows the order of complexing to be Th(IV) < Np(IV) < Pu(IV).

(ii) Neptunium(V)

The β values obtained for several chelate complexes of Np(V) are given in Table 15. The thermodynamic data are given in Table 16.

TABLE 13

Constants for the overall association of neptunium ions with different polycarboxylate ligands

Ion	Ligand	Method	Medium	Temp. °C	β_1	β_2	Ref.
Np(III)	NTA	Calc.	0	—	5.0×10^{12}	—	154
	EDTA	Calc.	0	—	3.1×10^{20}	—	154
	DTPA	Calc.	0	—	1.6×10^{25}	—	154
Np(IV)	NTA	Spec.	1.0 M ClO_4^-	25	1.9×10^{17}	1.15×10^{32}	26
	N-β-OH⁻-ED-Triacetate	Spec.	1.0 M ClO_4^-	25	6.6×10^{20}	3.9×10^{33}	26
	EDTA	Dist.	0.5 M HCl	23	2.0×10^{26}	—	196
	EDTA	Spec.	1.0 M ClO_4^-	25	3.55×10^{24}	—	26, 189
	EDTA	TTA	HNO_3(0)	25	7.9×10^{22}	—	197
	EDTA	?	?	?	6.3×10^{22}	—	198
	DTPA	Pot.	0.5 M HCl	20	1.95×10^{29}	—	199, 200
	DTPA	Spec.	1.0 M ClO_4^-	25	2.14×10^{30}	—	26, 189
	DTPA	Cix.	1.0 M ($[H^+] = 0.5$)	?	6.1×10^{29}	—	201
	DTPA	Cix.	HNO_3(0)	25	9.1×10^{30}	—	202
Np(V)	Citrate	Cix.	0.05 M	20	4.7×10^{3}	—	192
	Citrate	Spec.	1.0 M ClO_4^-	25	2.64×10^{4}	—	163
	NTA	Spec.	1.0 M ClO_4^-	25	7.16×10^{5}	5.85×10^{6}	163
	EDTA	Spec.	0.1 M NH_4ClO_4	25	1.0×10^{4}	2.14×10^{7}	203
	EDTA	TTA	1.0	?	1.1×10^{9}	—	204
	EDTA	?	?	?	2.2×10^{10}	—	205
	EDTA	?	?	?	4.9×10^{9}	—	206
	DTPA	Cix.	0.05 M NH_4Cl(pH = 6)	?	6.8×10^{10}	—	201

TABLE 14

Thermodynamic values for the Np(IV)-acetylacetone complexes [207]. $\mu = 1.0$; Temp. = 25° C

Equilibrium	$-\Delta G$ (Kcal $mole^{-1}$)	$-\Delta H$ (Kcal $mole^{-1}$)	ΔS (e.u.)
$Np(AA)_2^{2+} + AA^- \rightleftharpoons Np(AA)_3^+$	9.15 ± 0.03	2.3 ± 1.3	23.15 ± 0.14
$Np(AA)_3^+ + AA^- \rightleftharpoons Np(AA)_4$	8.57 ± 0.03	10.2 ± 1.2	5.92 ± 0.13

TABLE 15

Stability constants for the formation of Np(IV) chelates. $\mu = 0.1$; Temp. = 25°C

Ligand [a]	β_1	β_2	Ref.
Acetylacetone	1.2×10^4	1.0×10^7	208—210
Acetylacetone	1.2×10^4	1.2×10^7	209, 210 [b]
Tropolone	2.8×10^5	6.5×10^9	211 [c]
Tropolone	2.7×10^5	3.3×10^9	212
β-isopropyl tropolone	3.7×10^5	3.5×10^9	212
8-OH^--Quinoline	2.09×10^6	3.16×10^{11}	213
8-OH^--Quinoline 5-sulphonic acid	5.25×10^5	2.63×10^{10}	213
7-I-8-OHQ-5-sulphonic acid	6.76×10^4	2.51×10^9	213
Furoylacetone	2.5×10^4	7.1×10^7	209, 210
Thenoylacetone	1.7×10^4	2.6×10^7	209, 210
Benzoylacetone	9.8×10^4	7.2×10^8	209, 210
Trifluoroacetylacetone	3.7×10^2	—	209, 210
Furoyltrifluoroacetone	1.7×10^2	4.4×10^4	209, 210
Thenoyltrifluoroacetone	7.8×10^2	3.0×10^5	209, 210
Benzoyltrifluoroacetone	1.3×10^4	7.2×10^7	209, 210
Hexafluoroacetylacetone	8.7×10^1	—	209, 210
Difluoroylmethane	1.1×10^4	1.2×10^7	209, 210

[a] The actual ligand is the anion of the acids listed. [b] Ionic strength = 1.0. [c] Ionic strength = 1.0, temp. = 20° C, method = potentiometry.

TABLE 16

Thermodynamic values for the Np(V)—chelate complexes

Equilibrium	$-\Delta G$ (Kcal $mole^{-1}$)	$-\Delta H$ (Kcal $mole^{-1}$)	ΔS (e.u.)	Ref.
$NpO_2^+ + AA^- \rightleftharpoons NpO_2AA$	5.57	6.26	−2.33	209
$NpO_2AA + AA^- \rightleftharpoons NpO_2(AA)_2^-$	3.97	3.20	2.59	209
$NpO_2^+ + OXS^{2-} \rightleftharpoons NpO_2(OXS)^-$	7.9	10.6	9.4	213
$NpO_2(OXS)^- + OXS^{2-} \rightleftharpoons NpO_2(OXS)_2^{3-}$	6.5	8.5	6.7	213

P. GENERAL REMARKS

From the data on complex formation of neptunium ions that has been discussed in this review some general features and trends observed are summarized here. As mentioned in the introduction the problem of maintaining the oxidation state of the neptunium ions, whose complexing properties were being studied, has caused some uncertainty in the values of the stability constants.

There are practically no studies on the complex formation of Np(VI) with many organic ligands such as polycarboxylates and chelates. The same is the case with the chelate complexes of Np(IV). Wherever data are available complex formation trends have always been observed to be Np(IV) > Np(VI) > Np(V) as expected.

Thermodynamic data on complex formation equilibria have been very limited and wherever studied they have been obtained only by the temperature quotient method. As such there is a need to obtain reliable thermodynamic data, preferably by calorimetry, to gain more insight into the complexing behaviour. The spectrophotometric method has not been fully utilized even for calculating stability constants never mind establishing the nature of the complex species. As a rule, absorption spectral changes have been found to accompany complex formation in many cases. Also relatively recent techniques for elucidating the nature of the complex species, such as ultrasonic absorption studies, are yet to find their way to studies of this element.

Stabilities of the complexes of tetravalent actinides, in general, gave the trend Th(IV) < U(IV) $\simeq$ Np(IV) < Pu(IV) whereas for hexavalent actinides the observed trend has always been U(VI) > Np(VI) > Pu(VI) except in the case of sulphate where a reversed trend is seen.

In conclusion it can be said that the chemical properties of this pioneering transuranium element are as interesting, if not more, as those of uranium and plutonium. The chemical investigations on the latter two have been carried out quite extensively probably as they have imp[illegible]ant applications in nuclear technology. Neptunium has received relatively le[illegible]ttention. Recently, however, considerable effort has been devoted to the study of neptunium and it is hoped that much more work in the field of neptunium complexes will be forthcoming which is highly desirable.

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APPENDIX

Literature on qualitative data on complex formation; A—absorption spectra, B—solvent extraction, C—ion exchange, D—potentiometry, electromigration etc.

Ligand	Method	Reference nos. for		
		Np(IV)	Np(V)	Np(VI)
Hydroxide	A	—	36	—
Fluoride	A	—	47	—
	B	—	48, 54	—
Chloride	A	63	63, 80	63
	B	68—72	70—72, 79	68, 70—72, 79
	C	64—67	76—78	—
Bromide	A	—	49a	—
	C	84	—	—
Nitrate	A	95—99	49a, 63	63
	B	70—72, 100—113	79, 72, 79, 100, 102—104, 121—124	70—72, 79, 100—110, 113, 121, 123, 124
	C	99, 118—120	—	126
Thiocyanate	A	129, 130a	—	—
	B	130, 131	—	—
Sulphate	A	63	63	63
	B	49a, 71, 122	49a, 79	79
	C	—	48	—
	D	137, 138	—	137, 141, 142
Iodide	A	—	49a	—
Iodate	A	—	49a, 145	—
Carbonate	A	148, 149	152	149
Peroxide	A	49a	49a, 63	158
	D	157	—	—
Nitrite	A	—	49a	—
	B	158a	—	—
Formate	A	129	—	—
Acetate	A	129	36	—
	B	—	—	171, 172
Propionate	D	—	—	176
Salicylate	A	—	36	—
Oxalate	A	129, 187	194	—
	B	—	79	79
Phthalate	A	—	36	—

Hydrolysis of Np(VII), A, Ref. 40.

NOTE ADDED IN PROOF

Potentiometric values (β_1) obtained for dicarboxylate complexes of Np(V) in 1 M $NaClO_4$ medium at 20°C are [214]: oxalate (5.5×10^3; $\beta_2 = 2.04 \times 10^6$);

malonate (5.6×10^2); succinate (52.5); maleate (1.59×10^2); phthalate (1.66×10^2). Using proton magnetic relaxation methods (experimental conditions not specified) the following values (β_1) for the complexes of Np(V) are reported [215]: F^- (8.0); acetate (20.0); $SO_4^=$ (<0.2); Cl^- (<0.2); NO_3^- (<0.2). Recently, thiocyanate complexing of Np(V) in 9 M $NaClO_4$ at 25°C was studied [216] by potentiometry and spectrophotometry and the values of β reported are: potentiometry ($\beta_1 = 10.7$; $\beta_2 = 36.4$; $\beta_3 = 40.0$; $\beta = 36.0$); spectrophotometry ($\beta_1 = 17.0$; $\beta_2 = 81.0$; $\beta_3 = 109.0$; $\beta_4 = 52.8$; $\beta_5 = 2.9$).

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