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Studies of the Formation of Complexes of Np(V) with Inorganic Ligands by Means of Solvent Extraction with 2-Thenoyltrifluoroacetone and 1,10-Phenanthroline. II. Fluoro, Sulfato, and Phosphato Complexes

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The formation constants of the complexes of Np(V) with fluoride, sulfate, and phosphate have been determined in 1 mol dm^{-3} $NaClO_4$ at 25 °C by means of the solvent-extraction method using 2-thenoyltrifluoroacetone and 1,10-phenanthroline. Extractions at various pH values revealed that $H_2PO_4^-$ and HPO_4^{2-} participate in the complex formation of Np(V).

The study of the complex formation of quinquevalent uranides (U, Np, Pu, and Am) with a variety of ligands in aqueous solutions is important for understanding both the systematics and the nuclear chemical applications of these elements. Among uranides, neptunium is the only element which has a quinquevalent state which is stable enough to permit a study of complex formation in aqueous solutions.1) Recent compilations2–5) indicate a general lack of reliable data on the complex formation of Np(V), especially with inorganic ligands.

Previously,6–8) the formation constants of the complexes of Np(V) with some organic ligands and the carbonate ion have been determined by means of the solvent-extraction method using 2-thenoyltrifluoroacetone (TTA) and methyltrioctylammonium9) or TTA and 1,10-phenanthroline(phen).10) Inorganic anions, such as fluoride, chloride, nitrate, sulfate, and phosphate, are also important ligands in both natural and artificial systems. The present authors aimed to determine the formation constants of Np(V) complexes with these ligands by means of solvent extraction with TTA and phen. Among these anions, however, chloride and nitrate cannot be studied since they are expected to form only very weak complexes with Np(V). The complex formation of Np(V) with only fluoride, sulfate, and phosphate has, therefore, been investigated.

Experimental

The neptunium-239 tracer was prepared by milking from ^{243}Am by the method of Sill;11) it was then adjusted to the quinquevalent state by evaporation to dryness and dissolution in water.12) To avoid any possible contamination by any complex-forming substances or by neptunium with a valence state other than quinquevalent (which might be introduced during milking), the following back-extraction procedure was adopted. The ^{239}Np tracer was first extracted into an organic (3-methyl-1-butanol or dichloromethane) solution containing the desired concentrations of TTA and phen. A 4-cm^3 portion of this organic solution containing ^{239}Np was then mechanically shaken for 15 min (140 times/min) at 25±1 °C in a glass tube with the same volume of an aqueous solution containing 1 mol dm^{-3} sodium perchlorate, buffer reagents (a proper mixture of 0.1 mol dm^{-3} of 2-morpholinoethanesulfonic acid monohydrate(MES) and 0.1 mol dm^{-3} of tris(hydroxymethyl)aminomethane (THAM)), and a variable concentration of a complex-forming reagent. After phase separation, a 1-cm^3 portion of each phase was pipetted into a counting tube and the γ-activity of each phase was measured with a well-type NaI(Tl) scintillation counter. The remaining part of the aqueous phase was used for the pH measurement. The reagents and apparatus used in the experiments were those previously described.8)

Results

The distribution ratio of Np(V) in the absence of complexing agents, D_0, can be represented by:10)

$$D_0 = K_{ex}[HT]_o[phen]_o{}^m/[H^+], \tag{1}$$

where HT and phen denote the neutral forms of TTA and phen; K_{ex}, the extraction constant; m, the number of molecules of phen in the extracted species, and o, the organic phase. The concentration of HT in the organic phase, $[HT]_o$, is related to the total added concentration of TTA (C_{TTA}) by means of the following equations:

$$\begin{aligned} C_{TTA} &= [HT]_o + [HT] + [T^-] \\ &= [HT]_o(1+1/K_{DR} + K_a/K_{DR}[H^+]), \end{aligned} \tag{2}$$

where:

$$K_a = [H^+][T^-]/[HT] = 10^{-6.46}(\mu{=}0.1,\ 25°C),^{12)} \tag{3}$$

and

$$K_{DR} = [HT]_o/[HT], \tag{4}$$

for 3-methyl-1-butanol;

$$K_{DR} = 10^{1.63}(\mu{=}1.0,\ 20°C),^{13)}$$

and for dichloromethane;

$$K_{DR} = 10^{1.84}(\mu{=}0.1,\ 25°C).^{13)}$$

The concentration of phen in the organic phase, $[phen]_o$, can be assumed to be equal to the total added concentration of phen, C_{phen}, under the conditions adopted in the experiment.

Under some experimental conditions, the effect of complexation with the TTA anion must be taken into consideration. The corrected distribution ratio, D_0', which is obtained experimentally in the absence of complexing agents other than the TTA anion, can be expressed by the following equation:

$$D'_0 = D_0/a, \qquad (5)$$

$$a = 1 + \sum\beta^{\mathrm{T}}_n[\mathrm{T}^-]^n, \qquad (6)$$

where β^{T}_n is the overall formation constant of the neptunium complex with the TTA anion. Equations 2—4 can be used for the estimation of $[\mathrm{T}^-]$. The values of log β^{T}_1=2.89 and log β^{T}_2=5.48[14] were used for the calculation. As will be discussed later, uncertainties in the values of K_a, K_{DR}, and β^{T}_n give systematic errors to the calculation of the formation constants of Np(V) complexes through the conditional constant a in Eq. 6. Therefore, the total concentration of TTA was taken to be as low as was practicable in order to give values of a close to 1 (the largest value of a used in this study was 1.24). The complex formation of Np(V) with MES, THAM, or phen can be ignored under the conditions adopted in this experiment, because the change in the total concentration of MES plus THAM from 0.05 to 0.2 mol dm^{-3} has no effect on the distribution ratio of Np(V).

The distribution ratio of Np(V) in the presence of fluoride or sulfate can be expressed by:

$$D = D_0/(a+\sum\beta_n[\mathrm{L}]^n), \qquad (7)$$

where [L] is the concentration of F$^-$ or $\mathrm{SO_4}^{2-}$ and where β_n is the overall formation constant of the complex of Np(V) with the ligand L (the charges of the ions are omitted for the sake of simplicity):

$$\beta_n = [\mathrm{ML}_n]/[\mathrm{M}][\mathrm{L}]^n, \qquad (8)$$

where M=$\mathrm{NpO_2}^+$.

By substituting Eq. 5 into Eq. 7, we obtain:

$$1/D = 1/D'_0 + \sum(\beta_n/D'_0a)[\mathrm{L}]^n. \qquad (9)$$

By using this equation, the β_n values can be obtained, together with D'_0, from the analysis of the 1/*D* *vs.* [L] plots.

Figures 1 and 2 show the plots of log *D* *vs.* log ([L]/mol dm^{-3}) for fluoride and sulfate respectively. In each series of experiments, the distribution ratios were obtained in a medium buffered at a constant pH. Since the pH of the aqueous phase before and after shaking changed only slightly, the pH's of the aqueous phase at equilibrium (after shaking) differed from each other by less than 0.1 unit in each series. Because log D_0 changes with the pH according to Eqs. 1 and 2, the experimental values of *D* were corrected to those at a constant pH using the extraction curves which were obtained experimentally.[10] Although the value of a in Eqs. 5 and 6 may also change with the pH because of the change in $[\mathrm{T}^-]$, the value of a was assumed to be constant in each series of experiments, since the experimental conditions were such that $\sum\beta^{\mathrm{T}}_n[\mathrm{T}^-]^n<1$. As the degree of dissociation of HF and $\mathrm{HSO_4}^-$ is fairly large in solutions within the pH range studied (pK_a=2.96 for HF and pK_a=1.10 for $\mathrm{HSO_4}^-$),[4] the concentrations of F$^-$ and $\mathrm{SO_4}^{2-}$ were taken as equal to the added concentrations of NaF and $\mathrm{Na_2SO_4}$ respectively. The distribution of any species containing fluoride or sulfate in the organic phase was neglected.

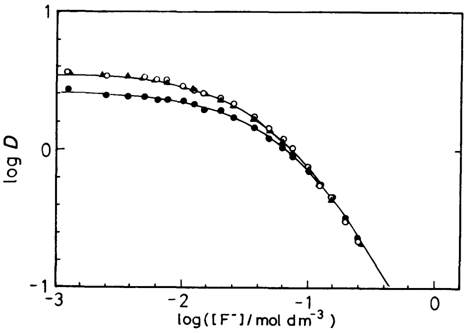

Fig. 1. Plots of log *D* *vs.* log([F$^-$]/mol dm^{-3}). Conditions: (○): No. 1, (▲): No. 2, (●): No. 3 in Table 1.

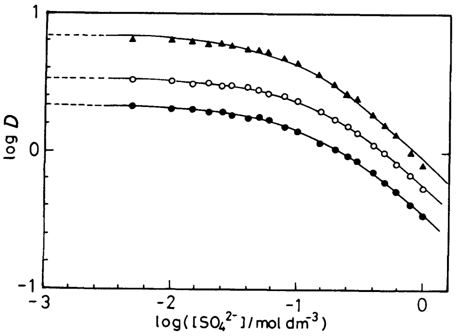

Fig. 2. Plots of log *D* *vs.* log([$\mathrm{SO_4}^{2-}$]/mol dm^{-3}). Conditions: (○): No. 4, (▲): No. 5, (●): No. 6 in Table 1.

To check the validity of the assumptions mentioned above, different kinds of organic diluents, 3-methyl-1-butanol and dichloromethane, and different pHs were adopted in different series of experiments.

The plots in Figs. 1 and 2 were analyzed to obtain the best fit to Eq. 9 as follows:

Equation 9 is equivalent to a linear function:

$$y = f(x), \qquad (10)$$

where:

$$y = 1/D, \qquad (11)$$

$$f(x) = 1/D'_0 + \sum(\beta_n/D'_0a)x^n, \qquad (12)$$

and:

$$x = [\mathrm{L}]. \qquad (13)$$

A set of data (x_i, y_i) (19—20 points) was analyzed by the least-squares method to determine the β_n and D'_0 values. Since the counting-time of the γ-activity was set to make the relative statistical errors of the total counts approximately constant (0.01—0.02), the residuals of the observed ratios, y, were expected to be proportional to the value of $1/D$, judging from error-propagation rules. Although the observed values of $1/D$ are not error-free, these values give a good basis for estimating the weight of the observation. Therefore, the least-squares fitting was carried out to minimize the following sum of the weighted squares of the residuals:

$$S = \sum\{y_i - f(x_i)\}^2/y_i^2. \tag{14}$$

The results of the analyses are shown in Table 1. Two series of experiments (Nos. 1 and 2) were carried out to check the reproducibility of the experiment, while others were carried out under different conditions in order to check if the unknown factors govern the distribution behavior of Np(V). Although the differences in β_n values were slightly larger than the standard deviations obtained from each series of experiments, the results agreed well with each other and enabled us to analyze the data altogether. Since Eq. 9 can be rearranged to:

$$aD'_0/D - (a-1) = 1 + \sum\beta_n[\mathrm{L}]^n, \tag{15}$$

the least-squares study was carried out between:

$$y = Y \equiv aD'_0/D - (a-1), \tag{16}$$

$$f(x) = 1 + \sum\beta_n x^n, \tag{17}$$

and:

$$x = [\mathrm{L}]. \tag{18}$$

The plots of log Y *vs.* log([L]/mol dm^{-3}) are shown in Figs. 3 and 4. The solid lines show the best fit of the data to Eq. 15, while the dashed lines show the contribution of each species of Np(V). The formation constants thus obtained are listed in Table 1.

In the presence of phoshate as a complexing agent, there is a possibility of the formation of different types of complexes, and the $1/D$ ratio can be expressed as:[8]

$$1/D = 1/D'_0 + \sum(\beta'_n/D'_0a)[\mathrm{H_2L}]^n + \sum(\beta_n/D'_0a)[\mathrm{HL}]^n, \tag{19}$$

where H_2L and HL denote $H_2PO_4^-$ and HPO_4^{2-} respectively. The overall formation constants and dissociation constants are given by these equations:

$$\beta'_n = [\mathrm{M(H_2L)}_n]/[\mathrm{M}][\mathrm{H_2L}]^n, \tag{20}$$

$$\beta_n = [\mathrm{M(HL)}_n]/[\mathrm{M}][\mathrm{HL}]^n, \tag{21}$$

$$K_i = [\mathrm{H}][\mathrm{H}_{3-i}\mathrm{L}]/[\mathrm{H}_{4-i}\mathrm{L}], \tag{22}$$

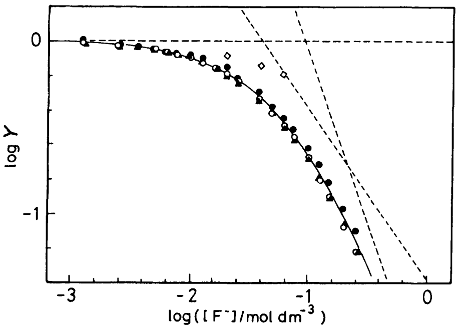

Fig. 3. Plots of log Y (Eq. 16) *vs.* log([F$^-$]/mol dm^{-3}). Conditions: (○): No. 1, (▲): No. 2, (●): No. 3 in Table 1, (◇): reproduced from Ref. 15, log $D_0 = -0.66$.

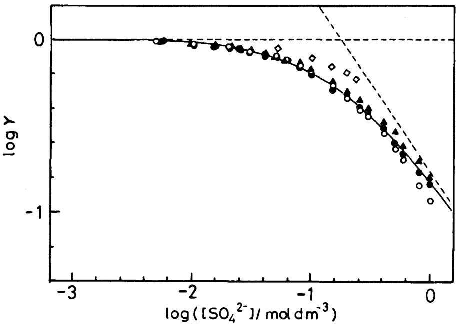

Fig. 4. Plots of log Y (Eq. 16) *vs.* log([SO_4^{2-}]/mol dm^{-3}). Conditions: (○): No. 4, (▲): No. 5, (●): No. 6 in Table 1, (◇): reproduced from Ref. 15, log $D_0 = -0.66$.

Table 1. Experimental results for Np(V)-fluoride and Np(V)-sulfate systems

Ligand	No.	pH	a	log(β_n/mol^{-n}dm^{3n})	
				n=1	n=2
F$^-$	1	6.63	1.00	1.38±0.01	2.17±0.01
	2	6.64	1.00	1.42±0.01	2.14±0.01
	3	7.62	1.14	1.34±0.01	1.98±0.01
	Mean			1.39±0.03	2.07±0.03
SO_4^{2-}	4	6.60	1.00	0.70±0.03	
	5	7.50	1.02	0.84±0.03	
	6	7.47	1.10	0.76±0.01	
	Mean			0.76±0.02	

1,2,4,5: $C_{\mathrm{TTA}}=1\times10^{-4}$ mol dm^{-3}, $C_{\mathrm{phen}}=1\times10^{-2}$ mol dm^{-3} in 3-methyl-1-butanol.
3,6: $C_{\mathrm{TTA}}=1\times10^{-3}$ mol dm^{-3}, $C_{\mathrm{phen}}=1\times10^{-2}$ mol dm^{-3} in dichloromethane.

where pK_1=1.70, pK_2=6.46, and pK_3=10.79.[4] Equation 19 may then be written as:

$$1/D = 1/D'_0 + \sum(B'_n/D'_0a)[\mathrm{H_2L}]^n, \tag{23}$$

where:

$$B'_n = \beta'_n + \beta_n K_2^n/[\mathrm{H}]^n, \tag{24}$$

or:

$$1/D = 1/D'_0 + \sum(B_n/D'_0a)[\mathrm{HL}]^n, \qquad (25)$$

where:

$$B_n = \beta'_n[\mathrm{H}]^n/K_2^{\,n} + \beta_n. \qquad (26)$$

Nine series of experiments were carried out to obtain the plot of log D *vs.* log([$H_2PO_4^-$]/mol dm^{-3}) or the plot of log D *vs.* log([HPO_4^{2-}]/mol dm^{-3}). The pH of the aqueous phase after shaking changed from the initial pH by less than 0.2 unit in each series of experiments; the experimental values of D were corrected to those at a constant pH using the experimental extraction curves which were obtained experimentally. The concentration of a particular species of phosphate was calculated at the pH of interest according to the following relationship:

$$\begin{aligned} C_\mathrm{L} &= [\mathrm{H_3PO_4}] + [\mathrm{H_2PO_4^-}] + [\mathrm{HPO_4^{2-}}] + [\mathrm{PO_4^{3-}}] \\ &= [\mathrm{H_3PO_4}](1 + K_1/[\mathrm{H^+}] + K_1K_2/[\mathrm{H^+}]^2 \\ &\quad + K_1K_2K_3/[\mathrm{H^+}]^3). \end{aligned} \qquad (27)$$

Some of the plots of log Y (Eq. 16) *vs.* log([HPO_4^{2-}]/mol dm^{-3}) are shown in Fig. 5 as illustrations. The values of B'_n and B_n obtained at various pH's are shown in Table 2, together with the experimental conditions used. Each series of experiments comprised 18 to 20 points of the data-set, and the standard deviations of the values of B'_n and B_n were less than 0.02. Since values of B'_n and B_n show the dependence on the pH in the opposite way, it can be concluded that both, and only, $H_2PO_4^-$ and HPO_4^{2-} ions form considerably stable complexes with Np(V). As the value of B'_n or B_n is a function of the pH, as is expressed by Eq. 24 or 26, a set of B'_n or B_n can be treated by the same least-squares method as explained before to determine the values of β'_n and β_n. Figure 6 shows the results of the least-squares fitting of the values of B_n to Eq. 26; the values of β'_n and β_n thus obtained are listed in Table 3. The fairly large standard deviations of the values can be ascribed to the rather restricted pH range studied, since a pH value than 4.5 is too high to allow the formation of a considerable amount of complexes of Np(V) with the $H_2PO_4^-$ ion. Moreover, uncertainties may be brought about in the observed values since the fraction of Np(V) in a particular chemical form is a quite complex function of both the total concentration of phosphate (C_L) and the pH. In

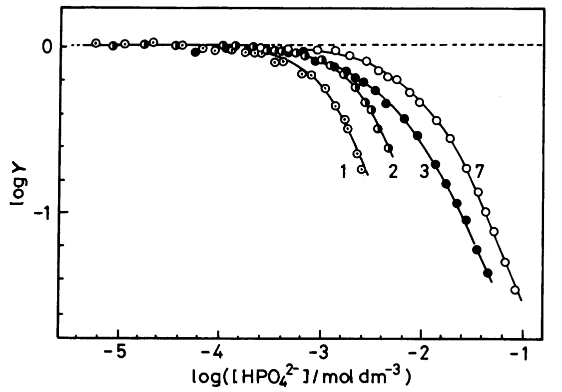

Fig. 5. Plots of log Y (Eq. 16) *vs.* log([HPO_4^{2-}]/mol dm^{-3}).
Conditions: See Table 2.

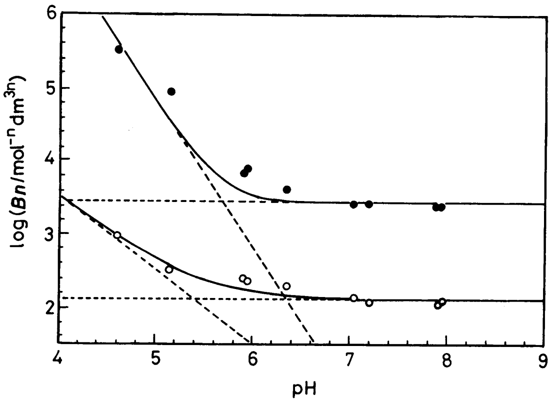

Fig. 6. Plots of log(B_n/mol^{-n}dm^{3n}) *vs.* pH for HPO_4^{2-} ligand.
○: $n=1$, ●: $n=2$. Solid lines (composites of the dashed lines) are the results of the least-squares treatment.

Table 2. Apparent constants obtained for the Np(V)-phosphate system

No.	pH	C_TTA/mol dm^{-3}	log D'_0	a	log(B_n/mol^{-n}dm^{3n}) *vs.*[$H_2PO_4^-$] n=1	*vs.*[$H_2PO_4^-$] n=2	*vs.*[HPO_4^{2-}] n=1	*vs.*[HPO_4^{2-}] n=2
1	4.60	2.0×10^{-3}	0.09	1.00	1.10	1.77	2.96	5.49
2	5.14	1.0×10^{-3}	0.29	1.00	1.17	2.28	2.49	4.92
3	5.90	1.0×10^{-2}	0.43	1.03	1.83	2.69	2.39	3.81
4	5.94	2.5×10^{-4}	0.45	1.00	1.83	2.85	2.35	3.89
5	6.34	1.0×10^{-4}	0.38	1.00	2.14	3.36	2.26	3.60
6	7.02	1.0×10^{-4}	0.71	1.00	2.69	4.53	2.13	3.41
7	7.20	1.0×10^{-4}	0.79	1.01	2.80	4.89	2.06	3.41
8	7.90	1.0×10^{-3}	0.52	1.24	3.48	6.23	2.04	3.35
9	7.94	1.0×10^{-4}	0.79	1.03	3.55	6.32	2.07	3.36

1,2,4-7,9: 3-methyl-1-butanol, 3,8: dichloromethane.
1,2,4-9: C_phen=1×10^{-2} mol dm^{-3}, 3: C_phen=2×10^{-2} mol dm^{-3}.

Table 3. Formation constants of Np(V)-complexes

Ligand	Method	Conditions	$\log(\beta_n/\mathrm{mol}^{-n}\mathrm{dm}^{3n})$		Ref.
			$n=1$	$n=2$	
F^-	TTA-phen	$\mu=1.0$, 25 °C	1.39 ± 0.03	2.07 ± 0.03	This work
	DNNS[a)]	$\mu=2.0$, 25 °C	0.99 ± 0.03		(15)
SO_4^{2-}	TTA-phen	$\mu=1.0$, 25 °C	0.76 ± 0.02		This work
	DNNS[b)]	$\mu=2.0$, 25 °C	0.45 ± 0.04		(15)
	DNNS[c)]	$\mu=2.0$, 25 °C	0.19 ± 0.02		(16)
	coppt.[d)]	$\mu\approx1.5$, 20 °C	1.04 ± 0.4		(18)
$H_2PO_4^-$	TTA-phen	$\mu=1.0$, 25 °C	1.04 ± 0.18	1.87 ± 0.29	This work
	cix.	$\mu=0.2$, 20 °C	0.81		(20)
HPO_4^{2-}	TTA-phen	$\mu=1.0$, 25 °C	2.11 ± 0.09	3.43 ± 0.16	This work
	cix.	$\mu=0.2$, 20 °C	2.85		(20)
	coppt.[e)]	$\mu=0.1$, 20 °C	2.90 ± 0.11		(18)
	cix.[f)]	$\mu=0.1$, 25 °C	2.36 ± 0.42		(21)
PO_4^{3-}	coppt.	$\mu=1.0$, 20 °C	5.78 ± 0.25		(18)

TTA-phen: solvent extraction with TTA plus phen, DNNS: solvent extraction with DNNS, coppt.: coprecipitation, cix.: cation exchange.

a) $[F^-]$: 0.02—0.06 mol dm^{-3}, b) $[SO_4^{2-}]$: 0.05—0.25 mol dm^{-3}, c) $[SO_4^{2-}]$: 0.05—0.3 mol dm^{-3}, d) $[SO_4^{2-}]$: 0.15—0.6 mol dm^{-3}, e) $[(NH_4)_2HPO_4]_t$: 0.05—0.34 mol dm^{-3}, f) $[HPO_4^{2-}]\approx C_L$: 0.001—0.01 mol dm^{-3}.

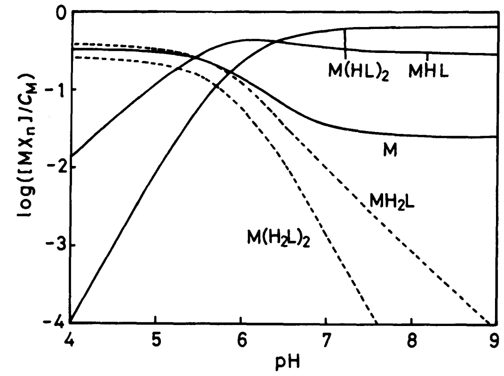

Fig. 7. Logarithmic diagram of the Np(V)-phosphate system at $C_L=0.1$ mol dm^{-3}. $M=NpO_2^+$, $H_2L=H_2PO_4^-$ and $HL=HPO_4^{2-}$.

the presence of $C_L=0.1$ mol dm^{-3}, for instance, the fraction of Np(V) in the form of a particular phosphate complex changes as a function of the pH, as is shown in Fig. 7, which was constructed by using the formation constants obtained in the present study.

Discussion

Table 3 lists the formation constants obtained in this study, together with the values reported by other workers.

Rao *et al.*[15)] have studied the complexing of Np(V) with F^-, SO_4^{2-}, and some other inorganic anions by the solvent-extraction method using 3,7-dinonylnaphthalenesulfonic acid (DNNS) as the extractant. Their values are smaller than the present values. Figures 3 and 4 show their extraction curves, which have been constructed by the present authors from the table in the original paper. Although they stated that the pH was maintained around 5 in their experiment, there was no description of the pH at equilibrium after the extraction. Since they used a stock solution of Np(V) in $HClO_4$ without any buffer, the aqueous phase might possibly be more acidic than expected. This may lead to the overestimation of $[F^-]$ by neglecting the association into HF. Since the distribution ratios of Np(V) were small even in the absence of the ligands ($D=0.219$ in the presence of 0.4 mol dm^{-3} DNNS), the range of the distribution ratio they measured was too narrow to obtain reliable formation constants (the percentages of the extraction of Np(V) varied within the small range from 18% to 11%).

Halperin and Oliver[16)] repeated the experiment on the sulfate complexing of Np(V) by the same method and under conditions almost equal to those adopted by Rao *et al.*[15)] Although they used the same technique, they obtained a considerably smaller value than that reported by Rao *et al.*; the discrepancy is outside the limits of experimental error. We suspect that the starting solution of Np(V) might have contained chemical species other than NpO_2^+, such as peroxide, since Halperin and Oliver used H_2O_2 as a reductant. If such kinds of species are not extractable into the organic phase, this will give systematic errors and lead to a lower formation constant. Hydrogen peroxide has been found to cause unusual behavior in neptunium when used as a redox reagent.[12,17)]

Moskvin and Poznyakov[18)] studied the complexing of Np(V) with SO_4^{2-}, SO_3^{2-}, HCO_3^-, HPO_4^{2-}, *etc.* by means of coprecipitation with iron(III) hydroxide at pH 8.5. As for the sulfate complex, they have reported a larger value than the present one, though the discrepancy is within the limits of experimental error. The main difficulty in their coprecipitation method is that the distribution ratio of Np(V) in the absence of complexing agents is too high to obtain reliable data, since the distribution ratio was determined from the difference in the activities of the centrifugate and a control (original) solution. The percentage of the adsorption is reported to around 95% and cannot be

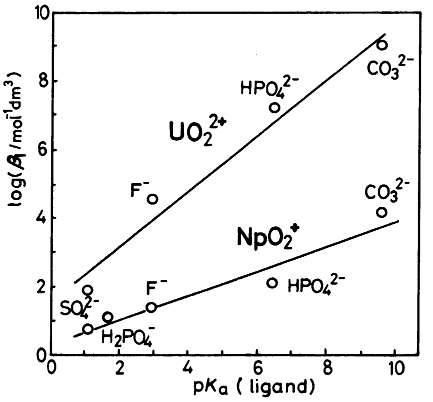

Fig. 8. Correlation between 1:1 chelate formation constants of UO_2^{2+} or NpO_2^+ and pK_a.

controlled, in contrast to the case with the solvent-extraction system adopted in this report.

The failure by Al-Niaimi *et al.*[19] to observe fluoride and sulfate complexing can be ascribed to the low fluoride and sulfate concentrations they used.

As for the formation constants of phosphate complexes, despite the large standard deviations in the present study, they may be considered to be more reliable than those listed in Table 3.

Moskvin *et al.*[18,20] obtained their values in a still more limited pH region (at pH 4.8—6.7 in Ref. 20 and at pH 8.5 in Ref. 18). Their formation constants for the complexes of Np(V) with $H_2PO_4^-$ and HPO_4^{2-} are not very different from the present values. However, if we accept the reported formation constant of the Np(V)-PO_4^{3-} complex, the main species of Np(V) at pH 8.5 should be $NpO_2PO_4^{2-}$, and the formation constants of Np(V)-HPO_4^{2-} complexes cannot be obtained at this pH.

Rees and Daniel[21] have determined the formation constant of the Np(V)-HPO_4^{2-} complex. They measured the distribution of Np(V) between the aqueous phase and a cation-exchange resin at pH 7.5. In their calculation, the concentration of HPO_4^{2-} was assumed to be equal to the total phosphate concentration at this pH. The agreement with the present value is reasonable, since Np(V) forms only a one-to-one complex with HPO_4^{2-} under the conditions they adopted (pH 7.5, $C_L=10^{-3}$—10^{-2} mol dm^{-3}).

In Fig. 8, the formation constants of the Np(V)-complexes with inorganic anions (including CO_3^{2-} by Ref. 8) obtained in the present study are compared with those of the UO_2^{2+}-complexes,[4,22] because UO_2^{2+} is also a dioxo cation of similar type. The good correlation of the stabilities of the Np(V)-complexes with the pK_a values of the ligands implies that all these complexes are formed by the interaction of a hard acid and a hard base.

In conclusion, since the present experiment was conducted to ensure the formation of various chemical species by covering a fairly wide range of ligand concentrations and pH's, the resultant formation constants can be used reliably to estimate the behavior of Np(V) in widely different natural or artificial systems.

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