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Electromigration of Carrier-free Radionuclides

11. Complex Formation of ^{239}Np(V) with Oxalate, Tartrate and Sulphate in Neutral Inert Electrolytes

By F. Rösch[1], S. Dittrich[2], G. V. Buklanov[3], M. Milanov[3], V. A. Khalkin[3], and R. Dreyer[2]

[1] **Academy of Sciences of G.D.R., CINR Rossendorf, 8051 Dresden, PF 19, G.D.R.**
[2] **Dresden University of Technology, G.D.R.**
[3] **JINR Dubna, P.O. Box 79, 10100 Moscow, USSR**

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Summary

Complex formation equilibria of Np(V) with oxalate, tartrate and sulphate ligands in neutral aqueous electrolytes at T = 298.1(1) K have been investigated by means of electromigration measurements of carrier-free ^{239}Np(V).

Stoichiometric stability constants for oxalate complexes of $\lg K_1$ = 3.77(2), 3.90(4), 3.57(4) and $\lg K_2$ = 2.21(20), 2.37(3), 2.38(12) in perchlorate systems of the overall ionic strength μ = 0.05, 0.10 and 0.30, respectively, were obtained. Similar results were found in nitrate electrolytes of μ = 0.10: $\lg K_1$ = 3.75(4), $\lg K_2$ = 2.38(5). The corresponding data are $\lg K_1$ = 1.76(7), $\lg K_2$ = 0.72(15) for tartrate ligand, μ = 0.10 (ClO_4^-) and $\lg K_1$ = 1.1(1) for sulphate ligand, μ = 0.30 (ClO_4^-).

However, signs and amounts of individual ion mobilities of the Np(V) complex ions calculated are difficult to interpret. Therefore, the existence of a Np(V) cation of type NpO^{3+} is postulated.

1. Introduction

By means of electromigration techniques the stability constants of different types of complexes can be obtained. But there is another fact of special importance. The electromigration method offers favourable prerequisites for studying individual ion mobilities of separate ions and resulting overall ion mobilities of elements. Additional effects of different ligands, essentially of H^+ and OH^- and of simple inorganic ions as well as of organic compounds can be tested.

These data are of special interest for the investigation of the phenomenon of migration and accumulation of various metals (radionuclides) in natural substances. Finally, in electrolyte systems free of any supporting materials one can ignore nuclide / adsorbent interactions and the role of different matrixes.

In the first part of the investigation of the electromigration behaviour of carrier-free ^{239}Np-neptunium(V) results on hydrolysis reactions and individual ion mobilities of neptunium(V) were obtained [1]. The present part of this series deals with various other problems. Using oxalate ligand, the general information on Np(V) complex formations in neutral aqueous solution can be obtained and compared with the literature data. Other ligands of L^{2-} type were selected because there exist only some inconsistent complex formation data. On the other hand, electromigration results for complexes of Np(V) with oxalate should be revised.

Finally, methodical aspects of electromigration measurements were of interest. Starting from common tendencies of electromigration, the ion mobility data on Np(V) – L^{2-} systems cannot be understood, if one considers a Np(V) cation of NpO_2^+ stoichiometry.

2. Experimental

^{239}Np(V)

Separation of ^{239}Np from the ^{243}Am / ^{239}Np generator system as well as stabilization of the pentavalent oxidation state of neptunium are described in ref. [1].

Modified electromigration technique

Technical details of the apparatus design, organization and analysis of electromigration are summarized in refs. [1 – 3]. Ref. [4] compares the results of electromigration measurements with regard to hydrolysis and complex formation of carrier-free radionuclides with the literature data.

Electrolyte solutions

Aqueous solutions of type Na_2L / $NaClO_4$, T = 298.1(1) K were used for the investigations, L = oxalate, tartrate and sulphate, respectively. To guarantee a high percentage of unprotonized L^{2-} ions in their protolysis equilibria and to avoid Np(V) hydrolysis, the pH of the solutions was adjusted to 5.5-8.9. The overall ionic strength of different systems was as follows:

L = oxalate: μ = 0.05 (pH 7.0 – 8.9)
μ = 0.10 (pH 5.5 – 6.5)
μ = 0.30 (pH 6.0 – 8.0)
L = tartrate: μ = 0.10 (pH 5.5 – 8.1)
L = sulphate: μ = 0.30 (pH 5.5 – 6.5) .

In addition, an electrolyte system Na_2Ox / $NaNO_3$, $\mu = 0.10$, pH 5.9 – 6.5, was used to test effects of the ground electrolyte composition.

No reducing agents like hydrazine, bromate or nitride, which are usually employed for the stabilization of the pentavalent oxidation state of neptunium, were added to the solutions. The dicarboxylic acids may act as reducing agents. On the other hand, overall ion mobilities of $^{239}Np(V)$ in electrolytes without and with 10^{-2} M $NaNO_2$ were found to be identical.

L^{2-} concentrations were calculated from the deprotonation constants of oxalic [5], tartaric [6] and sulphuric [7] acid. The electrolyte systems were prepared immediately before the experiments, using p.a. chemicals and bidistilled water. The pH of the electrolytes was measured by means of glass electrodes calibrated by standard buffer solutions. The pH of the $^{239}Np(V)$ sample was adjusted to the pH of the electrolyte systems. The volume of the $^{239}Np(V)$ stock solution injected into the electrolyte in the electromigration pipe was about 1 – 5 µl.

3. Results

The primary results of the electromigration measurements are overall ion mobilities $\bar{u}_{Np(V)}$. They will be discussed as functions of type $\bar{u}_{Np(V)} = f([L^{2-}])$.

The quantitative treatment of the complex formation results is based on mechanism (1), commonly accepted for the interpretation of Np(V) reactions:

$$NpO_2^+ + n\,L^{2-} \overset{\beta_n}{\rightleftarrows} [NpO_2L_n]^{1-2n} \qquad (1)$$

Application of the general electromigration equation for $n = 1, 2$ leads to

$$\bar{u}_{Np(V)} = \frac{u^0_{NpO_2^+} + u^0_{[NpO_2L]^-}\cdot K_1\cdot[L^{2-}] + u^0_{[NpO_2L_2]^{3-}}\cdot K_1K_2\cdot[L^{2-}]^2}{1 + K_1\cdot[L^{2-}] + K_1K_2\cdot[L^{2-}]^2} \qquad (2)$$

$\bar{u}_{Np(V)}$ – the overall ion mobility of neptunium(V),

$u^0_{[NpO_2L]^{1-2n}}$ – the individual ion mobilities of the neptunium(V) ions acting in the equilibrium,

β_n, K_n – the stoichiometric overall and stepwise complex formation constants, respectively.

Ion mobilities of cationic and anionic species were denoted by positive and negative signs.

The Np(V)-oxalate system

Fig. 1 shows the experimental electromigration results of $^{239}Np(V)$ in aqueous neutral perchlorate electrolytes of different overall ionic strength.

Starting from $[ox^{2-}] > 10^{-5}$ M, the overall ion mobilities of Np(V) decrease. At $[ox^{2-}] \geqq 1.5 \cdot 10^{-3}$ M, $2.5 \cdot 10^{-3}$ M and $4 \cdot 10^{-3}$ M ($\mu = 0.05$, 0.10 and 0.30, respectively) the radionuclide migrates in the direction of the anode. This immediately indicates formation of anionic complex species.

The behaviour of $^{239}Np(V)$ in nitrate background electrolytes is almost the same, Fig. 2.

Differences in the functions $\bar{u}_{Np(V)} = f([ox^{2-}]; ClO_4^-$ or $NO_3^-)$ mainly concern the different values of the individual ion mobilities of the metal cation itself. Compared with perchlorate electrolytes, individual ion mobilities of the Np(V) cation decrease in nitrate and chloride electrolytes [1].

Values of $u^0_{[NpO_2L_n]^{1-2n}}$ and K_n were obtained using the least squares method [8] and setting $n = 1, 2$ in eqs. (1, 2). The calculated functions $\bar{u}_{Np(V)} = f([ox^{2-}]; u^0_{[NpO_2ox_n]^{1-2n}}; K_n)$ are given in Figs. 1 and 2.

They are in satisfactory agreement with the experimental points. However, some problems must be noted. Surprisingly, calculated individual ion mobilities of the monooxalato complex ions $[NpO_2ox]^-$ are found to be positive (Table 1).

Another striking fact is the ratio of the $n^0_{[NpO_2ox_n]^{1-2n}}$ data. Usually, individual ion mobilities of complex ions are proportional to the individual ion mobility of the central metal cation according to the charges of the ions. This was shown for oxalate complexes of Bi(III), La(III) and Yb(III) for example [9–11]. Results of other electromigration and electrophoretic measurements reflect these correlations, too [12].

The Np(V)-tartrate system

Experimental results for $^{239}Np(V)$ electromigration in tartrate electrolytes are illustrated in Fig. 3.

Whereas in the case of oxalate ligand anionic species have been detected at $[L^{2-}] > 10^{-3}$ M, the overall ion mobilities of Np(V) in the tartrate solutions remain positive even at maximum concentrations of $[tart^{2-}] = 3.33 \cdot 10^{-2}$ M.

Comparison with the literature data is difficult because only one work on Np(V) complexes in aqueous tartrate solutions was published [13]. It is not easy to interpret the data given in ref. [13], because the ratios of stepwise stability constants obtained are unusual. For example, the value of $\lg K_1$ for NpO_2Htart is greater than the one for $[NpO_2tart]^-$. Moreover, even in $\mu = 0.05$ solutions the existence of $[NpO_2(tart)_3]^{5-}$ ions was discussed.

Complex formation constants $\lg K_n$ of $[NpO_2L_n]^{1-2n}$ seem to decrease from L = oxalate to L = tartrate. For this reason, one has to consider $n = 1$ as well as $n = 1, 2$ in order to calculate the complex formation parameters. In any case, even with $n = 1$, i.e. with exclusive formation of the monotartrato complex anionic species should be detected. This

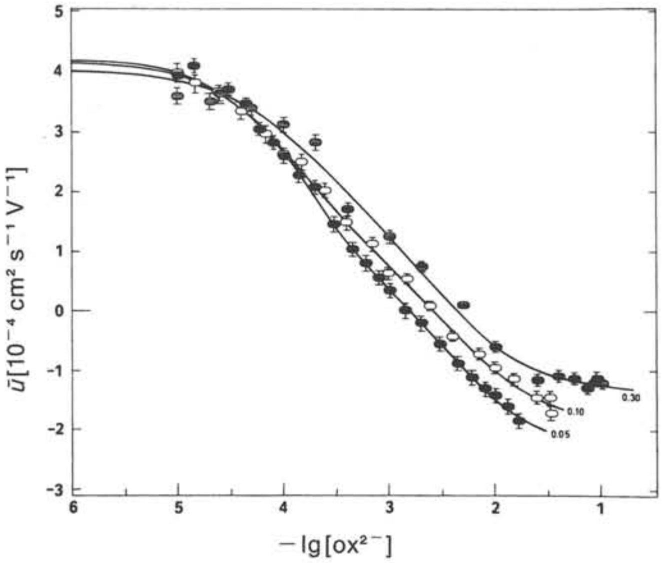

Fig. 1. Overall ion mobilities of $^{239}Np(V)$ vs. oxalate ligand concentration.
Na_2ox / $NaClO_4$ electrolytes, $T = 298.1(1)$ K,
$\mu = 0.05$ (●), $\mu = 0.10$ (○), $\mu = 0.30$ (◍).

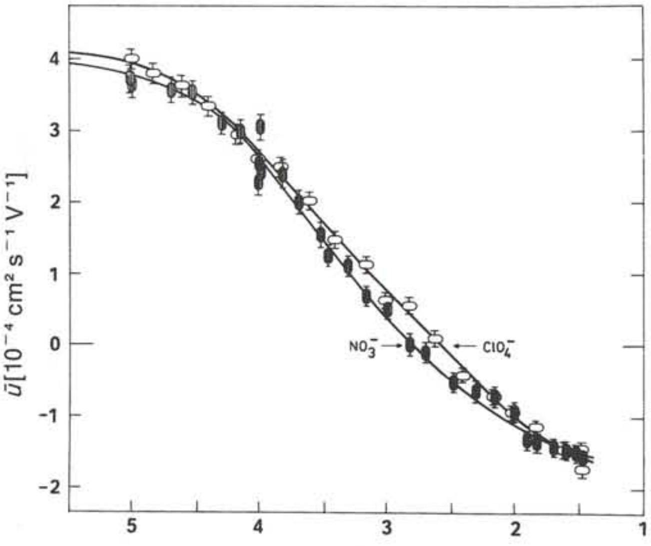

Fig. 2. Overall ion mobilities of $^{239}Np(V)$ vs. oxalate ligand concentration.
Na_2ox / $NaClO_4(NO_3)$ electrolytes, $\mu = 0.10$, $T = 298.1(1)$ K.

clearly contradicts experimental observations. The calculation of stability constants seems to be senseless under these conditions.

The Np(V)-sulphate system

Results of electromigration measurements in the sulphate electrolytes are compared in Fig. 4 with the results in the oxalate and tartrate systems.

Table 1. $u^0_{[NpO_2(ox)_n]^{1-2n}}$ data, $n = 0, 1, 2$, according to eqs. (1, 2). u^0_i in $10^{-4}\ cm^2 s^{-1} V^{-1}$

μ	$0.05(ClO_4^-)$	$0.10(ClO_4^-)$	$0.10(NO_3^-)$	$0.30(ClO_4^-)$
$n = 0$	$+4.18\ (6)$	$+4.17(10)$	$+4.00(10)$	$+3.78(11)$
$n = 1$	$+0.13(30)$	$+0.97\ (5)$	$+0.35(35)$	$+1.21(42)$
$n = 2$	$-2.51\ (6)$	$-1.86\ (8)$	$-1.67\ (7)$	$-1.35\ (5)$

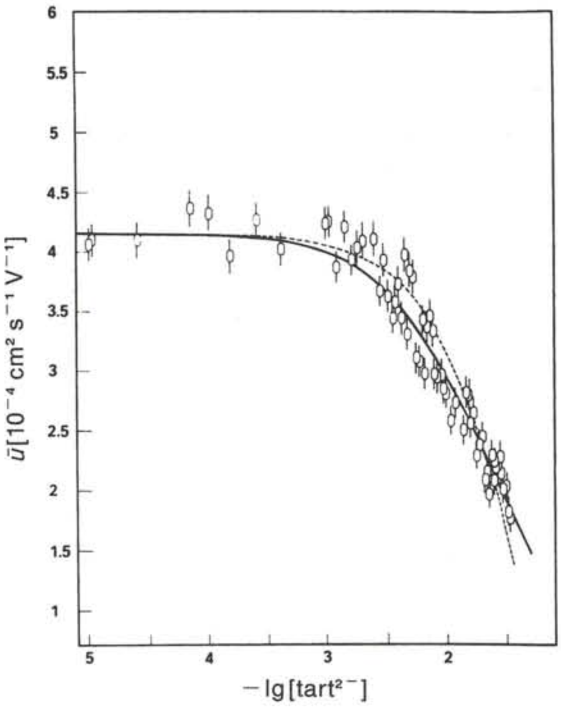

Fig. 3. Overall ion mobilities of $^{239}Np(V)$ vs. tartrate ligand concentration.
Na_2tart / $NaClO_4$ electrolytes, $\mu = 0.10$, $T = 298.1(1)$ K.

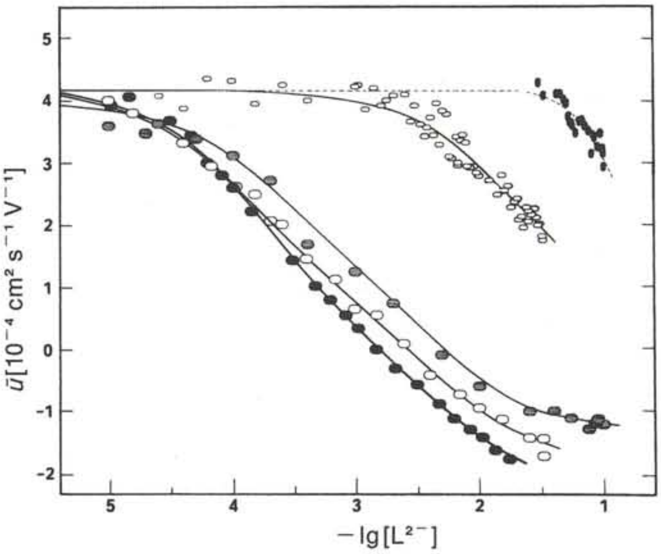

Fig. 4. Overall ion mobilities of $^{239}Np(V)$ vs. L^{2-} ligand concentrations.
Na_2L / $NaClO_4$ electrolytes, $T = 298.1(1)$ K.
L = oxalate: $\mu = 0.05$ (⬬), $\mu = 0.10$ (⬭), $\mu = 0.30$ (◍);
L = tartrate: $\mu = 0.10$ (○); L = sulphate; $\mu = 0.30$ (●).

As can be seen, the complex formation tendency of Np(V) with L = sulphate keeps on decreasing. Stepwise stoichiometric stability constants should be the lowest in this series. On the other hand, formation of the disulphato ions should be negligible at $[SO_4^{2-}] < 1.00 \cdot 10^{-1}$ M.

The literature data can corroborate this fact. Even at high overall ionic strength of $\mu = 1.0$, 2.0 and 8.5 no $\lg K_2$ data have been derived. The $\lg K_1$ data are 0.76, 0.45 and 0.86, respectively [14–16]. Rough extrapolations lead to the expected values of $\lg K_1 = 1.0 - 1.5$ at $\mu = 0.3$*. Consequently, the ratio $[NpO_2^+] / [NpO_2(SO_4)]^-$ at $[SO_4^{2-}] \geqq 10^{-1}$ M should be of the order of $\lessapprox 1$. Overall ion mobilities of Np(V) must then be $\bar{u}_{Np(V)} < 0$ at $[SO_4^{2-}] \geqq 10^{-1}$ M.

As in the case with L = tartrate, there are great discrepancies between expected and experimental results of electromigration measurements with L = sulphate.

4. Discussion

The electromigration investigations on complex formation of the carrier-free ^{239}Np-Np(V) in neutral aqueous electrolytes reveal the dependence $\bar{u}_{Np(V)} = f([L^{2-}])$, indicating a decreasing tendency of the complex stability in the series

oxalate < tartrate < sulphate.

However, quantitative treatment of the experimental data leads to striking discrepancies with the commonly accepted reactions of the NpO_2^+ cation.

The problems can be summarized as follows:

(i) The existence of anionic complex species was detected only with L = oxalate. With tartrate and sulphate even at maximum ligand concentrations of $3.33 \cdot 10^{-2}$ M and $1.00 \cdot 10^{-1}$ M, respectively, Np(V) migrates in the direction of the cathode.

Apparently, this is not connected with $n \geq 1$ in eq. (1).

(ii) Mathematic simulations based on eq. (2) yield cationic individual ion mobilities for the monooxalato ion. This is also the case for the tartrate ligand, regardless of whether $n = 1$ or $n = 1, 2$ is considered in eq. (2). (In the first case the K_2 therm is set to be 0).

(iii) Not only the signs, but also the ratios of the amounts of the $u^0_{[NpO_2L_n]^{1-2n}}$ data fail to follow the proportionality between their charges. Such correlations can be written as

$$\frac{u^0_{M^{m+}}}{u^0_{[ML_n]^{m-an}}} \approx \frac{z_{M^{m+}}}{z_{[ML_n]^{m-an}}} \qquad (3)$$

(z is the charge of the ions, L^{a-}).

(iv) A correlation between the overall ion mobility $\bar{u}_{Np(V)}$ and the mean ligand number $\bar{n}_{L^{2-}}$ [18] follows from eq. (3). Fig. 6 shows irregularities in the function $\bar{n}_{ox^{2-}} = f([ox^{2-}])$. A normalized function

$$\bar{u}'_{Np(V)} = f([ox^{2-}]) \qquad (4)$$

was introduced on the basis of $\bar{u}^{0'}_{NpO_2^+} = 1$.

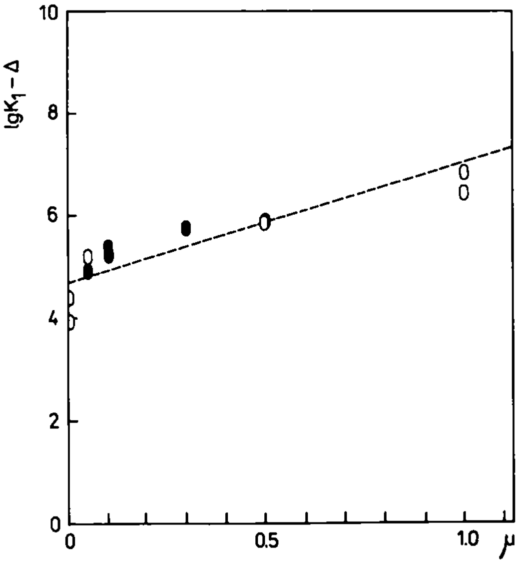

Fig. 5. $\lg K_1^{(\mu)}$ data of Np(V) — oxalate complex in aqueous electrolytes, $T = 298.1(1)$ K, according to eq. (7), ($\Delta = Az^2A \sqrt{\mu}(1 + \sqrt{\mu})^{-1}$). ○ — literature data, ● — present work.

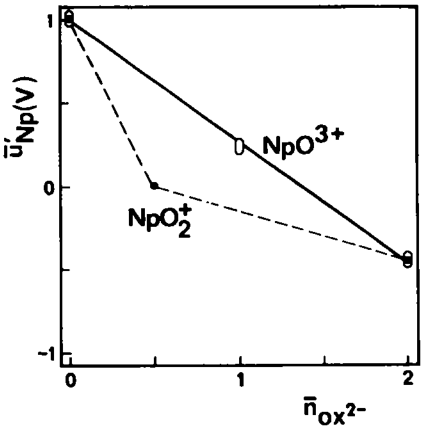

Fig. 6. Values of $(\bar{n}_{ox^{2-}}; \bar{u}'_{Np(V)})$ for NpO_2^+ and NpO^{3+} models. $\mu = 0.10(ClO_4^-)$, $T = 298.1(1)$ K.

Three points $(\bar{n}_{ox^{2-}}; \bar{u}'_{Np(V)})$ were selected: (0; 1) for the cation itself, (0.5; 0) according to the ratio $[NpO_2^+] / [NpO_2ox^-] = 1$ and (2; −0.45) for $u^{0'}_{NpO_2(ox)_2]^{3-}}$, $\mu = 0.10(ClO_4^-)$.

These four problems make it necessary to seek a new interpretation of the Np(V) complex formation.

It was found that on the assumption of a NpO^{3+} cation the above-mentioned contradictions are resolved.

With the reaction mechanism

$$NpO^{3+} + n\,L^{2-} \overset{\beta_n}{\rightleftarrows} [NpOL_n]^{3-2n} \qquad (5)$$

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* Values given in ref. [17] differ widely from other data and were not considered in this context.

and the resulting electromigration equation for $n = 1, 2$

$$\bar{u}_{\mathrm{Np(V)}} = \frac{u^0_{\mathrm{NpO^{3+}}} + u^0_{\mathrm{[NpOL]^+}} \cdot K_1 \cdot [\mathrm{L}^{2-}] + u^0_{\mathrm{[NpOL_2]^-}} \cdot K_1 K_2 \cdot [\mathrm{L}^{2-}]^2}{1 + K_1 \cdot [\mathrm{L}^{2-}] + K_1 K_2 \cdot [\mathrm{L}^{2-}]^2} \tag{6}$$

the numeric values of the parameters u^0 and K_n do not change which gives a better physico-chemical sense.

Table 2 summarizes all the individual ion mobilities computed according to eq. (6). For the tartrate ligand the data are included with the formation of the ditartrato complex neglected ($K_2 = 0$ in eq. (6)). In the other case ($n = 1, 2$), one has to consider the calculations of $\lg K_2$ and $u^0_{\mathrm{NpO(tart)_2]^-}}$ as tentative, because no direct evidence of this complex ion being formed was found. Fig. 3 contains the calculated functions both for $n = 1$ (dotted line) and $n = 1{,}2$.

Changes in $\bar{u}_{\mathrm{Np(V)}}$ in the sulphate system of only 30% even at the maximum sulphate concentration are insufficient for the calculation of complex formation data. Values given in Tables 2, 3 have been estimated.

The obtained stoichiometric stability constants of $[\mathrm{NpOL}_n]^{3-2n}$ complexes are compared with the literature data in Table 3. Generally, there is good agreement between the calculated data and those from literature. Fig. 5 illustrates this fact, comparing $\lg K_1$ of oxalate complexes, $T = 298.1$ K. For this reason, the correlation [25]

$$\lg K_1 = \lg K_1^0 + \Delta z^2 A \left\{ \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - B\mu \right\} \tag{7}$$

was applied. A is the Debye-Hückel constant, $\Delta z^2 = -12$, and B was fitted to 0.38. For $\lg K_1^0$ a value of 4.65(15) was calculated.

The problems involved in the interpretation of the signs and amounts of the individual ion mobilities can also be settled. For $[\mathrm{NpOL}]^+$ complexes the corresponding charge of the individual ion mobility was calculated. The ratios between the individual ion mobilities and the charges of the metal cation and complex ions are satisfactory:

$$\frac{u^0_{\mathrm{[NpOL_n]^{3-2n}}}}{u^0_{\mathrm{NpO^{3+}}}} \cdot \frac{z_{\mathrm{NpO^{3+}}}}{z_{\mathrm{[NpOL_n]^{3-2n}}}} \approx 1. \tag{8}$$

Derivations from eq. (8) are $-11(11)$% ($n = 1$, oxalate, tartrate; $\mathrm{ClO_4^-}$) and $+22(11)$% ($n = 2$, oxalate; $\mathrm{ClO_4^-}$, $\mathrm{NO_3^-}$), respectively; $\mu = 0.10, 0.30$. Results from the $\mu = 0.05$ system diverge from eq. (8). This may be explained by a more alkaline milieu of the

Table 3. Stepwise complex formation constants of Np(V) with L^{2-} ligands in aqueous solutions. $T = 298.1(1)$ K

	method	μ (electrolyte)	$\lg K_1$	$\lg K_2$	ref.
ox^{2-}	spec	0	3.93	3.13	[19]
	cix	0	4.4[a]	2.96[a]	[20]
	cix	0.05($\mathrm{ClO_4^-}$)	4.04[a]	3.32[a]	[21]
	em	0.05($\mathrm{ClO_4^-}$)	3.77(2)	2.21(20)	this work
	em	0.10($\mathrm{ClO_4^-}$)	3.90(4)	2.37(3)	this work
	em	0.10($\mathrm{NO_3^-}$)	3.75(4)	2.38(5)	this work
	em	0.30($\mathrm{ClO_4^-}$)	3.57(4)	2.38(12)	this work
	spec	0.50	3.29	3.77	[22]
	spec	0.50	3.30[b]	3.77[b]	[22]
pot		1.0($\mathrm{ClO_4^-}$)	3.74(5)[a]	2.57(10)[a]	[23]
	spec	1.0($\mathrm{ClO_4^-}$)	4.54	3.32	[23]
	dis	0.05($\mathrm{ClO_4^-}$)[c]	3.42	2.24	[24]
	dis	1.05($\mathrm{Cl^-}$)	3.42	2.22	[24]
	dis	0.05($\mathrm{Cl_4^-}$)[d]	3.41	2.25	[24]
tart^{2-}	cix	0.05($\mathrm{ClO_4^-}$)	2.32[a]	1.98[a]	[13]
	em	0.10($\mathrm{ClO_4^-}$)	1.76(7)	0.72(15)	this work
$\mathrm{SO_4^{2-}}$	em	0.30($\mathrm{ClO_4^-}$)	1.1(1)	–	this work
	dis	1.0($\mathrm{ClO_4^-}$)	0.76(2)	–	[14]
	dis	2.0($\mathrm{ClO_4^-}$)	0.45	–	[15]
	dis	8.5($\mathrm{ClO_4^-}$)	0.86	–	[16]
	dis	0.5($\mathrm{ClO_4^-}$)	−0.10(3)	–	[17]
	dis	1.0($\mathrm{ClO_4^-}$)	0.06(2)	–	[17]
	dis	2.0($\mathrm{ClO_4^-}$)	0.19(2)	–	[17]

[a] $T = 293.1$ K
[b] $T = 283.1$ K
[c] pH 5.5
[d] pH 8.4

Table 2. Parameter of ^{239}Np(V) complex formations of type $\mathrm{NpO^{3+}} + n\,\mathrm{L^{2-}}$, $\mathrm{Na_2L/NaClO_4}$ electrolytes, $T = 298.1(1)$ K. u_i^0 in 10^{-4} cm^{2}s^{-1}V^{-1}, K_n in l · mole^{-1}

	μ	$u^0_{\mathrm{NpO^{3+}}}$	$u^0_{\mathrm{NpOL^+}}$	$u^0_{\mathrm{NpOL_2^-}}$	$\lg K_1$	$\lg K_2$
ox^{2-}	0.05	+4.18 (6)	+0.13(30)	−2.51 (6)	3.77(2)	2.21(20)
	0.10	+4.17(10)	+0.97(5)	−1.86 (8)	3.90(4)	2.37 (3)
	0.10[d]	+4.00(10)	+0.35(35)	−1.67 (7)	3.75(4)	2.38 (5)
	0.30	+3.78(11)	+1.21(42)	−1.35 (5)	3.57(4)	2.38(12)
tart^{2-}	0.10	+4.17(10)	+1.33(66)	−0.92(71)	1.82(3)	0.72(15)
	0.10	+4.17(10)	+0.49(4)[a]	–	1.69(2)[a]	–
	0.10	+4.17(10)	+0.92(35)[b]	–	1.76(7)[b]	–
$\mathrm{SO_4^{2-}}$	0.30	+4.10(10)	+1.3(3)[c]	–	1.1(1)[c]	–

[a] $n = 1$ in eqs. (5, 6)
[b] mean values
[c] estimated values
[d] nitrate electrolyte

ground electrolyte and some effects of hydrolysis reactions.

Finally, good agreement between functions $\bar{u}_{Np(V)} = f([L^{2-}])$ and $\bar{n}_{L^{2-}} = f([L^{2-}])$ can be stated.

This is shown in Fig. 6 for L = oxalate, $\mu = 0.10(ClO_4^-)$. Fixed points $(\bar{n}_{ox^{2-}}; \bar{u}_{Np(V)})$ are the data for $u^{0'}_{[NpO(ox)_n]^{3-2n}}$ with $n = 0$ (0; 1), $n = 1$ (1; +0.23(2)) and $n = 2$ (2; −0.45(3)).

Conclusions

The properties of the actinyl cations MO_2^+ have not been studied so extensively as those of MO_2^{2+} cations. However a lot of concrete data exist which concern redox potentials, thermodynamic parameters of hydration [26] and physico-chemical properties of the ions in solution (hydrolysis, complex formation) and solids. In this context the IR and Raman spectra are of special interest [27, 28]. Besides the commonly accepted structure MO_2^+ the units MO^{3+} are also described: PaO^{3+} in strong acidic solutions [29] and NpO^{3+} in compounds $NpOF_3\ x\ H_2O$ ($x = 0, 1, 2$) [30], Cs_2NpOCl_5 [31] and $NpO(NO_3)_3x\ 3\ H_2O$ [32] depending on experimental circumstances. However, for these Np(V) compounds alternative stoichiometries in terms of coexistences of hepta- and hexavalent neptunium states were proposed [33–35].

Different stoichiometries were also discussed for Np(VII). In acidic solutions the cations NpO_3^+ or NpO_2^{3+} have been described and in alkaline solutions their hydrolysis products $NpO_4^-\ x\ H_2O$ and $NpO_4(OH)_2^{3-}$, NpO_5^{3-} or $NpO_5(OH)^{4-}$ and $NpO_2(OH)_6^{3-}$ have been characterized [36, 37].

Hence the possibility that a NpO^{3+} stoichiometry exists in aqueous solutions should not be absolutely excluded. However, the question of the differences between the results presented and the data of other authors arises. The answer is that we do not know the reasons. Possibly, the differences are connected with the carrier-free concentration of ^{239}Np. But the introduction of $^{237}Np(V)$ carrier into the $^{239}Np(V)$ sample also did not cause other electromigration behaviour of Np(V).

Therefore we can only state that experimental electromigration results on complex formation of $^{239}Np(V)$ with ligands of type L^{2-} in diluted neutral electrolytes cannot be explained by the reaction $NpO_2^+ + n\,L^{2-}$. On the other hand, good agreement between experiment and electromigration theory can be achieved if the existence of a NpO^{3+} cation is assumed. We emphasize that this is a postulate for the time being.

If this concept were true, data on Np(V) hydrolysis would have to be interpreted in a new way.

In our next publication on investigations of $^{239}Np(V)$, complex formations of the neptunium(V) cation with other ligands will be discussed. Further information on the structure of the Np(V) cation should be derived. The concept is based on the idea that at the first stage of the reactions with L^- ligands either neutral (NpO_2L) or cationic ($[NpOL]^{2+}$) compounds are produced, whereas complex formations with L^{3-} ligands lead to anionic ($[NpO_2L]^{2-}$) or neutral (NpOL) species. To verify this scheme, the electromigration method seems to be most suitable.

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