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Electromigration of Carrier-free Radionuclides

12. Reactions of ^{239}Np(V) with Acetate and Citrate Ligands in Neutral Solutions

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Neptunyl(V) / Complex formation / Stability constants / Electromigration / Ion mobilities

Summary

The complex formation reactions of carrier-free ^{239}Np(V) with acetate and citrate ligands in neutral solutions, $T = 298{,}1(1)$ K, have been studied by using a special type of on line electromigration measurements of γ-emitting radionuclides in homogeneous aqueous electrolytes free of supporting materials.

In the acetate system, $\mu = 0.30$ (ClO_4^-), stoichiometric stability constants of $\lg K_1 = 0.96$, $\lg K_2 = 0.61$, were obtained. In the citrate system reduction of Np(V) was observed.

1. Introduction

The present paper is the third in a series of publications dealing with the results of electromigration measurements of carrier-free ^{239}Np(V).

In ref. [1] hydrolysis of the pentavalent neptunium in aqueous perchlorate electrolytes has been studied. Formation of anionic hydrolysis products was observed. Stoichiometric hydrolysis constants and individual ion mobilities of species $[NpO_2(OH)_n]^{1-n}$, $n = 0, 1, 2$, were calculated; $\mu = 0.10(ClO_4^-)$, $T = 298.1(1)$ K. Results on complex formation of ^{239}Np(V) with L^{2-} ligands (oxalate, tartrate and sulphate, respectively) in neutral perchlorate electrolytes were published in ref. [2]. It was shown that the experimental overall ion mobilities $\bar{u}_{Np(V)} = f([L^{2-}])$ obtained, the individual ion mobilities $u^0_{[NpO_2L_n]^{1-2n}}$, $n = 0, 1, 2$ and the stoichiometric stability constants K_n, $n = 1, 2$, calculated, cannot be explained by assuming formation of $[NpO_2L_n]^{1-2n}$ species.

In contrast, by postulating the existence of a central Np(V) cation of stoichiometry NpO^{3+}, i.e. formation of $[NpOL_n]^{3-2n}$ complex ions, good correlations between electromigration experiments and theories could be obtained.

For reactions of the type

$$NpO^{3+} + n\,L^{2-} \overset{\beta_n}{\rightleftarrows} [NpOL_n]^{3-2n} \qquad (1)$$

values of the individual ion mobilities $u^0_{[NpOL_n]^{3-2n}}$, $n = 0, 1, 2$, and of stoichiometric stepwise stability constants K_n, $n = 1, 2$, have been fitted by the least squares computer simulation. Especially for L^{2-} = oxalate, where a lot of literature data on complex formations with Np(V) are available, the calculated $\lg K_n$ values at different overall ionic strength agree with the results obtained by other authors and by other analytical methods.

It is the aim of the present work on electromigration investigations of ^{239}Np(V) to revise the justification of postulating a NpO^{3+} unit by testing Np(V) complex formation in aqueous neutral perchlorate solutions with ligands of the type L^- and L^{3-}. The concept is based on the expectation that the first step of the complex formation leads either to neutral (NpO_2L) or cationic ($NpOL^{2+}$) products, or to anionic (NpO_2L^{2-}) or neutral (NpOL) products. The electromigration method is most suitable for directly analysing the existence of the alternative signs of the ions, and consequently for obtaining further information on the stoichiometry of the central neptunyl cation.

The intention was to test the ligands acetate (L^- type) and citrate (L^{3-} type). The corresponding acids HL and H_3L are sufficiently deprotonized in the pH range of interest (pH 5.5 – 8.5). In addition, the literature data on Np(V) complex formation with these ligands in aqueous solutions are available.

2. Experiments

Electromigration technique

Experimental procedure, apparatus and details of the electromigration measurements have been described in previous papers [1, 3, 4].

^{239}Np(V)

^{239}Np was obtained from a ^{243}Am generator. The pentavalent state of the carrier-free neptunium was stabilized by means of nitrite. Details of the separation and handling of the neptunium fractions are summarized in ref. [1].

Electrolyte systems

For investigations of the ^{239}Np(V) complex formation solutions of the types

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$NaClO_4/Na(ac)$, $\mu = 0.30$, pH $= 6.7-8.9$, $T = 298.1(1)$ K, and
$NaClO_4/Na_3(cit)$, $\mu = 0.10$, pH $= 7.2-8.4$, $T = 298.1(1)$ K,
were used.

The concentrations of the ligands were calculated by using concentration dissociation constants from ref. [5] and ref. [6].

Electrolyte solutions were prepared just before the electromigration measurements, using p.a. chemicals and bidistilled water. The pH of the solutions was measured by means of glass electrodes, calibrated by standard buffer solutions.

3. Results

To obtain the complex formation parameters, quantitative treatment of the experimental functions $\bar{u}_{Np(V)} = f([L^{a-}])$ starts from the electromigration equation

$$\bar{u}_j = \sum_{i=1}^{i} \alpha_i \cdot u_i^0 , \qquad (2)$$

$\bar{u}_j$: overall ion mobility of the migrating element j,
α_i: particular mole fractions of the ionic species i of the element j with respect to the equilibrium considered,
u_i^0: individual ion mobilities of the ionic species i of the element j with respect to the equilibrium considered and valid for $\alpha_i = 1$.

If either a NpO_2^+ or NpO^{3+} unit is assumed, complex formation reactions of Np(V) with L^{a-} ligands are

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

or

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

They lead to specific solutions of eq. 1:

$$\bar{u}_{Np(V)} = \frac{u^0_{NpO_2^+} + \sum_{n=1}^{n} u^0_{[NpO_2L_n]^{1-an}}}{1 + \sum_{n=1}^{n} \beta_n [L^{a-}]^n} \qquad (4)$$

or

$$\bar{u}_{Np(V)} = \frac{u^0_{NpO^{3+}} + \sum_{n=1}^{n} u^0_{[NpOL_n]^{3-an}}}{1 + \sum_{n=1}^{n} \beta_n [L^{a-}]^n} \qquad (5)$$

in the case of eq. 2 and eq. 3, respectively.

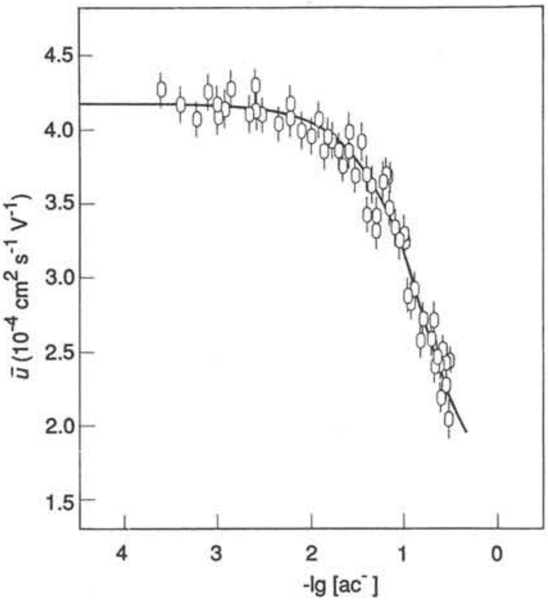

Fig. 1. Overall ion mobility of $^{239}Np(V)$ versus acetate ligand concentrations in aqueous perchlorate electrolytes.
$\mu = 0.30(ClO_4^-)$, pH 6.7–8.9, $T = 298.1(1)$ K.

There β_n are the stoichiometric overall stability constants and K_n the stoichiometric stepwise stability constants; $\beta_n = \Pi K_n$.

The Np(V) - acetate system

The experimental results from electromigration measurements of $^{239}Np(V)$ in neutral aqueous perchlorate solutions containing different acetate ion concentrations are summarized in Fig. 1.

With $[ac^-] > 10^{-3}$ M, the overall ion mobilities of the pentavalent neptunium start to decrease with respect to the value of the individual ion mobility of the $^{239}Np(V)$ cation of $+4.1(1) \cdot 10^{-4}$ cm^{2}s^{-1}V^{-1}, $\mu = 0.30(ClO_4^-)$, $T = 298.1(1)$ K.

At the maximum acetate concentration $[ac^-] = 3 \cdot 10^{-1}$ M the relative degradation of $\bar{u}_{Np(V)}$ compared to the value at $[ac^-] = 0$ is about 50%. No formation of anionic complex ions was registered.

Considering the literature data of $\lg K_1 \approx 1.1(2)$ and $\lg K_2 \approx 0.4(3)$, see Table 1, the formation of mono- and diacetato complexes of Np(V) is to be expected under the electrolyte conditions applied. Therefore, mathematical solutions of eqs. 4,5 start with $n \geqq 1$. The correctness of the calculated parameters u_i^0 and K_n of different complex formation mechanisms can be proved by comparing

(i) chemical signs of the complex ions and the calculated values,
(ii) obtained values of stoichiometric stability constants and the corresponding literature data,
(iii) values of the sum of the least squares function FCN of the computer minimization program MINUIT [7] for both models.

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Table 1. Stoichiometric stability constants and individual ion mobilities of $[NpO(ac)_n]^{3-n}$ species, $\mu = 0.30(ClO_4^-)$, pH 6.7–8.9, $T = 298.1(1)$ K
Results of computer simulations of eq. (5) with $n = 1, 2, 3$, respectively. K_n in $l \cdot mol^{-1}$; u_i^0 in $10^{-4}\ cm^2s^{-1}V^{-1}$.

Parameter	$n = 1$	$n = 2$	$n = 3$
$u^0_{NpO^{3+}}$	+4.17(4)	+4.16(4)	+4.17(4)
$u^0_{NpOAc^{2+}}$	+0.78(32)	+2.73(53)	+2.75(16)
$u^0_{NpOAc_2^+}$	–	+1.29(41)	+1.54(8)
$\lg K_1$	0.65(8)	0.96(8)	0.97(4)
$\lg K_2$	–	0.61(43)	0.66(20)
$\lg K_3$	–	–	−0.62(54)
FCN	47.28	46.87	47.08

Table 2. Stability constants of acetato complexes of Np(V) in aqueous solutions
(*) this work, (a) $\lg\beta_2$

μ	$\lg K_1$	$\lg K_2$	Lit.
0	1.30	–	13
0.3 (ClO_4^-)	0.96	0.61	*
1.0 (ClO_4^-)	0.73	–	14
1.0 (ClO_4^-)	0.73	–	15
1.5 (ClO_4^-)	1.08	–	14
1.5 (Cl^-)	1.04	0.50	16
1.5 (ClO_4^-)	–	1.85^a	17
2.0 (ClO_4^-)	0.97	–	18
2.0 (ClO_4^-)	0.89	0.33	12

For example, with $n = 1$ in eq. 4 the calculated values are $u^0_{NpO_2^+} = +4.14(20) \cdot 10^{-4}\ cm^2s^{-1}V^{-1}$, $\lg K_1 = 0.48$, FCN = 50.74. Apparently, this value of $\lg K_1$ is significantly low.

On the other hand, an assumption of $n \geqq 2$ in eq. 4, i.e. formation of anionic complex species $[NpO_2(ac)_2]^-$ or $[NpO_2(ac)_3]^{2-}$, distinctly contradicts the experimental results, because no electromigration of the $^{239}Np(V)$ in the direction of the anode was detected.

Therefore, the alternative reaction (5) was considered for calculations of complex formation parameters. The results are summarized in Table 1. In each case ($n = 1, 2, 3$) better FCN values are obtained for the $[NpO(ac)_n]^{3-}$ model, compared with the $[NpO_2(ac)_n]^{1-n}$ model.

The value of FCN of the reaction with $n = 2$ is the best. The values of $\lg K_1$ and $\lg K_2$ as well as $u^0_{[NpO(ac)]^{2+}}$ and $u^0_{[NpO(ac)_2]^+}$ are also chemically obvious. First of all this concerns agreement of the stoichiometric stability constants with the literature data (Table 2).

Moreover, the signs of, and the ratio between, the $u^0_{[NpO(ac)_n]^{3-n}}$ data, $n = 0, 1, 2$, correspond to generally accepted regularities of individual ion mobilities of central and complex ions in equilibria reactions in aqueous solutions.

Derivations from the limiting correlation

$$\frac{u^0_{NpO^{3+}}}{u^0_{[NpO(ac)_n]^{3-n}}} \cdot \frac{z_{[NpO(ac)_n]^{3-n}}}{z_{NpO^{3+}}} = 1 \tag{6}$$

are negligible; z is the charge of the ions.

The concrete values of eq. 6 are 1.02(21) and 1.08(43) for $n = 1$ and $n = 2$, respectively.

The experimental errors of $\lg K_2$ and of the individual ion mobility of the diacetato complex cation should be discussed in connection with the relatively low particular mole fraction of the ion.

In this context, the $n = 3$ model is also understandable. The individual ion mobility of the triacetato complex is given: $u^0_{[NpO(ac)_3]} = 0$. However, no overall ion mobilities $\bar{u}_{Np(V)} < +2 \cdot 10^{-4}\ cm^2\ s^{-1}\ V^{-1}$ have been observed, but only in this range the existence of $[NpO(ac)_3]$ is probable.

Consequently, the calculation of exact data of $\lg K_n$ as well as of $u^0_{[NpO(ac)_n]^{3-n}}$, $n = 2, 3$ is more of a mathematical interest: The set of the stability constants of individual ion mobilities calculated is chemically correct, but the data on $\lg K_3$ and $u^0_{[NpO(ac)_2]^+}$ should not be overestimated.

However, the value of $\lg K_3 = -0.6$ proves the assertion that formation of the triacetato complex can be neglected under the electrolyte conditions of $[ac^-] = 3 \cdot 10^{-1}$ M, $\mu = 0.30(ClO_4^-)$, $T = 298.1(1)$ K.

The Np(V)-citrate system

The strong complex formation tendency of the citrate ligand with actinide cations is well known. Values of the stability constants of Np(V)-citrate compounds are relatively high. At the usual overall ionic strength of $\mu \leqq 1$ and temperatures of $T = 293.1 - 298.1$ K mean values of $\lg K_1 \approx 4$ [8–12] and $\lg K_2 \approx 2.4 - 3$ [8, 11] have been found.

The different data published are (in terms of $\lg K_n$; μ; T):

$n = 1$ (2.49; 0.05; ?) [8],
(3.67; 0.05; 293.1 K) [9],
(4.84; 0.10; 298.1 K) [10],
(3.93; ? ; 298.1 K) [11],
(4.42; 1.00; 298.1 K) [12], and for
$n = 2$ (2.38; 0.05; ?) [8],
(2.97; ? ; 298.1 K) [11].

The results vary considerably. This can be explained by general problems of the quantitative treatment of complex formation reactions of Np(V) with the citrate ligand in aqueous solutions. The results from electromigration measurements of $^{239}Np(V)$ in aqueous neutral electrolyte systems are shown in Fig. 2.

In contrast to the Np(V) - acetate system and to the Np(V) - L^{2-} systems [2] no continuous changes in the overall ion mobilities of $^{239}Np(V)$ versus ligand concentrations were observed. Here, an abrupt fall of $u_{Np(V)}$ at $[cit^{3-}] \approx 1 \cdot 10^{-4}$ M occurs.

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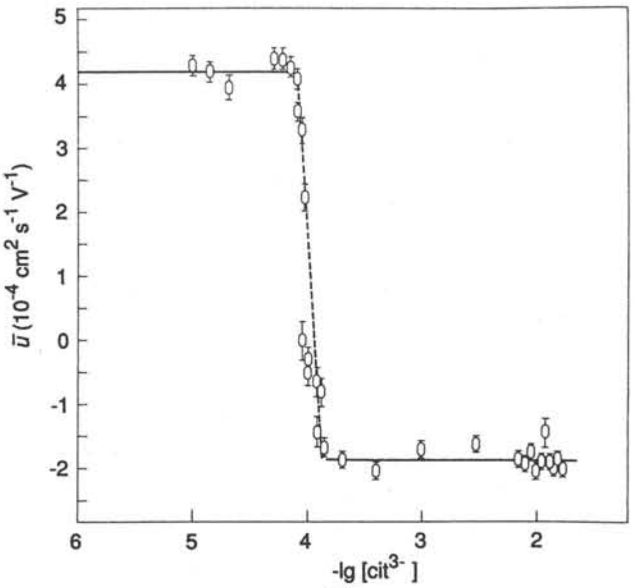

Fig. 2. Overall ion mobility of ^{239}Np(V) versus citrate ligand concentration in aqueous perchlorate electrolytes.
$\mu = 0.10(ClO_4^-)$, pH 7.2–8.4, $T = 298.1(1)$ K.

The final product of this reaction migrates as an anion with an ion mobility of $-1.9(1) \cdot 10^{-4}$ cm^{2}s^{-1}V^{-1}, $\mu = 0.10(ClO_4^-)$, $T = 298.1(1)$ K. Further increase in the citrate concentration does not affect this value.

Because of the small range of [cit^{3-}] in which $\bar{u}_{Np(V)}$ changes, no complex formation of the type $\bar{u}_{Np(V)} = f([cit^{-3}])$ with the starting and end points of the individual ion mobilities of $+4.1(1) \cdot 10^{-4}$ cm^{2}s^{-1}V^{-1} and $-1.9(1) \cdot 10^{-4}$ cm^{2}s^{-1}V^{-1} can be formulated.

4. Discussion

In the preceding work, the use of a mechanism like $NpO_2^+ + nL^{2-}$ to explain the complex formation of carrier-free ^{239}Np(V) with the L^{2-} ligands oxalate, tartrate and sulphate in neutral perchlorate electrolytes, gave rise to four problems:

(i) Formation of anionic complexes – as it was to be expected from the literature data on stoichiometric stability constants of the complexes – was not observed with tartrate and sulphate ligands.

(ii) Mathematical computer simulations of the experimental ($[L^{2-}]$; $\bar{u}_{Np(V)}$) data lead to cationic individual ion mobilities of the complex ions $[NpO_2L]^-$, L = oxalate, tartrate, sulphate.

(iii) The $u^0_{[NpO_2L_n]^{1-2n}}$ data obtained, $n = 1, 2$, were found to be not proportional to the value of $u^0_{NpO_2^+}$ with respect to the ratios of the corresponding charges of the ions.

(iv) Correlations between the dependences of $\bar{u}_{Np(V)}$ and of the mean ligand number $\bar{n}_{L^{2-}}$ on ligand concentrations are chemically senseless.

There have been attempts to solve these problems by postulating the existence of a neptunyl(V) cation of stoichiometry NpO^{3+}. According to the $NpO^{3+} + n\,L^{2-}$ model, the correct chemical signs and amounts of individual ion mobilities of the ions acting in the complex formation equilibria have been obtained. Besides, the stoichiometric complex formation constants calculated agree with the corresponding literature data.

There is a complete analogy to the electromigration results in the Np(V) - acetate system.
The facts are:
No evidence of formation of anionic complex formation products was found though the $[NpO_2(ac)_2]^-$ ion should exist in aqueous solutions of $\mu = 0.30(ClO_4^-)$, $[ac^-] = 3 \cdot 10^{-1}$ M, $T = 298.1(1)$ K. The assumption that only the monoacetato complex is formed leads to a value of $\lg K_1$ which is much too low with respect to the literature data.

Alternatively, the stoichiometric stability constants which theoretically allow for the existence of $[NpO(ac)_n]^{3-n}$ complexes, $n = 1, 2$, are chemically correct.

Table 2 compares the calculated stoichiometric stability constants for $n = 1, 2, 3$, with the literature data. The values are arranged according to the overall ionic strength of the electrolyte systems used in the investigations. The dependence of the $\lg K_n$ data on the overall ionic strength is low.

Unfortunately, the electromigration results obtained in the Np(V)-citrate system do not reflect the complex formation reaction. In contrast, the experimental dependence of $\bar{u}_{Np(V)}$ on the citrate ion concentration should be explained by reduction of the pentavalent neptunium. The reduction potential is reached in solutions of 10^{-4} M [cit^{3-}], $\mu = 0.10(ClO_4^-)$, $T = 298.1(1)$ K.

The reduced neptunium, probably Np(IV), is stabilized according to the concentrations of cit^{3-} and OH$^-$ in the solution.

The general formulation of the stoichiometry of the ion should be $[Np^{IV}cit_n(OH)_m]^{4-(3n+m)}$. Taking into account the amount of the final individual ion mobility of the product, a charge in the range of -1, -2 or -3 is probable. Variants are ($n = 2$; $m = 0$) and ($n = 1$; $m = 2$ or 3). The latter alternative is preferable, because the neptunium(IV) cation is hydrolysed in a neutral milieu and the citrate ligand acts as a strong complex-forming agent. On the other hand, the ratios between individual ion mobilities and charges of the ions cannot be compared because of the change in the physico-chemical character of the central metal cation itself.

In the reduction process no evidence of the existence of either a NpO_2^+ or a NpO^{3+} in complex formations with L^{3-} citrate ligand could be obtained.

However, the results of the electromigration investigations in the ^{239}Np(V) acetate system support the postulate of the existence of a NpO^{3+} cation.

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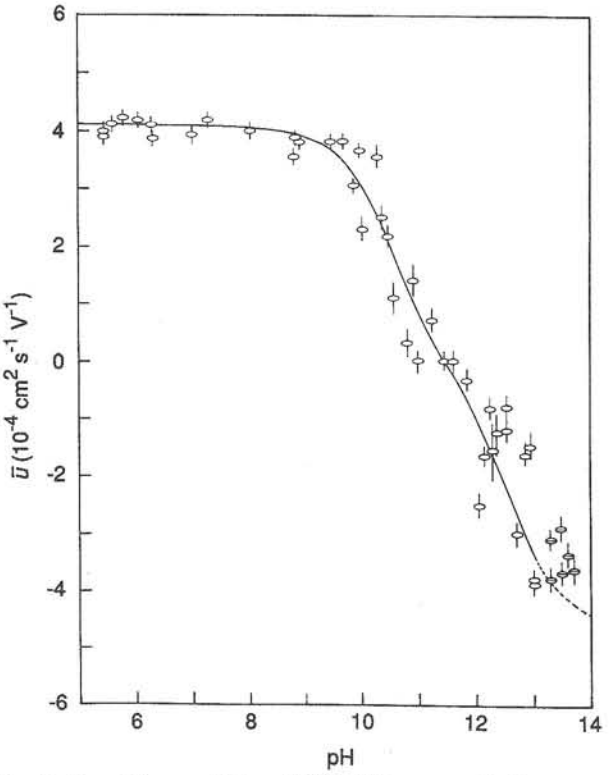

Fig. 3. Overall ion mobility of ^{239}Np(V) versus pH of aqueous perchlorate electrolytes [1].
$\mu = 0.10(\mathrm{ClO_4^-})$, pH 5.6–12.9, $T = 298.1(1)$ K.
(⊖) 0.2, 0.3, 0.4 and 0.5 M NaOH, respectively.

Accepting the existence of such an ion gives rise to some questions. For example, are there differences between the stability constants of the complexes containing $\mathrm{NpO_2^+}$ or $\mathrm{NpO^{3+}}$ units?

The literature data on Np(V) complex formation are clearly based on the existence of the $\mathrm{NpO_2^+}$ cation.

However, there is good agreement of the stoichiometric stability constants calculated in [2] for oxalate, tartrate and sulphate, and in the present work for acetate, with the literature data. Thus, similar parameters of the $\mathrm{Np^V}$ state would decisively determine the similar complex formation behaviour of $\mathrm{NpO_x^{5-2x}}$ cations, $x = 2$ or $x = 1$. It would be of special interest to investigate how the primary experimental literature data can be explained on the basis of a new mechanism of the type of eq. (2).

Only in some publications structure investigations have been carried out and it cannot be excluded that the experimental results of the investigations are also explained by mechanism (2).

It is one of the advantages of the electromigration method that charges of the acting ions are detectable immediately.

If a central $\mathrm{Np^VO_x^{5-2x}}$ cation with $x = 1$ exists, the hydrolysis behaviour of the ^{239}Np(V) published in ref. [1] and shown here in Fig. 3, should be discussed in a new way.

Then eq. (7) must be written as

$$\mathrm{NpO^{3+}} + n\,\mathrm{H_2O} \overset{\beta'_n}{\rightleftarrows} [\mathrm{NpO(OH)}_n]^{3-n} + n\,\mathrm{H^+}. \quad (7)$$

Since absolute amounts of the individual ion mobilities of the central cation and the anionic final hydrolysis product are almost the same, $n = 6$ should be assumed. An estimation yields a value of $p\beta'_6 \approx 66$ (3).

5. Conclusions

The investigation on the electromigration behaviour of carrier-free ^{239}Np(V) in neutral aqueous perchlorate electrolytes resulted in experimental dependences of the overall ion mobility of the pentavalent neptunium on concentrations of L^{a-}-ligands, $a = 1, 2$. The functions $\bar{u}_{\mathrm{Np(V)}} = f([\mathrm{L}^{a-}])$ were simulated by a computer minimization program based on the mechanism of the type $\mathrm{NpO_2^+} + n\,\mathrm{L}^{a-}$. It was shown that this leads to chemically incorrect values of stoichiometric stability constants and individual ion mobilities.

In contrast, assuming pentavalent neptunium of stoichiometry $\mathrm{NpO^{3+}}$, satisfactory data of $\lg K_n$ and $u^0_{[\mathrm{NpOL}_n]^{3-an}}$ are obtained. The stoichiometric stability constants of oxalate, tartrate, sulphate and acetate complexes of Np(V), respectively, were found to agree with the corresponding literature data.

The changes and absolute amounts of individual ion mobilities as well as correlations between individual ion mobilities and charges of complexes and central ions follow the general electromigration character.

Of course, the postulation of the existence of a $\mathrm{NpO^{3+}}$ cation contradicts the general and fundamental knowledge about Np(V) chemistry in aqueous solutions.

In this context, the formulation of a neptunium(V) cation with the charge +3 is a primarily formal attempt to interpret the well reproducible electromigration results.

In principle, any attempt of interpretation has to explain the increase of positive charges of the Np(V) compleexes:
The investigated complexes of ^{239}Np(V) with L^{a-}-ligands of the types $[\mathrm{NpO_2L}_n]^{1-an}$ with $a = 2$, $n = 1$ (oxalate, tartrate, sulphate) as well as $a = 1$, $n = 2$ (acetate) do not migrate like anions but like cations.

The discussion of a $\mathrm{Np^VO_x^{5-2x}}$ stoichiometry with $x = 1$ satisfies the electromigration behaviour of the Np(V) complexes. However, actual existence of a $\mathrm{NpO^{3+}}$ cation in aqueous solutions seems to be not acceptable for a lot of reasons. This is clearly confirmed also by the own experimental electromigration data on ^{239}Np(V) hydrolysis [1], Fig. 3, indicating existence of $\mathrm{NpO_2^+}$. A $\mathrm{NpO^{3+}}$ cation should be hydrolyzed at significant lower values of pH, i.e. in neutral or acidic media.

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Therefore, it is necessary to look for other mechanisms which may increase positively the charge of the Np(V) complexes.

For example, the formation of ion pairs between the $[NpO_2L_n]^{1-an}$ anions and the cation of the ground electrolyte Na^+ was proposed yielding species of the type $[Na_x(NpO_2L_n)]^{(x-an)}$. But these equilibria are unprobable. Nevertheless, they will be investigated in further works. However, there is another possibility to interprete the electromigration phenomenon:
In complex chemistry of some pentavalent metal cations MeO_2^+ reactions of type

$$(OMeO)^+ + n\,L^{a-} + H_2O \rightarrow [(OMeOH)L_n]^{-an} + OH^- \quad (8)$$

are known, Me = Tc, Re [19]. The protonizations are consequences of changes in the electron density at the yl-oxygens within the O=Me=O bonds, caused by the Me-ligand bondings.

Possibly, these reactions occur also in the case of the pentavalent neptunium with concern to one or both of the yl-oxygens, respectively.

Unfortunately, the experimental electromigration data do not allow to detect such mechanisms unambiguously. On the other hand, this interpretation offers some advantages.

For example, the model can describe that in aqueous inert electrolyte solutions the NpO_2^+ cation exists, whereas in the process of the complex formation the oxygen(s) of the O=Np=O is (are) protonizated gradually.

Further experimental investigations will be carried out to examine the proposed models.

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