

- [51] B. Guillaume, D. E. Hobart, J. Y. Bourges, *J. inorg. nucl. chem.* **43** (1981) 3295
 B. Guillaume, G. M. Begun, R. L. Hahn, *Inorg. Chem.* **21** (1981) 3295
 P. G. Varlashkin, D. E. Hobart, G. M. Begun, J. R. Peterson, *Radiochim. Acta* **35** (1984) 91
- [52] A. G. Rykov, A. A. Frolov, *Radiokhimiya* (in Russian) **16** (1974) 569
 A. G. Rykov, A. A. Frolov, *Radiokhimiya* (in Russian) **14** (1972) 709
- [53] A. R. Eberle, M. W. Lerner, C. G. Goldbeck, NBL-252 1970
- [54] U. Niese, „Zur Analytik des Neptuniums“, Thesen, Prom. B., T.U. Dresden, 1984, ZfK-553 (1985)
 U. Niese, J. Vecernik, *Isotopenpraxis*, **18** (1981) 191
- [55] R. A. Schneider, *Anal. Chem.* **34** (1962) 522
- [56] F. L. Moore, *Anal. Chem.* **29** (1957) 941
- [57] G. W. C. Milner, G. Phillips, *Advances in Analytical Chemistry*, H. W. Nürnberg (ed), London, p. 159
- [58] M. C. Musikas, *Radiochim. Acta*, **1** (1963) 92
- [59] C. E. Plock, *J. Electroanal. Chem.* **18** (1968) 289
- [60] R. C. Propst, *Anal. Chem.* **43** (1971) 994
- [61] P. G. Hagan, J. M. Cleveland, *J. inorg. nucl. chem.* **28** (1966) 2905
- [62] R. Gauthier, V. Ilmstaedter, K. H. Lieser, *Radiochimica Acta* **33** (1983) 35
- [63] P. A. Bertrand, G. R. Choppin, *Radiochim. Acta*, **31** (1982) 135
 G. R. Choppin, Akairo Saito, *Radiochim. Acta*, **35** (1984) 149
- [64] Yasuchi Inoue, Osamu Tochiyama, *J. inorg. nucl. Chem.* **39** (1977) 1443
- [65] S. B. Savvin, Arsenazo III, *Methods of Photometric Determination of Rare and Actinide Elements*, Moscow, 1966
- [66] Yu. P. Novikov, *J. Radioanal. Chem.* **21** (1974) 519
 Yu. P. Novikov, B. F. Myasoedov, M. N. Margorina, *Radiochem. Radioanal. Lett.* **10** (1972) 11
- [67] B. Stahr, W. Faubel, P. M. Menzler, H. J. Ache, Abstracts, Second Karlsruhe International Conference on Analytical Chemistry in Nuclear Technology, June 5–9, 1989, Karlsruhe
- [68] A. V. Stepanov, V. M. Alexandruk, A. S. Babaev, T. A. Demyanova, S. A. Nikitina, E. B. Preobrazhenskaya, Abstracts, Second Karlsruhe Conference on Analytical Chemistry in Nuclear Technology, June 5–9, 1989, Karlsruhe, p. 33
- [69] B. F. Myasoedov, *Inorg. chim. Acta*, **140** (1986) 231
- [70] B. F. Myasoedov, *Talanta*, **34** (1987) 31
- [71] B. F. Myasoedov, I. A. Lebedev, *Radiochim. Acta*, **32** (1983) 55
- [72] H. Ruf, M. Friedrich, *Nucl. Techn.* **37** (1977) 79
- [73] U. Niese, S. Niese, *J. Trace and Microprobe Techn.* **1** (1983) 339
- [74] U. Niese, S. Niese, *Isotopenpraxis*, **20** (1984) 131
- [75] M. Yamamoto, K. Chatani, K. Komura, K. Ueno, *Radiochim. Acta*, **47** (1989) 63
- [76] D. C. Lauria, D. Yang, S. Möbius, C. Keller, Abstracts, Actinides-89, September 24.–29. 1989, Taschkent, p. 450
- [77] F. Rösch, S. Dittrich, T. Reimann, G. V. Buklanov, M. Milanov, R. Dreyer, V. A. Khalkin, Abstracts, Actinides-89, September, 24.–29. Taschkent, 1989, p. 263
- [78] G. Rosner, *J. Radioanal. Chem.* **64** (1981) 55
- [79] U. Niese, S. Niese, *J. Radioanal. Nucl. Chem.* **91** (1985) 17
- [80] B. L. Cohen, *Health Physics*, **42** (1982) 133
- [81] G. R. Choppin, Abstracts, Actinides-89, September 24.–29. 1989, Taschkent, p. 426
- [82] K. H. Lieser, U. Mühlenweg, *Radiochim. Acta*, **43** (1988) 27, 44/45 (1988) 129
- [83] Shinichi Nakayama, Hajime Arimoto, Norikazu Yamada, Hirotake Moriyama, Kunio Migashi, *Radiochim. Acta*, **44/45** (1988) 179
- [84] Shinichi Nakayama, Tsunetaka Banba, *J. Nucl. Sci. Technol.* **26** (1989) 45
- [85] V. Hirsch, K. H. Lieser, *Radiochim. Acta*, **44/45** (1988) 7
- [86] G. Bidoglio, A. Avogadro, A. De Plano, G. P. Lazzari, *Radiochim. Acta*, **44/45** (1988) 29
- [87] F. Baumgärtner (Hrsg.), *Chemie der nuklearen Entsorgung*, Teil 2, München: Verlag Karl Thiemeig 1978, S. 47

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Electromigration Studies of Carrier-Free $^{239}\text{Np(V)}$ in Aqueous Solutions*)

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Ion mobilities of carrier-free $^{239}\text{Np(V)}$ have been measured in aqueous solutions, $T = 298.1(1)$ K. Ion mobilities of $^{239}\text{NpO}_2^+$ and its dependencies on pH of acidic inert electrolytes have been measured. In alkaline solutions the stoichiometric hydrolysis constants of $\text{NpO}_2(\text{OH})$ as well as $[\text{NpO}_2(\text{OH})_2]^-$ have been obtained. Complex formations of $^{239}\text{Np(V)}$ with oxalate, tartrate, sulphate, acetate and citrate ligands have been studied in neutral solutions.

In wäßrigen Lösungen, $T = 298,1(1)$ K, sind die Ionenbeweglichkeiten von trägerfreiem $^{239}\text{Np(V)}$ gemessen worden. Es wurden die Ionenbeweglichkeiten von $^{239}\text{NpO}_2^+$ sowie deren Abhängigkeiten vom pH-Wert saurer Inertelektrolyte bestimmt. In alkalischen Lösungen wurden die stoichiometrischen Hydrolysekonstanten von $\text{NpO}_2(\text{OH})$ bzw. $[\text{NpO}_2(\text{OH})_2]^-$ erhalten. In neutralen Lösungen wurden die Komplexbildungen des $^{239}\text{Np(V)}$ mit den Liganden Oxalat, Tartrat, Sulfat, Acetat und Citrat untersucht.

Keywords

complex formations; electromigration; neptunyl complexes; neptunyl compounds; neptunium 239; ion mobilities; hydrolysis

Introduction

The electromigration method offers favourable prerequisites for studying individual ion mobilities of separate ions and resulting overall ion mobilities of elements. These data are unique ones.

Many ion mobilities of cations in infinitely diluted solutions are available from conductivity data according to Nernst equation.

In contrary, individual ion mobilities of most of the complex or hydroxo ions are unknown both in real and infinitely diluted electrolytes.

It is one of the most important achievements of the modified version of the continuous electromigration technique, developed in our group, to measure immediately these experimental data.

The values of the individual ion mobilities can be used for determinations of physico-chemical parameters of the ions, to study chemical equilibria (protolysis and complex formations) and to obtaine informations on the specific interactions of the migrating ions with the ground electrolyte system. For practical purposes, the data are of special interest for the investigation of the phenomenon of migration and accumulation of various metals (radionuclides) in natural substances and for separations of elements, for example.

The present work summarizes results of electromigration investigations of some aspects of the chemistry of carrier-free $^{239}\text{Np(V)}$ in aqueous solutions.

Dealing with the pentavalent actinide $^{239}\text{Np(V)}$ individual ion mobilities of the NpO_2^+ cation were studied in acidic and neutral aqueous inert electrolytes.

Additional effects of different ligands, essentially of H^+ and OH^- and of simple inorganic ions as well as of organic compounds were

*) Part 18 of the series: Electromigration of Carrier-Free Radionuclides

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tested. This lead to the hydrolysis and complex formation studies of the pentavalent neptunyl cation.

Study of hydrolysis of neptunium in various valence states, in particular in the most stable pentavalent one is still of importance for investigation of the element's chemical behaviour. The first hydrolysis constant of neptunyl ion was determined many times by different methods in solutions with neptunium contents of $10^{-2} - 10^{-5}$ M (Tab. 1) [1–7], except for Ref. [7] where carrier-free ^{239}Np was used.

Anionic forms of Np(V) were detected in alkaline solutions with $\text{pH} > 12$ by electrophoretic [4] and ion-exchange methods [8]. Detailed study of $\text{NpO}_2(\text{OH})$ solubility versus concentration of hydrogen ions with fine-pore membranes [6] used to separate precipitate and solution allowed the conclusion, that only the anion $[\text{NpO}_2(\text{OH})_2]^-$ is produced up to $\text{pH} < 13$. Mathematical treatment of the results allowed also determination of the second hydrolysis constant $p\beta_2 = 23.11$. Noteworthy is that the first hydrolysis constant from Ref. [6] is about two orders smaller than the constants calculated by other authors [1, 4, 5, 7]. That is why we have found it reasonable to determine both hydrolysis constants with a radically different method.

After obtaining the range of $\text{pH} = 5.5 - 8.5$, where hydrolysis and other interactions of the neptunyl cation with inert ground electrolytes are negligible, the complex formations of $^{239}\text{Np(V)}$ were studied.

Using oxalate ligand, general information on Np(V) complex formations in neutral aqueous solution should be obtained and compared with the literature data. Other ligands of L^{2-} (tartrate, sulphate) type were selected because there exist only some inconsistent complex formation data.

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 could not be understood, if one considers a Np(V) cation of NpO_2^+ stoichiometry. A formal attempt to consider a NpO_3^{3+} stoichiometry of the Np(V) was able to correlate electromigration results and reaction model. In this context, the next plan was to test the ligands acetate (L^- type) and citrate (L^{3-} type). The corresponding acids HL and H_2L are sufficiently deprotonised in the pH range of interest ($\text{pH} 5.5 - 8.5$). Additionally the literature data on Np(V) complex formation with these ligands in aqueous solutions are available.

The concept was based on the expectation that the first step of the complex formation leads either to neutral ($[\text{NpO}_2\text{L}]$) or cationic ($[\text{NpOL}]^{2+}$), or to anionic ($[\text{NpO}_2\text{L}]^{2-}$) or neutral ($[\text{NpOL}]$) products, respectively. The electromigration method is most suitable for direct analyse of the existence of the alternative signs of the ions, and consequently for obtaining further information on the stoichiometry of the central neptunyl cation.

2. Experimental

^{239}Np

The carrier-free isotope ^{239}Np ($T_{1/2} = 2.35$ days; β^- , γ) was used for the investigations. It was obtained by wellknown generation method from ^{243}Am ($T_{1/2} = 7370$ years) [9]. The separated sample of ^{239}Np was acidified with 8 M HNO_3 , then neptunium(V) was reduced by hydrazine to the tetravalent state. The nitrate complex anion of Np(IV) was sorbed from this solution in a chromatographic column filled with anion exchange resin Dowex $7 \times 8.200 - 400$ mesh [10]. The column was washed with 8 M HNO_3 to eliminate possible contamination of americium and hydrazine, and neptunium was washed out with 0.1–1 M HNO_3 .

The solution was dried by evaporation, then water was added and evaporation repeated in a test tube with a conical bottom. Np(V) stock solutions of $0.25 \text{ ml} \cdot 10^{-2} \text{ M H(Na)ClO}_4 + 1 \cdot 10^{-3} \text{ M NaNO}_2$ (to stabilize the pentavalent state) were used for the electromigration experiments. The obtained solution had specific volume activity of about 100 to 200 MBq/ml.

Electromigration method

This is a horizontal low-voltage electrophoresis of ions in solutions of inert electrolyte systems without stabilizing materials (e.g. papers, quartz powder or others). We have used a specialized version of the method, based on multiple on-line measurements of the carrier-free radioelement electromigration velocity during the experiment [11–13]. Reliability of results obtained by this method was earlier checked determining individual ion mobilities, hydrolysis constants and complex stability constants of other carrier-free radioelements [14–20].

Migration velocities of Np(V) ions were measured in a glass tube, 40 mm long, 3 mm in diameter, by means of a NaI (Tl) scintillation detector, detecting X-ray and γ -radiation of ^{239}Np . The detector continuously scanned the tube during the experiment. At the same time a multichannel analyser, operating in the multiscale mode recorded time and distance covered by the radioelement zone from the beginning of the experiment.

Continuous electrolyte exchange in vessels with platinum electrodes guaranteed pH constancy in the electromigration tube. Connection of this tube of electrode vessels through hydrodynamic resistors (nuclear filters with holes 30 nm in diameter) prevented generation of liquid flows, distortion of the shape of the radioelement zone and uncontrollable affection of the ion migration velocities. Absence of the above-mentioned factors in the Np(V) experiments was proved by practically constant half-widths of radioelement zones and migration velocities of ions during 1.5–2 hours of electrophoresis. To obtain a relatively narrow zone, not more than 5 μl of ^{239}Np stock solution with pH and μ close to those of the background electrolyte solution were injected into the electromigration tube by means of a microsyringe. Neptunium electromigration mobility was determined at a constant field strength $E = 10.00(1) \text{ V} \cdot \text{cm}^{-1}$.

Electrolyte solutions

Dependence of neptunium electromigration velocity and direction (cationic or anionic, respectively) upon hydrogen ion concentration was studied in inert electrolytes using HClO_4 , NaClO_4 , NaOH with overall ionic strength $\mu = 0.10$ and temperature $T = 298.1(1) \text{ K}$. To stabilize neptunium in the pentavalent state, NO_2^- or N_2H_5^+ were added; their concentration in solutions was of the order of 10^{-3} M .

To avoid effects caused by the $^{239}\text{Np(V)}$ ultramicroquantities on Np mobilities $^{237}\text{NpO}_2^+$ was added to the background electrolytes to get neptunium concentration $1 \cdot 10^{-4} \text{ M}$ in several experiments. An independent series of experiments was also carried out to determine the $^{239}\text{Np(V)}$ individual ion mobility in acidic and neutral nitrate and chloride solutions, $\mu = 0.1$ and $\mu = 1.0$.

Investigations of the hydrolysis of $^{239}\text{Np(V)}$ were carried out in $\text{H(Na)ClO}_4/\text{NaOH}$ electrolytes, $\mu = 0.10$. For several experiments solutions of 0.20, 0.30, 0.40 and 0.50 M NaOH were used. All these electrolyte systems contained 10^{-3} M hydrazine. The temperature was 298.1(1) K.

To study the complex formation of $^{239}\text{Np(V)}$, aqueous solutions of type $\text{Na}_2\text{L}/\text{NaClO}_4$, $T = 298.1(1) \text{ K}$ were used for the investigations; L = oxalate, tartrate, sulphate, citrate and acetate, respectively.

To guarantee a high percentage of unprotonated L^{2-} ions in their protolysis equilibria and to avoid Np(V) hydrolysis, the pH of the solutions was adjusted to 5.5–8.5. The overall ionic strength of different systems was as follows:

L = oxalate:	$\mu = 0.05$ (pH 7.0–8.9)
	$\mu = 0.10$ (pH 5.5–6.5)
	$\mu = 0.30$ (pH 6.0–8.0)
L = tartrate:	$\mu = 0.10$ (pH 5.5–8.1)
L = sulphate:	$\mu = 0.30$ (pH 5.5–6.5)
L = acetate:	$\mu = 0.30$ (pH 6.7–8.9)
L = citrate:	$\mu = 0.10$ (pH 7.2–8.4).

In addition, an electrolyte system $\text{Na}_2\text{ox}/\text{NaNO}_3$, $\mu = 0.10$, pH 5.9–6.5, was used to test effects of the ground electrolyte composition.

The concentrations of the ligands were calculated by using concentration dissociation constants from refs. [21–24].

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

The pH of the electrolytes was measured by means of glass electrodes calibrated by standard buffer solutions. The pH of the $^{239}\text{Np(V)}$ sample was adjusted to the pH of the electrolyte systems.

3. Results and Discussion

3.1. Individual ion mobility of $^{239}\text{NpO}_2^+$ in acidic solution

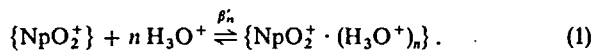
The primary results of the electromigration experiments in acidic aqueous perchlorate electrolytes are summarized in Fig. 1.

At pH 7.5–5.5 the values of $u_{\text{NpO}_2^+}^0$ are constant. Between pH 5.5–3 with decreasing pH the individual ion mobility of the neptunyl cation decreases too. At pH < 3 a new and constant value of $u_{\text{NpO}_2^+}^0$ is obtained. For conditions of $\mu = 0.10$ (ClO_4^-) the differences between the two standards are $1.35 \cdot 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$, i.e. 32.5%.

The effect was still observed both with NO_2^- and with N_2H_5^+ in the solutions, at $^{237}\text{NpO}_2$ concentration of $1 \cdot 10^{-4} \text{ M}$ in the background electrolyte, at the increase of overall ionic strength to $\mu = 1.0$, and in chloride and nitrate solutions of background electrolytes. To explain the effect, it is logic to assume that it is related to different valence states of neptunium in acid or neutral solutions, or to interaction of Np(V) with hydrogen ions whose concentration was the only variable in this experimental series.

On the basis of the first assumption one should admit that the single-charged Np(V) ion is unstable in solutions with pH < 3 and is oxidized to a more mobile double-charged Np(VI) ion, even in presence of NO_2^- or N_2H_5^+ . We think it to be improbable, since it is well-known that nitrites and hydrazine quickly reduce Np(VI) to Np(V) in weakly acidic solutions [18]. Though these reactions were investigated in solutions with relatively high concentrations of H^+ , Np(VI) and strong overall ionic strength, it follows from the data in Ref. [18] that their velocities are inversely proportional to $[\text{H}^+]$ and μ . Consequently, also under our conditions we only deal with Np(V) in the whole interval of hydrogen ion concentration.

Difference in mobility of neptunyl ion in acidic and neutral solutions can be explained on the basis of the second assumption on its interaction with hydrogen ions:



On the basis of model calculations corresponding to eq. (1), one can write down the relation $\bar{u}_{\text{Np(V)}} = f([\text{H}^+])$ in the following form:

$$\bar{u}_{\text{Np(V)}} = \frac{u_{\text{NpO}_2^+}^0 + u_{\text{NpO}_2^+ \cdot \text{H}_3\text{O}^+}^0 \cdot \beta_1' [\text{H}^+] + \dots + u_{\text{NpO}_2^+ \cdot (\text{H}_3\text{O}^+)_n}^0 \cdot \beta_n' [\text{H}^+]^n}{1 + \beta_1' [\text{H}^+] + \dots + \beta_n' [\text{H}^+]^n} \quad (2)$$

where u_i^0 are the individual mobilities of neptunium(V) ions, building up an equilibrium system. Solution of eq. (2) showed that the calculated function $\bar{u}_{\text{Np(V)}} = f([\text{H}^+])$ has the closest coincidence with results of our measurements of Np(V) ion mobilities in the interval $2.5 < \text{pH} < 4.5$ at $n = 1$. There is $\beta_1' \approx 10^4 \text{ mole}^{-1} \cdot \text{l}$.

There are similar results on electromigration of other radiocations in aqueous acidic perchlorate electrolytes, $\mu = 0.10$ (ClO_4^-), $T = 298.1(1) \text{ K}$. Individual ion mobilities of $^{140}\text{La}^{3+}$, $^{147,148}\text{Eu}^{3+}$, $^{149}\text{Gd}^{3+}$, $^{152,153}\text{Tb}^{3+}$, $^{167}\text{Tm}^{3+}$, $^{169}\text{Yb}^{3+}$, $^{169-171}\text{Lu}^{3+}$, $^{241}\text{Am}^{3+}$ and $^{87\text{m}}\text{Sr}^{2+}$ change between pH 5.5 and 3.0 [25, 16]. Consequently, the results described for $^{239}\text{NpO}_2^+$ should be of general nature.

Details of this effect have been investigated using $^{241}\text{Am}^{3+}$ [20].

As shown for $^{241}\text{Am}^{3+}$, with decreasing overall ionic strength the differences of u_i^0 data become lower and lower. An identical value u_i^∞ seems to be obtained at infinite dilution of the electrolyte.

Hitherto unknown interactions of the migrating radiocation with the ground electrolyte system, induced by changes of the hydrogen concentration, should be studied in further works.

However, the difference of u_i^0 -data in acidic and neutral solutions in the case of $^{239}\text{NpO}_2^+$ is the greatest one, compared to the other cations noted. This may be understood as a special contribution of yl-oxygens in this process.

Besides the effect of pH-depending changes of $u_{\text{NpO}_2^+}^0$ its absolute values are of interest.

The individual ion mobilities of $^{239}\text{NpO}_2^+$ in some real electrolytes are summarized in Tab. 1.

Fig. 2 illustrates the dependence of $u_{\text{NpO}_2^+}^0$ on the overall ionic strength μ of neutral perchlorate electrolytes. Although mathematical extrapolations of the function $u_{\text{NpO}_2^+}^0 = f(\mu)$ up to $\mu = 0$ are not

Tab. 1. Individual ion mobility of Np(V) in acidic and neutral solutions of background electrolytes of different chemical composition, $T = 298.1(1) \text{ K}$. $u_{\text{NpO}_2^+}^0$ in $10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$

μ	$1 < \text{pH} < 2$			$5.5 < \text{pH} < 7.5$		
	Na(H)ClO ₄	K(H)NO ₃	Na(H)Cl	NaClO ₄	KNO ₃	NaCl
0.1	+2.80(15)	+2.35(15)	+2.25(10)	+4.15(15)	+3.90(20)	+3.80(20)
1.0	+2.25(20)	+1.80(20)	+1.15(20)	+2.80(10)	+2.70(15)	+2.35(15)

possible because results in very diluted electrolytes are missing, the value of $u_{\text{NpO}_2^+}^\infty$ at $\mu = 0$ should be of the order of $+5.7(4) \cdot 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$. It may be compared with a value, obtained by means of conductivity measurements in acidic solutions of NpO_2NO_3 :

$$\lambda_{\text{NpO}_2^+}^\infty = 51(1) \Omega \text{ cm}^2 \text{ val}^{-1};$$

$$u_{\text{NpO}_2^+}^\infty = 5.3(3) \cdot 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1} [27].$$

Results on pulse radiolysis measurements of NpO_2^+ – solutions were carried out using 0.01 M ethanol as catcher [28] and will not be considered here.

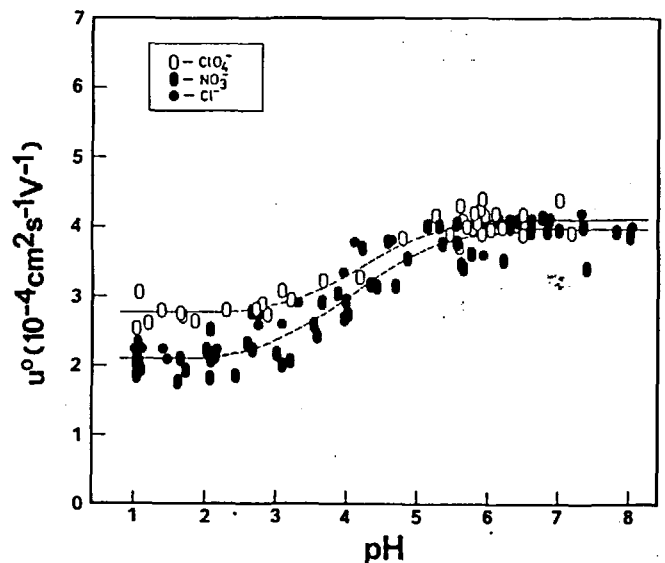


Fig. 1. Individual ion mobilities of $^{239}\text{NpO}_2^+$ vs. pH of acidic perchlorate, nitrate and chloride electrolytes, $\mu = 0.10$, $T = 298.1(1) \text{ K}$

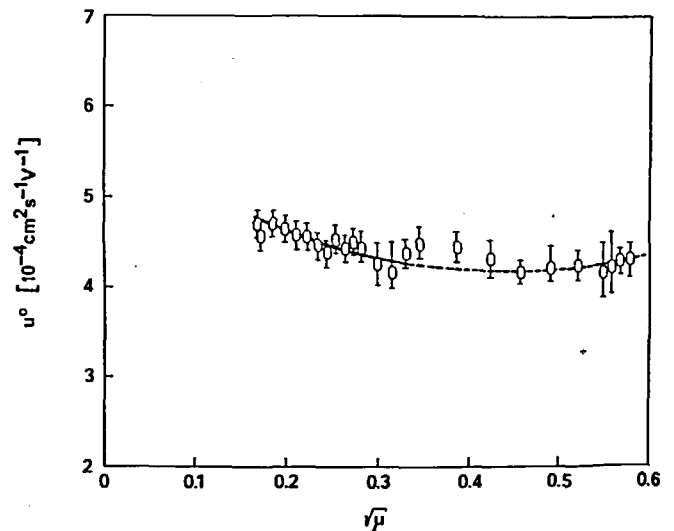


Fig. 2. Individual ion mobilities of $^{239}\text{NpO}_2^+$ vs. overall ionic strength of neutral NaClO_4 electrolytes, $\mu = 0.025 - 0.350$ (ClO_4^-), 10^{-3} M hydrazine, $T = 298.1(1) \text{ K}$

Other data on ion mobilities of NpO_2^+ in aqueous solutions are not available.

In this context, both the absolute values of $u_{\text{NpO}_2^+}^\infty$ in real aqueous inert electrolytes as well as the effect of changes of individual NpO_2^+ ion mobility in acidic aqueous solutions are unique data.

3.2. Ion mobilities of $^{239}\text{Np(V)}$ in alkaline solution

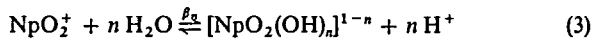
Starting from a constant value of

$$u_{\text{NpO}_2^+}^0 = +4.2(1) \cdot 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$$

the measured electromigration data of $^{239}\text{Np(V)}$ reduces in alkaline solutions at $\text{pH} > 8.5$. At $\text{pH} > 10$ the $^{239}\text{Np(V)}$ migrates in direction of the anode, indicating formation of anionic hydrolysis products.

The primary results of these electromigration measurements are shown in Fig. 3. They will be discussed as functions of type $\bar{u}_{\text{Np(V)}} = f([\text{H}^+])$.

To calculate equilibrium constants of hydrolysis reactions for pentavalent neptunium



on the basis of the above conclusion, we used NpO_2^+ individual ion mobility obtained in the interval $5.5 < \text{pH} < 13$. For this interval we assumed on the basis of results reported in Ref. [6] that $n = 1, 2$ in eq. (3). In this case the overall ion mobility of Np(V) must be described by the following equation:

$$\bar{u}_{\text{Np(V)}} = \frac{u_{\text{NpO}_2^+}^0 [\text{H}^+]^{-2} + u_{[\text{NpO}_2(\text{OH})_2]^-}^0 \beta_2}{[\text{H}^+]^{-2} + \beta_1 [\text{H}^+]^{-1} + \beta_2} \quad (4)$$

Eq. (4) was solved by the least squares method using MINUIT [29] program. The solid line in Fig. 3 give the relation $\bar{u}_{\text{Np(V)}} = f([\text{H}^+])$

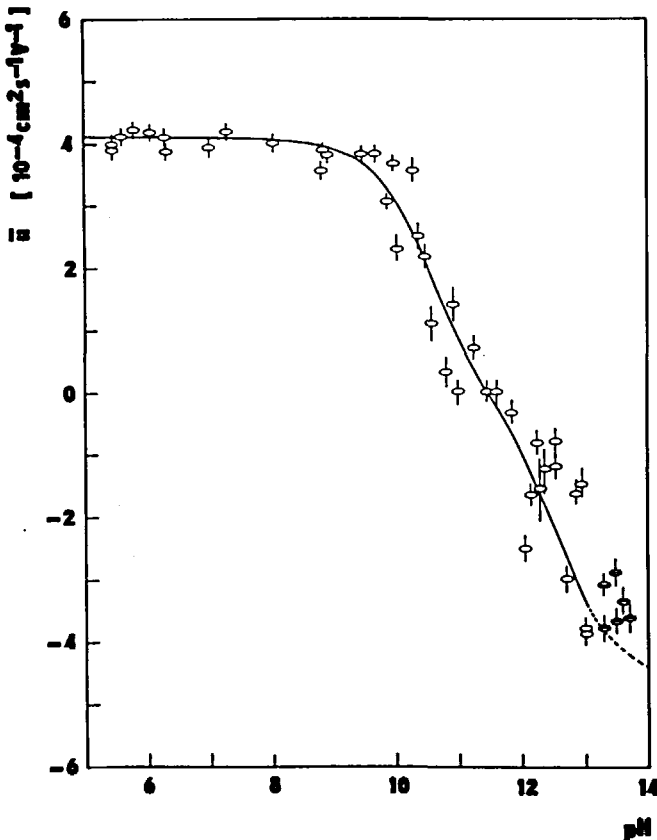


Fig. 3. Overall ion mobilities of $^{239}\text{Np(V)}$ vs. pH of inert electrolytes $\text{HClO}_4\text{-NaClO}_4\text{-NaOH}$, $\mu = 0.10$, NO_2^- or N_2H_5^+ , $1 \cdot 10^{-3} \text{ M}$ (○); NaOH , $0.2\text{-}0.5 \text{ M}$, $\text{N}_2\text{H}_5\text{OH}$, $1 \cdot 10^{-3} \text{ M}$ (●), $T = 298.1(1) \text{ K}$

calculated. It is in good agreement with experimental data. The relation was calculated with the following values of constant terms from eq. (4):

$$\begin{aligned} p\beta_1 &= 10.45(25), & p\beta_2 &= 21.95(35), \\ u_{\text{NpO}_2^+}^0 &= +4.2(1) \cdot 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}, \\ u_{[\text{NpO}_2(\text{OH})_2]^-}^0 &= -4.55(30) \cdot 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}. \end{aligned}$$

It is significant that absolute values of individual ion mobilities of Np(V) cation and anion were found to be practically the same. It could be expected by analogy with the results of previous works where we obtained close absolute values for individual ion mobilities of single-charged cationic and anionic complex ions of trivalent metals in background electrolyte solutions with dicarboxylic acids [15, 17, 18]. We think that approximate equality of absolute values for individual ion mobilities of NpO_2^+ and $[\text{NpO}_2(\text{OH})_2]^-$ indirectly indicate a reliability of Np(V) hydrolysis constants obtained in electromigration experiments with carrier-free ^{239}Np . The same can be said with respect to the satisfactory agreement of β_1 values found by us and by Bidoglio et al. [7], who also worked with carrier-free ^{239}Np .

Tab. 2 summarizes the literature data on the hydrolysis of pentavalent neptunium. Also results of paper and column electrophoresis measurements published recently [30, 31] are included.

Satisfactory agreement of the presented electromigration results with the values, obtained by means of other analytical techniques, can be stated.

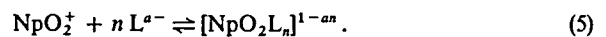
Tab. 2. Stoichiometric hydrolysis constants of pentavalent neptunium in aqueous solutions, $T = 298.1 \text{ K}$. (for methods see Tab. 5)

Meth.	μ	$p\beta_1$	$p\beta_2$	pK_2	ref.
pot, sol	0.1	9.07			1
tit	0.2 ^{b)}	10.08			2
est		10.0			3
pot	0.02 ^{a)}	8.9			4
spec	0.001 ^{b)}	8.9			4
sol	1.0	9.32			5
tit	1.0	11.67(62)	23.11	11.4	6
dis	0.2	9.84			7
pr	$5.10 \cdot 10^{-4}$ ^{c)}	$8.7^{+1.0}_{-0.5}$			28
em	0.1	10.45(25)	21.95(35)	11.5	this work
pep	0.1	8.0	18.1		30
pep	0.005	8.3	18.8		30
sol	0.01	8.3	19.4	11.1	31

a) - 296.1 K, b) - 293.1 K, c) - including 0.01 M ethanol

3.3. Complex formations of $^{239}\text{Np(V)}$ in neutral solution

The quantitative treatment of the complex formation results is based on mechanism (5), commonly accepted for the interpretation of Np(V) reactions:



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

$$\begin{aligned} \bar{u}_{\text{Np(V)}} &= \frac{u_{\text{NpO}_2^+}^0 + u_{[\text{NpO}_2\text{L}]^{1-a}}^0 \cdot K_1 \cdot [\text{L}^{a-}] + u_{[\text{NpO}_2\text{L}_2]^{1-2a}}^0 \cdot K_1 K_2 \cdot [\text{L}^{a-}]^2}{1 + K_1 \cdot [\text{L}^{a-}] + K_1 K_2 \cdot [\text{L}^{a-}]^2} \quad (6) \end{aligned}$$

The Np(V) - oxalate system

Fig. 4 shows the experimental electromigration results of $^{239}\text{Np(V)}$ in aqueous neutral perchlorate electrolytes of different overall ionic strength.

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

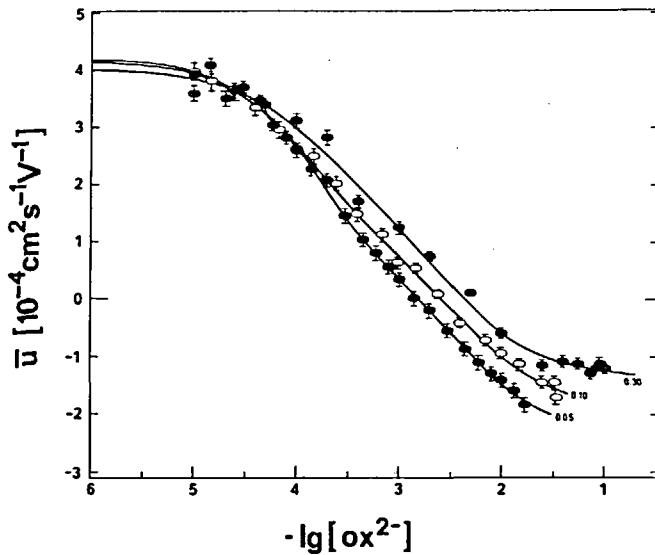


Fig. 4. Overall ion mobilities of ²³⁹Np(V) vs. oxalate ligand concentration. Na₂ox/NaClO₄ electrolytes, T = 298.1(1) K, μ = 0.05 (●), μ = 0.10 (○), μ = 0.30 (⊙)

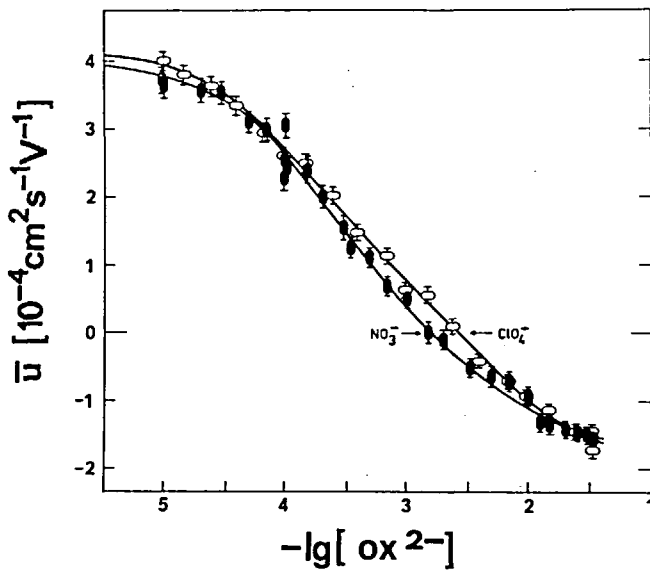


Fig. 5. Overall ion mobilities of ²³⁹Np(V) vs. oxalate ligand concentration. Na₂ox/NaClO₄(NO₃) electrolytes, μ = 0.10, T = 298.1(1) K

The behaviour of ²³⁹Np(V) in nitrate background electrolytes is almost the same, Fig. 5.

Differences in the functions $\bar{u}_{Np(V)} = f([ox^{2-}]; ClO_4^- \text{ or } NO_3^-)$ mainly concern the different values of the individual ion mobilities of the metal cation itself, chapter 3.1.

Values of $u_{[NpO_2L_n]^{1-2n}}^0$ and K_n were obtained, using the least squares method [29] and setting $n = 1, 2$ in eqs. (5, 6). The calculated functions $\bar{u}_{Np(V)} = f([ox^{2-}]; u_{[NpO_2L_n]^{1-2n}}^0; K_n)$ are given in Figs. 4 and 5.

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 (Tab. 3).

Another striking fact is the ratio of the $u_{[NpO_2L_n]^{1-2n}}^0$ 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 [15, 17, 18] as well as for the hydroxo complexes of ²³⁹Np(V) itself. Results of the other electromigration and electrophoretic measurements reflect these correlations too [32].

The Np(V) – tartrate system

Experimental results for ²³⁹Np(V) electromigration in tartrate electrolytes are illustrated in Fig. 6.

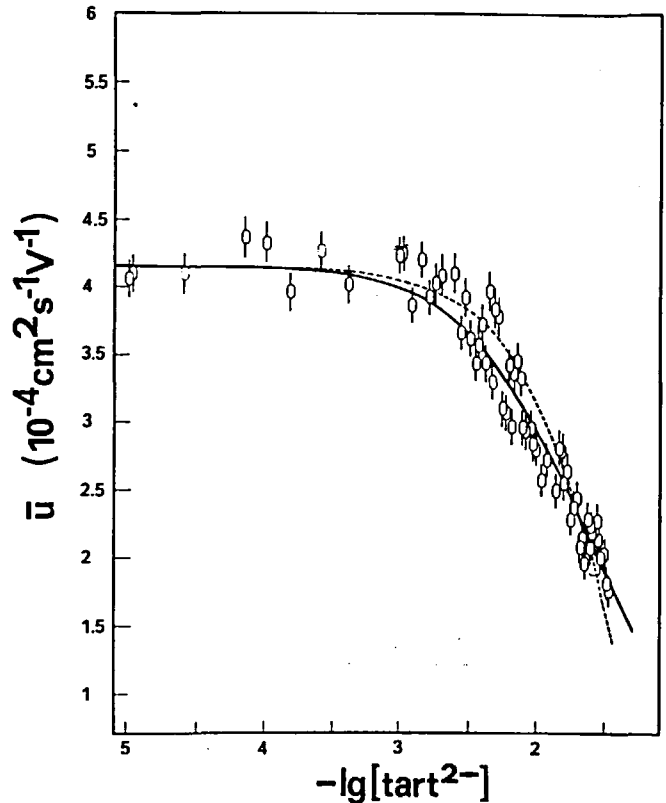


Fig. 6. Overall ion mobilities of ²³⁹Np(V) vs. tartrate ligand concentration. Na₂tart/NaClO₄ electrolytes, μ = 0.10, T = 298.1(1) K

Tab. 3. Parameters of ²³⁹Np(V) complex formations according to eqs. (5, 6). Na₂L/NaClO₄ electrolytes, L = oxalate, tartrate, sulphate. T = 298.1(1) K. u_i^0 in $10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$, K_n in $\text{l} \cdot \text{mole}^{-1}$

L	μ	$u_{NpO_2^+}^0$	$u_{[NpOL_n]^{1-}}^0$	$u_{[NpOL_2]^{1-}}^0$	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	+4.00(10)	+0.35(35)	-1.67(7)	3.75(4)	2.38(5)
tart ²⁻	0.30	+3.78(11)	+1.21(42)	-1.35(5)	3.57(4)	2.38(12)
	0.10	+4.17(10)	+1.33(66)	-0.92(71)	1.82(3)	0.72(15)
SO ₄ ²⁻	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	-
	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

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

Comparison with the literature data is difficult because only one work on Np(V) complexes in aqueous tartrate solutions was published.

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 $n = 2$ in order to calculate the complex formation parameters. In any case, even with $n = 1$, i.e. with exclusive formation of the monotartrate complex, anionic species should be detected. This 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 shown in Fig. 7.

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 disulphate ions should be negligible under $[SO_4^{2-}] \leq 1.00 \cdot 10^{-1} \text{ M}$ concentration conditions.

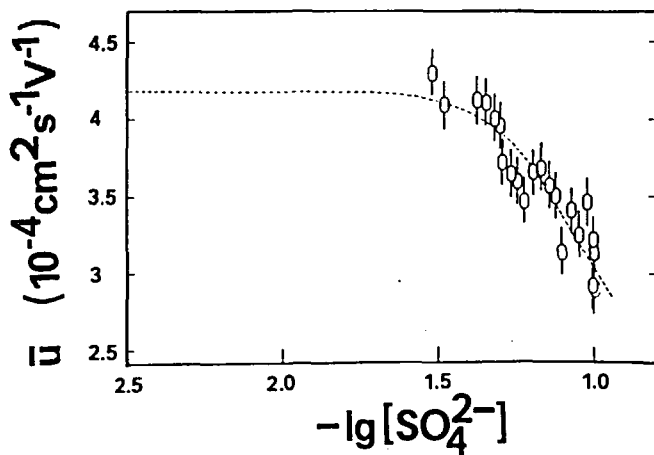


Fig. 7. Overall ion mobilities of $^{239}\text{Np(V)}$ vs. sulphate ligand concentration. $\text{Na}_2\text{SO}_4/\text{NaClO}_4$, $\mu = 0.30$, $T = 298.1(1)\text{ K}$

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 [33–35]. Rough extrapolations lead to the expected values of $\lg K_1 = 1.0–1.5$ at $\mu = 0.3$. Consequently, the ratio $[\text{NpO}_2^+]/[\text{NpO}_2(\text{SO}_4)^-]$ at $[\text{SO}_4^{2-}] = 10^{-1}\text{ M}$ should be of the order of ≥ 1 . Overall ion mobilities of Np(V) must then be $\bar{u}_{\text{Np(V)}} \leq 0$ at $[\text{SO}_4^{2-}] = 10^{-1}\text{ M}$.

As in the case with $\text{L} = \text{tartrate}$, there are great discrepancies between expected and experimental results of electromigration measurements.

The results of the calculations according to eq. (6) are summarized in Tab. 3.

The $\text{Np(V)} - \text{acetate}$ system

The experimental results on electromigration measurements of $^{239}\text{Np(V)}$ in neutral aqueous perchlorate solutions containing different acetate ion concentrations are summarized in Fig. 8.

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

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

Considering the literature date of $\lg K_1 \approx 1.1(2)$ and $\lg K_2 \approx 0.4(3)$, formation of mono- and diacetato complexes of Np(V) are to be expected under the electrolyte conditions applied.

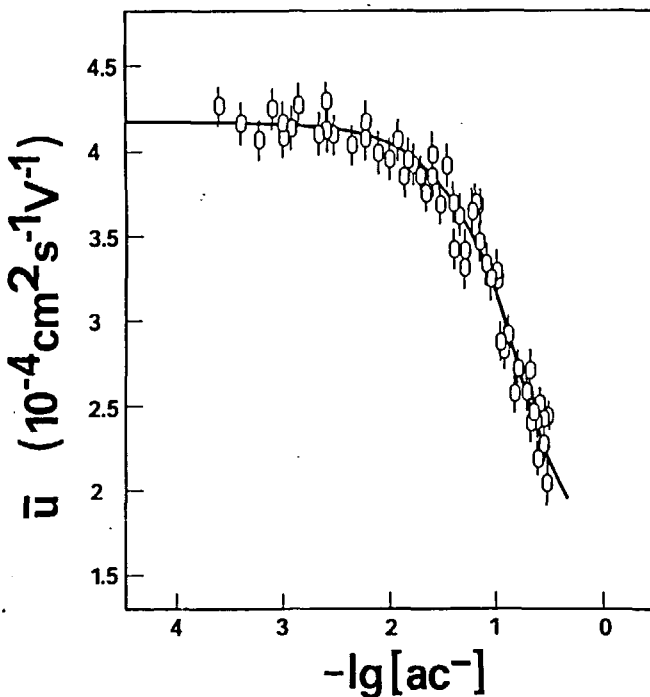


Fig. 8. Overall ion mobility of $^{239}\text{Np-Np(V)}$ vs. acetate ligand concentration. $\text{Na}(\text{ac})/\text{NaClO}_4$, $\mu = 0.30$ (ClO_4^-), $T = 298.1(1)\text{ K}$

For example, with $n = 1$ in eq. (6) the calculated values are $u_{\text{NpO}_2^+}^0 = +4.14(20) \cdot 10^{-4}\text{ cm}^2\text{ s}^{-1}\text{ V}^{-1}$, $\lg K_1 = 0.48$, $\text{FCN} = 50.74$. Apparently, this value of $\lg K_1$ is significantly low.

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

Tab. 4 summarizes the calculated values on the basis of eq. (6).

Tab. 4. Parameters of $^{239}\text{Np(V)}$ complex formations according to eqs. (5, 6), $\text{Na}(\text{ac})/\text{NaClO}_4$ electrolytes. $T = 298.1(1)\text{ K}$. u_i^0 in $10^{-4}\text{ cm}^2\text{ s}^{-1}\text{ V}^{-1}$, K_n in $\text{l} \cdot \text{mole}^{-1}$.

n	$u_{\text{NpO}_2^+}^0$	$u_{[\text{NpO}_2(\text{ac})]}^0$	$u_{[\text{NpO}_2(\text{ac})_2]^-}^0$	$\lg K_1$	$\lg K_2$	$\lg K_3$
1	+4.17(4)	+0.78(32)	—	0.65(8)	—	—
2	+4.16(4)	+2.73(53)	+1.29(41)	0.96(8)	0.61(43)	—
3	+4.17(4)	+1.29(41)	+1.54(8)	0.97(4)	0.66(20)	-0.62(54)

The $\text{Np(V)} - \text{citrate}$ system

The strong complex formation tendency of the citrate ligand with actinide cations is well known. Values of the stability constants of $\text{Np(V)} - \text{citrate}$ compounds are relatively high. At the usual overall ionic strength of $\mu \leq 1$ and temperature of $T = 239.1–298.1\text{ K}$ the mean values of $\lg K_1 \approx 4$ [36–40] and $\lg K_2 \approx 2.4–3$ [36, 39] have been found.

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

- $n = 1$ (2.49; 0.05; ?) [36],
- (3.67; 0.05; 293.1 K) [37],
- (4.84; 0.10; 298.1 K) [38],
- (3.94; ?; 298.1 K) [39],
- (4.42; 1.00; 298.1 K) [40],

and for

- $n = 2$ (2.38; 0.05; ?) [36],
- (2.97; ?; 298.1 K) [38].

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 on electromigration measurements of $^{239}\text{Np(V)}$ in aqueous neutral electrolyte systems are shown in Fig. 9.

In contrast to the $\text{Np(V)} - \text{acetate}$ system and to the $\text{Np(V)} - \text{L}^{2-}$ systems no continuous changes in the overall ion mobilities of $^{239}\text{Np(V)}$ versus ligand concentrations were observed. Here an abrupt fall of $\bar{u}_{\text{Np(V)}}$ at $[\text{cit}^{3-}] \approx 1 \cdot 10^{-4}\text{ M}$ occurs. The final product of this reaction migrates as an anion with an ion mobility of $-1.9(1) \cdot 10^{-4}\text{ cm}^2\text{ s}^{-1}\text{ V}^{-1}$, $\mu = 0.10$ (ClO_4^-), $T = 298.1(1)\text{ K}$. Further increase in the citrate concentration does not affect this value.

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

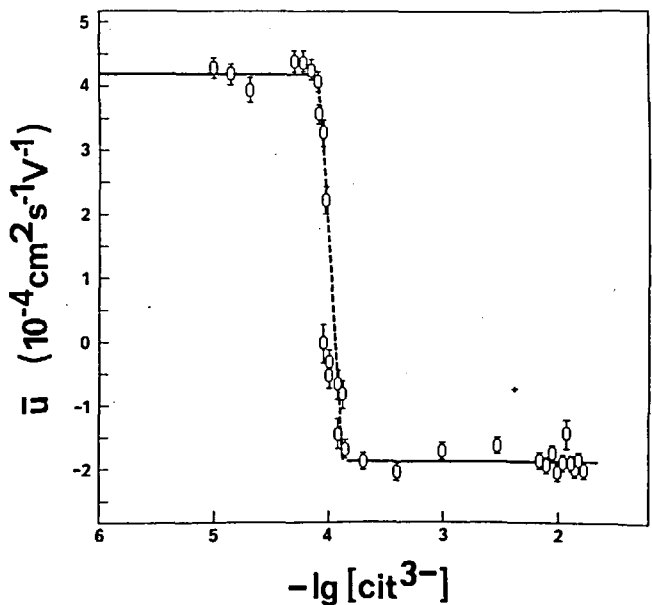


Fig. 9. Overall ion mobility of $^{239}\text{Np(V)}$ vs. citrate ligand concentration. $\text{Na}_3(\text{cit})/\text{NaClO}_4$, $\mu = 0.10$ (ClO_4^-), $T = 298.1(1)\text{ K}$

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 [cit³⁻], $\mu = 0.10$ (ClO₄⁻), $T = 298.1(1)$ K.

The reduced neptunium, probably the Np(IV) state, is stabilized according to the concentrations of cit³⁻ 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)}. The amount of the final individual ion mobility of the product taken into account, 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 one can not compare the ratios between individual ion mobilities and charges of the ions because of the change in the physico-chemical character of the central metal cation itself.

The use of the mechanism like NpO₂²⁺ + n L^{a-} to explain the complex formation of carrier-free ²³⁹Np(V) with L²⁻ ligands oxalate, tartrate, sulphate and acetate in neutral perchlorate electrolytes, gave rise to four problems:

- (i) Formation of anionic complex products — as one has to expect according to the literature data on stoichiometric stability constants of the complexes — were not observed with tartrate, sulphate and acetate ligands.
- (ii) Mathematical computer simulations of the experimental ([L^{a-}]; $\bar{u}_{Np(V)}$) data lead to cationic individual ion mobilities of the complex ions [NpO₂L]^{1-a}, L = oxalate, tartrate, sulphate, acetate.
- (iii) The obtained $u_{[NpO_2L]^{1-a}}^0$ data, n = 1, 2, were found to be not proportional to the value of $u_{NpO_2}^0$ 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^a} on ligand concentrations are chemically senseless.

Besides the stoichiometric complex formation constants calculated agree with the corresponding literature data.

There were attempts to solve these problems by postulating the existence of a neptunyl(V) cation of stoichiometry NpO³⁺. According to the NpO³⁺ + n L^{a-} model, the correct chemical signs and amounts of individual ion mobilities of the ions acting in the complex formation equilibria have been obtained.

Correctness of the calculated parameters u^0 and K_n of different complex formation mechanisms is proved 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 [29] for both models.

With the reaction mechanism



and the resulting electromigration equation for n = 1, 2

$$\bar{u}_{Np(V)} = \frac{u_{NpO^{3+}}^0 + u_{[NpOL]^{1-a}}^0 \cdot K_1 \cdot [L^{a-}] + u_{[NpOL_2]^{1-2a}}^0 \cdot K_1 K_2 \cdot [L^{a-}]^2}{1 + K_1 \cdot [L^{a-}] + K_1 K_2 \cdot [L^{a-}]^2} \quad (8)$$

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

Tab. 3, 4 summarize 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 K₂ and $u_{[NpO(Ltar)]^{1-a}}$ as tentative, because no direct evidence of this complex ion being formed was found. Fig. 6 contains the calculated functions both for n = 1 (dotted line) and n = 1, 2.

Changes in $\bar{u}_{Np(V)}$ 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 Tab. 5 have been estimated.

Also for L = acetate better FCN values are obtained for the [NpO(ac)_n]³⁻ⁿ model compared with the [NpO₂(ac)_n]¹⁻ⁿ one.

The value of FCN of the reaction with n = 2 is the best one. The values of lg K₁ and lg K₂ as well as $u_{[NpO(ac)_2]^{1-2a}}^0$ and $u_{[NpO(ac)_2]^{1-2a}}^0$ are also chemically understandable. First of all this concerns agreement of the stoichiometric stability constants with the literature data.

The experimental errors of lg K₂ 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: $u_{[NpO(ac)_3]^{1-3a}}^0 = 0$. However, no overall ion mobilities $\bar{u}_{Np(V)} < +2 \cdot 10^{-4}$ cm² s⁻¹ V⁻¹ have been observed, but only in this range existence of [NpO(ac)₃] is probable.

Consequently, calculation of exact data on lg K_n as well as of $u_{[NpO(ac)_n]^{1-na}}^0$, n ≥ 2, is more of mathematical interest: The set of the stability constants and of the individual ion mobilities calculated are chemically correct, but the data on lg K₃ and $u_{[NpO(ac)_3]^{1-3a}}^0$ should not be overestimated.

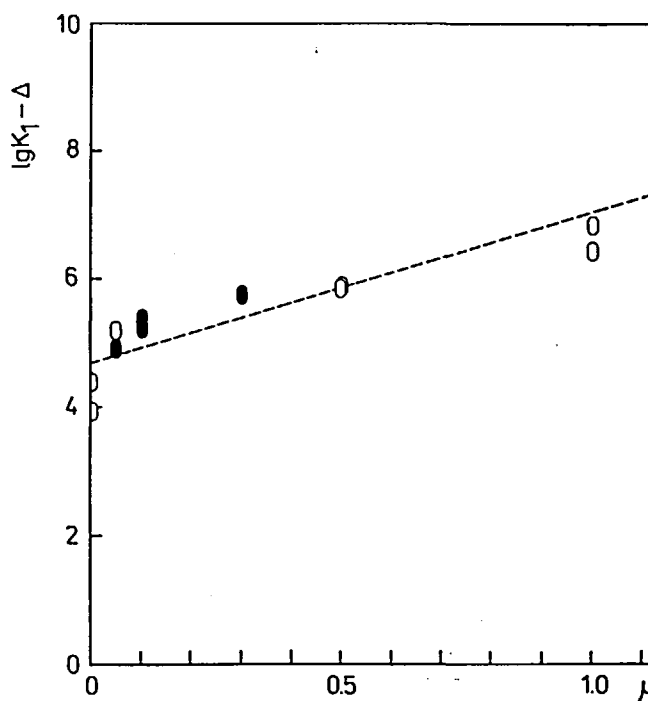


Fig. 10. lg K₁^(u) data of Np(V) — oxalate complex in aqueous electrolytes, T = 298.1(1) K, according to eq. (9), ($\Delta = \Delta z^2 A \sqrt{\mu} (1 + \sqrt{\mu})^{-1}$) (○) literature data, (●) present work

However, the value of lg K₃ = -0.6 proves the assertion, that formation of the triacetato complex can be neglected under the electrolyte conditions of [ac⁻] = 3 · 10⁻¹ M, μ = 0.30 (ClO₄⁻), T = 298.1(1) K.

The obtained stoichiometric stability constants of [NpOL_n]^{3-na} complexes are compared with the literature data in Tab. 5. Generally speaking, there is

Tab. 5. Stability constants of ²³⁹Np(V) complexes in aqueous solutions, T = 298.1 K, K_n in l · mole⁻¹

L	Meth.	μ	lg K ₁	lg K ₂	Lit.	
ox ²⁻	spec	0	3.93	3.13	[84, 85]	
	cix	0 ^{a)}	4.4	2.96	[85, 86]	
	cix	0.05 (ClO ₄ ⁻) ^{a)}	4.04	3.32	[86, 87]	
	em	0.05 (ClO ₄ ⁻)	3.77(2)	2.21(20)	[*]	
	em	0.10 (ClO ₄ ⁻)	3.90(4)	2.37(3)	[*]	
	em	0.10 (NO ₃ ⁻)	3.75(4)	2.38(5)	[*]	
	em	0.30 (ClO ₄ ⁻)	3.57(4)	2.38(12)	[*]	
	spec	0.50	3.29	2.77	[87, 88]	
	spec	0.50 ^{b)}	3.30	2.77	[87, 88]	
	pot	1.0 (ClO ₄ ⁻) ^{a)}	3.74(5)	2.57(10)	[88, 89]	
	spec	1.0 (ClO ₄ ⁻)	4.54	3.32	[88, 89]	
	tart ²⁻	dis	0.05 (ClO ₄ ⁻)	3.42	2.24	[89, 90]
dis		1.05 (ClO ₄ ⁻)	3.42	2.22	[89, 90]	
dis		0.05 (ClO ₄ ⁻)	3.41	2.25	[89, 90]	
cix		0.05 (ClO ₄ ⁻) ^{a)}	2.32	1.98	[90, 91]	
em		0.10 (ClO ₄ ⁻)	1.76(7)	0.72(15)	[*]	
sulf ²⁻		em	0.30 (ClO ₄ ⁻)	1.1(1)	—	[*]
		dis	1.0 (ClO ₄ ⁻)	0.76(2)	—	[91, 92]
		dis	2.0 (ClO ₄ ⁻)	0.45	—	[92, 93]
		dis	8.5 (ClO ₄ ⁻)	0.86	—	[93, 94]
		dis	0.5 (ClO ₄ ⁻)	-0.10	—	[94, 95]
	dis	1.0 (ClO ₄ ⁻)	0.06	—	[94, 95]	
	dis	2.0 (ClO ₄ ⁻)	0.19	—	[94, 95]	
	pmr	0	1.30	—	[95, 96]	
ac ⁻	cix	0	1.33	0.53(1.80) ⁺	[96]	
	em	0.30 (ClO ₄ ⁻)	0.96	0.61	[*]	
	?	1.0 (ClO ₄ ⁻)	0.73	—	[97]	
	cix	1.5 (ClO ₄ ⁻)	1.08	0.47(1.55) ⁺	[96, 98]	
	spec	1.5 (Cl ⁻)	1.04	0.50	[98, 99]	
	cix	2.0 (ClO ₄ ⁻)	0.97	—	[100]	
	spec	2.0 (ClO ₄ ⁻)	0.89	0.3(1.23) ⁺	[88, 89]	

^{a)} 293.1 K, ^{b)} 283.1 K, ⁺ lg β₂, ^{*} this work.

methods: (spec) — spectroscopy, (pmr) — proton magnetic resonance, (cix) — ion exchange, (em) — electromigration, (pot) — potentiometry, (dis) — distribution between two phases, (sol) — solubility, (est) — calculated data, (tit) — titration, (pr) — pulse radiolysis, (pep) — paper electrophoresis

good agreement between the calculated data and these from literature. Fig. 10 illustrates this fact, comparing $\lg K_1$ of oxalate complexes, $T = 298.1 \text{ K}$. For this reason, the correlation [58]

$$\lg K_1 = \lg K_1^0 + \Delta z^2 A \left(\frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - B\mu \right) \quad (9)$$

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 $[\text{NpOL}]^+$ complexes the corresponding charge of the individual ion mobility was calculated. The proportions between the individual ion mobilities and charges of the metal cation and complex ions are realized to a great extent.

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

These three aspects are discussed in detail in [59, 60].

4. Conclusions

The modified version of on line electromigration measurements of carrier-free radionuclides in homogeneous aqueous electrolytes free of any supporting chromatographic materials lead to some interesting results on the physico-chemistry of $^{239}\text{Np(V)}$ in aqueous solutions.

Unique values of the absolute individual ion mobility of $^{239}\text{NpO}_2^+$ in different solutions have been measured immediately. They seem to agree with the results of conductivity measurements [27]. Additionally, a hitherto unknown effect of dependence of $u_{\text{NpO}_2^+}^0$ on the pH of acidic aqueous inert electrolytes was detected. This may be understood as a stimulation of further investigations of special interactions of carrier-free $^{239}\text{Np(V)}$ with aqueous solutions.

The results of the studies of the Np(V) hydrolysis corroborate general data on this important equilibrium reaction. Compared with the other analytical techniques applied for these studies, the electromigration results should be of high accuracy because of the sensible registration of changes of the charges of the acting species.

With respect to the complex formation experiments, the electromigration results lead to discussions of the stoichiometry of the Np(V) and its complexes.

The investigations of electromigration behaviour of carrier-free $^{239}\text{Np(V)}$ in neutral aqueous perchlorate electrolytes resulted in experimental dependences of the overall ion mobility of the pentavalent neptunium on concentration of $[\text{L}^{a-}]$ ligands, $a = 1, 2$. The functions $\bar{u}_{\text{Np(V)}} = f([\text{L}^{a-}])$ were simulated by a computer minimization program based on the accepted mechanism of the type $\text{NpO}_2^+ + n \text{L}^{a-}$. It was shown that this leads to chemically incorrect values of stoichiometric stability constants and individual ion mobilities.

In contrast, on the assumption of pentavalent neptunium of stoichiometry NpO_2^+ satisfactory data $\lg K_n$ and $u_{[\text{NpOL}_n]^{1-a}}^0$ were 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 complex and central ions follow general electromigration character.

The properties of the actinyl cations MO_2^+ have not been studied so well as those of MO_2^{2+} cations. However, a lot of concrete data exist. These concern redox potentials, thermodynamic parameters of hydration [61] 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 [62, 63]. Besides the commonly accepted structure MO_2^+ the units MO^{3+} were also described: PaO^{3+} in strong acidic solutions [64] and NpO^{3+} in compounds $\text{NpOF}_3 \times x \text{H}_2\text{O}$ ($x = 0, 1, 2$) [65], $\text{Cs}_2\text{NpOCl}_5$ [65] and $\text{NpO}(\text{NO}_3) \times 3 \text{H}_2\text{O}$ [67], depending on experimental circumstan-

ces. However, for these Np(V) compounds alternative stoichiometries in terms of the coexistence of hepta- and hexavalent neptunium states were proposed [68–70].

Different stoichiometries were also discussed for Np(VII). In acidic solutions the cations NpO_3^+ or NpO_3^{2+} have been described and in alkaline solutions their hydrolysis products $\text{NpO}_4^- \times \text{H}_2\text{O}$ and $\text{NpO}_4(\text{OH})_2^{3-}$, NpO_5^{3-} or $\text{NpO}_5(\text{OH})^{4-}$ and $\text{NpO}_2(\text{OH})_6^{3-}$ have been characterized [71, 72].

In this context the formulation of a neptunium(V) cation with the charge +3 is first of all a formal try to interpret the well reproducible electromigration results. However, a NpO^{3+} cation is unprobable to exist in aqueous solutions.

The postulation of existence of a NpO^{3+} cation contradicts the general and fundamental knowledge about Np(V) chemistry in aqueous solutions.

In principle, any other attempt of interpretation has to explain the increase of positive charges of the Np(V) complexes:

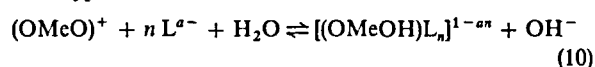
The investigated complexes of $^{239}\text{Np(V)}$ with L^{a-} -ligands of the types $[\text{NpO}_2\text{L}_n]^{1-a}$ with $a = 2, n = 1$ (oxalate, tartrate, sulphate) as well as $a = 1, n = 2$ (acetate) do not migrate like anions but like cations.

The discussion of a $\text{Np}^{\text{V}}\text{O}_x^{2-x}$ stoichiometry with $x = 1$ satisfies the electromigration behaviour of the Np(V) complexes, though actual existence of a 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 $^{239}\text{Np(V)}$ hydrolysis, indicating existence of NpO_2^+ . A NpO^{3+} cation should be hydrolyzed at significant lower values of pH, i.e. in neutral or acidic media.

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 $[\text{NpO}_2\text{L}_n]^{1-a}$ anions and the cation of the ground electrolyte Na^+ was proposed yielding species of the type $[\text{Na}_x(\text{NpO}_2\text{L}_n)]^{(x-a)}$. But these equilibria are unprobable. Nevertheless, they will be investigated in further works. However, there is another possibility to interpret the electromigration phenomenon:

In complex chemistry of some pentavalent metal cations MeO_2^+ reactions of type



are known, $\text{Me} = \text{Tc, Re}$ [73]. The protonizations are consequences of changes in the electron density at the yl-oxygens within the $\text{O}=\text{Me}=\text{O}$ 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 examples, 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 $\text{O}=\text{Np}=\text{O}$ is are protonized gradually.

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

Finally, the modified experimental technique applied here lead to a lot of results, corroborating known data.

On the other hand, new and suprising aspects were detected. Some of these aspects need further investigations, especially in combination with other analytical methods.

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References

- [1] K. A. Kraus, Proc. Int. Conf. Peaceful Uses At. Energy, Geneva 1955, Moscow: Goskhimizdat, 7, 312 (1958)
- [2] A. I. Moskvina, Radiokhimiya 13 (1971) 681
- [3] V. A. Mikhailov, Analiticheskaya Khimiya Neptunia, Izdat. Moscow: Nauka 1972, p. 20
- [4] A. P. Sevostyanova, G. V. Khalturin, Radiokhimiya 18 (1976) 870
- [5] L. Maya, Inorg. Chem. 22 (1983) 2093
- [6] Ch. Lierse, W. Treiber, J. I. Kim, Radiochim. Acta 38 (1985) 27
- [7] G. Bidoglio, G. Tanet, A. Chatt, Radiochim. Acta 38, (1985) 21
- [8] B. Cohen, P. Shorman, Inorg. Nucl. Chem. Lett. 5 (1969) 653
- [9] C. W. Sill, Anal. Chem. 38 (1966) 802
- [10] J. Garraway, P. D. Wilson, J. Less. Common Met. 91 (1983) 13
- [11] M. Milanov, W. Doberenz, R. Dreyer, M. Noak, V. A. Khalkin, Radiokhimiya 24 (1982) 520
- [12] M. Milanov, A. Marinov, Tran Kim Hung, W. Doberenz, V. A. Khalkin, JINR 7-83-209, Dubna 1983
- [13] M. Milanov, Tran Kim Hung, D. Shoninski, F. Rösch, V. A. Khalkin, JINR P6-86-549, Dubna 1986
- [14] M. Milanov, F. Rösch, V. A. Khalkin, J. Henniger, Tran Kim Hung, Radiokhimiya 29 (1987) 21
- [15] F. Rösch, Tran Kim Hung, M. Milanov, V. A. Khalkin, Talanta 34 (1987) 375
- [16] F. Rösch, Tran Kim Hung, M. Milanov, V. A. Khalkin, Isotopenpraxis 24 (1988) 383, 386
- [17] F. Rösch, R. Herrmann, Tran Kim Hung, M. Milanov, J. Radioanal. Nucl. Chem. 111 (1987) 319
- [18] F. Rösch, Tran Kim Hung, M. Milanov, N. A. Lebedev, V. A. Khalkin, J. Chromatogr. 396 (1987) 43
- [19] F. Rösch, T. Reimann, G. V. Buklanov, M. Milanov, V. A. Khalkin, Radiochimica Acta 47 (1989) 187
- [20] F. Rösch, T. Reimann, G. V. Buklanov, M. Milanov, V. A. Khalkin, R. Dreyer, J. Radioanal. Nucl. Chem. 134 (1989) 109
- [21] G. F. Condike, A. E. Martell, J. Inorg. Nucl. Chem. 31 (1968) 2455
- [22] S. Ramamoorthy, P. G. Manning, J. Inorg. Nucl. Chem. 35 (1973) 1571
- [23] R. M. Smith, A. E. Martell, Critical Stability Constants, Vol. 4, Inorganic Ligands, New York: Plenum Press, 1976
- [24] I. Feldmann, L. Koval, Inorg. Chem. 2 (1963) 145
- [25] F. Rösch, ZfK-665, Rossendorf, 1989
- [26] F. Rösch, R. Ludwig, T. Reimann, G. V. Buklanov, M. Milanov, R. Dreyer, V. A. Khalkin, Int. Conf. Actinides-89, Tashkent, USSR, Sept. 24-29, 1989, Abstracts p. 274
- [27] H. Nitsche, Thesis, FU Berlin, 1980
- [28] K. H. Schmidt, S. Gordon, R. C. Thompson, J. C. Sullivan, J. Inorg. Nucl. Chem. 42 (1980) 611
- [29] F. James, M. Roos, MINUIT Programm, CERN Computer Centre, Programm Library, Long, Write-Up D 506, D 596 (1971)
- [30] S. Nagasaki, S. Tanaka, Y. Takahashi, J. Radioanal. Nucl. Chem. 124 (1988) 383
- [31] S. Nakayama, H. Arimoto, N. Yamada, H. Moriyama, K. Higashi, Radiochimica Acta 44/45 (1988) 179
- [32] F. Rösch, ZfK-651, Rossendorf, 1988
- [33] Y. Inoue, O. Tochiyama, Bull. Chem. Soc. Japan 58 (1985) 2228
- [34] P. P. V. Rao, N. M. Gudi, S. V. Bagawde, J. Inorg. Nucl. Chem. 41 (1979) 235
- [35] S. K. Patil, V. V. Ramakrishna, N. M. Gudi, Nucl. Radiochem. Symp. Waltair, 1980, Abstr. 1, 67 (1980)
- [36] E. P. Sevastyanova, Radiokhimiya 27, (1985) 24
- [37] A. I. Moskvina, I. N. Marinov, Yu. A. Zolotov, Zhur. Neorg. Kim. 6 (1961) 1813
- [38] F. F. Rees, S. R. Daniel, Polyhedron 3 (1984) 667
- [39] Y. Inoue, O. Tochiyama, T. Takahashi, Radiochimica Acta 31 (1982) 197
- [40] H. Stober, KfK-1657, Karlsruhe, 1972
- [41] C. Keller, The Chemistry of the Transuranium Elements. Weinheim: Verlag Chemie, GmbH, 1971
- [42] Yu. A. Zolotov, I. N. Marov, A. I. Moskvina, Radiokhimiya 6 (1961) 539
- [43] E. Nebel, K. Schwabe, Z. Phys. Chem. 244 (1963) 29
- [44] Yu. A. Zolotov, I. P. Alimarin, J. Inorg. Nucl. Chem. 25 (1963) 691
- [45] D. M. Gruen, J. J. Katz, J. Am. Chem. Soc. 75 (1953) 3772
- [46] H. Stober, KfK-1657, Karlsruhe, 1972
- [47] Y. Inoue, O. Tochiyama, Radiochim. Acta 31 (1982) 197
- [48] A. I. Moskvina, I. N. Marov, Yu. A. Zolotov, Zh. Neorg. Khim. 6 (1961) 1813
- [49] Y. Inoue, O. Tochiyama, Bull. Chem. Soc. Jpn. 58 (1985) 2228
- [50] P. Vasudeva Rao, N. M. Gudi, S. V. Bagawde, J. Inorg. Nucl. Chem. 41 (1979) 235
- [51] S. K. Patil, V. V. Ramakrishna, N. M. Gudi, Nucl. Radiochem. Symp. Waltair, Abstr. 1 (1980) 67
- [52] J. Halperin, J. H. Oliver, Radiochim. Acta 33 (1983) 29
- [53] V. A. Vodoratov, V. B. Kolokoltsov, T. V. Koraleva, L. C. Maciroc, D. N. Suglebov, V. T. Sles, Radiokhimiya 17 (1975) 889
- [54] S. H. Eberle, H. Stober, private communication, quoted in Ref. [83]
- [55] A. I. Moskvina, I. Geletseanu, A. V. Lapitskij, Dokl. Akad. Nauk SSR 149 (1963) 611
- [56] M. P. Mefodova, P. I. Artjuchin, A. D. Gelman, Radiokhimiya 1 (1959) 309
- [57] S. V. Bagawde et al., unpublished work, quoted in Ref. [100]
- [58] C. W. Davies, Ion Association, Washington, D.C.; Butterworth Inc., 1961
- [59] F. Rösch, S. Dittrich, G. V. Buklanov, M. Milanov, V. A. Khalkin, R. Dreyer, Radiochimica Acta, in press
- [60] F. Rösch, S. Dittrich, G. V. Buklanov, M. Milanov, V. A. Khalkin, R. Dreyer, Radiochimica Acta, in press
- [61] F. David, J. Less-Common Met. 121 (1986) 27
- [62] R. Gauthier, K. K. Lieser, Radiochimica Acta 33 (1983) 35, 41
- [63] C. Madic, G. M. Begun, D. E. Hobart, R. L. Hahn, Inorg. Chem. 23 (1984) 1914
- [64] L. Thakur, A. K. Thakur, Ind. J. Pure Appl. Phys. 17 (1979) 538
- [65] K. W. Bagnall, D. Brown, J. F. Easey, J. Amer. Chem. Soc. 9 (1968) 2223
- [66] K. W. Bagnall, J. B. Laidler, J. Amer. Chem. Soc. 6 (1966) 516
- [67] J. B. Laidler, J. Amer. Chem. Soc. 6 (1966) 780
- [68] V. I. Blochin, V. P. Shilov, N. N. Krot, Zhur. Neorg. Khim. 17 (1972) 2742
- [69] D. G. Karkaker, I. A. Stone, J. Inorg. Nucl. Chem. 41 (1979) 1153
- [70] M. P. Mefodova, N. N. Krot, Sojedinenie transuranovykh elementov, (in Russ.) Moscow: Nauka, 1987, pp. 175
- [71] N. N. Krot et al. (eds.), Semivalentnoye sostoyaniya Np, Pu, Am (in Russ.), Moscow: Nauka 1977
- [72] C. Keller, in: A. J. Freeman, C. Keller (eds.): Handbook on the Physics and Chemistry of the Actinides, Amsterdam: Elsevier Science Publishers B. V., 1985, pp. 177
- [73] J.-L. Vanderheyden, A. R. Kekring, K. Libson, M. J. Heeg, L. Roecker, P. Motz, R. Whittle, R. C. Elder, E. Deutsch, Inorg. Chem. 23 (1984) 3184