

ELECTROMIGRATION OF CARRIER-FREE RADIONUCLIDES

13. ION MOBILITIES AND HYDROLYSIS OF $^{241}\text{Am-Am(III)}$ IN AQUEOUS INERT ELECTROLYTES

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The electromigration behaviour of carrier-free $^{241}\text{Am-Am(III)}$ in inert electrolytes, $\mu = 0.1$ (C10 $\bar{4}$), $T = 298.1(1)$ K, was studied. On the basis of the overall ion mobilities of $^{241}\text{Am-Am(III)}$ on pH between pH 5.5 and 12.9, the stoichiometric hydrolysis constants $\beta_3^{\text{H}^+} = 23.8(9)$, and $\text{p}K_1 = 6.9(2)$ were obtained. For K_4 a limitation of $\text{p}K_4 \geq 14.4(3)$ was possible, because no formation of anionic hydrolysis products in solutions $\text{pH} \leq 12.9$ was registered. The individual ion mobility of the $^{241}\text{Am-Am}^{3+}$ decrease in the range pH 5.5 – 3 from $+ 6.85(15)$ up to $+ 5.50(15) \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$. Dependences of this effect on overall ionic strength, inert electrolyte anion, and the temperature of the electrolytes were studied in acidic and neutral solutions.

Introduction

Investigations on the chemical behaviour of actinide ions in aqueous solutions are the main topic of radioanalytical chemistry. Today these studies are additionally motivated by the necessity to know how reactor isotopes interact with solids and fluids under natural geological conditions.

The problem to deal with the transport behaviour of the radionuclides is caused by increasing industrial, military, medical and other applications of radioactive isotopes. For calculations of the radionuclide transport properties, knowledge of the separate processes (1) hydrolysis of the metal cations, (2) complex formations and (3) ion migration is to be obtained. Current publications deal with conceptions and experimental work in this field.^{1–14}

On the other hand, ion migration in geological formations must be considered as a coincidence of two fundamental processes: the chemical equilibria interactions (I) of

the migrating species with the aqueous electrolyte of natural composition and the physico-chemical interactions (II) of the migrating species with solid geological materials in terms of the stopping effect with respect to ion mobilities characterized by process (I).

The aim of the present work is to study the ion mobilities and hydrolysis reactions of carrier-free ^{241}Am —Am(III) in aqueous perchlorate electrolyte systems.

A modified version of horizontal low-voltage electromigration measurements of γ -emitting radionuclides in homogeneous electrolytes free of supporting chromatographic materials was applied for the investigations. The trivalent americium was chosen because there exist a lot of analytical data on its chemical properties. Consequently, results of the electromigration studies may be compared with the representative literature data. Electrophoretic techniques were usually employed for separation of radioelements. However, hydrolysis equilibria of 4f or 5f elements have seldom been treated. Experimental results ($\text{p}K_1$ values) of electromigration measurements frequently differ from other results.¹⁵⁻¹⁷ This is connected with unsatisfactory experimental conditions due to applications of supporting materials, and with the inconstancy of important apparatus and electrolyte parameters. In contrast, the modified electromigration technique^{18,19} offers new opportunities. Because of the absence of supporting materials and the constancy of apparatus and electrolyte parameters the primary experimental ion mobilities are "absolute" and can be understood exclusively as interactions of the migrating species with the electrolyte solution.

Materials and methods

Electromigration technique

The experimental procedure, apparatus construction as well as details of the electromigration measurements were described in previous papers.^{18,19,20-26} Briefly, migration velocities were measured in a glass tube 40 mm long, 3 mm in diameter, by means of a NaI(Tl) scintillation detector. The detector continuously scanned the tube during the experiment. At the same time, a multichannel analyzer, 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. The connection of this tube of electrode vessels through hydrodynamic resistors (nuclear filters) prevented the generation of liquid flows, distortion of the shape of the radioelement zone and uncontrollable disturbance of the ion migration velocities.

²⁴¹Am–Am(III)

The isotope ²⁴¹Am (433 a; α, sf) decays into ²³⁷Np emitting low energy γ-rays with the main ray at $E_\gamma = 59.5$ keV. It should be stated that under these conditions of decay the radioisotope ²⁴¹Am is useful for the electromigration measurements by means of the special technique applied.

²⁴¹Am–Am(III) solutions in 0.10M Na(H)ClO₄ were used as stock solutions for the experiments. Volumes of about 1–2 μl per experiment were injected into the start position of the migration tube. The pH of the samples was adjusted to the pH of the electrolyte systems in the electromigration apparatus.

Electrolyte systems

For the investigation of hydrolysis of trivalent americium the solutions of type (i) Na(H)ClO₄/NaOH, $\mu = 0.10$, pH = 1.05–12.9, T = 298.1(1) K, were prepared. Individual ion mobilities of ²⁴¹Am–Am³⁺ and dependences of the values on the overall ionic strength μ were studied in systems (ii) x M NaClO₄, $x = 1.0 \cdot 10^{-2} - 2.0 \cdot 10^{-1}$, pH = 5.85(20), and x M Na(H)ClO₄, $x = 5.0 \cdot 10^{-3} - 2.0 \cdot 10^{-1}$, pH = 3.0(1), respectively, T = 298.1(1) K. Additional investigations on solutions of type (iii) 0.10M Na(H)X, X = NO₃⁻ and Cl⁻, respectively, T = 298.1(1) K, were carried out to obtain information on effects of the anion of the inert electrolyte on ²⁴¹Am–Am³⁺ individual ion mobilities.

The temperature dependence of the individual ion mobilities of the americium cation was measured in electrolytes (iv) 0.10M NaClO₄, pH = 5.85(20), and 0.10M Na(H)ClO₄, pH = 1.4(1), respectively, in the range of 287.9 K – 318.1 K; $\Delta T = 0.1$ K. Temperature effects on ²⁴¹Am–Am(III) hydrolysis were additionally investigated at T = 318.1(1) K in solutions of type (i) at pH = 1.05–7.

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

Results*Registration of ²⁴¹Am–Am(III) electromigration*

As already noted, the decay scheme of ²⁴¹Am offers excellent opportunities of detecting the americium electromigration behaviour. Figure 1 shows a typical example of primary results of the on-line scanning of the migration tube containing the migrating radioelement, i.e. the distribution of ²⁴¹Am(III) in the migration tube at dif-

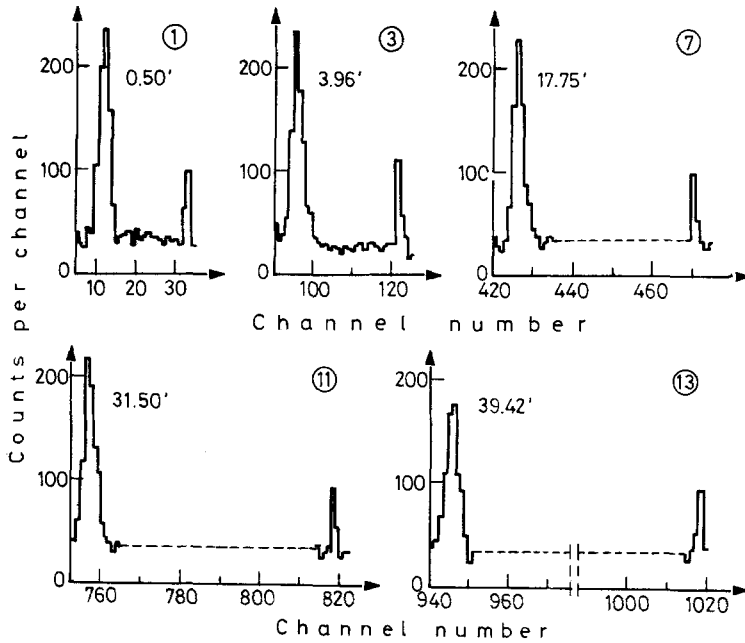


Fig. 1. Time-place correlations of a typical electromigration registration of $^{241}\text{Am}-\text{Am(III)}$; electrolyte: 0.10M HClO_4 , $T = 298.1(1)\text{ K}$; parameters: $\Delta E = 10.00(1)\text{ V} \cdot \text{cm}^{-1}$; correlations: $1\text{ canal} = 2.9\text{ mm}$. The small peak on the right sides shows the radioactive marker

ferent times scanned by a moving scintillation detector. As described in detail in References 19, 24, the ion mobilities u (in $10^{-4}\text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$) were calculated from these linear time-place correlations and after normalization of the electric field strength gradient $\Delta E = 1\text{ V} \cdot \text{cm}^{-1}$.

Hydrolysis of $^{241}\text{Am}-\text{Am(III)}$

When the hydrolysis of the trivalent americium in aqueous solutions is studied, the dependence of $^{241}\text{Am}-\text{Am(III)}$ overall ion mobility $\bar{u}_{\text{Am(III)}}$ on the pH of inert electrolytes is to be registered:

$$\bar{u}_{\text{Am(III)}} = f(\text{pH}). \quad (1)$$

Figure 2 summarizes the experimental results obtained in system (i). Some results of the measurements in similar nitrate electrolytes are included.

These results allow three deviations. They concern

- the dependence of type $\bar{u}_{Am(III)} = f(\text{pH})$ at $\text{pH} > 5.5$,
 - the behaviour of $^{241}\text{Am}-\text{Am}^{3+}$ individual ion mobilities $u_{Am^{3+}}^0$ in acidic solutions, and
 - the difference in ion mobilities obtained in perchlorate and nitrate electrolytes.
- The last two effects will be discussed later.

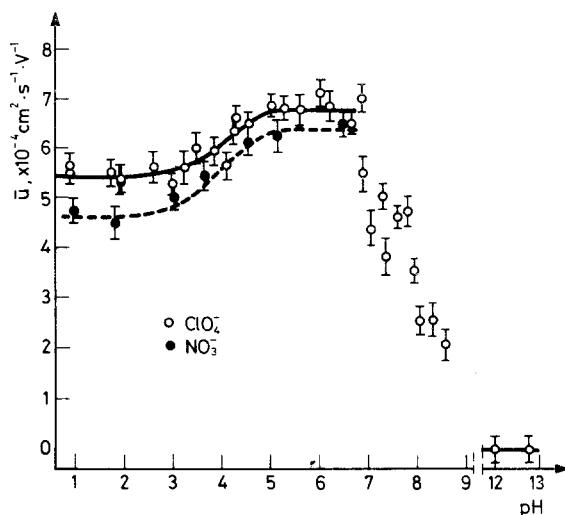
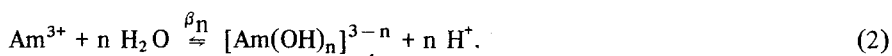


Fig. 2. Overall ion mobilities of $^{241}\text{Am}-\text{Am(III)}$ as a function of pH of aqueous inert electrolyte $\mu = 0.10$ (ClO_4^-) (\circ), $\mu = 0.10$ (NO_3^-) (\bullet); $T = 298.1(1)$ K

For the investigation of the hydrolysis equilibrium of $^{241}\text{Am}-\text{Am(III)}$ the dependence $\bar{u}_{Am(III)} = f([\text{H}^+])$ between $\text{pH } 5.5$ and 12.9 , $\mu = 0.10$ (ClO_4^-), is of interest.

The dropping of the overall ion mobilities from a constant value at $\text{pH } 5.5-6.8$ up to $\bar{u}_{Am(III)} = 0$ in alkaline solutions with $\text{pH} > 10$ is to be interpreted as the formation of the hydroxide Am(OH)_3 . A general chemical equilibrium is formulated by



In strong alkaline solutions ($\text{pH} \rightarrow 12.9$) no electromigration of $^{241}\text{Am}-\text{Am(III)}$ in the direction of the anode was found. Consequently, the formation of anionic hydrolysis products, e.g. $n > 3$ in Eq. (2), can be neglected under the experimental conditions applied.

Calculation of stoichiometric hydrolysis constants: Based on the fundamental electromigration equation for equilibria [Eq. (2)] of the type

$$\bar{u}_{Am(III)} = \sum_{n=0}^n u_{[Am(OH)_n]^{3-n}}^0 \cdot \alpha_{[Am(OH)_n]^{3-n}} \quad (3)$$

the concrete formulation with $n = 3$ is

$$\bar{u}_{Am(III)} = \frac{u_{Am^{3+}}^0}{1 + \beta_3 [H^+]^{-3}}$$

- where $\bar{u}_{Am(III)}$ – overall ion mobility of the carrier-free trivalent americium,
 $\alpha_{[Am(OH)_n]^{3-n}}$ – particular mole fractions of the species with respect to Eq. (2),
 $u_{[Am(OH)_n]^{3-n}}^0$ – individual ion mobilities of the ions, $n = 0, 1, 2$,
 $(u_{Am(OH)_3}^0 = 0, \text{ valid at } \alpha_{[Am(OH)_n]^{3-n}} = 1,$
 β_n – stoichiometric overall hydrolysis constant,
 K_n – stoichiometric stepwise hydrolysis constants ($\beta_n = \prod K_n$).

By means of a computer minimization program²⁷ the values of $u_{Am^{3+}}^0 = +6.85(15) \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$ and $p\beta_3 = 23.8(9)$ were calculated. For the calculation

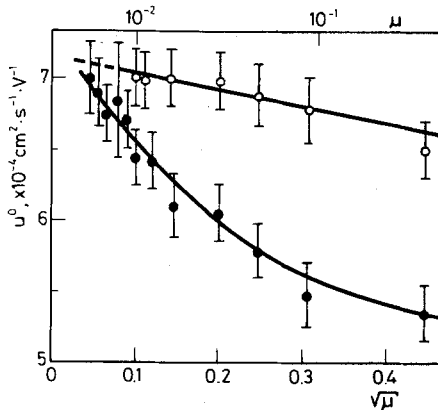


Fig. 3. Individual ion mobilities of $^{241}\text{Am}-\text{Am}^{3+}$ as a function of overall ionic strength of aqueous perchlorate electrolytes, (○) pH 5.85(20), (●) pH 3; $T = 298.1(1) \text{ K}$

of the important pK_1 data an estimation is possible according to

$$\bar{u}_{Am(III)} = \frac{u_{Am^{3+}}^0 + u_{[Am(OH)]^{2+}}^0 K_1 [H^+]^{-1}}{1 + K_1 [H^+]^{-1}} \quad (5)$$

Based on the experimental results in the range of pH 5.5–7.9 (Fig. 2), the values of $u_{Am^{3+}}^0 = +7.03(14) \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$, $u_{[Am(OH)]^{2+}}^0 = +4.12(32) \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$, and $pK_1 = 6.9(2)$ were obtained.

With individual ion mobility of Am^{3+} calculated by means of Eq. (4), the results are $u_{[Am(OH)]^{2+}}^0 = +3.82(15) \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$ and $pK_1 = 7.0(1)$.

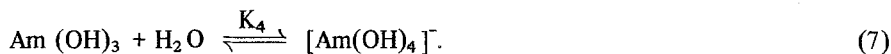
For the individual ion mobility of the $[Am(OH)]^{2+}$ a correlation of

$$u_{[Am(OH)]^{2+}}^0 \approx u_{Am^{3+}}^0 \left\{ \frac{z_{[Am(OH)]^{2+}}}{z_{Am^{3+}}} \right\} \quad (6)$$

can be substituted according to the results of other electromigration experiments,²⁰⁻²⁶ z are the charges of the ions. When comparing the expected $u_{[Am(OH)]^{2+}}^0$ value $+4.5 \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$ [Eq. (6)] with the calculated one [mean value $+3.95(35) \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$, Eq. (5)], differences of about 10% are found. These differences are acceptable according to the simplified calculation mechanism introduced. Both $pK_1 = 6.9(2)$ and $p\beta_3 = 23.8(9)$ correspond to the data available in the literature.

Further subdivisions in order to obtain all the pK_n data ($n = 1-3$), seem to be possible by fixing the individual ion mobilities of $[Am(OH)]^{2+}$ and $[Am(OH)_2]^+$. Then, with $u_{Am(OH)_3}^0 = 0$ and with the experimental value of $u_{Am^{3+}}^0$ the whole set of individual ion mobilities would be known. The calculations yield $pK_2 \approx 8-9$ and $pK_3 \approx 9-10$. However, there are too few experimental points $\{[H^+]; \bar{u}_{Am(III)}\}$ between pH 7 and 10, and calculations of this type are not satisfactory. In Reference 28 an alternative way of calculating the individual ion mobilities and the stoichiometric stepwise hydrolysis of a trivalent f-element will be discussed.

For K_4 a limitation is possible considering Eq. (7).



Absence of evidence for the formation of anionic hydrolysis products at pH 12.9 can be explained by the ratio $[[Am(OH)_4]^-] : [Am(OH)_3]$, which is lower than about

1:30, a fact detectable by means of the electromigration method. Accordingly, a value of $\text{p}K_4 \geq 14.4(3)$ can be derived.

The results of hydrolysis constants of Am(III) in aqueous solutions are summarized in Table 1.

Individual ion mobilities of $^{241}\text{Am}-\text{Am}^{3+}$ in acidic inert electrolytes

The individual ion mobility $u_{\text{Am}^{3+}}^0 = +6.85(15) \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$, $\mu = 0.10 (\text{ClO}_4^-)$, $\text{pH} > 5.5$, $T = 298.1(1) \text{ K}$, corresponds to $\alpha_{\text{Am}^{3+}} = 1$ with respect to the hydrolysis equilibria [Eq. (2)]. Both values should be expected not to change if the pH of the inert electrolyte system (i) varies in the range of $\text{pH} < 5.5$. No chemical equilibria of the americium cation with components of the electrolyte solution can be formulated, which affect the reactions (2). Reduction or oxidation of trivalent americium should be excluded under the concrete experimental conditions. Changes of the macroscopic physico-chemical parameters of the electrolyte systems between pH 1.05 and 5.5 are not responsible for changes in $\alpha_{\text{Am}^{3+}}$ or $u_{\text{Am}^{3+}}^0$ as well. However, the experimental results of $^{241}\text{Am}-\text{Am(III)}$ electromigration in acidic inert electrolytes demonstrate an unambiguously significant dependence of $u_{\text{Am}^{3+}}^0$ data on the pH of the aqueous solutions.

Ion mobilities change from a constant value at $\text{pH} > 5.5$ to a new standard at $\text{pH} < 3$. The differences between both plateaus are considerable. Seen absolutely, about $1.4 \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$ and relatively about 20%, $\mu = 0.10 (\text{ClO}_4^-)$, $T = 298.1(1) \text{ K}$. A similar effect was observed in the case of the pentavalent neptunyl cation.²⁴ It was attempted to interpret this behaviour in terms of protonation reactions and new migration character of the cation in acidic solutions. Since the character of changes in the u^0 data of both migrating, chemically different radiocations is almost identical, this interpretation should be corrected.

The only ion which dramatically changes its concentration by orders of magnitude between pH 5.5 and 3, is the hydrogen cation. By contrast, the concentration of the inert electrolyte cation Na^+ decreases continuously from 0.100 to 0.099M. This is only a relative change of 1%. Consequently, the reasons for the registered changes in the individual ion mobility of the migrating cation in acidic solutions should be seen in special interactions of the migrating radiocation with the hydrogen cation and/or the hydrogen-bond induced structure of the aqueous electrolyte and/or in different types of the hydration character of the migrating cation and its interactions with the electrolyte components, respectively.

Below, some experimental aspects of this effect will be considered in detail by studying the dependence of the individual ion mobilities of $^{241}\text{Am}-\text{Am}^{3+}$ in both acidic and neutral solutions on the overall ionic strength, electrolyte anion and temperature, respectively.

Table 1
Hydrolysis constants of trivalent americium in aqueous solutions

Method	μ	T (K)	pK ₁	pK ₂	pK ₃	pK ₄	Year	Reference
em	0.005 (Cl ⁻)	278.1	3.05	-	-	-	1969	29
dis	0.1 (ClO ₄ ⁻)	296.1	5.92	-	-	-	1969	30
em	0.005 (ClO ₄ ⁻)	298.1	3.30	7.1	-	-	1972	31, 32
dis	0.1 (ClO ₄ ⁻)	298.1	5.30	-	-	-	1973	33
	0.1	298.1	6.1	-	-	-	1976	34
	0	298.1	8.0 (5)	-	-	-	1976	35
	0	298.1	5.8	13 ^a	21 ^a	31 ^a	1978	36
	0.1	298.1	7.63 (30)	-	-	-	1982	37
	1.0	298.1	8.0 (5)	16.9 ^a	26.5 ^a	37.1 ^a	1982	38
em	1.0 (ClO ₄ ⁻)	298.1	7.5 (3)	-	-	-	1982	39
sol	0.2 (ClO ₄ ⁻)	298.1	-	15.2 ^a	-	-	1982	13
pH	1.0 (ClO ₄ ⁻)	298.1	7.03 (5)	-	-	-	1982	40
	0.1	294.1	8.02 (35)	6.62 (25)	9.89 (11)	-	1982	41
dis	0.7 (Cl ⁻)	298.1	7.54 (20)	-	-	-	1983	42
sol	0	298.1	8.2	17.1 (5) ^a	27 ^a	40 ^a	1983	43
sol	0.003	298.1	7.8	8.72	-	-	1984	44
sol	0.1 (ClO ₄ ⁻)	298.1	8.15	15.21 ^a	25.37 ^a	-	1984	45, 46
sol	0.1 (Cl ⁻)	298.1	7.5	15.4 ^a	27.2 ^a	-	1984	47, 48
sol	0.6 (Cl ⁻)	298.1	8.7	16.2 ^a	28.1 ^a	-	1985	47, 48
em	0.1 (ClO ₄ ⁻)	298.1	6.9 (2)	-	23.8 (9) ^a	-	1988	b
em	0.1 (ClO ₄ ⁻)	298.1	-	-	-	≥14.4 (3) ≥38 (1) ^a	1988	b

^apβ_n values.

^bthis work.

em - electromigration,

dis - extraction,

est - calculated,

pH - titration,

sol - solubility.

Variation of overall ionic strength of the electrolyte systems

The overall ionic strength μ of the ground electrolytes varied both in neutral (pH 5.85) and acidic (pH 3) solutions [electrolyte systems (ii)]. The experimental results are summarized in Fig. 3. As noted before, the $u_{Am^{3+}}^0$ data in neutral solutions are higher than in acidic ones. In both systems individual ion mobilities of $^{241}Am-Am^{3+}$ decrease with increasing overall ionic strength. Absolute differences of type Δu^0 :

$$\Delta u_{Am^{3+}}^0(\mu) = u_{Am^{3+}}^0(\text{pH } 5.85) - u_{Am^{3+}}^0(\text{pH } 3) \quad (8)$$

as well as ratios in per cent Δu^0 :

$$\Delta u_{Am^{3+}}^0(\mu) = u_{Am^{3+}}^0(\text{pH } 5.85) / u_{Am^{3+}}^0(\text{pH } 3) \quad (9)$$

decrease with the overall ionic strength. The correlations are demonstrated in Fig. 4.

The experimental functions

$$u_{Am^{3+}}^0 = f(\mu) \quad (10)$$

can be extrapolated up to the infinitely diluted electrolyte condition ($\mu = 0$). The resulting individual ion mobilities $u_{Am^{3+}}^\infty$ seem to be identical both in neutral and

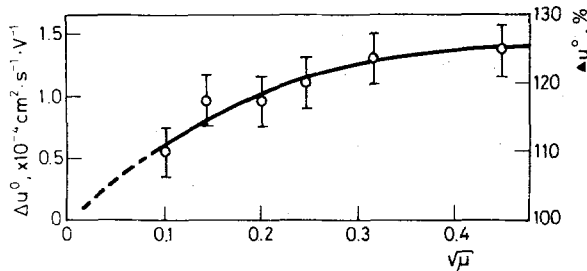


Fig. 4. Absolute [Eq. (8)] differences $\Delta u_{Am^{3+}}^0(\mu)$ and ratios [Eq. (9)] $\Delta u_{Am^{3+}}^0(\mu)$ of individual ion mobilities of $^{241}Am-Am^{3+}$ in acidic and neutral aqueous perchlorate electrolytes as a function of overall ionic strength

acidic solutions. However, experimental data in the range $\mu < 10^{-3}$, which are important for exact extrapolations, are missing. Based on the existing pairs $\{\mu, u_{Am^{3+}}^0(\text{pH } 5.85)\}$, the mathematical simulations of type

$$u_{Am^{3+}}^0 = u_{Am^{3+}}^\infty - a\sqrt{\mu} \quad (11)$$

is possible. In the acidic systems, one has to substitute a nonlinear term for $f(\mu)$ in Eq. (10). Here, the formulations of the FUOSS-DEBYE-ONSAGER theories^{50,51} or semiempiric correlations as, for example, JONES-DOLE equations⁴⁹ can be applied. These solutions demand far more experimental data. Therefore, theoretical discussions of the electromigration results $u_{Am^{3+}}^0 = f(\mu)$ are neglected here, and only experimental trends are illustrated. However, two facts should be stated. Similar or identical individual ion mobilities $u_{Am^{3+}}^\infty$ were obtained both from neutral and acidic aqueous electrolyte solutions. The final value of $u_{Am^{3+}}^\infty$ at $T = 298.1(1)$ K and for pure water should be of the order of $+7.3(2) \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$. On the other hand, the increasing overall ionic strength causes different degrees of dependence of $u_{Am^{3+}}^0$ data on the overall ionic strength in a neutral or acidic environment. The dependence in neutral solutions is lower than in acidic ones, whereas the dependence in acidic solutions may be called "normal" with respect to the known conductivity data.⁵² Consequently, differences $\Delta u_{Am^{3+}}^0 = f(\mu)$ increase with the overall ionic strength in an exponential way. At about $\mu \gtrsim 0.3$ the differences seem to become constant: $\Delta u_{Am^{3+}}^0(\mu) = 1.45 \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$ or $\Delta u_{Am^{3+}}^0(\mu) = 20\%$, respectively.

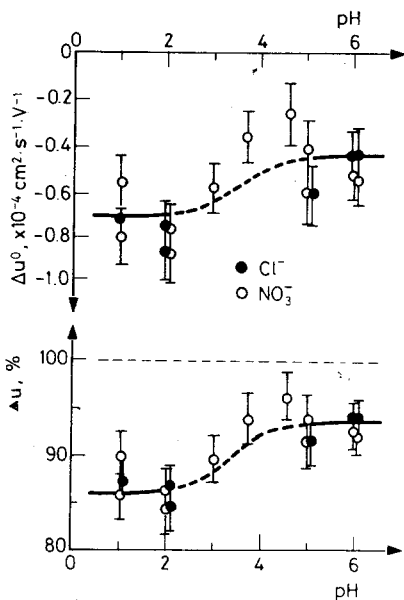


Fig. 5. Absolute [Eq. (12)] differences $\Delta u_{Am^{3+}}^0(X)$ and ratios $\Delta u_{Am^{3+}}^0(X)$ of individual ion mobilities of $^{241}\text{Am}-\text{Am}^{3+}$ in acidic and neutral aqueous electrolytes $\text{Na}(\text{H})\text{X}$ as a function of the back ground electrolyte anion $\text{X} = \text{ClO}_4^-, \text{NO}_3^-, \text{Cl}^-$, (\circ) $\text{X} = \text{NO}_3^-$, (\bullet) $\text{X} = \text{Cl}^-$, $\mu = 0.10$, $T = 298.1(1)$ K

Variations of the background electrolyte anion

As is seen from Fig. 2, the experimental ion mobilities of $^{241}\text{Am}-\text{Am}^{3+}$ in nitrate electrolytes differ from those in perchlorate electrolytes. Figure 5 shows the changes in individual ion mobilities of the americium cation in $\text{Na}(\text{H})\text{X}$ solutions at pH 1.05–6.0 [electrolyte systems (iii)] as a function of $\text{X} = \text{ClO}_4^-, \text{NO}_3^-, \text{Cl}^-$. Correlations are given both in per cent ($u_{\text{Am}^{3+}}^0(\text{X} = \text{ClO}_4^-) = 100\%$) and in the absolute form

$$\Delta u_{\text{Am}^{3+}}^0(\text{X}) = u_{\text{Am}^{3+}}^0(\text{X} = \text{NO}_3^-, \text{Cl}^-) - u_{\text{Am}^{3+}}^0(\text{X} = \text{ClO}_4^-). \quad (12)$$

Absolute differences $\Delta u_{\text{Am}^{3+}}^0(\text{X})$ of $u_{\text{Am}^{3+}}^0$ data between perchlorate and nitrate electrolytes are $0.7(2) \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$ and $0.5(2) \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$, respectively, in acidic and neutral solutions. The results in chloride electrolytes are the same.

More important are the relations in per cent, because in this case the functions $u_{\text{Am}^{3+}}^0 = f(\text{pH})$ are included. The values of $\Delta u_{\text{Am}^{3+}}^0(\text{X})$ are 86(3)% in acidic solutions and 93(3)% in neutral ones; $\text{X} = \text{NO}_3^-, \text{Cl}^-$. This means that the degradation of $u_{\text{Am}^{3+}}^0$ data after substitution the perchlorate anion of the background electrolytes by nitrate or chloride is a little greater in acidic than in neutral solutions.

Variation of the temperature

The functions $u_{\text{Am}^{3+}}^0(\text{pH}) = f(T)^u$ have been investigated in electrolyte systems (iv), in the range of $T = 287.9\text{--}318.1 \text{ K}$. The primary results are illustrated in Figs 6 and 7. They show that an increase in the electrolyte temperature leads to an increase in individual ion mobilities, too. Figure 6 shows linear correlations of the temperature dependence of $u_{\text{Am}^{3+}}^0$ both at pH 5.85 and 1.40. Besides, the relative increase in the individual ion mobility of Am^{3+} with the temperature of the electrolyte is similar in the whole range of H^+ concentration investigated. The quotient

$$qu_{\text{Am}^{3+}}^0(T) = \frac{u_{\text{Am}^{3+}}^0(T=318.1 \text{ K})}{u_{\text{Am}^{3+}}^0(T=298.1 \text{ K})} = f(\text{pH}) \quad (13)$$

for example, is almost constant: $qu_{\text{Am}^{3+}}^0(T=298.1\text{--}318.1 \text{ K}) = 1.44(5)$. This effect is shown in Fig. 8 with the normalization of $u_{\text{Am}^{3+}}^0(T=298.1 \text{ K}) = 1$.

Finally, with normalizations $u_{\text{Am}^{3+}}^0(\text{pH} < 3) = 1$, Eq. (1) can be summarized for different temperatures. Figure 9 shows that the electrolyte temperature in the range investigated does not affect the dependence of changes in $u_{\text{Am}^{3+}}^0$ on pH.

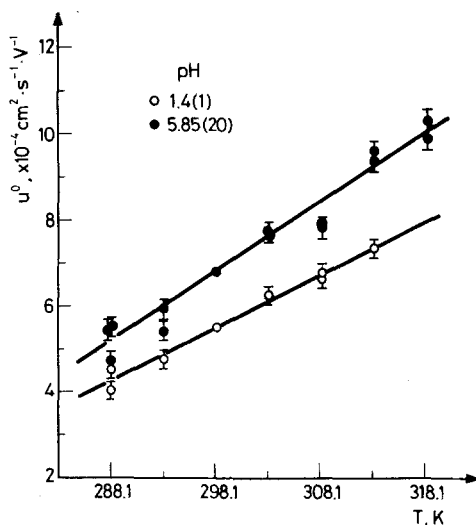


Fig. 6. Individual ion mobilities of $^{241}\text{Am}-\text{Am}^{3+}$ in acidic and neutral aqueous perchlorate electrolytes as a function of electrolyte temperature; (○) pH 1.4(1), (●) pH 5.85(20), $\mu = 0.10$ (ClO_4^-)

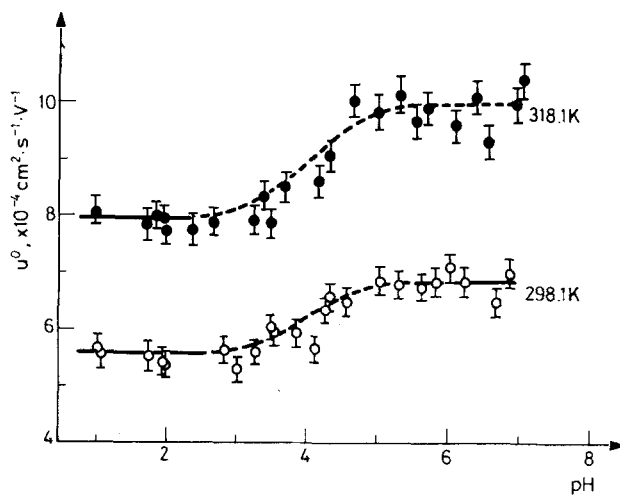


Fig. 7. Individual ion mobilities of $^{241}\text{Am}-\text{Am}^{3+}$ in aqueous perchlorate electrolytes of 298.1(1) K and 318.1(1) K as a function of pH; (○) $T = 298.1(1) \text{ K}$, (●) $T = 318.1(1) \text{ K}$, $\mu = 0.10$ (ClO_4^-)

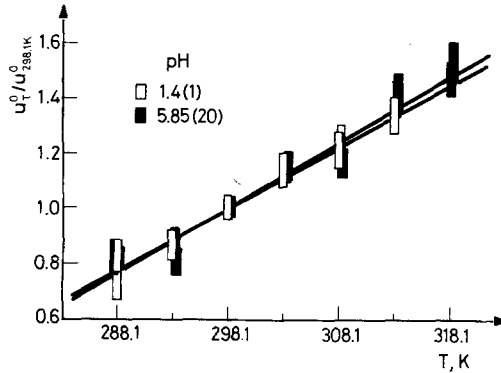


Fig. 8. Relative changes of individual ion mobilities of $^{241}\text{Am}-\text{Am}^{3+}$ in acidic and neutral aqueous perchlorate electrolytes as a function of electrolyte temperature with respect to $u_{\text{Am}^{3+}}^0$ (298.1 K); (\square) pH 1.4(1), (\blacksquare) pH 5.85(20), $\mu = 0.10$ (ClO_4^-)

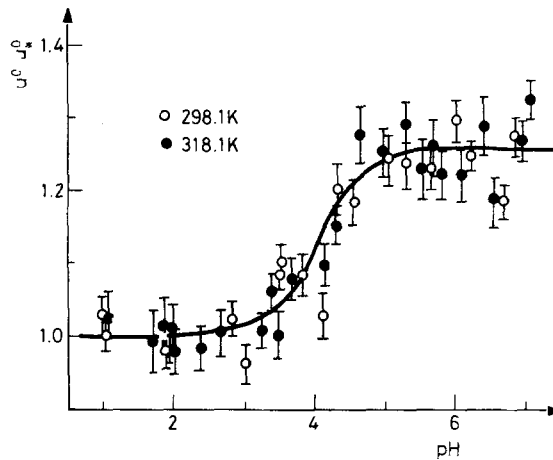


Fig. 9. Relative changes of individual ion mobilities of $^{241}\text{Am}-\text{Am}^{3+}$ in aqueous perchlorate electrolytes of 298.1(1) K and 318.1(1) K as a function of pH; with respect to mean individual ion mobilities u_*^0 ($\text{pH} < 3$). (\circ) $T = 298.1(1)$ K, (\bullet) $T = 318.1(1)$ K, $\mu = 0.10$ (ClO_4^-)

Discussion

Hydrolysis investigations of trivalent metal cations are intricate. Only in few cases has the division of all the stepwise hydrolysis constants been obtained by means of the same method. By using, e.g., $^{205,206}\text{Bi}$ -Bismuth(III) and the determination of

the hydrolysis parameters for $[\text{Bi}(\text{OH})_n]^{3-n}$, $n = 0-4$, it was demonstrated that the modified electromigration technique allows the problems to be solved in principle.²⁰ For most trivalent metals it is possible to get information only on the first hydrolysis step or the overall reaction (formation of the hydroxide). This is especially valid for lanthanides and actinides.

In the present study the stoichiometric hydrolysis constants $p\beta_3 = 23.8(9)$ and $pK_1 = 6.9(2)$ were calculated. A limitation of $pK_4 \geq 14.4(3)$ was obtained. Comparison with literature data shows that the modified electromigration method can successfully compete with conventional analytical techniques. In addition, the aggravating influence of supporting chromatographic materials,²⁹ $(\text{SiO}_2)^{31}$ on the hydrolysis equilibria and on the values of the ion mobilities of Am^{3+} are demonstrated. Contrary to this, the electromigration technique applied allows measurements of "absolute" ion mobility data. Interactions of the migrating species with surfaces of solid supporting carriers or with inhomogeneous solution compounds of the electrolyte fail to take place. Primary experimental data can be interpreted as relations between migrating species and electrolyte.

In neutral electrolytes, $\mu = 0.10$ (ClO_4^-) the individual ion mobilities of Am^{3+} are $+6.85(15) \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$ and $+9.97(20) \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$ at 298.1(1) K and 318.1(1) K, respectively.

The temperature dependence of the individual ion mobilities of the trivalent americium cation is due to the changes in the electrolyte viscosity with temperature in the range investigated.

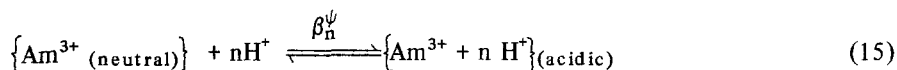
Simple extrapolations of type (10) lead to the individual ion mobility of $^{241}\text{Am}-\text{Am}^{3+}$ in pure water at $T = 298.1(1) \text{ K}$ of $u_{\text{Am}^{3+}}^\infty = +7.3(2) \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$. This result can be compared with diffusion coefficients $D_{\text{Am}^{3+}}^\infty$ via

$$u^\infty = D^\infty \left\{ \frac{|z| e}{k T} \right\} \quad (14)$$

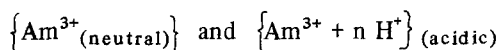
For $D_{\text{Am}^{3+}}^\infty = 6.24 \cdot 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$, obtained from diffusion measurements in $\text{Li}(\text{H})\text{Cl}$ solutions ($\text{pH } 2.5$, $T = 298.1 \text{ K}$)⁵³ one gets $u_{\text{Am}^{3+}}^\infty = +7.3 \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$. A value of $+7.2(2) \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$, $T = 298.1 \text{ K}$, was obtained from conductivity measurements.⁵⁴ Beside hydrolytic reactions of trivalent americium, the changes in individual ion mobilities of the radiocation in acidic inert electrolytes have to be discussed. The changes in $u_{\text{Am}^{3+}}^0$ between the two plateaus at $\text{pH } 3$ and $\text{pH } 5.5-7$, respectively, are of special interest. Redox reactions or complex formations of the cation as well as changes in macroscopic parameters of the background electrolyte can be excluded.

Changes in the properties of the central cation or special relationships between the migrating cation and the electrolyte components in the range of pH 3–5.5 have not been discussed in the literature. However, a similar electromigration behaviour of carrier-free $^{239}\text{Np-Np(V)}$ was reported.²⁴

For the first interpretation of the specific changes in $u_{\text{Am}^{3+}}^0$ data in acidic inert electrolytes we single out two alternative states of $^{241}\text{Am-Am}^{3+}$ acting in an equilibrium of type



Using the formulations



we describe different situations of interactions of the migrating cation with the electrolyte system, caused by changes in $[\text{H}^+]$. Unfortunately, exact formulations of these situations are not possible for the time being.

Equation (15) was treated by computer program²⁷ to obtain the first parameters of the equilibrium reactions. The results of calculations are summarized in Table 2 for $T = 298.1$ K. Using a minimization of the least squares function FCN, we con-

Table 2
Calculation results for eq. (15) $\mu = 0.10$ (ClO_4^-),
 $T = 298.1$ (1) K; β_n^ψ in $l^n \text{mole}^{-n}$, u^0 in $10^{-4} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$

n	FCN	$\lg \beta_n^\alpha$	$u^0 \{\text{Am}^{3+}_{(\text{neutral})}\}$	$u^0 \text{Am}^{3+} + n\text{H}^+_{(\text{acidic})}$
1	0.53	4.14 (25)	+6.93 (15)	+5.47 (9)
2	0.59	8.37 (35)	+6.83 (13)	+5.55 (8)
3	0.63	12.61 (35)	+6.80 (12)	+5.57 (8)

clude that Eq. (15) is of the first order in $[\text{H}^+]$, and the stoichiometric stability constant is $\log \beta_1^\psi = 4.14(25)$, $\mu = 0.10(\text{ClO}_4^-)$. Possibly, the existence of a definite standard of the hydrogen bonds produces changes in the hydration character of the cation. Then a concrete ratio $Q = [\text{H}_2\text{O}]/[\text{H}^+]$ may be derived. The value of Eq. (15) for $^{241}\text{Am-Am}^{3+}$ ($\log \beta_1^\psi \approx 4$ in the case of pentavalent neptunium)²⁴ and the known values of $[\text{H}_2\text{O}]$ at $\mu = 0.10(\text{ClO}_4^-)$ ⁵⁵ yield a quotient $Q \approx 7(1) \cdot 10^5$.

The alternative states of $^{241}\text{Am}-\text{Am}^{3+}$ can be detected by different individual ion mobilities in real electrolyte solutions. Besides, the dependence of individual Am^{3+} mobilities on electrolyte consistence is different in acidic and neutral solutions. In general, we can assume a "sensitivity" of $^{241}\text{Am}-\text{Am}^{3+}$ in acidic solutions with respect to the overall ionic strength and the anion of the inert electrolyte.

Replacement of the "inert" perchlorate anion by chloride or nitrate causes a decrease in the individual ion mobilities of the americium cation. This behaviour is connected with formations of inner-sphere complexes $[\text{Am}(\text{H}_2\text{O})_m\text{X}_n]^{3-n}$, $m+n=N=8$ or 9 , $n \geq 1$. For $\text{X} = \text{ClO}_4^-$ these complexes are improbable, whereas for $\text{X} = \text{NO}_3^-$ or $\text{X} = \text{halide}$, the compounds are detectable.^{5,6,7}

The most important fact in this context is that the degradation of $u_{\text{Am}^{3+}}^0$ is stronger in acidic solutions than in neutral ones. Here, the distinct dependence $u_{\text{Am}^{3+}}^0 = f(\mu)$ in acidic solutions is also appreciated. On the contrary, the specific behaviour of the electromigration of $^{241}\text{Am}-\text{Am}^{3+}$ in neutral solutions can be described as a "screening" of interactions of the migrating cation with the electrolyte components. Substitutions in the series $\text{X} = \text{ClO}_4^-, \text{NO}_3^-, \text{Cl}^-$ or changes in the overall ionic strength in neutral solutions affect the values of $u_{\text{Am}^{3+}}^0$ to a small degree only. Unfortunately, descriptions of this type follow only phenomenological criteria. Questions about the character of the hydration sphere were not answered. It is not clear which parameters of the hydration sphere change and what are the reasons for these processes.

It is of interest that discontinuous variations of parameters of the hydration sphere (in terms of coordination numbers N and hydration numbers h , for example) are known^{5,8} in the 4f- and 5f-series as a function of the ionic radii. A value of $r_{\text{M}^{3+}} = 1.07 \text{ \AA}$ was given as a "critical" ionic radius for the changes from $N = 9$ to $N = 8$ or $h = 12.7$ to $h = 14.1$. However, there is no evidence of thermodynamic data of the same cation changing with the pH. Similar processes are known for complex formations, see References 59 and 60, for example.

To study the nature of the electromigration effect described, further investigations are necessary. In particular, ion – solvent interactions should be considered in detail. For the time being the experimental facts can be summarized as follows:

1. Electromigration measurements of $^{241}\text{Am}-\text{Am}^{3+}$ in aqueous inert electrolytes free of supporting materials revealed two different plateaus of individual ion mobilities $u_{\text{Am}^{3+}}^0$ in solutions of $\text{pH} < 3$ and $\text{pH} 5.5-7$, respectively. The result is similar to that of $^{239}\text{Np}-\text{Np(V)}$.²⁴
2. The differences do not correspond to conventional equilibria reactions or to changes in macroscopic parameters of the background electrolytes.
3. What induces the changes in $u_{\text{Am}^{3+}}^0$ is the change in concentrations of the hydrogen cation. Because of this fact two different situations in interactions of the

migrating cation with the solvent or water – hydrogen-bond structures are proposed. The alternative states were indicated by different individual ion mobilities of the migrating radiocation as well as by different dependences of $u_{Am^{3+}}^0$ data on the overall ionic strength or on the type of the anion of the inert electrolyte systems in acidic and neutral environments.

4. As the overall ionic strength decreases, the differences of the $u_{Am^{3+}}^0$ data between acidic and neutral solutions decrease, too. In infinitely diluted solutions, $u_{Am^{3+}}$ seems to be of the same value. The differences between the individual ion mobilities of the americium cation in acidic and neutral solutions increase exponentially with the overall ionic strength. At $\mu \gtrsim 0.3$ a constant difference $\Delta u_{Am^{3+}}^0(\mu)$ appears.

In nitrate or chloride electrolytes individual ion mobilities of $^{241}Am-Am^{3+}$ are reduced against the values in perchlorate electrolytes due to the formation of $[Am(H_2O)_m X_n]^{3-n}$ compounds. In acidic solutions the effects are more significant than in analogous neutral ones.

5. Similarly to the known definitions of “stick” and “slip” with respect to ion migration, the effects described here may be characterized by a “sensitivity” of the migrating ion interactions with the electrolyte components and by “screening” with respect to the interactions of the migrating ion with electrolyte components in acidic and neutral solutions, respectively.

ANNEX

The preceding parts of this series of electromigration studies of carrier-free radionuclides in homogeneous aqueous electrolytes free of any supporting materials deal with

- hydrolysis and complex formation of $^{205,206}Bi-Bi(III)$ (MILANOV M., RÖSCH F., KHALKIN V. A., HENNIGER J., TRAN KIM HUNG, Radiokhimiya, 29 (1987) 21–29; RÖSCH F., TRAN KIM HUNG, MILANOV M., KHALKIN V. A., Talanta, 34 (1987) 375–380),
- complex formations of $^{140}La-La(III)$ and $^{169}Yb-Yb(III)$ (RÖSCH F., TRAN KIM HUNG, MILANOV M., LEBEDEV N. A., KHALKIN V. A., J. Chromatogr., 396 (1987) 43–50; RÖSCH F., HERRMANN R., TRAN KIM HUNG, MILANOV M., KHALKIN V. A., J. Radioanal. Nucl. Chem., 111 (1987) 319–327),
- hydrolysis of $^{239}Np-Np(V)$ (RÖSCH F., MILANOV M., TRAN KIM HUNG, LUDWIG R., BULANOV G. V., KHALKIN V. A., Radiochim. Acta, 42 (1987) 43–46),
- complex formations of $^{201}Tl-Tl(I)$ with iodide, bromide and sulfate, respectively (RÖSCH F., TRAN KIM HUNG, MILANOV M., KHALKIN V. A., Isotopenpraxis, 24 (1988) 383–386; 386–388),
- hydrolysis and complex formation with oxalate of $^{249}Cf-Cf(IV)$, (RÖSCH F., REIMANN T., BUKLANOV G. V., MILANOV M., KHALKIN V. A., DREYER R., ZfK-636, Rossendorf, 1988),
- protonation of $^{131}I-IO_3^-$, (RÖSCH F., TRAN KIM HUNG, MILANOV M., KHALKIN V. A., J. Chromatogr., 457 (1988) 362),
- hydrolysis of $^{209-211}At-At(I)$, (RÖSCH F., TRAN KIM HUNG, MILANOV M., KHALKIN V. A., ZfK-613, Rossendorf, 1988),

- complex formations of ^{239}Np –Np(V) in neutral solutions with oxalate, tartrate, sulfate and acetate, citrate, respectively, (RÖSCH F., DITTRICH S., BUKLANOV G. V., MILANOV M., KHALKIN V. A., DREYER R., ZfK-614, 615, Rossendorf, 1988),
- hydrolysis and complex formations with sulfate of ^{169}Yb –Yb(III), (RÖSCH F., TRAN KIM HUNG, MILANOV M., KHALKIN V. A., ZfK-650, Rossendorf, 1988).

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