

Electromigration of Carrier-free Radionuclides 8. Hydrolysis of ^{249}Cf (III) in Aqueous Solution

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(Received July 12, 1988)

Californium (III) / Hydrolysis / Stability constants / Electromigration / Ion mobilities

Summary

The overall ion mobilities of carrier-free Cf(III) have been measured in aqueous perchlorate solutions by means of a modified version of the electromigration method. By mathematical processing of the experimental data the stoichiometric hydrolysis constants $p\beta_3 = 18.6(3)$ and $pK_1 = 6.2(2)$ at $\mu = 0.10$, $T = 298.1(1)$ K, were calculated. A limit of $pK_4 \geq 14.4(3)$ results from the fact that no evidence of formation of anionic hydrolysis products in alkaline solutions has been found.

The individual ion mobility of Cf^{3+} was found to be $u_{\text{Cf}^{3+}}^0 = +5.15(16) \cdot 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$.

Introduction

The investigation of the hydrolysis behaviour of trivalent lanthanides and actinides commonly yields the first stoichiometric hydrolysis constant pK_1 as the most important analytical data. Only few results on pK_2 values can be found in the literature. Formation of anionic species $[\text{M}(\text{OH})_{3+m}]^{m-}$, $m \geq 1$, is not described. The pK_1 data published for lanthanides Ln(III) differ sometimes in order of magnitude, depending on the analytical method applied, even for the same element. However, satisfactory knowledge of quantitative values as well as trends of Ln(III) hydrolysis in aqueous solution exist [1]. A similar hydrolysis character of trivalent actinides An(III) is proposed. But only a few experimental results are published, most of them for americium. This has two reasons: Actinides lighter than Am form higher oxidation states. Their trivalent state must be stabilized by means of extremely strong reducing reagents. On the other hand, actinides with atomic number higher than americium are available only in relatively low concentrations, whereas many analytical methods are based on investigations with weightable amounts of the elements. Because of this fact the number of published pK_1 data for the group Cm, Bk, Cf, Es decreases. Also due to the short half-lives and the complicated production processes, for the heavier actinides no results on hydrolysis exist.

For this reason we tried to apply a modified on-line horizontal low-voltage electromigration technique in aqueous electrolyte solutions free of any supporting materials to study the hydrolysis and complex formation equilibria of carrier-free γ -emitting transamericium elements. This paper deals with the hydrolytic behaviour of ^{249}Cf (III) in aqueous perchlorate solutions.

Experiments

Electromigration method

Construction and experimental principles of the electromigration technique are described in refs. [2–4]. Special features guarantee constancy of the apparatus and of the electrolyte parameters (electric field strength gradient ΔE , temperature and chemical composition of the electrolytes), in particular of the pH of the solutions.

Some experimental results demonstrating the analytical applicability of this electromigration method are summarized in ref. [5]. In the field of hydrolysis equilibria the investigation of the formation of $[\text{Bi}(\text{OH})_n]^{3-n}$ ($n = 1, 2, 3, 4$) and of $[\text{NpO}_2(\text{OH})_n]^{1-n}$ ($n = 1, 2$) has been described [6, 7].

^{249}Cf . ^{249}Cf ($t_{1/2} = 352$ a; α , sf), produced by β^- decay of ^{249}Bk , emits γ -rays of 252.8, 266.6, 333.4, 388.2 keV and is suitable for electromigration measurements using a NaI(Tl) scintillation detector. Fig. 1 shows an example of the time-distance correlation of ^{249}Cf (III) electromigration registration.

For the electromigration experiments a stock sample of ^{249}Cf (III) in 0.10 M Na(H)ClO₄ solution was prepared. The pH of this solution was adjusted to the pH of the electrolyte. Volumes of 1–5 μl of the californium stock solution, yielding registration of about 100 counts per second were injected into the start position of the electromigration pipe. The electric field strength gradient was $\Delta E = 10.00(1) \text{ V} \cdot \text{cm}^{-1}$.

Electrolyte

To minimize Cf(III) association with electrolyte components the Na(H)ClO₄/NaOH system was used; $\mu = 0.10$, pH 1.05–12.8, $T = 298.1(1)$ K. The pH was measured by means of glass electrodes, calibrated by standard buffer solutions ($\Delta \text{pH} \approx 0.03$).

Chemicals were of p. a. grade, water was bidistilled.

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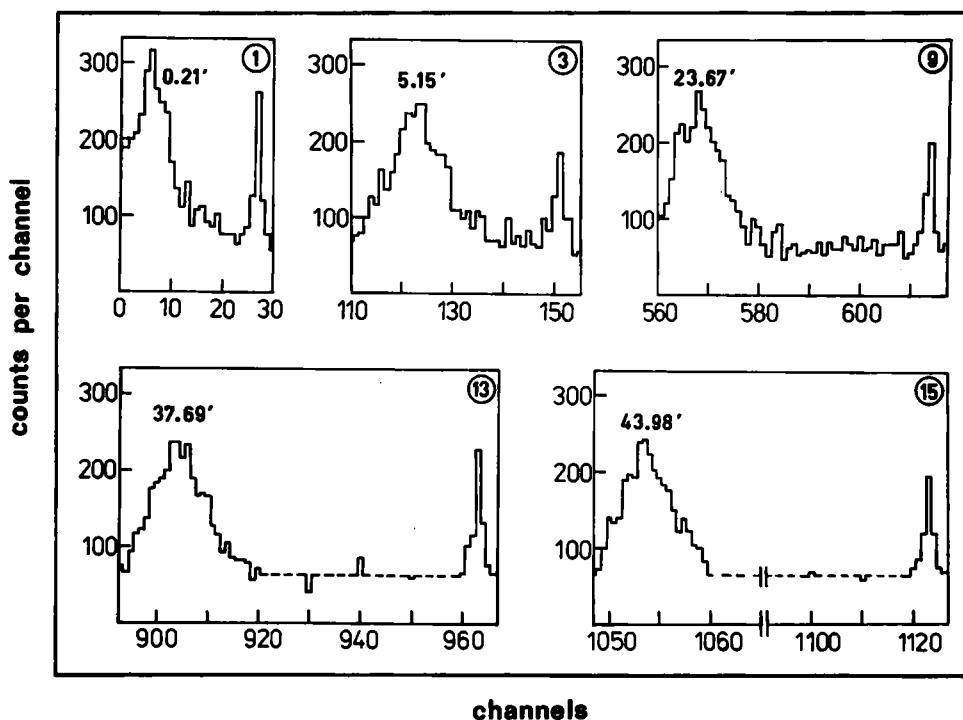


Fig. 1. Time-distance correlations of a $^{249}\text{Cf(III)}$ electromigration experiment; 0.10 M HClO_4 , $T = 298.1(1)$ K, $\Delta E = 10.00(1)$ V \cdot cm $^{-1}$. (time scale: 1 channel = 2.5 s, distance scale: 1 channel = 2.85 mm; distances are given in relation to a radioactive mark (right side of each plot); numbers of plots (in circles) correspond to numbers of scan operations selected).

Results and discussion

For investigations of Cf(III) hydrolysis reactions the experimental dependence of the $^{249}\text{Cf(III)}$ overall ion mobility $\bar{u}_{\text{Cf(III)}}$ on pH of the inert electrolytes was measured. The results are summarized in Fig. 2.

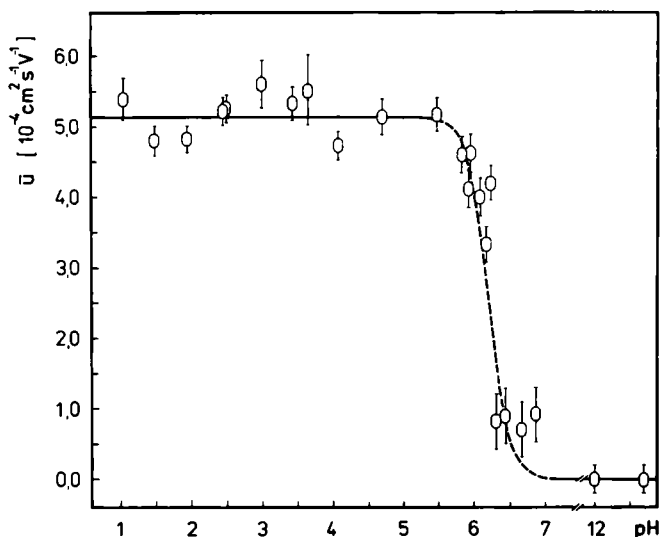


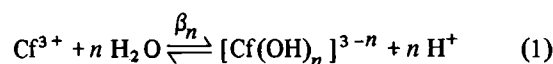
Fig. 2. Overall ion mobilities of $^{249}\text{Cf(III)}$ versus pH. Na(H)ClO $_4$ /NaOH electrolytes, $\mu = 0.10$, $T = 298.1(1)$ K.

Three details should be emphasized.

- (i) Between pH 1 and 5.5 the registered overall ion mobility is constant. This result can be interpreted as absence of hydrolytic reactions and yields the

individual ion mobility of Cf^{3+} in aqueous perchlorate electrolytes at $\mu = 0.10$ and $T = 298.1(1)$ K.

(ii) In the range of $5.5 < \text{pH} < 7.0$ the overall ion mobilities decrease. This should be understood as consequence of the hydrolysis equilibria



$n = 1 - 3$. Finally, at $\text{pH} \approx 7$ the hydroxide Cf(OH)_3 is formed, indicated by $\bar{u}_{\text{Cf(III)}} = 0$.

- (iii) In alkaline solutions of $\text{pH} \leq 12.8$ no electromigration of $^{249}\text{Cf(III)}$ in the direction of the cathode was detected. Formation of hydrolysis products with $n \geq 4$ in eq. (1), i. e. existence of anionic $[\text{Cf(OH)}_{3+m}]^{m-}$ species ($m \geq 1$), can therefore be excluded under these conditions.

Calculation of stoichiometric hydrolysis constants

The basic electromigration equation in the case of Cf(III) hydrolysis

$$\bar{u}_{\text{Cf(III)}} = \sum_{n=1}^n u^0 [\text{Cf(OH)}_n]^{3-n} \cdot \alpha [\text{Cf(OH)}_n]^{3-n} \quad (2)$$

with $n = 3$ leads to eq. (3) which allows the calculation of the stoichiometric overall hydrolysis constant β_3 :

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

Here

$\bar{u}_{\text{Cf(III)}}$ is the overall ion mobility of trivalent californium, α_i are the particular mole fractions of the ionic species i , u_i^0 are the individual ion mobilities of i at values of

$$\alpha_i = 1,$$

β_3 is the stoichiometric overall hydrolysis constant, $\beta_3 = K_1 K_2 K_3$, where K_1, K_2, K_3 are the stoichiometric stepwise hydrolysis constants.

To obtain values of $u_{\text{Cf}^{3+}}^0$ and β_3 eq. (3) was fitted by the least square method using the minimization program MINUIT [8].

The results are $u_{\text{Cf}^{3+}}^0 = +5.13(16) \cdot 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ and $p\beta_3 = 18.6(3)$; β_3 in $\text{mol}^3 \cdot \text{l}^{-3}$.

For pK_1 an estimation is possible if one assumes an individual ion mobility of $[\text{Cf}(\text{OH})]^{2+}$ according to the relation

$$\frac{u_{[\text{Cf}(\text{OH})]^{2+}}^0}{z_{[\text{Cf}(\text{OH})]^{2+}}} \approx \frac{u_{\text{Cf}^{3+}}^0}{z_{\text{Cf}^{3+}}};$$

z_i are the charges of the ions. With $u_{[\text{Cf}(\text{OH})]^{2+}}^0 \approx +3.4(4) \cdot 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ a value of $pK_1 = 6.2(2)$ can be derived.

Further subdivisions, i. e. calculation of all the stepwise hydrolysis constants and individual ion mobilities of the species seems to be not appropriate. Simultaneous calculation of the tree stepwise hydrolysis constants of trivalent lanthanides and actinides by other analytical methods is rarely successful, too. Formation of the hydroxides proceeds rapidly and is commonly irreversible.

However, estimation of pK_4 and $p\beta_4$ values is possible.

The fact that no evidence of $[\text{Cf}(\text{OH})_4]^-$ formation was found at $\text{pH} \leq 12.8$ gives a limit of $pK_4 \geq 14.4(3)$.

In Table 1 the hydrolysis constants obtained are compared with data available in the literature. The values $pK_1 = 5.62$ and 5.05 , respectively, are the results of extraction measurements [9, 10]; the value given by SMITH and MARTELL is derived from a critical discussion of systematics in hydrolysis equilibria [11]. These data are in satisfactory agreement and may be taken as demonstration of the applicability of the electromigration technique. Additionally, the values of β_3 and K_4 (or β_4) have been determined for the first time.

Finally, the method also yields absolute individual ion mobilities in aqueous solution. The Cf^{3+} individual ion mobility was obtained immediately. Comparable data have been found by means of diffusion measurements [12, 13]. On the other hand, ion mobilities measured by electromigration in solutions containing hydrodynamic stabilizers, e. g. SiO_2 (Bk(IV)) [14] and paper (trivalent Cm, Cf, Es, Fm, Md) [15] are only relative values.

Table 1. Stoichiometric hydrolysis constants of trivalent californium in aqueous solutions

Solution (μ ; T(K))	pK_1	$p\beta_3$	pK_4	Ref.
0.10 (ClO_4^-); 296.1	5.62	—	—	[9]
0.10 (ClO_4^-); ?	5.05	—	—	[10]
0.10 — ; 298.1	5.8	—	—	[11]
0.10 (ClO_4^-); 298.1	6.2(2)	18.6(3)	$\geq 14.4(3)$	this work

Transformation of the diffusion coefficients of Cf^{3+} measured in lithium chloride solutions of pH 2.5 and $T = 298.1 \text{ K}$ using the NERNST' equation leads to $u_{\text{Cf}^{3+}}^\infty = +6.87 \cdot 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$. Assuming similar dependences of diffusion coefficients and individual ion mobilities on the overall ionic strength μ in dilute aqueous solutions, values of $u_{\text{Cf}^{3+}}^0 = 6.3 \cdot 10^{-4}$ and $6.1 \cdot 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ are to be expected at $\mu = (0.68 - 1.6) \cdot 10^{-2} \text{ M}$ and $5.0 \cdot 10^{-2} \text{ M}$ [11, 12], respectively. In this context the $u_{\text{Cf}^{3+}}^0$ value obtained experimentally at $\mu = 0.10$ is in relatively good agreement.

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