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D.Schumann, A.F.Novgorodov, V.A.Khalkin

ELECTROPHORETIC INVESTIGATIONS OF HYDROLYSIS AND FORMATION OF FLUORIDE COMPLEXES OF CARRIER-FREE ^{155}Eu

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INTRODUCTION

The published information on the constants of hydrolysis and stability of fluoride complexes of lanthanides is quite scarce. For example, for europium one has determined only the first hydrolysis constant $p\beta_{1h} = 8.5$ [1] and two fluorocomplex stability constants $\lg\beta_{1K} = 3.39$, $\lg\beta_{2K} = 6.48$ ($\mu = 0.5$) [2] and $\lg\beta_{1K} = 3.08$ ($\mu = 1.0$) [3].

In our investigations we followed the experimentally proved ideas that additional information on these processes can be obtained by means of a new version of the electromigration method developed in our Laboratory earlier [4,5]. Its specific feature is electrophoresis in electrolyte solutions free of finely divided hydrodynamic stabilizers, which is very suitable for the study of the behaviour of carrier-free radionuclides.

EXPERIMENTAL

The ^{155}Eu radionuclide ($T_{1/2} \approx 5$ years) was obtained from ^{154}Sm irradiated with neutrons in a nuclear reactor.* The target was kept untreated for about half a year till the complete decay of ^{156}Eu ($T_{1/2} = 15$ days). Samarium oxide was diluted in citric acid, and europium was extracted from the solution by the sodium amalgam. The amalgam was destroyed by the hydrochloric acid solution, and europium was precipitated with $Fe(OH)_3$. Iron was separated from europium on an anion-exchange column filled with anionite Domex 1x8. The electromigration measurements were carried out in solutions of constant ion strength $\mu = 0.1$ at 25°C.

RESULTS AND DISCUSSION

The behaviour of the carrier-free $^{155}Eu(III)$ mobility in the interval $1 \leq pH \leq 13$ allows the conclusion that hydrolysis of the element begins at pH > 8 and ends at pH 9-9.5 with formation of $Eu(OH)_3$ (Fig.1).

*Institute for Nuclear Research of the Ukrainian Academy of Sciences (Kiev).

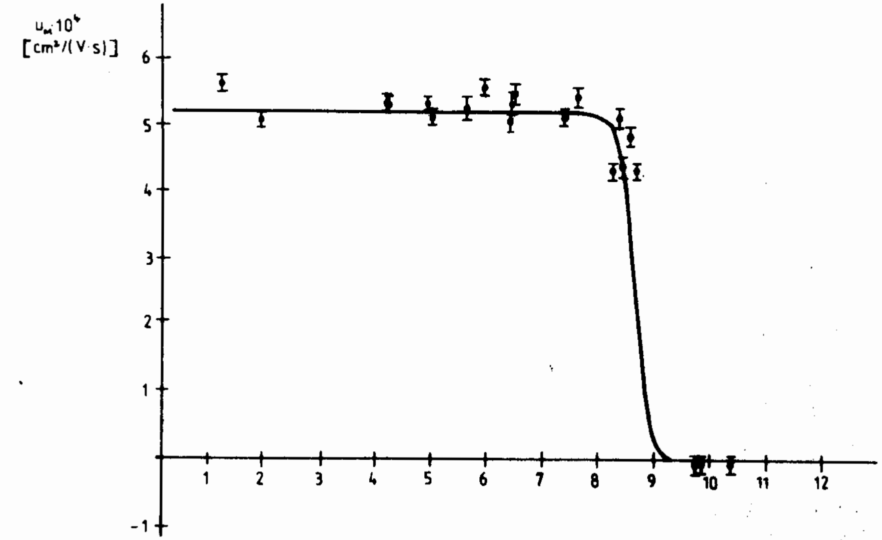

Fig.1. Mobility of carrier-free $^{155}Eu(III)$ in perchlorate solutions of background electrolytes, $\mu = 0.1$, 25°C. The curve is calculated by equation (2): $\beta_{3h} = 3\cdot10^{-26}$ $mol^3\cdot l^{-3}$, $u_o = 5.3\cdot10^{-4}$ $cm^2V^{-1}s^{-1}$.

Investigation of europium electromigration in highly alkaline solutions (pH ≈ 13) did not reveal transformation of hydroxides into complex hydroxyanions. The sharp decrease in the mobility in a narrow interval of pH indicates that neutral moleculae dominate in the equilibrium mixture of europium hydrolysis products:

$$Eu^{2+} + 3H_2O \underset{}{\overset{\beta_{3h}}{\rightleftarrows}} Eu(OH)_3 + 3H^+ \qquad (1)$$

so the migration equation can be written down as

$$\bar{u}_{Eu(III)} = \frac{u_o}{1 + \beta_{3h}\,|H^+|^{-3}} \,. \qquad (2)$$

The curve in Fig.1 is calculated by equation (2) at $u_o = 5.3\cdot10^{-4}$ $cm^2V^{-1}s^{-1}$ and $p\beta_{3h} = 25.5$. The above information on β_{1h} [1] and our estimation of β_{3h} allow a conclusion that the stepwise constants of europium hydrolysis have close values of the same order: $K_i = n\cdot10^{-9}$ $mol\cdot l^{-1}$.

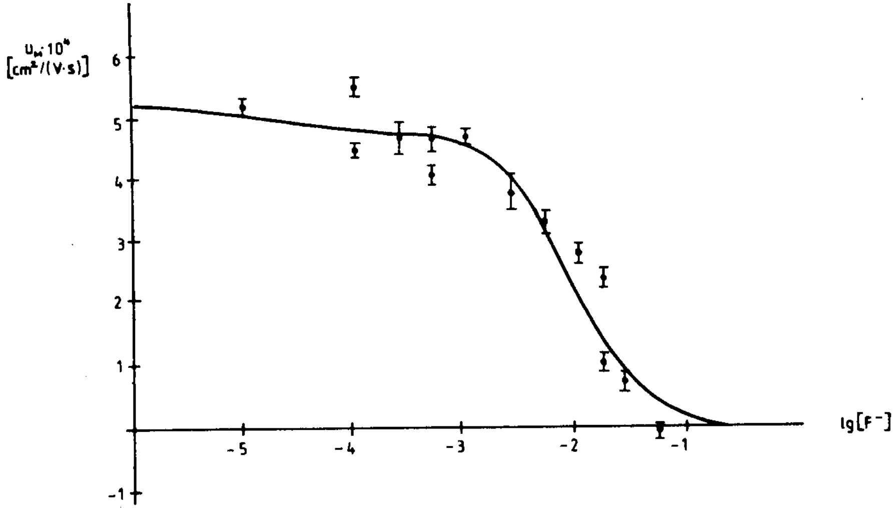

Fig.2. Dependence of the ^{155}Eu(III) mobility in neutral (pH 6-7) perchlorate solutions of background electrolytes on the concentration of fluoride ions. $\mu = 0.1$, 25°C. The curve is calculated by equation (4): $\beta_{1K} = 4\cdot10^{4}$ $mol\cdot l^{-1}$, $\beta_{2K} = 1.45\cdot10^{7}$ $mol^{2}\cdot l^{-2}$, $\beta_{3K} = 2.5\cdot10^{9}$ $mol^{3}\cdot l^{-3}$, $u_1 = 4.6\cdot10^{-4}$ $cm^{2}V^{-1}s^{-1}$, $u_2 = 5.0\cdot10^{-4}$ $cm^{2}V^{-1}s^{-1}$.

Dependence of the ^{155}Eu(III) mobility on the concentration of F^- in neutral solutions of electrolytes (pH 6-7) is shown in Fig.2. The experimental results allow one to calculate constants of the following equilibrium reactions:

$$Eu^{3+} + F^- \overset{K_1}{\rightleftarrows} EuF^{2+} \qquad K_1 = \beta_{1K} \tag{3a}$$

$$EuF^{2+} + F^- \overset{K_2}{\rightleftarrows} EuF_2^{+} \qquad K_1K_2 = \beta_{2K} \tag{3b}$$

$$EuF_2^{1+} + F^- \overset{K_3}{\rightleftarrows} EuF_3 \qquad K_1K_2K_3 = \beta_{3K} \tag{3c}$$

solving the electromigration equation (4) using the MINUIT programme [6]:

$$\bar{u}_{Eu(III)} = \frac{u_0 + u_1\beta_{1K}|F^-| + u_2\beta_{2K}|F^-|^2}{1 + \beta_{1K}|F^-| + \beta_{2K}|F^-|^2 + \beta_{3K}|F^-|^3}\,. \tag{4}$$

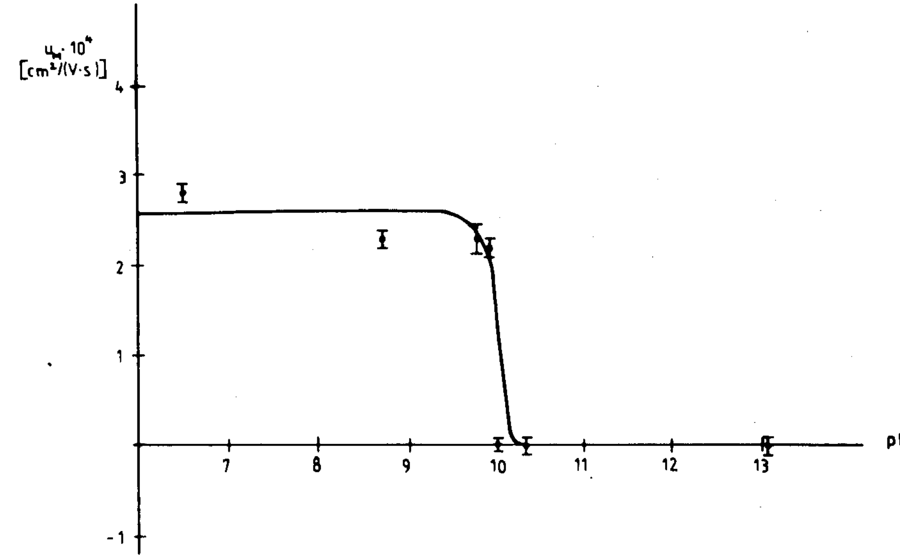

Fig.3. Mobility of ^{155}Eu(III) as a function of pH at the constant concentration $1\cdot10^{-2}$ $mol\cdot l^{-1}$ of F^-, $\mu = 0.1$, 25°C. The curve is calculated by the electromigration equation with the values of the europium cation mobility and the complex formation and hydrolysis constants obtained in this paper.

Our values of the constants $\lg\beta_{1K} = 4.6(2)$ and $\lg\beta_{2K} = 7.16(4)$ appear to be close to the values obtained by other methods and under other conditions [2,3]. The third constant $\lg\beta_{3K} = 9.40(7)$ has been determined for the first time.

It was also interesting for us to study the influence of the competition between the processes of fluoride complex formation and hydrolysis on the europium mobility. So we carried out several experiments with ^{155}Eu(III) in solutions of background electrolytes with a constant concentrations of the fluoride (10^{-2} $mol\cdot l^{-1}$) in the pH interval from 6.5 to 13. With these concentrations of the ligand, following the calculations by the electromigration equation that takes into account both complex formation and hydrolysis, one could expect a sharp decrease in the europium mobility at lower concentrations of hydrogen ions (pH ~ 10) than in pure fluoride-free solutions.

As is seen from Fig.3, the experimental and calculated data are in good agreement with each other, which can additionally prove the correctness of all values determined by us.

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