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Complexes of Europium(III) with Nitrate and Chloride Ions in 4 M $H(ClO_4)$ and $Na(ClO_4)$

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The complex formation of europium(III) with nitrate and chloride ions in 4 M $H(ClO_4)$ and 4 M $Na(ClO_4)$ was studied at 25°C, using radioactive tracers at very low concentrations and in conjunction with cation exchange resin. The stability constants were determined graphically by a "curve-fitting" method. The stability constants obtained were as follows:

Ligand	Ionic medium	$\log\beta_1$	$\log\beta_2$	$\log\beta_3$
NO_3^-	4 M $H(ClO_4)$	0.17	−0.72	—
NO_3^-	4 M $Na(ClO_4)$	0.12	−0.52	—
Cl^-	4 M $H(ClO_4)$	−0.27	−0.90	∼−2.0
Cl^-	4 M $Na(ClO_4)$	−0.06	−0.48	∼−1.7

It was concluded that the stability of the nitrate complexes is nearly comparable with that of the chloride complexes.

The present authors have studied the complex formation of europium(III) with nitrate and chloride ions in 4 M perchlorate media at 25°C, using radioactive tracers at very low concentrations in conjunction with cation exchange resin. Both hydrogen and sodium ions were employed as counter-ions of nitrate, chloride, or perchlorate ions in order to observe how the changes in the bulk cation in the ionic media affect the stability constants.

Experimental

Tracer and Reagents. Europium 152 + 154 obtained from the Oak Ridge National Laboratory was diluted with perchloric acid, nitric acid, hydrochloric acid, sodium perchlorate, or sodium nitrate solution at 4.0 M. These solutions were then used as the stock tracer solutions. All of the reagents were of an analytical grade. The concentrations of the acids were determined by titration, using potassium acid carbonate as the standard. The concentrations of the stock sodium perchlorate and nitrate solutions were determined by titration after they had been passed through a cation exchange resin column in the H^+-form.

Dowex 50W X-12, 100—200 mesh was used throughout the experiments. It was conditioned several times with sodium chloride and hydrochloric acid solutions, and was made into the H^+-form or Na^+-form. These forms were equilibrated in the open air and then stored in closed bottles. The exchange capacity of the resin in the H^+-form was 3.62 meq/g, and that in the Na^+-form was 3.40 meq/g.

Procedures. All of the procedures were carried out in a thermostatted room at 25±0.5°C. The Na^+-form resin was used for the experiments in 4 M $Na(ClO_4)$ while the H^+-form resin was used for the experiments in 4 M $H(ClO_4)$. About 100 mg of the resin was placed in glass-stoppered tubes (volume 20 m*l*). The tracer solution and various amounts of perchlorate and ligand solutions were then placed in the tubes. The initial volume of the aqueous phase was always 5.0 m*l*. The initial concentration of europium(III) in the aqueous phase was less than 10^{-6} M. The tubes, with the contents, were then agitated mechanically for fifteen minutes and centrifuged for three minutes at 2000 rpm. A two-milliliter aliquot was pipetted out and transferred into a small glass tube. The γ-radioactivity of the solution was measured with a well-type (NaI) scintillation counter.

Statistical Treatment

The statistical treatment was just the same as that described in a previous work[1]; only a summary will be given in this paper.

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[1] T. Sekine and Y. Hasegawa, This Bulletin, **39**, 240 (1966).

M^{3+}: a trivalent metal ion
D : the net distribution ratio of europium (III)
T : the total radioactivity added to the whole system
A : the radioactivity per m*l* of the aqueous phase in equilibrium with the resin phase
v : the volume of the aqueous phase (m*l*)
G : the weight of the resin (g)
L^- : a monovalent complex forming a ligand
the subscript "R": a species in the resin phase
4 M $H(ClO_4)$: this expression signifies that the aqueous phase consists of mixtures of 4 M perchloric acid and 4 M nitric or hydrochloric acid various mixing ratios
K_{d_n} : the distribution constant of the ML_n^{3-n} species, $K_{d_n} = [ML_n^{3-n}]_R/[ML_n^{3-n}]$
β_n : the formation constant of the ML_n^{3-n} complex, $\beta_n = [ML_n^{3-n}]/[ML^{3+}][L^-]^n)$

Using these notations, the following equations are obtained:

$$D = [M(III)_{R,\text{total}}]/[M(III)] \tag{1}$$

$$= \frac{\text{Eu(III) per g of resin}}{\text{Eu(III) per m}l\text{ of solution}} \tag{2}$$

$$= \frac{(T-vA)}{(G\times A)} \tag{3}$$

When the complex-forming ligand is absent in the system, Eq. (1) can be described as;

$$D = [M^{3+}]_R/[M^{3+}] = K_{d_0} \tag{4}$$

When, on the other hand, the metal ion forms complexes with L^-, Eq. (1) can be described as;

$$\begin{aligned} D = {} & ([M^{3+}]_R + [ML^{2+}]_R + [ML_2{}^+]_R) \\ & \times ([M^{3+}] + [ML^{2+}] + [ML_2{}^+] \\ & + [ML_3] + \cdots)^{-1} \end{aligned} \tag{5}$$

By introducing the distribution constants and the stability constants, Eq. (5) can be described as;

$$\begin{aligned} D/K_{d_0} = {} & \left(1 + \frac{K_{d_1}}{K_{d_0}} \times \beta_1[L^-] + \frac{K_{d_2}}{K_{d_0}} \times \beta_2[L^-]^2\right) \\ & \times (1 + \beta_1[L^-] + \beta_2[L^-]^2 \\ & + \beta_3[L^-]^3 + \cdots)^{-1} \end{aligned} \tag{6}$$

The distribution constants, K_{d_n}, and the stability constants, β_n, are determined by a "curve-fitting" method, as has described in Ref. 1.

Results

Figures 1 to 4 give the $\log D/K_{d_0}$ *vs.* $\log [L^-]$ plots. The values for K_{d_0} in Eq. (4) were found by separate experiments to be 64.9 in 4 M $HClO_4$ and 131 in 4 M $NaClO_4$. The stability constants, β_n, as determined by the "curve-fitting" method, are given in Table 1.

The uptake of the ML^{2+} or $ML_2{}^+$ species on the resin was concluded to be negligible. The solid curves given in Figs. 1 to 4 show the distribution curves which calculated from the constants in Table 1.

Discussion

The results in Figs. 1 to 4 and Table 1 can be summarized as follows; (i) The stabilities of nitrate and chloride complexes are not very different, although the nitrate complexes seem to be a little more stable than the chloride complexes.

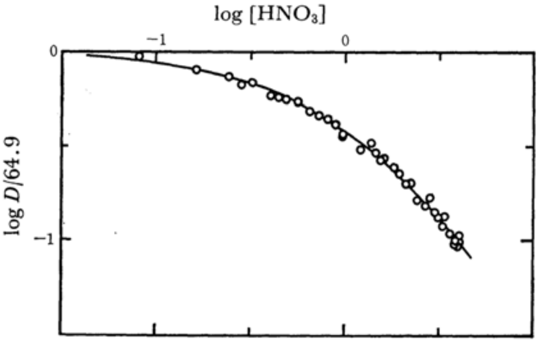

Fig. 1. The plot $\log D/K_{d_0}$ *vs.* $\log [HNO_3]$ of europium(III) in perchloric acid medium.
Ion-exchange resin: Dowex 50W X-12, 100—200 mesh in H^+-form
Aqueous phase: 4.0 M $H(NO_3, ClO_4)$
The curve drawn for the plot is
$\log D/64.9 = -\log(1+1.5[HNO_3]+0.19[HNO_3]^2)$

TABLE 1. STABILITY CONSTANTS OF EUROPIUM(III) NITRATE AND CHLORIDE COMPLEXES IN 4 M PERCHLORATE MEDIA AT 25°C

	Ligand	Ionic medium	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	Remark
(A)	NO_3^-	4 M $H(ClO_4)$	0.17	−0.72	—	Present work**
	NO_3^-	4 M $Na(ClO_4)$*	0.12	−0.52	—	Present work**
(B)	Cl^-	4 M $H(ClO_4)$	−0.27	−0.90	∼−2.0	Present work**
	Cl^-	4 M $Na(ClO_4)$*	−0.06	−0.48	∼−1.7	Present work**
	Cl^-	4 M $Na(ClO_4)$*	−0.15	−0.72	—	Ref. 4***

* The hydrogen ion concentration is 0.01 M.
** Ion-exchange method.
*** Liquid-liquid distribution method.

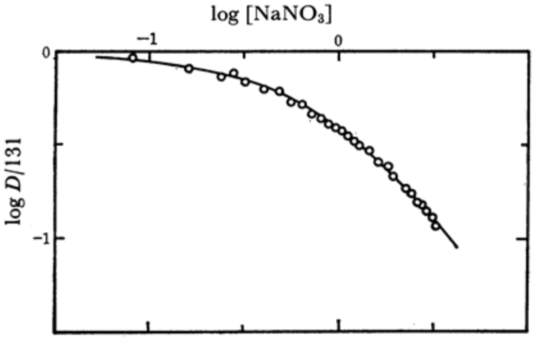

Fig. 2. The plot $\log D/K_{d_0}$ *vs.* $\log [NaNO_3]$ of europium(III) in sodium perchlorate medium.
Ion-exchange resin: Dowex 50W X-12, 100—200 mesh in Na^+-form
Aqueous phase: 4.0 M $Na(NO_3, ClO_4)$, $[H^+]=0.010$ M
The curve drawn for the plot is
$\log D/131 = -\log(1+1.3[NaNO_3]+0.30[NaNO_3]^2)$

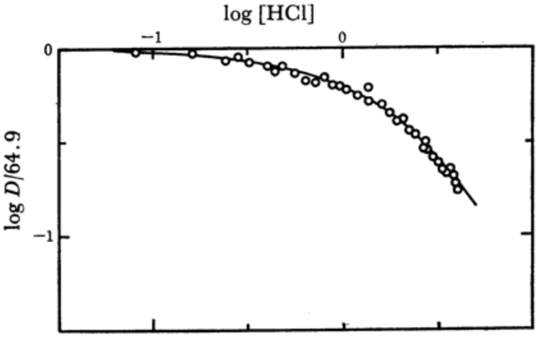

Fig. 3. The plot $\log D/K_{d_0}$ *vs.* $\log [HCl]$ of europium(III) in perchloric acid medium.
Ion-exchange resin: Dowex 50W X-12, 100—200 mesh in H^+-form
Aqueous phase: 4 M $H(Cl, ClO_4)$
The curve drawn for the plot is
$\log D/64.9 = -\log(1+0.53[HCl]+0.13[HCl]^2+0.01[HCl]^3)$

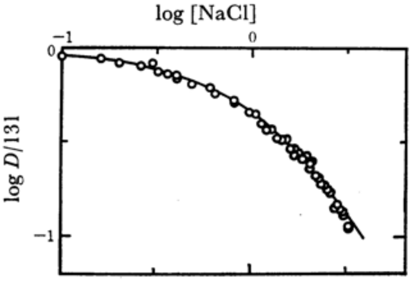

Fig. 4. The plot $\log D/K_{d_0}$ *vs.* $\log [NaCl]$ of europium(III) in sodium perchlorate medium.
Ion-exchange resin: Dowex 50W X-12, 100—200 mesh in Na^+-form
Aqueous phase: 4.0 M $Na(Cl, ClO_4)$, $[H^+]=0.010$ M
The curve drawn for the plot is
$\log D/131 = -\log(1+0.87[NaCl]+0.33[NaCl]^2+0.02[NaCl]^3)$

TABLE 2. STABILITY CONSTANTS OF AMERICIUM(III) CHLORIDE COMPLEXES IN 4 M PERCHLORATE MEDIA

Ionic medium	Temp.	$\log \beta_1$	$\log \beta_2$	Ref.
4 M $H(ClO_4)$	20°C	−0.16	−0.74	5**
4 M $Na(ClO_4)$*	25°C	−0.15	−0.72	4***

* The hydrogen ion concentration is 0.01 M.
** Ion-exchange method.
*** Liquid-liquid distribution method.

(ii) No remarkable difference exists between the stablity constants of the nitrate complexes in 4 M $H(ClO_4)$ and those in 4 M $Na(ClO_4)$, but the chloride complexes in 4 M $H(ClO_4)$ seem to be a little less stable than those in 4 M $Na(ClO_4)$.

(iii) Only the Eu^{3+} species is adsorbed on the resin in all of the systems.

(iv) A third complex is observed in the chloride systems, but no certain identification of this species is possible.

In the present work, the equilibrium constants are calculated by the stoichiometrical concentrations. The thermodynamical equilibrium constants may be described as follows;

$$^T\beta_n = (\gamma_{EuL_n{}^{3-n}}/\gamma_{Eu^{3+}} \times \gamma_{L_n{}^{-n}})\beta_n \tag{7}$$

$$^TK_{d_0} = (\gamma_{Eu_R{}^{3+}}/\gamma_{Eu^{3+}})K_{d_0} \tag{8}$$

The activity coefficients of an ionic species in aqueous solutions are assumed to be constant in constant-ionic-strength media only at low concentrations.[2,3] In the present work, however, the $\gamma_{EuL_n{}^{3-n}}/\gamma_{Eu^{3+}} \times \gamma_{L_n{}^{-n}}$ and $\gamma_{Eu_R{}^{3+}}/\gamma_{Eu^{3+}}$ terms could not always be constant, because the experiments were carried out in solutions at high electrolyte concentrations in order to determine the weak complexes. The use of the total ligand concentration for the calculation of the constants may also have caused some errors due to the association between the cation (H^+ or Na^+) and the ligand anion in high-electrolyte solutions.[7] Thus, there could exist some difference between the stoichiometrical stability constants in 4 M $H(ClO_4)$ and in 4 M $Na(ClO_4)$ as calculated from the experimental data when no correction is made for these factors.

However, the stability constants obtained in the present study and those of americium(III) chloride complexes obtained in the previous work are not very different in the 4 M $H(ClO_4)$ and in 4 M $Na(ClO_4)$.

The stability constants for chloride complexes in 4 M $Na(ClO_4)$ as determined by the cation-exchange method (in the present work) are a

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2) G. Biedermann and L. G. Sillén, *Arkiv Kemi*, **5**, 425 (1953).

3) F. J. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill, Inc., London (1961).

4) T. Sekine, *J. Inorg. Nucl. Chem.*, **26**, 1468 (1964); *Acta Chem. Scand.*, **19**, 1435 (1965).

5) I. Grenthe, *Acta Chem. Scand.*, **16**, 2300 (1962).

TABLE 3. STABILITY CONSTANTS OF EUROPIUM(III) NITRATE AND CHLORIDE COMPLEXES FROM THE PREVIOUS WORK

	Ligand	Ionic medium	Temp.	log β_1	log β_2	Ref.
(A)	NO_3^-	1 M $H(ClO_4)$	22°C	0.30	—	6*
	NO_3^-	1 M $H(ClO_4)$	25°C	0.30	—	7*
(B)	Cl^-	1 M $H(ClO_4)$	22°C	−0.10	—	6*
	Cl^-	1 M $H(ClO_4)$	25°C	−0.10	−0.70	8*

* Carried-out by liquid-liquid distribution methods.

little larger than those obtained by the liquid-liquid distribution method (Ref. 4), but, without further information, it seems difficult to find a reasonable explanation for the differences.

Table 3 gives the stability constants of europium(III) nitrate and chloride complexes which appeared in the previous work. The present results in 4 M $H(ClO_4)$ or 4 M $Na(ClO_4)$ may not be compared directly with these previous results which were obtained in 1 M $H(ClO_4)$. The second nitrate complex was determined only in 4 M perchlorate media; this shows that the use of a higher electrolyte concentration media is favorable for the study of the higher complexes.

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6) D. F. Peppard, G. W. Mason and I. Hucher, *J. Inorg. Nucl. Chem.*, **24**, 881 (1962).

7) G. R. Choppin and W. F. Strazik, *Inorg. Chem.*, **4**, 1250 (1965).

8) G. R. Choppin and P. J. Unreim, *J. Inorg. Nucl. Chem.*, **25**, 387 (1963).