ACTA CHEMICA SCANDINAVICA 16 (1962) 1695–1712

On the Stability of the Acetate, Glycolate and Thioglycolate Complexes of Tervalent Europium and Americium

INGMAR GRENTHE

Department of Inorganic and Physical Chemistry, Chemical Institute, University of Lund, Lund, Sweden

The stability constants for the acetate, glycolate and thioglycolate complexes of tervalent europium and americium were determined in a perchlorate medium of the ionic strength $I = 0.5$ M and at a temperature of 20.0°C. The europium complexes were studied by a potentiometric method [1a] and the americium complexes using the cation exchange method of Fronæus [2a-2c]. The quantitative results for the acetate and glycolate systems were checked by an anion exchange study. In all the systems investigated the americium complexes were stronger than the corresponding europium complexes. The difference was most pronounced for the glycolate systems. For both europium and americium the stability constants of the complexes decreased in the following order: glycolate, acetate, thioglycolate.

The acetate and glycolate complexes of several tervalent lanthanides have previously been studied by Sonesson [1a-1e]. Qualitative studies of the cation and anion exchange behaviour of both europium and americium in glycolate solutions have been published by Stewart [3] and Holm *et al* [4]. In the present investigation these measurements were extended in order to determine the stability constants of europium and americium complexes with acetate, glycolate and thioglycolate ions.

As only tracer amounts of ^{241}Am were available, the experimental methods were restricted to ion exchange and solvent extraction studies. In the present investigation the first method, with the cation exchanger in the sodium form, was used. Previous experience [5] did prove that reliable results could be obtained even on the tracer scale. The method has one serious drawback, however: no information about the existence of anionic complexes can be obtained. For this reason an anion exchange study was added to the investigation. Macro amounts of europium oxide were available and therefore the europium systems could be studied by a potentiometric standard method, *viz.* the determination of the concentration free ligand by means of pH-measurements.

All measurements were made at a temperature of 20.0°C and in a perchlorate medium of the ionic strength of $I = 0.5$ M.

CALCULATION OF STABILITY CONSTANTS FROM CATION EXCHANGE DATA

The following notation was used:

C'_M, C'_A = the total concentrations of metal ion and ligand before addition of ion exchanger
C_M, C_A = the total concentrations of metal ion and ligand in equilibrium with the ion exchanger
$[M^{3+}]$, $[MA_j^{3-j}]$ = equilibrium concentrations of the various species in solution
$[M^{3+}]_R$, $[MA_j^{3+j}]_R$ = equilibrium concentrations of the various species in the resin phase.
β_j = the stability constant for the complex MA_j^{3-j} in solution
$l_j = \dfrac{[MA_j^{3-j}]_R}{[MA_j^{3-j}]}$; $(j = 0, 1, 2)$
$l'_j = \beta_j \cdot \dfrac{l_j}{l_0}$; $(j = 1, 2)$
v = the volume of the solution before the addition of the ion exchanger
m = the weight of dried ion exchanger
δ = the swelling factor of the ion exchanger
$X_n = \sum\limits_{j=n}^{N} \beta_j [A^-]^{j-n}$; $(\beta_0 = 1)$

For the determination of the stability constants β_j the functions, φ_1, f and g were used. For further details see Refs.[1a,2b,2c]

$$\varphi = \frac{v}{m}\left(\frac{C'_M}{C_M} - \delta\right) = l_0 \cdot \frac{1 + l'_1[A^-] + l'_2[A^-]^2}{X} \tag{1}$$

$$\varphi_1 = \left(\frac{l_0}{\varphi} - 1\right) \cdot \frac{1}{[A^-]} \tag{2}$$

$$f = \left\{\frac{l_0}{\varphi}\,[(\beta_1 - l'_1)[A^-] - 1] + 1\right\} \cdot \frac{1}{[A^-]^2} = \beta_1\varphi_1 - X_2 - \frac{l'_1 \cdot l_0}{\varphi} \tag{3}$$

$$g = \left\{f - \beta_1\varphi_1 + \frac{l_0}{\varphi}\,(\beta_2 - l'_2)\right\} \cdot \frac{1}{[A^-]} = \beta_2\varphi_1 - \beta_3 - X_4[A^-] \tag{4}$$

$$\lim_{[A^-]\to 0} \varphi_1 = \overset{0}{\varphi_1} = \beta_1 - l'_1 \tag{5}$$

$$\lim_{[A^-]\to 0} f = f^0 = \beta_1\overset{0}{\varphi_1} - (\beta_2 - l'_2) \tag{6}$$

$$\Delta\varphi_1 = \varphi_1 - \overset{0}{\varphi_1} \tag{7}$$

$$\Delta f = f - f^0 \tag{8}$$

$$\beta_1 = \frac{\Delta f}{\Delta\varphi_1} + \beta_3 \cdot \frac{[A^-]}{\Delta\varphi_1} + \beta_4[A^-] \cdot \frac{[A^-]}{\Delta\varphi_1} - l'_2 \cdot \varphi_1 \frac{[A^-]}{\Delta\varphi_1} \tag{9}$$

As a rule β_1 can be determined from eqn. (9) written as

$$\frac{\Delta f}{[A^-]} = \beta_1 \cdot \frac{\Delta\varphi_1}{[A^-]} - \beta_3 - \beta_4[A^-] + l'_2 \cdot \varphi_1 \tag{10}$$

By plotting $\Delta f/[A^-]$ *versus* $\Delta\varphi_1/[A^-]$, β_1 is obtained as the slope. This method could not be used here, because the values of $\Delta f/[A^-]$ and $\Delta\varphi_1/[A^-]$ were approximately constant. The following method of successive approximations was used instead: In the first approximation of β_1 from eqn. (9) all terms except $\Delta f/\Delta\varphi_1$ were neglected. Using this approximate β_1-value the function g was computed. β_2 and β_3 were then determined by plotting g *versus* φ_1. In the second approximation of β_1 all correction terms were included (*vide infra*, p. 1698 and p.1699). In order to compute the last term in eqn. (9) it was necessary to estimate l_2'. This was done using the relation $\beta_1^2 \cdot \beta_2^{-1} = (l_1')^2(l_2')^{-1}$ (*cf.* Ref. [2c], p. 20). A satisfactory value of β_1 was obtained after three approximations.

In order to determine the concentration of free ligand $[A^-]$ from the C_A-values, two corrections had to be applied to the latter figures. The first was due to ligand produced by protolysis of the acid HA. This correction was computed from the acid constant of HA. The second correction was due to ligand produced, when sodium ions in the ion exchanger were replaced by hydrogen ions from the solution. This correction was computed on the assumption (for the validity of this assumption *vide infra*, p. 1699) that $[H^+]_R \cdot [H^+]^{-1} \approx [Na^+]_R \cdot [Na^+]^{-1}$. For further details see Ref. [1d], pp. 1442 and 1445.

EXPERIMENTAL

Chemicals used. A hydrochloric acid solutions of tervalent americium was obtained from A.E.R.E. Harwell. The sample consisted of ^{241}Am to more than 99.93 %, the rest was ^{239}Pu. From this stock solution more dilute americium solutions were prepared by dilution with a 0.5 M sodium perchlorate solution. The acidity of these solutions was determined by a potentiometric determination of their hydrogen ion concentration.

All other chemicals used except thioglycolic acid were of analytical grade. Thioglycolic acid (Fluka purum) was purified by a vacuum distillation before it was used.

The stock solutions of acetic and glycolic acid were standardized by an alkalimetric titration. Thioglycolic acid was standardized by oxidation with a standard iodine solution [6]. The stock solutions of acetate and sodium perchlorate were analysed by passing a known volume of the solutions through an ion exchanger in the hydrogen form followed by an alkalimetric titration of the acid. The cation exchange resin (Dowex 50 W × 8, 50—100 mesh, exchange capacity 3.81 mequiv. $\cdot$ g^{-1}) was used in the sodium form. The swelling factor δ was determined to 0.99 for the value of $v \cdot m^{-1} = 33.9 \times 10^{-3}\ l \cdot g^{-1}$ used in the following experiments. The buffer solutions used all had the following compositions:

$$C_A \text{ mM NaA},\ C_{HA} = k \cdot C_A \text{ mM HA},\ \ I = 0.5\text{ M}$$

where k is close to unity. Buffer stock solutions were prepared by mixing acetic acid and sodium acetate stock solutions or by partial neutralization of glycolic or thioglycolic acid with sodium hydroxide. Sodium perchlorate was added to give the correct ionic strength. From these stock solutions more dilute solutions were obtained by dilution with a 0.5 M sodium perchlorate solution.

The distribution coefficient φ was determined by shaking 5 ml of the buffer solutions, to which 0.086 ml of the americium stock solutions had been added, with 150 mg ion exchange resin. The time necessary for the attainment of equilibrium was < 20 h. For each ligand, series with varying C_A' were performed at two or three different values of C_M' and each series was repeated at least twice.

The americium concentration of the solutions was determined by measuring the γ-activity of a 4 ml sample in a scintillation counter (Tracerlab P 20, using a NaI (Tl) crystal). In order to determine the absolute concentration of americium the amount in a thin solid sample was determined by measuring the α-activity in a 2 π proportional counter (Tracerlab SC-16 P, was used in this investigation). For details about the preparation of the sample see Ref.[7], p. 1063. By measuring the same amount of americium diluted

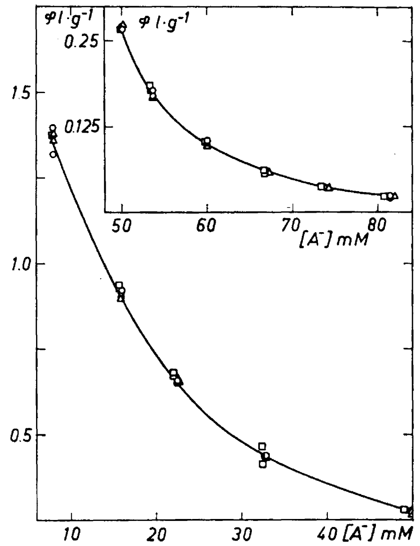

Fig. 1. φ as a function of [A⁻] for the Am^{3+}-acetate system. $C'_M = 1.14 \times 10^{-7}$ M □, $C'_M = 1.40 \times 10^{-7}$ M ○, $C'_M = 2.12 \times 10^{-7}$ M △.

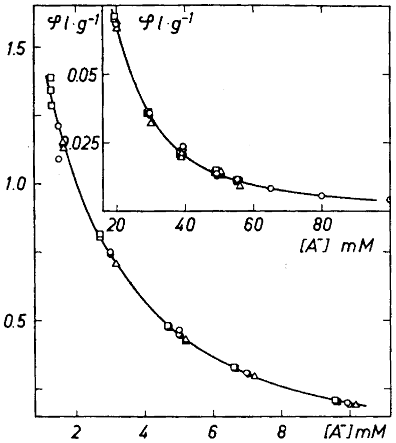

Fig. 2. φ as a function of [A⁻] for the Am^{3+}-glycolate system. $C'_M = 1.14 \times 10^{-7}$ M □, $C'_M = 1.40 \times 10^{-7}$ M ○, $C'_M = 2.66 \times 10^{-7}$ M △.

to 4 ml in the scintillation counter it was possible to relate the concentration in cpm to the concentration in moles. l^{-1}. 1000 cpm was equal to 1.5×10^{-8} M.

All operations with more concentrated americium solutions were performed in a glove box, while the more dilute solutions were handled in a well ventilated fume hood.

RESULTS

The americium-acetate system

The distribution coefficient φ as a function of the acetate concentration at the different values of C'_M is given in Fig. 1. No corrections needed be applied to the C_A-values because of the low acidity of the buffer solutions (pH $\approx$ 4.5). From Fig. 1 it is evident that there is no variation in φ with the load C_{MR}. The various functions used for the computation of the stability constants are given in Table 1. φ_1 and f were plotted *versus* [A⁻] and extrapolated to [A⁻] = 0 to give φ_1^0 and f^0. The following values were obtained:

$$\varphi_1^0 = 94 \pm 2 \text{ M}^{-1}$$
$$f^0 = 7400 \pm 200 \text{ M}^{-2}$$

β_1 was calculated from eqn. (9) in the way described earlier (*vide supra* p. 1697). In the final approximation values of $\beta_2 = 1.9 \times 10^3$ M^{-2}, $\beta_3 = 1 \times 10^4$ M^{-3}, $\beta_4 = 0$ and $l'_2 = 6$ M^{-2} were used. The following stability constants were obtained:

$$\beta_1 = 98.5 \pm 3\ \mathrm{M}^{-1}$$
$$\beta_2 = (1.9 \pm 0.2) \times 10^3\ \mathrm{M}^{-2}$$
$$\beta_3 = (8 \pm 3) \times 10^3\ \mathrm{M}^{-3}$$

From eqn. (6) a value of $\beta_2 = 1.86 \times 10^3$ (with the assumption $l_2' = 0$) was obtained.

The americium-glycolate system

The experimental values of φ as a function of $[\mathrm{A}^-]$ and C_M' are given in Fig. 2 and the functions used for computing the stability constants in Table 2. The pH of the glycolate buffers was about one unit lower than that of the acetate buffers and the two corrections to the C_A-values (*vide supra* p. 1697) had to be applied. These corrections were checked in a few cases by determining the hydrogen ion concentration of the solutions equilibrated with ion exchanger. The $[\mathrm{A}^-]$-values determined by the two methods differed by 0.5 % at most. Values of φ_1^0 and f^0 were determined as described earlier. The following values were obtained:

$$\varphi_1^0 = 630 \pm 5\ \mathrm{M}^{-1}$$
$$f^0 = (3.42 \pm 0.03) \times 10^5\ \mathrm{M}^{-2}$$

In the final approximation of β_1 from eqn. (9) values of $\beta_2 = 7.2 \times 10^4\ \mathrm{M}^{-2}$, $\beta_3 = 2 \times 10^6\ \mathrm{M}^{-3}$, $\beta_4 \approx 5 \times 10^6\ \mathrm{M}^{-4}$ (estimated from the position of φ_max in the anion exchange experiment, *vide infra* p. 1708) and $l_2' = 150\ \mathrm{M}^{-2}$ were used.

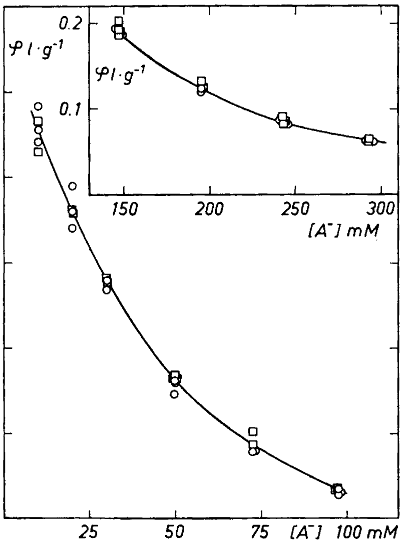

Fig. 3. φ as a function of $[\mathrm{A}^-]$ for the Am^{3+}-thioglycolate system. $C_\mathrm{M}' = 1.14 \times 10^{-7}$ M □, $C_\mathrm{M}' = 2.56 \times 10^{-7}$ M ○.

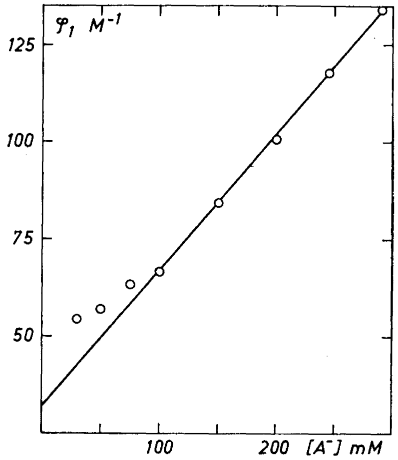

Fig. 4. $\varphi_1 = f\,([\mathrm{A}^-])$ for the Am^{3+}-thioglycolate system.

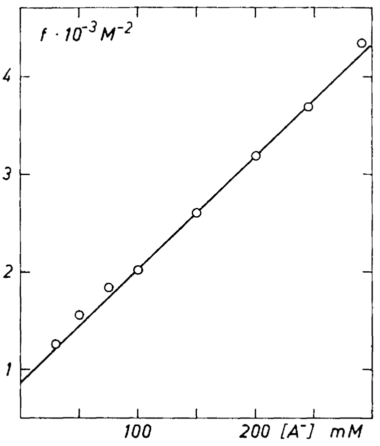

Fig. 5. The function f for the Am^{3+}-thioglycolate system.

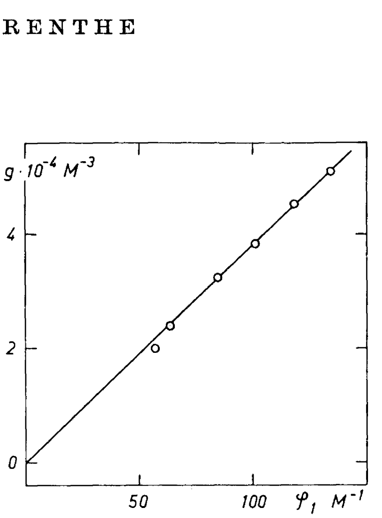

Fig. 6. g as a function of φ_1 for the Am^{3+}-thioglycolate system.

The stability constants obtained were:

$$\beta_1 = 657 \pm 15 \text{ M}^{-1}$$
$$\beta_2 = (7.2 \pm 1) \times 10^4 \text{ M}^{-2}$$
$$\beta_3 = (2 \pm 1) \times 10^6 \text{ M}^{-3}$$

The americium-thioglycolate system

The experimental material is given in Fig. 3 and the functions φ_1, f and g in Table 3. In Figs. 4, 5 and 6 the functions φ_1, f and g are plotted. It is obvious from the figures that the functions deviate from the expected course at lower values of C_A'. This was probably due to an oxidation of the ligand to dithiodi-

Table 1. Corresponding values of [A⁻], φ, φ_1, f and g for the americium acetate system. The values of β_1 in column 5 have been computed from eqn. (9) using a value of β_2 = 1.9×10^3 M^{-2}, $\beta_3 = 10^4$ M^{-3} and $l_2' = 6$ M^{-2}.

[A⁻] mM	φ $l \cdot g^{-1}$	φ_1 M^{-1}	$f \times 10^{-4}$ M^{-2}	β_1 M^{-1}	$g \times 10^{-5}$ M^{-3}
0	2.51	*94*	*0.74*		*−0.8*
8.00	1.37	105	0.85	108.6	1.99
16.00	0.897	112	0.94	120.0	2.24
22.00	0.660	127	1.05	97.7	2.26
33.00	0.430	147	1.22	96.8	2.61
50.00	0.273	164	1.40	101.1	2.99
68.00	0.175	196	1.69	99.4	3.57
100.0	0.101	239	2.10	99.8	4.37
135.0	0.059	308	2.73	98.4	5.64
170.0	0.0375	388	3.47	97.6	7.11
215.0	0.0245	472	4.26	97.3	8.68

Table 2. Corresponding values of $[A^-]$, φ, φ_1, f and g for the americium-glycolate system. The values of β_1 in column 5 have been computed from eqn. (9) using values of $\beta_2 = 7.4 \times 10^4$ M^{-2}, $\beta_3 = 2 \times 10^6$ M^{-3}, $l_2' = 150$ M^{-2} and $\beta_4 \approx 5 \times 10^6$ M^{-4}

$[A^-]$ mM	φ $l \cdot g^{-1}$	φ_1 M^{-1}	$f \times 10^{-5}$ M^{-2}	β_1 M^{-1}	$g \times 10^{-5}$ M^{-3}
0	2.51	*630*	*3.42*		*−1.8*
1.50	1.21	715	3.94	645	4.87
3.00	0.739	799	4.47	655	5.53
5.00	0.450	916	5.20	655	6.38
7.00	0.307	1025	5.89	659	7.20
10.00	0.197	1174	6.85	665	8.30
15.00	0.107	1497	8.85	658	10.59
20.00	0.0670	1823	10.89	657	12.92
30.00	0.0344	2399	14.52	658	17.07
40.00	0.0200	3113	18.99	655	22.20
50.00	0.0135	3698	22.68	655	26.41
55.50	0.0113	3984	24.50	656	28.47
65.00	0.0083	4637	28.62	655	33.17
80.00	0.0054	5798	35.89	652	41.50

glycolic acid. The oxidation was about 10 % in the solutions with the lower values of C_A' and 1—2 % in the solutions with higher C_A'-values. The presence of the oxidation product means that the results for this particular ligand are more uncertain than those for the other two systems. The stability constants however have been computed as before. The following values were obtained:

$$\beta_1 = 35.5 \pm 5 \text{ M}^{-1}$$
$$\beta_2 = 400 \pm 100 \text{ M}^{-2}$$
$$\beta_3 = 0 \text{ M}^{-3}$$

β_1 was computed from eqn. (9) using values of $\beta_3 = \beta_4 = l_2' = 0$.
β_2 was also computed from eqn. (6) with the value of $l_2' = 0$. A value of $\beta_2 = 400$ M^{-2} was obtained.

Table 3. Corresponding values of $[A^-]$, φ, φ_1, f and g for the americium-thioglycolate system. β_1 has been computed from eqn. (9) using a value of $\beta_3 = 0$ and $l'_2 = 0$.

$[A^-]$ mM	φ $l \cdot g^{-1}$	φ_1 M^{-1}	f M^{-2}	β_1 M^{-1}	$g \times 10^{-4}$ M^{-3}
0	2.51	*35*	*860*		*0.00*
10	1.39	80.6			
20	1.15	59.6			
30	0.950	54.7	1258		
50	0.650	57.2	1559	31.5	2.01
75	0.435	63.6	1845	34.4	2.39
100	0.327	66.8	2019	36.4	2.58
150	0.184	84.3	2621	35.7	3.23
200	0.119	100.5	3188	35.5	3.84
245	0.084	117.9	3787	35.3	4.50
290	0.063	133.9	4346	35.2	5.11

Table 4. The distribution coefficients l_j and l'_j for the various americium species.

Ligand	l_0 $\mathrm{l \cdot g^{-1}}$	l_1 $\mathrm{l \cdot g^{-1}}$	l'_1 $\mathrm{M^{-1}}$	$l_2 \times 10^3$ $\mathrm{l \cdot g^{-1}}$	l'_2 $\mathrm{M^{-2}}$
Acetate	2.51	0.11	4.5	7.9	6
Glycolate	2.51	0.10	30	5.3	150
Thioglycolate	2.51	~0.1	~1	0	0

The distribution coefficients l'_j and l_j for the various species in the solutions are given in Table 4. The sorption of the complex species is very much lower than the sorption of the hydrated Am^{3+}-ion. This means that when the first complex is transformed to the second and higher complexes, the absolute decrease in φ will be small and for higher $[A^-]$-values smaller than the random errors. These will thus seriously affect the determination of β_3 and make it impossible to compute any constants for complexes higher than the third.

CALCULATION OF STABILITY CONSTANTS FROM POTENTIOMETRIC DATA

The following notation was used:

$[H^+]$, $[H^+]'$ = the hydrogen ion concentration in buffer solution with and without metal ion.
C_H = the concentration free perchloric acid in the metal perchlorate solution.
C'_{HA}, C'_A = the stoichiometric concentrations of acid and sodium salt in the buffer solutions.
C_A = the actual total concentration of the ligand A, where $C_A = C'_A + [H^+] - C_H$.
$[M^{3+}]$, $[A^-]$ = the concentration of free central ion and free ligand.
β_j = the stability constant of the j:th mononuclear complex.

$$\bar{n} = \frac{C'_A + [H^+] - C_H - [A^-]}{C_M} \tag{10}$$

$$[A^-] = \frac{[H^+]'}{[H^+]} \cdot \frac{(C'_A + [H^+]')(k \cdot C'_A + C_H - [H^+])}{k \cdot C'_A - [H^+]'} \tag{11}$$

If only mononuclear complexes are formed the following expression is valid

$$\ln X([A^-]_j) = \int_0^{[A^-]_j} (\bar{n}/[A^-]) \mathrm{d}[A^-] \tag{12}$$

$X([A^-]_j)$ and k are the same as before (*vide supra*, pp. 1696, 1695). For details of the method of calculation the reader is referred to Refs. [1a–1c].

EXPERIMENTAL

Chemicals used. Europium perchlorate was prepared from Eu_2O_3 (purity > 99.8 %, from Lindsay Chemical Co) by treatment with perchloric acid. The excess of acid was evaporated with a heating lamp. The stock solution was standardized by an ion exchange analysis. The other chemicals were the same as used in the cation exchange investigation.

Procedure. The emf E of galvanic cells of the following composition were measured:

$$\begin{array}{c|c|c|l|c}
 & & & C_{\mathrm{M}} \text{ mM Eu (ClO}_4)_3 & \\
 & 10.01 \text{ mM HClO}_4 & 0.5\text{ M} & C_{\mathrm{H}} \text{ mM H ClO}_4 & \\
\text{Au} & I = 0.5\text{ M} & & C'_{\mathrm{A}} \text{ mM NaA} & \text{Au} \\
 & & \text{Na ClO}_4 & C'_{\mathrm{HA}} = k \cdot C'_{\mathrm{A}} \text{ mM HA} & \\
 & & & \quad I = 0.5\text{ M} & \\
 & \text{Quinhydrone} & & \quad \text{Quinhydrone} &
\end{array}$$

Here A means acetate or glycolate. For the thioglycolate system the quinhydrone electrode could not be used and so the right half-cell had to be replaced according to:

$$\begin{array}{c|l|l}
 & C_{\mathrm{M}} \text{ mM Eu (ClO}_4)_3 & \\
 & C_{\mathrm{H}} \text{ mM H ClO}_4 & \text{glass} \\
\text{S} & C'_{\mathrm{A}} \text{ mM NaA} & \text{electrode} \\
 & C'_{\mathrm{HA}} = k \cdot C'_{\mathrm{A}} \text{ mM Ha} & \\
 & \quad \text{I} = 0.5\text{ M} &
\end{array}$$

The solution in the right half-cell was prepared by adding known amounts of a buffer solution T to 3 ml of a solution S. The small volumes of T were added from an Agla micrometer syringe with an error of 0.5 % at most.

The solutions S and T had the following composition:

$$\text{S} \begin{cases} C_{\mathrm{M}} \text{ mM Eu (ClO}_4)_3 \\ C_{\mathrm{H}} \text{ mM H ClO}_4 \\ \\ I = 0.5\text{ M} \end{cases} \qquad \text{T} \begin{cases} C_{\mathrm{M}} \text{ mM Eu (ClO}_4)_3 \\ C_{\mathrm{H}} \text{ mM H ClO}_4 \\ C'_{\mathrm{A}} \text{ mM NaA} \\ C'_{\mathrm{HA}} = k \,.\, C'_{\mathrm{A}} \text{ mM HA} \\ I = 0.5\text{ M} \end{cases}$$

The solutions were mixed by passing nitrogen through the right half-cell.

In all the potentiometric titrations described here only one buffer solutions (a 1—1 buffer) was used. For the lanthanide acetate and glycolate systems Sonesson has shown that buffer solutions with different ratios of acid salt give the same $\bar{n}$-values for the same concentration free ligand. Consequently neither the acetate nor the glycolate systems form complexes with HA. This is certainly true also of the europium systems investigated here.

Titrations were also made at $C_{\mathrm{M}} = 0$. The measured emfs were in this case E′. From the titrations with and without central ion present, $[\mathrm{H}^+]/[\mathrm{H}^+]'$ was computed from the following expression:

$$E' - E = E_{\mathrm{A}} = 58.16 \log [\mathrm{H}^+]/[\mathrm{H}^+]' \tag{13}$$

Each titration was repeated at least twice and the reproducibility of the potentials was in general within ± 0.2 mV.

RESULTS

The europium-acetate system

E' and the dissociation constant of acetic acid were determined as a function of the total concentration of ligand C'_{A} and the results are given in Table 5.

Titrations were performed at two values of C_{M} (40 mM and 20 mM). It turned out that $\bar{n}/[\mathrm{A}^-]$ as a function of $[\mathrm{A}^-]$ was dependent on C_{M} (*cf*. Fig. 7). This might be caused by polynuclear complexes, qualitative changes of the ionic medium, when C_{M} is varied, or changes of the ionic strength caused by the complex formation. By extrapolation to $C_{\mathrm{M}} = 0$, these possible causes of the variation have all been eliminated and β_j can be calculated from the functions X.

Table 5. E' and the dissociation constant K_c for the various ligands as a function of C'_A.

Acetate buffer			Glycolate buffer			Thioglycolate buffer		
C'_A mM	E' mV	$K_c \times 10^5$ M	C'_A mM	E' mV	$K_c \times 10^4$ M	C'_A mM	E' mV	$K_c \times 10^4$ M
5.00	146.7	3.04	2.48	96.2	2.69	4.95	87.7	3.54
14.70	146.7	3.02	4.90	93.9	2.72	9.80	86.3	3.53
24.04	146.7	3.01	9.62	92.6	2.74	14.56	85.7	3.55
41.67	146.7	3.01	14.15	92.2	2.75	28.30	85.5	3.49
69.57	146.8	3.00	18.52	91.9	2.74	53.57	85.7	3.43
119.2	147.1	2.97	26.79	91.7	2.74	90.16	86.1	3.35
170.0	147.4	2.93	34.48	91.6	2.74	142.9	86.8	3.25
208.8	147.7	2.89	54.69	91.6	2.72	187.5	88.0	3.09
			76.39	91.6	2.72	250.0	89.5	2.91
			93.75	91.7	2.70			
			111.1	91.7	2.70			
			136.4	91.9	2.68			

The functions X, X_1 and X_2 are given in Table 6 for different values of [A$^-$]. All values are referred to solutions with $C_M = 0$. The stability constants were determined by the standard graphical method. The following results were obtained:

Table 6. The functions X, X_1 and X_2 for the europium-acetate system.

[A$^-$] mM	$\int_0^{[A^-]} \frac{\bar{n}}{[A^-]} d[A^-]$	X	X_1 M^{-1}	$X_2 \times 10^{-3}$ M^{-2}
0.00		*1.000*	*87.5*	*1.54*
1.00	41.75	1.087	87.0	
3.00	122.00	1.276	92.0	
5.00	195.90	1.480	96.0	
7.00	264.00	1.696	99.4	
10.00	357.00	2.042	104.2	1.67
13.00	441.75	2.419	109.2	1.67
16.00	519.90	2.829	114.3	1.68
20.00	615.60	3.426	121.3	1.69
25.00	722.97	4.246	129.8	1.69
30.00	820.47	5.161	138.7	1.71
40.00	994.97	7.315	157.9	1.76
50.00	1146.60	9.906	178.1	1.81
60.00	1281.97	12.99	199.8	1.87
70.00	1405.47	16.63	223.3	1.94
85.00	1571.22	23.16	260.7	2.04
100.0	1717.09	31.01	300.1	2.13
120.0	1890.14	43.83	356.9	2.25
140.0	2040.89	59.25	416.1	2.35

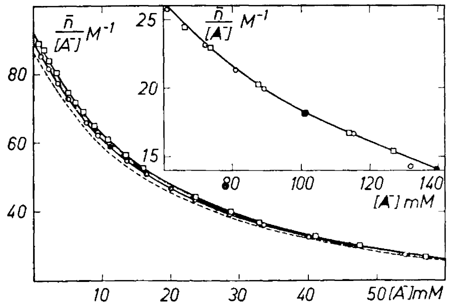

Fig. 7. $\bar{n}/[A^-]$ as a function of $[A^-]$ for the europium-acetate system. □ $C_M = 38.98$ mM, ○ $C_M = 19.49$ mM. The dashed curve was obtained on extrapolation to $C_M = 0$.

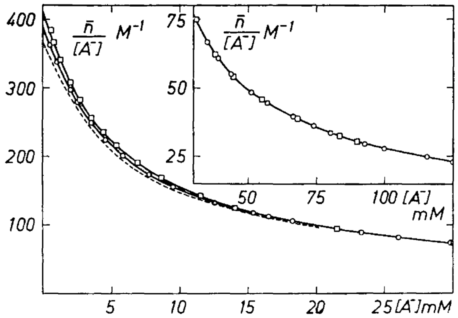

Fig. 8. $\bar{n}/[A^-]$ as a function of $[A^-]$ for the europium glycolate system. □ $C_M = 39.60$ mM, ○ $C_M = 19.80$ mM. The dashed curve was obtained on extrapolation to $C_M = 0$.

$$\beta_1 = 87.5 \pm 1.0 \text{ M}^{-1}$$
$$\beta_2 = (1.54 \pm 0.05) \times 10^3 \text{ M}^{-2}$$
$$\beta_3 = (6.1 \pm 0.3) \times 10^3 \text{ M}^{-3}$$

The europium-glycolate system

This system was investigated in the same way as the acetate system. The experimental values of E' as a function of C_A' are given in Table 5. In Fig. 8 the experimental values of $\bar{n}/[A]$ as a function of $[A^-]$ for $C_M = 40$ mM, 20 mM and 0 mM (extrapolated) are given. The functions necessary for computing the stability constants are given in Table 7. The following stability constants were obtained:

$$\beta_1 = 369 \pm 3 \text{ M}^{-1} \quad ; \quad \beta_3 = (8.1 \pm 0.7) \times 10^5 \text{ M}^{-3}$$
$$\beta_2 = (4.1 \pm 0.3) \times 10^4 \text{ M}^{-2} \quad ; \quad \beta_4 = (2.3 \pm 0.5) \times 10^6 \text{ M}^{-4}$$

The europium-thioglycolate system

The ligand is oxidized by quinhydrone and therefore $[H^+]$ had to be measured by the glass electrode. The emfs were measured with a Radiometer type PHM 4 b pH-meter. E' and E were determined as a function of C_A' as before. Because the complex formation was so weak that at low C_M the E_A-values could not be determined with any accuracy (the E_A-values are small, *cf.* Table 8), only one value of C_M (= 40 mM) was used. The decrease in ionic strength caused by the complex formation was corrected by the addition of solid sodium perchlorate. The titrations could usually be reproduced within ± 0.2 mV. Before and after each titration it was checked that the asymmetry potential of the glass electrode had not changed.

As the ligand was easily oxidized, the experiments were carried out in a nitrogen atmosphere but nevertheless a slight oxidation could not be avoided, amounting to 1—2 % in 5 h at most.

Table 7. The functions X, X_1, X_2 and X_3 for the europium glycolate system.

$[A^-]$ mM	$\int_0^{[A^-]_j} \frac{\bar{n}}{[A^-]} \cdot d[A^-]$	X	X_1 M^{-1}	$X_2 \times 10^{-4}$ M^{-2}	$X_3 \times 10^{-5}$ M^{-3}
0.00		*1.000*	*369*	*4.10*	*8.1*
1.00	69.45	1.415	415		
2.00	130.38	1.919	460		
3.00	184.45	2.515	505		
5.00	276.85	3.992	598	4.58	
7.00	353.90	5.869	696	4.67	
11.00	479.30	10.99	908	4.90	
17.00	626.60	22.95	1291	5.42	
25.00	777.60	48.82	1913	6.18	5.20
35.00	924.20	101.6	2874	7.16	8.74
50.00	1094.39	237.9	4738	8.74	9.28
70.00	1266.39	562.4	8020	10.93	9.76
90.00	1402.39	1110	12322	13.28	10.20
125.00	1589.48	2829	22620	17.80	10.96

The experimental results for the various titrations are given in Tables 5 and 8. The functions used for the computation of the stability constants are given in Table 9. The following results were obtained:

$$\beta_1 = 35.2 \pm 1.0 \text{ M}^{-1}$$
$$\beta_2 = 188 \pm 10 \text{ M}^{-2}$$

A slight variation in the $\bar{n}/[A^-]$-values with C_M was found for both the acetate and glycolate systems (see Figs. 7 and 8). This may be caused either by polynuclerar complexes or by changes in the medium. Sonesson did not find any formation of polynuclear complexes for the rare earths before dysprosium, so the second explanation is perhaps the more probable, particularly

Table 8. Experimental values of C'_A, E, E_A, $[A^-]$ and $\bar{n}/[A^-]$ for the europium thioglycolate system (C_M = 39.60 mM).

C'_A mM	E mV	E_A mV	$[A^-]$ mM	$\bar{n}/[A^-]$ M^{-1}
0.00	77.3		0.00	*35.2*
4.26	66.1	22.1	1.92	34.2
12.38	65.3	20.3	5.72	30.6
23.64	65.8	19.0	11.3	28.0
37.14	66.7	17.3	19.0	24.5
49.19	68.1	15.8	26.6	21.7
65.00	69.5	14.3	37.2	19.0
90.43	71.9	12.2	56.2	15.5
118.2	73.9	10.8	77.5	13.3
140.0	75.4	9.8	95.4	11.8
173.3	77.5	8.3	125	9.7
204.3	79.3	7.2	154	8.2

Table 9. The functions X and X_1 for the europium-thioglycolate system.

$[\mathrm{A}^-]$ mM	$\int_0^{[\mathrm{A}^-]_j} \frac{\bar{n}}{[\mathrm{A}^-]} \mathrm{d}[\mathrm{A}^-]$	X	X_1 M^{-1}
0.00		*1.000*	*35.2*
5.00	32.85	1.179	35.8
10.00	62.90	1.370	37.0
15.00	90.40	1.571	38.1
20.00	115.65	1.782	39.1
40.00	199.15	2.707	42.7
60.00	266.35	3.788	46.5
80.00	323.15	5.031	50.4
100.0	371.75	6.417	54.2
120.0	414.35	7.940	57.8
140.0	452.35	9.600	61.4
155.0	478.15	10.92	64.0

as the central ion in this investigation gives a large contribution to the ionic strength of the solutions. This was not the case in Sonessons study because of the higher ionic strength used by him (2 M instead of 0.5 M in the present investigation).

For the thioglycolate system it was not possible to make corrections for these changes in the medium (except for the decrease in ionic strength caused by the complex formation). This fact and the slight oxidation of the ligand imply that the stability constants are more uncertain for this particular system. The maximum deviations are expected to be within the error limits given previously.

INVESTIGATION OF THE EUROPIUM AND AMERICIUM ACETATE AND GLYCOLATE SYSTEMS WITH AN ANION EXCHANGER

A theory for the distribution of a central ion M between a solution phase containing a ligand A and an anion exchange resin saturated with A has been given by Fronæus[8]. This paper should be consulted for further details about the theoretical treatment.

The distribution of the charged species is given by the Donnan equation:

$$[\mathrm{M}^{3+}]_\mathrm{R} \cdot [\mathrm{A}^-]^3_\mathrm{R} = K[\mathrm{M}^{3+}] \cdot [\mathrm{A}^-]^3$$

where the constant K also includes the activity coefficients of the ion species in the two phases. The following relation can be derived:

$$\varphi = \frac{C_\mathrm{MR}}{C_\mathrm{M}} = K \cdot \frac{X([\mathrm{A}^-]_\mathrm{R})}{[\mathrm{A}^-]^3_\mathrm{R}} \cdot \frac{[\mathrm{A}^-]^3}{X([\mathrm{A}^-])} = l_3 \cdot \frac{\alpha_3}{\alpha_{3\mathrm{R}}} \tag{14}$$

where X ($[\mathrm{A}^-]$) and X ($[\mathrm{A}^-]_\mathrm{R}$) are the functions X for the solution and the resin phases respectively. l_3 is the Nernst distribution coefficient for the third uncharged complex and $l_3 = K \cdot \beta_{3\mathrm{R}} \cdot \beta_3^{-1}$.

If anionic complexes are formed, φ should first increase with increasing values of $[A^-]$, then pass through a maximum at the value of $[A^-]$, where $\bar{n} = 3$, in the outer solution and finally decrease again. On the other hand, if no anionic complexes are formed, φ is expected to increase uniformly with increasing values of $[A^-]$. Part of the sorption C_{MR} on the resin at lower values of $[A^-]$ may be due to a surface sorption, as has been pointed out by Froænus [8]. This surface sorption might be estimated by studying a system, where no anionic complexes are formed, in this case the acetate complexes. From Table 10 one can see that the surface sorption will cause the φ-values for the acetate systems to decrease, instead of increasing, as could be expected from the theory.

EXPERIMENTAL

A 2.86×10^{-2} mM Eu $(ClO_4)_3$ solution containing the isotopes ^{152,154}Eu was prepared by dissolving 50 mg irradiated Eu_2O_3 (from A.E.R.E. Harwell) in perchloric acid. A solution of the perchlorate was then prepared as described before. A water solution of Am^{3+} was prepared by dilution of the stock solution. The excess of acid was $\approx$ 0.5 mM.

The anion exchanger Dowex 1 × 4, 50—100 mesh was saturated with acetate or glycolate by passing the acids through a column of the ion exchanger in the hydroxyl form. For the value of $v \cdot m^{-1} = 25 \times 10^{-3}\ l \cdot g^{-1}$ used in the following experiments, the swelling factors of the resin in the acetate and glycolate forms were determined to 0.96 and 0.99, respectively. They were constant in the concentration range investigated here.

The experimental procedure was the same as that in the cation exchange experiments. No additional sodium perchlorate was used in the buffer solutions in order to avoid exchange of perchlorate from the solution for ligand from the resin. Because of the very low distribution coefficients it was not possible to obtain sufficiently accurate values of φ by measuring C'_M and C_M. Instead, the resin phase had to be analysed in the way described by Sonesson [1d]. Both the americium and europium concentrations were determined radio metrically as described earlier (*vide supra*, p. 1697).

RESULTS

The experimental results are given in Table 10. In Fig. 9 the distribution coefficient φ_{corr} (the distribution coefficient corrected for the surface sorption) is plotted *versus* $[A^-]$. Both europium and americium were quite strongly sorbed at low acetate concentrations while the φ-values were constant (within

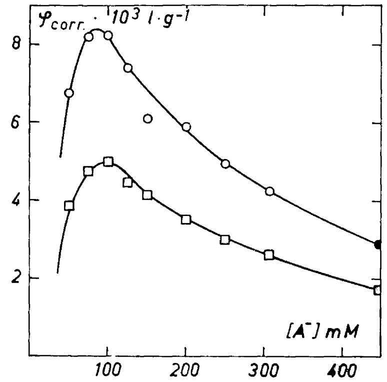

Fig. 9. The anion exchange distributions $\varphi_{corr} = f([A^-])$, for the europium and americium glycolate systems. ○ the Am^{3+}-glycolate system, □ the Eu^{3+}-glycolate system.

Table 10. The anion exchange distributions for acetate and glycolate systems of europium and americium.

$[A^-]$ mM	$Eu^{3+}-Ac^-$	$Am^{3+}-Ac^-$	$[A^-]$ mM	$Eu^{3+}-glyc^-$	$Am^{3+}-glyc^-$
	$\varphi \times 10^3\ l \cdot g^{-1}$	$\varphi \cdot 10^3\ l \cdot g^{-1}$		$\varphi \cdot 10^3\ l \cdot g^{-1}$	$\varphi \cdot 10^3\ l \cdot g^{-1}$
25	3.95	9.74	25	3.95	9.75
50	0.95	2.22	50	4.83	8.98
75	0.50		75	5.26	9.22
125	0.48	0.69	100	5.49	8.95
250		0.26	125	4.97	8.04
350		0.62	150	4.64	6.73
500	0.47	0.61	200	4.02	6.51
650		0.57	250	3.52	5.56
900		0.53	311	3.12	4.80
			444	2.23	3.43

the experimental error) between $[A^-] = 100$ and 900 mM. Thus no anionic complexes are formed in the resin phase but this does not necessarily imply that no anionic species are present in the solution (see Ref.[1d] p. 1451).

Both the europium and americium glycolate systems have maxima which appear very clearly, when the surface sorption (estimated from the acetate measurements) has been corrected for. The maximum value of φ is much lower for europium than for americium and appears for europium at a higher value of $[A^-]$. It is safe to conclude that anionic glycolate complexes are formed both by europium and americium. In the case of europium this was found already by the potentiometric measurements. The low values of the distribution coefficient for the glycolate system indicate that it is difficult for the anionic complexes to be formed in the resin phase, presumably because of a steric hindrance.

According to Fronæus [8] the values of $\varphi_{\max}$ for systems of equal type should give a qualitative measure of the strength of the anionic complexes. The higher $\varphi_{\max}$ value for the americium glycolate system and the fact that the maximum appears at a slightly lower $[A^-]$-value indicate that americium gives stronger complexes than europium, an already established fact, based on the ion exchange and potentiometric measurements described before. The thioglycolate systems could not be investigated by anion exchangers as the ligand was attacked by the resin.

DISCUSSION

The stability constants for the complexes investigated are collected in Table 11. It is evident that americium forms stronger complexes than europium for all the systems investigated here. This difference is most pronounced for the glycolates, where the stability constants β_j for the americium complexes are $\approx 80\ \%$ greater than those for the corresponding europium complexes. This fact can also be observed in an earlier investigation [3] where cation exchanger columns loaded with europium and americium have been eluted with glycolate

Table 11. The formation constants β_j for the acetate, glycolate and thioglycolate system of europium and americium.

Central ion →	Eu^{3+}				Am^{3+}			
Ligand ↓	β_1 M^{-1}	β_2 M^{-2}	β_3 M^{-3}	β_4 M^{-4}	β_1 M^{-1}	β_2 M^{-2}	β_3 M^{-3}	β_4 M^{-4}
Acetate	87.5±1.0	$(1.54 \pm 0.05) \times 10^3$	$(6.1 \pm 0.3) \times 10^3$	no evidence of anionic complexes	98.5±3.0	$(1.9 \pm 0.2) \times 10^3$	$(8 \pm 3) \times 10^3$	no evidence of anionic complexes
Glycolate	369±3	$(4.1 \pm 0.3) \times 10^4$	$(8.1 \pm 0.7) \times 10^5$	$(2.3 \pm 0.5) \times 10^6$	657±15	$(7.2 \pm 1.0) \times 10^4$	$(2 \pm 1) \times 10^6$	anionic complexes formed
Thioglycolate	35.2±1.0	188±10	0		35.5±5	400±100	0	

buffers and the position of the elution peaks for the two elements has been determined. From the position of the elution peaks the separation factor $\alpha_{\mathrm{Am}}^{\mathrm{Eu}}$ was determined where:

$$\alpha_{\mathrm{Am}}^{\mathrm{Eu}}=\frac{\varphi_{\mathrm{Eu}}}{\varphi_{\mathrm{Am}}}=\frac{{}^{\mathrm{Eu}}l_0 \cdot (1+{}^{\mathrm{Eu}}l'_1 \cdot [\mathrm{A}^-]+{}^{\mathrm{Eu}}l'_2 \cdot [\mathrm{A}^-]^2)}{{}^{\mathrm{Am}}l_0 \cdot (1+{}^{\mathrm{Am}}l'_1 \cdot [\mathrm{A}^-]+{}^{\mathrm{Am}}l'_2 \cdot [\mathrm{A}^-]^2)} \cdot \frac{X^{\mathrm{Am}}}{X^{\mathrm{Eu}}}$$

Neither the composition of the buffer solutions in Ref. [3] nor the values of l_1' and l_2' for the europium and americium complexes are known. This fact makes it impossible to make a quantitative comparison between the two methods. If the ratio between the activity factors for the europium and americium species does not vary with the ionic strength and if the distribution coefficients l_1' and l_2' are approximately the same for both the europium and americium glycolates, then the ratio $X^{\mathrm{Am}}/X^{\mathrm{Eu}}$ can be computed with the use of the values of the separation factor $\alpha_{\mathrm{Am}}^{\mathrm{Eu}} = 0.69 \pm 0.16$ determined by Stewart [3]. ${}^{\mathrm{Eu}}l_0$ was determined in a separate experiment and was equal to $1.26\ l \cdot g^{-1}$.
Thus:

$$\frac{X^{\mathrm{Am}}}{X^{\mathrm{Eu}}}= (0.69 \pm 0.16) \times \frac{2.51}{1.26} = 1.38 \pm 0.32$$

This ratio is only valid for the constant but unknown value of $[\mathrm{A}^-]$ in the buffer solution used by Stewart.

The main factors, affecting the relative stability of the europium and the americium complexes investigated here, are the ionic radius and the properties of the outer electron shells. If the radius factor is the more important one, then europium with its smaller ionic radius is expected to form stronger complexes than americium. This was not the case for the system in the present investigation (see Table 11). As to the properties of the outer electron shells, both elements have the same structure apart from a difference of one unit in the principal quantum number.

The 5f orbitals are more affected by the environment [9] than the 4f orbitals, which means that the former are more available for bond formation. Americium is thus expected to form stronger complexes than europium, if the properties of the outer electron shells are more important than the radius factor. This seems to be the case for the systems in this investigation.

The strongly electropositive lanthanide and actinide elements are according to Ahrland *et al.* [10] class A acceptors and are thus expected to have a greater affinity to oxygen than to sulphur. Glycolate forms stronger complexes than thioglycolate with both europium and americium (see Table 11). From the magnitude of the stability constants it is safe to conclude that the hydroxyl oxygen of the glycolate ion is coordinated to the central ion. A five membered chelate ring is thus formed by the using of this oxygen and the carboxylate group. It is not possible to decide whether the sulphur of the thioglycolate ion is coordinated or not, only that the affinity to sulphur is much smaller than that to oxygen for both europium and americium in accordance with the views given by Ahrland *et al.*

The fact that thioglycolate is even weaker bonded than acetate must be correlated [11] with the greater acidity of thioglycolic acid as compared to acetic acid.

In order to compare Sonessons data[1a-1c] (which were determined at an ionic strength $I = 2$ M) with those of the present investigation, it was necessary to estimate the influence of the ionic strength on the stability constants. The gadolinium systems were assumed to be representative of this variation for all rare earths. For the acetate system no appreciable differences between the stability constants at $I = 0.5$ M and $I = 2$ M were found. For the glycolate systems the β_1-values for $I = 0.5$ M should be decreased by 10 %, the β_2- and β_3-values by 20 % in order to be comparable with the corresponding values at $I = 2$ M. From a comparison with Sonesson's data it is evident that the stability constants of both the acetate and glycolate complexes of Eu^{3+} have values between the corresponding values of Sm^{3+} and Gd^{3+}.

It can be pointed out that the dithiodiglycolate complexes of tervalent americium must be rather weak. The concentration of the ligand is much higher than that of the central ion and the stability constants for the thioglycolate systems are still of the right order of magnitude (estimated from the stability constants of the Eu^{3+}-thioglycolate system). For europium the stability constants can not be influenced more than 1—2 % by the presence of dithiodiglycolate even if the complexes were very stable.

This investigation has been supported by a grant form *Statens Råd för Atomforskning*. The author is indebted to Professor Sture Fronæus and Dr. Sten Ahrland for many fruitful discussions.

REFERENCES

1 a. Sonesson, A. *Acta Chem. Scand.* **12** (1958) 165.
1 b. Sonesson, A. *Ibid.* **12** (1958) 1937.
1 c. Sonesson, A. *Ibid.* **13** (1959) 998.
1 d. Sonesson, A. *Ibid.* **13** (1959) 1437.
1 e. Sonesson, A. *Ibid.* **14** (1960) 1495.
2 a. Fronæus, S. *Acta Chem. Scand.* **5** (1951) 859.
2 b. Fronæus, S. *Svensk Kem. Tidskr.* **64** (1952) 317.
2 c. Fronæus, S. *Ibid.* **65** (1953) 19.
3. Stewart, D. C. *Proc. Intern. Conf. Peaceful Uses Atomic Energy*, Geneva 1955, Vol. 7, p. 321.
4. Holm, L. W., Choppin, G. R. and Moy, D. *J. Inorg. & Nuclear Chem.* **19** (1961) 251.
5. Grenthe, I. and Norén, B. *Acta Chem. Scand.* **14** (1960) 2216.
6. Klason, P. and Carlson, T. *Ber.* **39** (1906) 2216.
7. Ahrland, S., Grenthe, I. and Norén, B. *Acta Chem. Scand.* **14** (1960) 1059.
8. Fronæus, S. *Svensk Kem. Tidskr.* **65** (1953) 1.
9. Katz, J. J. and Seaborg, G. T. *The Chemistry of the Actinide Elements*, Methuen, London 1957, pp. 463—470.
10. Ahrland, S., Chatt, J. and Davies, M. R. *Quart Rev.* 265, vol. XII No. 3, 1958.
11. Lewis, J. and Wilkins, R. G. *Modern Coordination Chemistry*, Interscience New York 1960, pp. 51—57.

Received January 31, 1962.