On the Complex Chemistry of the Tervalent Rare-Earth Ions

III. The Glycolate Systems

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The complexity constants of the glycolate systems of ten rare earths have been determined by potentiometric measurements similar to those used previously in the investigation of the acetate systems [1,2]. The results are given in Tables 5 and 6 and Fig. 5.

The glycolate systems show a considerably higher complexity than the corresponding acetate systems. This is probably due to the formation of chelates in the glycolate systems. The value of the first complexity constant, $\beta_1 = [MA] \cdot [M]^{-1} \cdot [A]^{-1}$, increases from La to Sm. For the Gd-system a somewhat lower value of β_1 is found than for the Sm-system. From Gd to Yb, however, β_1 increases again, contrary to the variation of β_1 for the corresponding acetate systems.

The potentiometric measurements show that the formation of anionic glycolate complexes must be assumed.

The neodymium glycolate system has also been investigated extinctiometrically. The complexity constants obtained in this way are in good agreement with those obtained potentiometrically.

The glycolate ion, $HO \cdot CH_2 \cdot COO^-$, contains a hydroxide group but has in other respects the same constitution as the acetate ion, $CH_3 . COO^-$. On account of the OH-group the glycolate ion has a more or less pronounced tendency to form chelates. A five-membered ring can be formed. In those cases where chelates are not formed, the glycolate solutions ought to show a lower degree of complexity than the corresponding acetate solutions, in as much as glycolic acid is stronger than acetic acid (*cf.* Sundén [3] and Ahrland [4]). If on the other hand chelates are formed, we would expect the first complexity constants (the very first one at least) to be greater than the constants of the corresponding acetate complexes.

Investigations indicating that the glycolate systems of the rare earths probably contain chelates are to be found in the literature (Jantsch and Grünkraut [5]), but no attempts to compute the complexity onstants have been made. In order to make possible a comparison between the complexity of the

corresponding acetate and glycolate systems, the investigation of the glycolate systems described in this paper has been performed in the same way as the investigation of the acetate systems reported in papers I [1] and II [2]. Thus all measurements have been made at 20°C and with an ionic strength of 2.0 M. The main method of investigation has been the potentiometric determination of the hydrogen-ion concentration in solutions with known total concentrations of rare-earth ions, glycolate ions and glycolic acid. As a check on the potentiometric investigations the neodymium glycolate system has been examined extinctiometrically in the way described in II for the erbium acetate system.

Concerning the symbols and the formulae used in the calculations, the reader is referred to I and II.

CHEMICALS USED

Glycolic acid ((Fluca puriss. and Kahlbaum puriss.) was dried *in vacuo* over concentrated H_2SO_4. Both preparations gave after drying the equivalent weight 76.1 (calc. 76.0).

A stock solution of glycolic acid * HAcOH and sodium glycolate NaAcOH in the proportion 2 M HAcOH: 2 M NaAcOH was prepared by partial neutralization of calculated amounts of dried acid by carbonate-free sodium hydroxide. Afterwards the concentrations of HAcOH and NaAcOH were checked.

Buffer solutions with $\delta = 1.0$, 2.5 and 4.0 were prepared from calculated amounts of the stock solution and dried glycolic acid. Sodium perchlorate from a stock solution was added to make $I = 2.0$ M. Besides, a buffer solution with the composition 0.387 M HAcOH, 1.107 M NaAcOH and $NaClO_4$ to make $I = 2.0$ M was used.

A. POTENTIOMETRIC MEASUREMENTS

The cells in which the electromotive forces were measured were of the following composition (Me^{3+} = the rare earth ion):

$$
\text{Au} \left| \begin{array}{c} \text{Quinhydrone} \\ \text{10.2 mM } HClO_4 \\ NaClO_4 \text{ to } I = 2.0 \text{ M} \end{array} \right| \begin{array}{c} \text{2.0 M} \\ NaClO_4 \end{array} \left| \begin{array}{l} \text{Quinhydrone} \\ C_M \text{ mM } Me(ClO_4)_3 \\ C_H = \nu \cdot C_M \text{ mM } HClO_4 \\ C'_A \text{ mM } NaAcOH \\ C'_{HA} = \delta \cdot C'_A \text{ mM } HAcOH \\ NaClO_4 \text{ to } I = 2.0 \text{ M} \end{array} \right| \text{Au} \quad (1)
$$

The solution of the right cell was prepared from a known volume of the rare-earth perchlorate solution S_1 and increasing volumes of the buffer solution S_2:

	S_1	S_2	
$Me(ClO_4)_3$	C°_M	0	mM
$HClO_4$	$C^\circ_H = \nu \cdot C^\circ_M$	0	mM
NaAcOH	0	C°_A	mM
HAcOH	0	$C^\circ_{HA} = \delta \cdot C^\circ_A$	mM
$NaClO_4$	$2\,000 - 6\,C^\circ_M - C^\circ_H$	$2\,000 - C^\circ_A$	mM

(2)

The relation between C_M and C'_A is given by

$$C_M = C^\circ_M (1 - C'_A \times 10^{-3}) \text{ mM} \qquad (3)$$

except in the case where $C^\circ_A = 1\,107$ mM.

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* AcOH⁻ = the glycolate ion.

Table 1. Determination of E' as a function of C_A' by the addition of glycolate buffers with different values of δ to a 2 M solution of sodium perchlorate.

$\delta = 0.350$			$\delta = 1.0$			$\delta = 4.0$	
C_A' mM	E' mV	$K_c \times 10^{+4}$	C_A' mM	E' mV	$K_c \times 10^{+4}$	E' mV	$K_c \times 10^{+4}$
10.96	129.2	1.79	9.90	102.9	1.77	68.4	1.82
21.71	128.8	1.80	19.61	102.1	1.80	67.0	1.85
			29.1	101.8	1.81	66.5	1.86
42.6	128.5	1.81	38.5	101.7	1.81	66.1	1.88
			56.6	101.6	1.81	65.6	1.90
72.4	128.4	1.81	74.1	101.5	1.82	65.2	1.93
109.7	128.2	1.83	99.1	101.3	1.83	64.7	1.96
			122.8	101.2	1.84	64.2	2.00
168.9	128.1	1.83	152.5	101.1	1.84	63.7	2.03
			200.0	100.9	1.86	62.9	2.09
287.0	128.0	1.84	285.7	100.6	1.88	61.6	2.2
			375	100.2	1.91	60.4	2.3
492	127.9	1.84	500	99.7	1.94	58.6	2.5
604	127.8	1.85	546	99.6	1.95	58.1	2.6

The emf of the element in (1) is denoted by E when $C_M \neq 0$, and by E' when $C_M = 0$, that is, when the right cell contains only the buffer solution. During the experiments the solutions were kept in a thermostat in which the temperature was 20.0° ± 0.1°C.

Every titration series was repeated at least once. With the exception of the cases where the rare-earth glycolate was precipitated, the potential was steady and could with few exceptions be reproduced within 0.2 mV.

The variation of the stoichiometric acid constant K_c with C_A' and C_{HA}' is shown in Table 1. It is evident that the addition of glycolic acid and the exchange of perchlorate ions for glycolate ions have a marked influence on the ionic medium. The variation of E' may to some degree depend on the salt error of the quinhydrone electrode. As only $E_A = E'-E$ is used for the computation of [A] (except for the determination of some correction terms), the salt error caused by the addition of the buffer solution is reduced to a minimum.

However, the medium changes probably also influence the activity factors of other ion species in the complex solution. Then it is possible that the complexity constants β_n vary with C_A' and C_{HA}'. As the variation of E' is especially significant at high values of δ, some difference might be expected between the $\bar{n}/[A]$-values obtained with buffer solutions having great differences in δ. Therefore buffer solutions with $\delta = 0.350$ and $\delta = 4.0$ were used in investigating the complexity systems. The results of the measurements on the gadolinium glycolate system are shown in Tables 2a and 2b and Fig. 1. The agreement between the $\bar{n}/[A]$-values obtained with the two buffers is rather good. The differences fall generally within the limits of the random errors. Thus it appears that a high concentration of glycolic acid does not have any great influence on the complexity constants.

Table 2 a. Corresponding values of $\bar{n}/[A]$ and $[A]$ for the gadolinium glycolate system determined by means of a glycolate buffer with $\delta = 0.350$ (*cf.* Fig. 1).

	$C_M = C_M^o \, (1 - 0.903 \cdot C_A' \cdot 10^{-3})$ mM					
	$C_M^o = 23.65$ mM $C_H = 8.30 \cdot 10^{-2} \cdot C_M$ mM Buffer 0.387:1.107 Symbol: O			$C_M^o = 47.3$ mM $C_H = 3 \cdot 10^{-5} \cdot C_M$ mM Buffer 0.387:1.107 Symbol: □		
C_A' mM	$E_A - \Delta E_A$ mV	$[A]$ mM	$\dfrac{\bar{n}}{[A]}$ M^{-1}	$E_A - \Delta E_A$ mV	$[A]$ mM	$\dfrac{\bar{n}}{[A]}$ M^{-1}
10.96	60.6 − 0.1	1.365	261	60.4 − 0.1	0.847	272
21.71	52.0 − 0.1	3.35	217	61.5 − 0.2	1.756	254
32.25	45.6 − 0.2	6.13	175	60.1 − 0.2	2.85	230
42.6	40.6 − 0.2	9.58	144	58.1 − 0.3	4.16	206
52.7	35.9 − 0.2	14.03	117	55.7 − 0.3	5.73	184
72.4	28.8 − 0.3	25.05	82.5	50.3 − 0.4	9.90	144
91.4	23.3 − 0.3	38.8	60.6	44.6 − 0.5	15.81	110.5
109.7	19.5 − 0.3	53.6	47.6	39.1 − 0.5	23.67	85.5
136.0	15.6 − 0.3	76.9	36.0	32.3 − 0.5	38.5	61.1
168.9	12.3 − 0.3	108.0	27.4	25.6 − 0.5	62.4	42.6
221.4	8.9 − 0.3	160.7	19.5	18.5 − 0.5	108.5	27.5
287.0	6.5 − 0.2	226.9	14.8	13.2 − 0.5	173.5	18.7
369	4.8 − 0.2	310.7	11.6	9.3 − 0.5	260.4	13.3
492	3.0 − 0.2	443	8.2	6.0 − 0.4	394	9.4
604	2.0 − 0.2	565	6.3	4.2 − 0.3	517	7.8

As the glycolic acid has a OH-group, it is possible that the unprotolyzed acid molecules form complexes with the rare-earth ions. We have therefore examined the question as to whether the addition of glycolic acid to an acidified solution of a rare-earth perchlorate has any effect on the extinction curve of the rare earth. It was found that the extinction of the holmium ions within the wave length range 320—700 mμ was unchanged, except for the peak at 450 mμ, when C_{HA} was increased from 0 mM to 750 mM ($C_M = 50$ mM, $[H^+] = 125$ mM, NaClO$_4$ to $I = 2.0$ M). The molar extinction coefficient of the peak at 450 mμ increased from 4.0 to 4.8. This increase, however, can be attributed to a complex formation between holmium ions and glycolate ions, as $[A] \approx 1.1$ mM in a solution having $C_{HA} = 750$ mM ($K_c = 1.8 \times 10^{-4}$) and $[H^+] = 125$ mM. This assumption was confirmed by an examination of the extinction of holmium perchlorate solutions ($C_H^o \approx 0.5$ mM), to which different amounts of glycolate buffer ($\delta = 1$) were added. It was found that the molar extinction coefficient of the peak at 450 mμ was about 4.8 when $[HA] \approx 18$ mM and $[A] \approx 1.0$ mM ($\bar{n} \approx 0.3$ according to the potentiometric measurements) *. Thus, complex formation between unprotolyzed glycolic

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* The formation of holmium glycolate complexes is accompanied by a rather strong increase of the extinction band at 450 mμ, whereas the increase of the band at 360 mμ is considerably lower. The band at 450 mμ has two peaks at a distance of about 1 mμ. It is the peak with the shorter wave length that increases when glycolate complexes are formed.

Table 2 b. Corresponding values of $n/[A]$ and $[A]$ obtained for the gadolinium glycolate system by means of a buffer solution with $\delta = 4.0$ (*cf.* Fig. 1).

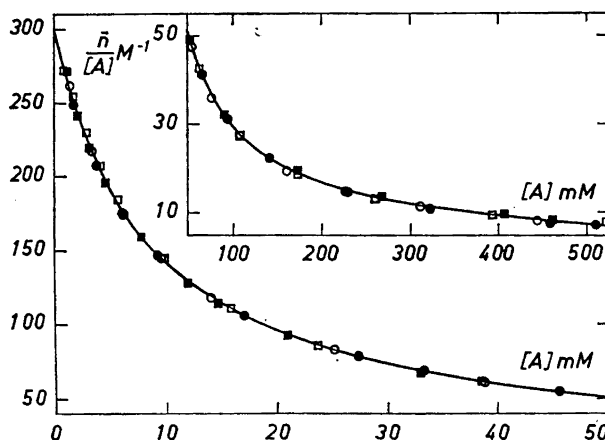|	$C_M = C_M^o\,(1 - C_A' \cdot 10^{-3})$ mM					
	$C_M^o = 23.65$ mM $C_H = 8.30 \cdot 10^{-2} \cdot C_M$ mM Buffer 4:1 Symbol: ●			$C_M^o = 47.3$ mM $C_H = 3.10^{-5} \cdot C_M$ mM Buffer 4:1 Symbol: ■		
C_A' mM	$E_A - \Delta E_A$ mV	$[A]$ mM	$\dfrac{\bar{n}}{[A]}$ M^{-1}	$E_A - \Delta E_A$ mV	$[A]$ mM	$\dfrac{\bar{n}}{[A]}$ M^{-1}
9.90	44.3 − 0.1	1.776	248	52.8 − 0.1	1.147	271
19.61	42.5 − 0.1	3.73	208	55.0 − 0.2	2.152	241
29.13	39.8 − 0.2	6.18	174	55.0 − 0.2	3.24	219
38.5	36.7 − 0.2	9.21	146	53.8 − 0.3	4.55	196
56.6	30.8 − 0.2	17.09	106	50.5 − 0.4	7.73	159
74.1	25.8 − 0.3	27.3	78.7	46.3 − 0.4	12.00	127.5
82.6	23.6 − 0.3	33.2	68.8	44.0 − 0.4	14.70	114
99.1	20.2 − 0.3	45.5	55.3	39.8 − 0.5	20.93	92.0
122.8	16.2 − 0.3	66.0	41.3	33.8 − 0.5	33.0	68.0
152.5	12.8 − 0.3	93.7	31.2	27.7 − 0.5	52.1	49.3
200.0	9.4 − 0.3	140.3	22.4	20.5 − 0.5	90.9	32.3
285.7	5.9 − 0.2	229.0	14.6	13.2 − 0.5	173.3	19.4
375	4.0 − 0.2	323.5	10.7	8.9 − 0.4	268.5	13.6
500	2.4 − 0.2	459	7.5	5.5 − 0.3	408	9.7
546	1.9 − 0.1	509	6.7	4.5 − 0.3	463	8.4

Fig. 1. The relation between $\bar{n}/[A]$ and $[A]$ for the gadolinium glycolate system according to the titration series in Tables 2a and 2b.

acid and holmium ions (and other rare-earth ions) may probably be excluded.

Any significant signs of polynuclear complexes have not been found, as the $\bar{n}$/[A]-functions of series with different C_M coincide at low [A] within the limits of the random errors.

The rare-earth glycolates are rather slightly soluble. The solubilities of the glycolates of the lighter rare earths have been determined by Jantsch and Grünkraut [5]. They found that the solubility at 18°C increases from 9.1 mmole/l at La to 12.5 mmole/l at Nd and 17.0 mmole/l at Sm. These glycolates have the composition Me(AcOH)$_3$ when dried in air at room temperature. The gadolinium glycolate showed a considerably higher solubility, 33.8 mmole/l, and contained 2 H$_2$O after drying.

The solubilities of the higher rare-earth glycolates seem to decrease from Gd to Yb. No determinations of the solubilities have been performed, but Jantsch and Grünkraut found that if a solution containing a mixture of rare-earth nitrates was partially precipitated with sodium glycolate, the higher rare earths were concentrated in the precipitate. It was also found by the present author in the investigation of the complexity of the glycolate systems that in order to avoid precipitation solutions with considerably lower rare-earth concentrations must be used for the higher rare earths than for gadolinium. The precipitate obtained in the Ho^{3+}—AcOH$^-$-system was analyzed after drying in air at room temperature. Its composition was Ho(AcOH)$_3 \cdot 2$H$_2$O (Found: Ho 38.3; H$_2$O 8.4. Calc. Ho 38.7; H$_2$O 8.45).

The precipitates of the rare-earth glycolates were formed rather slowly, except at $\bar{n} \approx 3$. Therefore it was also possible to investigate the glycolate systems at high ligand concentrations and relatively high rare-earth concentrations.

According to the potentiometric measurements anionic glycolate complexes are formed. Then it was expected that the precipitate of the rare-earth glycolate should dissolve at least partially when the concentration of glycolate ions was increased. However, such a dissolution could not be proved directly.

As the complex solutions have pH < 4, the degree of hydrolysis of the rare-earth ions must be so slight that it can be neglected (cf. I[p. 171] and II[p. 1940]).

As the ionic strength of the complex solutions decreases by the complex formation, the E_A-values must be corrected. By using the method indicated in Paper I the relation between the correction term, ΔE_A, and the depression of the ionic strength, ΔI, has been determined. The correction term should be subtracted from E_A to give the true E_A at $I = 2.0$ M. For the glycolate systems the following function was obtained:

$$\Delta E_A = 2.3 \cdot \Delta I \qquad (4)$$

Thus the E_A-values of the glycolate systems are not so sensitive to changes of the ionic strength as the E_A-values of the acetate systems.

For the calculation of ΔI the following formula was used:

$$\Delta I = 0.5 \cdot C_M \cdot \bar{n}(7-\bar{n}) \qquad (5)$$

where $\bar{n}$ was obtained by means of the uncorrected E_A-values (cf. I[p. 171]).

Table 3. The corresponding values of $\bar{n}/[A]$ and $[A]$, given at some round values of $[A]$ (in mM), for the rare-earth glycolate systems investigated potentiometrically.

	$\bar{n}/[A]$ for $[A] =$									
	0	2	5	10	15	20	30	40	50	70
La	153	132	112	90	76.5	67	54.5	46	40.5	32.3
Ce	226	180	142	109	88.5	75.5	60	49.5	42.5	34.0
Pr	270	208	161	121	98.5	83	65	54	46	36.2
Nd	320	238	177	130	103.5	86.5	66.5	55	47	36.6
Sm	364	270	202	145	114	95	72.5	59	50	38.3
Gd	297	244	190	142	113.5	95	73	59.5	50.5	39.1
Dy	330	259	197	146	116	96.5	74.5	60.5	51	39.3
Ho	350	262	199	146	116	96.5	74	60	51	39.5
Er	402	288	212	150	118	98	74	60	51	39.1
Yb	520	348	246	167	129	106	78.5	63	53	40.2

	$\bar{n}/[A]$ for $[A] =$									
	100	150	200	250	300	350	400	450	500	550
La	25.3	18.3	14.6	12.4	10.6	9.4	8.5	7.7	7.2	6.8
Ce	26.1	19.3	15.5	13.0	11.2	9.8	8.7	7.8	7.1	—
Pr	28.0	20.3	16.1	13.4	11.6	10.2	9.1	8.1	7.6	7.1
Nd	28.0	20.0	15.8	13.2	11.3	10.0	8.8	8.0	7.4	—
Sm	29.2	20.9	16.5	13.6	11.7	10.3	9.1	8.3	7.6	7.0
Gd	29.5	21.3	16.6	13.8	11.9	10.6	9.3	8.3	7.4	6.8
Dy	29.7	21.5	17.0	14.0	12.0	10.4	9.2	8.3	7.5	7.0
Ho	29.8	21.5	17.0	14.2	12.2	10.7	9.5	8.6	7.8	7.3
Er	29.6	21.0	16.7	13.9	12.0	10.7	9.6	8.7	7.8	7.1
Yb	30.2	21.2	16.7	14.0	12.2	11.0	9.8	8.9	8.0	7.3

Table 3 gives $\bar{n}/[A]$ for various values of $[A]$ for all the rare-earth glycolate systems examined. $[A]$ and $\bar{n}/[A]$ have been calculated according to eqns. II(2), II(3) and II(4). Fig. 2 shows the complex formation curve $\bar{n} = f(\log[A])$ for the glycolate systems of La^{3+}, Sm^{3+}, Dy^{3+}, and Yb^{3+}.

The complexity constants $\beta_n = [MA_n]\cdot[M]^{-1}\cdot[A]^{-n}$ have been computed according to eqns. II(5), II(7) and II(8) after a graphical integration of the function $\bar{n}/[A] = f([A]))$. The complexity constants are given in Table 5.

B. THE EXTINCTIOMETRIC INVESTIGATION

The neodymium glycolate system was examined extinctiometrically in the same way as the erbium acetate system described in II[p. 1947]. As the potentiometric investigation showed that polynuclear complexes can be formed only to a very limited extent, the terms depending on polynuclear complexes are neglected in the extinctiometric equations.
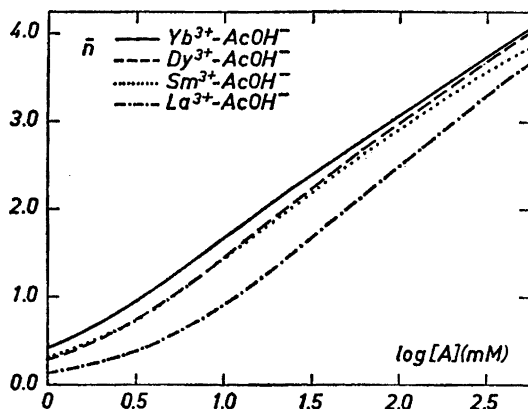
Fig. 2. The complex formation curves $\bar{n} = f(\log[A])$ for four rare-earth glycolate systems.

The measurements were performed at 20°C by means of a Hilger Uvispek with tungsten lamp and glass prism. As seen in Fig. 3 the complex formation has the greatest effect on the absorption band at 580 mμ. The band is shifted towards longer wave length, and the extinctiometric measurements were therefore performed at 586 mμ. At this wave length the slope of the absorption band has approximately the same value for all the solutions measured, and therefore the errors caused by the imperfect monochromaticity of the light are reduced (cf. Fronæus [6, p. 98]). The effective band width was about 5 Å.

In order to reduce the error caused by the partial reflection of the light at the end plates of the absorption cells (cf. Fronæus [6, p. 98]), solutions with the same value of ε should
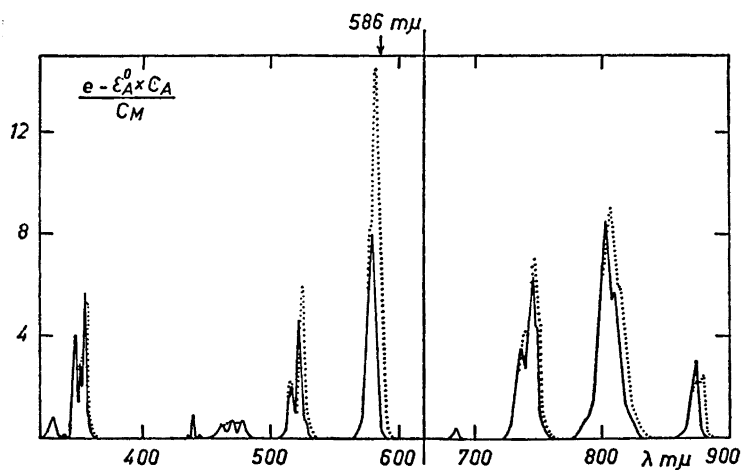

Fig. 3. The extinction curves for a neodymium perchlorate solution (the fulldrawn curve) and a complex solution with $C_{Nd^{3+}} = 50$ mM and $C_A = 500$ mM (the dotted curve). The ionic strength of both solutions was 2.0 M.
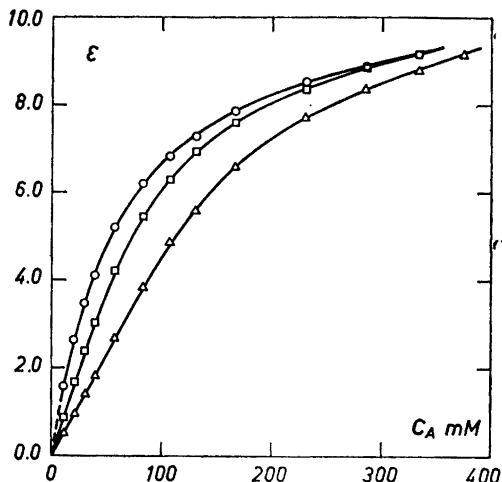
Fig. 4. ε for the neodymium glycolate system as a function of the glycolate concentration at different values of d. $\bigcirc : d = 4$ cm, $\square : d = 2$ cm, $\triangle : d = 1$ cm. The relation between C_M, C'_A and d is given by eqn. (6). By correcting C'_A according to the formula $C_A = C'_A + [H^+] - C_H$ the true total concentration C_A of glycolate ions is obtained.

have the same total extinction (E). This condition has been fulfilled approximately by holding the following relation between the rare-earth concentration (C_M mM), the glycolate concentration (C'_A mM) and the length of the absorption cell (d in cm):

$$C_M = \frac{50}{d} \ (1 - C'_A \times 10^{-3}); \qquad (C_M \text{ and } C'_A \text{ in mM}) \tag{6}$$

The solutions to be measured have been prepared by mixing different volumes of two solutions:

$$S_1 : \frac{50}{d} \ \text{mM Nd(ClO}_4)_3 + \left(2\ 000 - 6 \cdot \frac{50}{d}\right) \text{mM NaClO}_4$$

$$S_2 : 1\ 000 \ \text{mM HAcOH} + 1\ 000 \ \text{mM NaAcOH} + 1\ 000 \ \text{mM NaClO}_4$$

In the calculation of the true total concentration of glycolate ions ($C_A = C'_A + [H^+] - C_H$) the potentiometrically obtained values of the correction terms $[H^+]$ and C_H have been used. C_H depends on the presence of free perchloric acid in the rare-earth perchlorate solution ($C_H = 1.34 \times 10^{-3} \times C_M$ mM).

The relation between the lengths of the absorption cells was found to be 4.00:2.00:0.998 by means of extinction measurements performed with an alkaline solution of sodium picrate.

The validity of Beer's law was checked for neodymium perchlorate solutions with $C_M \leq 50$ mM.

The relation between

$$\varepsilon = \frac{e - \varepsilon_M^\circ \cdot C_M - \varepsilon_A^\circ \cdot C_A}{C_M}$$

and the glycolate concentration C_A has been determined experimentally for three values of d in eqn. (6). The three functions $\varepsilon = f(C_A)$ are shown in Fig. 4. By means of the three curves and eqn. (6) the pairs of values $(C_M, C_A)_\varepsilon$ — that is, the corresponding values of C_M and C_A at a given value of ε — have been calculated for the three values of d (Table 4).

According to eqn. II(13) the following equation is valid if only mononuclear complexes are formed:

$$\varepsilon = \frac{\xi}{X} = \frac{1}{X} \cdot \sum_{n=1}^{N} (\varepsilon_n - \varepsilon_M^\circ - n \cdot \varepsilon_A^\circ)\beta_n \cdot [A]^n \tag{7}$$

Therefore solutions with the same value of ε must have the same concentration $[A]$ of free glycolate ions. Thus if $\bar{n}_\varepsilon$ is the ligand number, the relation between $(C_A)_\varepsilon$ and $(C_M)_\varepsilon$ is given by the straight line

$$(C_A)_\varepsilon = \bar{n}_\varepsilon \cdot (C_M)_\varepsilon + [A] \tag{8}$$

The pairs of values $(C_M, C_A)_\varepsilon$ given in Table 4 for $2.0 \leq \varepsilon \leq 6.5$ represent approximately a straight line. Therefore it is possible to calculate $\bar{n}_\varepsilon$ and $[A]$ according to eqn. (8). The determinations of $\bar{n}_\varepsilon$ and $[A]$ have been performed graphically. The accordance between $\bar{n}_\varepsilon/[A]$ and $\bar{n}/[A]$ obtained potentiometrically is relatively good. On account of the method of extrapolation, the determination of $\bar{n}_\varepsilon/[A]$ begins to be very uncertain for $[A] < 4$ mM.

Table 4. Determination of the corresponding values of $[A]$ and $\bar{n}_\varepsilon$ for the neodymium glycolate system and a comparison between $\bar{n}_\varepsilon/[A]$ and the potentiometrically obtained values of $\bar{n}/[A]$.

ε	$d = 1$ cm		$d = 2$ cm		$d = 4$ cm		$C_M = 0$ $[A]$ mM	$\bar{n}_\varepsilon$	$\dfrac{\bar{n}_\varepsilon}{[A]}$ M⁻¹	$\dfrac{\bar{n}}{[A]}$ M⁻¹ pot.
	C_A mM	C_M mM	C_A mM	C_M mM	C_A mM	C_M mM				
2.0	43.5	47.9	24.5	24.4	13.8	12.4	4.0	0.82	205	192
2.25	48.5	47.6	28.0	24.3	16.0	12.4	5.0	0.93	185	175
2.5	54.0	47.4	31.0	24.2	18.5	12.3	6.0	1.02	170	165
2.75	59.0	47.0	34.5	24.1	21.0	12.2	8.0	1.10	138	144
3.0	65.0	46.7	38.5	24.0	24.0	12.2	9.5	1.20	126	133
3.25	70	46.5	42.0	24.0	27.0	12.2	11.2	1.28	114	122
3.5	76	46.2	46.0	23.9	30.0	12.1	13.5	1.35	100	110
3.75	81	45.9	50.0	23.8	33.5	12.1	16.2	1.40	87	98
4.0	87	45.7	54	23.7	37	12.0	19.0	1.50	79	89
4.5	98	45.1	62.5	23.5	44.5	11.9	25	1.62	65	75
5.0	111.5	44.4	72.5	23.1	52.5	11.8	30.5	1.83	60	66
5.5	128	43.6	84	22.9	62	11.7	38	2.05	54	57
6.0	145	42.8	99	22.6	76	11.6	49	2.25	46	48
6.5	163	41.8	116	22.2	93	11.3	65	2.3	35	38

Table 5. The complexity constants of the rare-earth glycolate systems with their random errors (temperature = 20°C, ionic strength = 2 M).

Rare earth	β_1 M^{-1}	$\beta_2 \times 10^{-3}$ M^{-2}	$\beta_3 \times 10^{-4}$ M^{-3}	$\beta_4 \times 10^{-5}$ M^{-4}	$\beta_5 \times 10^{-5}$ M^{-5}
A. Potentiometric investigation					
57 La	155 ± 8	5.7 ± 0.4	6.5 ± 0.6	1.2 ± 0.3	~ 0.7
58 Ce	225 ± 10	10.5 ± 0.7	14 ± 1.5	3.5 ± 0.7	~ 2
59 Pr	270 ± 15	15.5 ± 1	25 ± 3	9 ± 2	~ 5
60 Nd	320 ± 20	22 ± 2	37 ± 5	11 ± 4	~ 5
62 Sm	360 ± 20	34 ± 2	72 ± 8	28 ± 5	~ 10
64 Gd	300 ± 15	27 ± 2	62 ± 8	26 ± 5	~ 10
66 Dy	330 ± 20	30 ± 3	79 ± 10	30 ± 5	~ 20
67 Ho	350 ± 20	30 ± 3	81 ± 10	27 ± 5	~ 30
68 Er	400 ± 20	38 ± 3	98 ± 15	30 ± 5	~ 30
70 Yb	520 ± 30	66 ± 5	210 ± 25	60 ± 10	~100
B. Extinctiometric investigation					
60 Nd	350 ± 50	25 ± 5	~ 20		

As the function $\bar{n}/[A] = f([A])$ is very steep for low values of [A] for the rare-earth glycolate systems, it is not possible to extrapolate $\bar{n}_\varepsilon/[A]$ to [A] = 0 from [A] = 4 × 10^{-3} M, the lowest value at which $\bar{n}_\varepsilon/[A]$ could be determined. In the computation of the X-function (*cf.* eqn. II(7)), [A] = 0.004 M has been chosen as the inferior limit of the integration

$$\ln \frac{X([A])}{X(0.004)} = \int_{0.004}^{[A]} \frac{\bar{n}_\varepsilon}{[A]} \, d([A]) \tag{9}$$

In this way $X([A])/X(0.004)$ has been computed. The value of $X(0.004)$ was obtained by extrapolation of the function $X([A])/X(0.004) = f([A])$ to [A] = 0. As $X(0) = 1$ according to eqn. II(5), we have $X(0)/X(0.004) = 1/X(0.004)$. The extrapolation gave $1/X(0.004) = 0.35 \pm 0.03$. After the calculation of the X-function the complexity constants have been computed in the same way as before (Table 5).

The complexity constants have also been computed directly by means of eqn. II(4a) from the values of $\bar{n}_\varepsilon$ obtained for [A] = 4, 6, 15, and 30 mM ($\bar{n}_\varepsilon = 0.82$, 1.02, 1.37, and 1.82, respectively). Assuming that only three complexes are formed at these low concentrations of the free ligand, we get $\beta_1 = 350$, $\beta_2 = 28 \times 10^3$, and $\beta_3 \approx 2 \times 10^5$, in good accordance with the constants in Table 5.

RESULTS

The complexity constants of the rare-earth glycolate systems are found in Table 5. The stability constants and the ratios for consecutive stability constants are shown in Table 6.

Table 6. The stability constants ($b_1 = \beta_1$, $b_n = \beta_n/\beta_{n-1}$ for $n \geq 2$) and the ratio b_n/b_{n+1} between the consecutive stability constants of the rare-earth glycolate systems.

Rare earth	b_1	b_2	b_3	b_4	b_1/b_2	b_2/b_3	b_3/b_4
La	155	37	11.5	1.8	4.2	3.2	6
Ce	225	46.5	13.3	2.5	4.8	3.5	5.5
Pr	270	57.5	16.1	3.6	4.7	3.6	4.5
Nd	320	69	16.8	3.4	4.6	4.1	5
Sm	360	94	22.5	3.9	3.8	4.2	5.5
Gd	300	90	23.0	4.2	3.3	3.9	5.5
Dy	330	91	26.5	3.8	3.6	3.5	7
Ho	350	86	27	3.3	4.1	3.2	8
Er	400	95	26	3.1	4.2	3.7	8
Yb	520	127	32	2.9	4.1	4.0	11

A comparison between the complexity constants of the glycolate and the acetate systems (Tables II:13 and II:14) shows that the glycolate systems, especially those of the heavier rare earths, are complex to a much higher degree than the corresponding acetate systems.

The complexity constants β_1, β_2 and β_3 of the higher rare-earth glycolates vary with the atomic number of the rare earth in another way than the constants of the corresponding acetates, as shown in Fig. 5. β_1, β_2 and β_3 of the glycolate systems increases from Gd to Yb, contrary to the corresponding constants of the acetate systems.
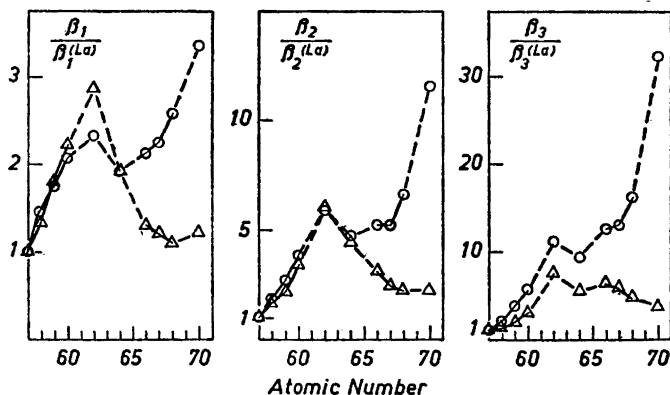

Fig. 5. The variation of β_1, β_2 and β_3 for the acetate and the glycolate systems with the atomic number of the rare earth. In order to facilitate a comparison between the variations of the complexity constants of the two systems, the quotients $\beta_n/\beta_n^{(\text{La})}$ have been chosen as ordinates, $\beta_n^{(\text{La})}$ denotes the complexity constant of the lanthanum system in question. ---- O: the glycolate systems; $\triangle$: the acetate systems. The symbols have been linked together with a broken line if the complexity system has not been examined for a rare earth lying between them.

Statistical calculations indicate, according to Bjerrum [7], that we ought to have the following relation between the stability constants for systems with simply bound ligands

$$b_1 : b_2 : b_3 : b_4 : b_5 : b_6 = 6 : \frac{5}{2} : \frac{4}{3} : \frac{3}{4} : \frac{2}{5} : \frac{1}{6}$$

It is expected from purely statistical reasons that the quotients b_n/b_{n+1} should have greater values in systems with chelating ligands than in systems with only simply bound ligands, as the chelating ligand leaves fewer sites vacant for coordination, where the next ligand can be bound, than does the simply bound ligand. If the central ion has six octahedrically-arranged coordination sites and if the ligand occupies two adjacent coordination sites, we ought to have, according to Bjerrum [7]

$$b_1 : b_2 : b_3 = 12 : 2 : 1/3$$

The values of b_n/b_{n+1} of the glycolate systems are not so high as six, and moreover they do not differ much from the quotients b_n/b_{n+1} of the corresponding acetate systems. It may, however, be noticed that b_1/b_2 and b_2/b_3 for the glycolate systems of Dy, Ho, Er, and Yb are somewhat higher than the corresponding values for the acetate systems.

Because of the high values of β_n for the glycolate systems relative to β_n for the corresponding acetate systems, although glycolic acid is stronger than acetic acid, it is probable that the glycolate ion acts as a chelating ligand, even if the quotients b_n/b_{n+1} do not have the expected values.

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