On the Complex Chemistry of the Tervalent Rare Earth Ions

II. The Acetate Systems of Praseodymium, Samarium, Dysprosium, Holmium, Erbium and Ytterbium

ARTUR SONESSON

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

Six rare earth acetate systems have been examined potentiometrically and one of these moreover extinctiometrically. The complexity constants are listed in Table 13 and the stability constants in Table 14 (together with four systems reported in Part I [1]). All measurements have been performed in perchlorate medium of ionic strength 2 M at 20°C.

The extinctiometric investigation of the $Er^{3+} - Ac^- -$ system* shows that the formation of the acetate complexes is accompanied by the appearance of new peaks close to the original absorption bands at about 380 mμ and 525 mμ. The new peaks, one at every band, have a somewhat shorter wavelength than the original peaks. The agreement between the potentiometrically and the extinctiometrically obtained complexity constants is good.

The stability constant of the first complex, b_1, increases with the atomic number from La to Sm. Then it decreases for Gd and Dy and remains approximately constant for Dy, Ho, Er and Yb. To begin with, b_2 and b_3 also increase with the atomic number of the rare earth. For the heaviest rare earths, however, b_2 and b_3 decrease slightly.

The heavier rare earths (Gd — Yb) seem to form polynuclear complexes which, however, are rather weak.

In Part I[1] the complexity constants of the acetate systems of La, Ce, Nd, and Gd were reported. The first three ions belong to the lightest rare earths, whilst Gd is situated in the middle of the series. In the present paper the investigation of the acetate systems of two light rare earths (Pr and Sm) and four heavy ones (Dy, Ho, Er, and Yb) is reported.

---

* Ac^- = acetate ion.

CHEMICALS USED

Rare earth perchlorates. Praseodymium and samarium perchlorates were prepared from the nitrates (> 98 % pure) by repeated evaporations with perchloric acid. In the preparations of the other rare earth perchlorates oxides with purity > 99 % were dissolved in perchloric acid.

The concentrations of the stock solutions were determined by gravimetric analysis. Pr and Sm were precipitated as oxalates, Dy, Ho, Er, and Yb as hydroxides. Moreover, the concentrations of the stock solutions were controlled by means of a cation exchanger column.

The concentration of free perchloric acid of the stock solutions was determined by electrometric titration with sodium hydroxide.

The *other chemicals* used were of analytical grade as in Part I. The concentrations of the stock solutions of NaAc and NaClO$_4$ were checked by means of a cation exchanger column.

A. THE POTENTIOMETRIC INVESTIGATION

Notations and general formulae (for deductions of the formulae the reader is referred to Part I and to Fronæus [2]).

$[H^+]'$, $[H^+]$ = the hydrogen ion concentration of the buffer solution and the complex solution, respectively.

C_H° = the concentration of free perchloric acid of the rare earth perchlorate solution before buffer is added. Thus $C_H^\circ = v \cdot C_M^\circ$, v being a constant and C_M° the starting concentration of the rare earth perchlorate.

C_H = $v.C_M$, C_M being the total concentration of rare earth of the complex solution.

C_{HA}', C_A' = the stoichiometric concentrations of acid HA and salt NaA, calculated from the amount of buffer added to the complex solution.

δ = C_{HA}'/C_A'

C_A = the actual total concentration of the ligand A, thus

$C_A = C_A' + [H^+] - C_H$.

$[M]$, $[A]$ = the concentrations of free central ion and free ligand respectively.

E_A = $E' - E$ = the difference between the emfs (in mV) of two elements according to I(15)*, which have $C_M = 0$ and $C_M \neq 0$, respectively.

ΔE_A = a correction term applied to E_A to correct for the increase of emf caused by the reduction of the ionic strength through the complex formation. ΔE_A is computed according to the eqns. I(16) and I(17).

β_n, β_n' = the complexity constants of the mononuclear and the dinuclear complexes, respectively.

b_n = the stability constants: $b_1 = \beta_1$, $b_n = \beta_n/\beta_{n-1}$ ($n = 2, 3, \ldots$).

$\bar{n}$ = the ligand number.

$\bar{n}_I$ = the ligand number of the mononuclear complexes.

$\bar{n}_c$ = the ligand number of the mononuclear complexes, calculated by means of the complexity constants.

$$\beta_n = \frac{[MA_n]}{[M] \cdot [A]^n} \tag{1a}$$

$$\beta_n' = \frac{[M_2A_n]}{[M]^2 \cdot [A]^n} \tag{1b}$$

_____
* Formulae in Part I are referred to in this way.

$$[A] = \frac{[H^+]'}{[H^+]} \cdot \frac{(C_A' + [H^+]')(\delta C_A' + C_H - [H^+])}{\delta C_A' - [H^+]'} \qquad (2)$$

$$E_A - \Delta E_A = 58.16 \log \frac{[H^+]}{[H^+]'} \qquad (3)$$

$$\bar{n} = \frac{C_A' + [H^+] - C_H - [A]}{C_M} \qquad (4)$$

$$\bar{n}_I = [A] \cdot \frac{X'}{X} = \frac{\sum\limits_{n=1}^{N} n\beta_n [A]^n}{1 + \sum\limits_{n=1}^{N} \beta_n [A]^n} \qquad (4a)\ {}^*$$

$$X = 1 + \sum_{n=1}^{N} \beta_n \cdot [A]^n \qquad (5)$$

$$X = \frac{C_M}{[M]} \text{ , if only mononuclear complexes are formed} \qquad (5a)$$
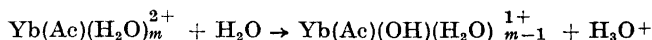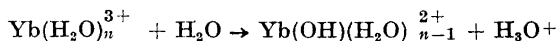
$$Y = \sum_{n=1}^{L} \beta_n' \cdot [A]^n \qquad (6)$$

$$\ln X([A]_j) = \int_0^{[A]_j} \frac{\bar{n}_I}{[A]} \cdot d[A] \qquad (7)$$

$$X_1 = (X-1)/[A]\ ;\ X_n = (X_{n-1} - \beta_{n-1})/[A]\ (n = 2, 3, \ldots) \qquad (8)$$

Experimental. The experimental procedure has been the same as that described in Part I. The quinhydrone elements measured have had the composition shown in I(15).

As was shown in Part I, the hydrolysis of the lower rare earths caused by the addition of acetate buffer can be neglected. However, the hydrolysis increases considerably with the atomic number of the rare earth, and therefore the $Yb^{3+}-Ac^-$—system has been examined by use of buffers with different concentrations of acetic acid ($\delta = 0.5$, 2.0 and 5.0; $C_M = 25$ mM). As seen in Table 8A—C and Fig. 2 the buffer $\frac{1}{2}$HAc:1 NaAc gives somewhat higher values of $\bar{n}/[A]$ at low [A] than the other buffers. This indicates formation of OH-complexes. Hydrolytic reactions, *e.g.*

$$Yb(H_2O)_n^{3+} + H_2O \rightarrow Yb(OH)(H_2O)_{n-1}^{2+} + H_3O^+$$

$$Yb(Ac)(H_2O)_m^{2+} + H_2O \rightarrow Yb(Ac)(OH)(H_2O)_{m-1}^{1+} + H_3O^+$$

produce hydrogen ions, which then combine with acetate ions ($H_3O^+ + Ac^- \rightleftharpoons HAc + H_2O$) until equilibrium has been reached. The result will be a decrease of [Ac$^-$] in the same way as if rare earth acetate complexes were formed, and the ligand number $\bar{n}$ obtained by the potentiometric measurements will include also the OH-complexes.

---

* This formula is a correction of eqn. I (7), which has been written in an erroneous form.

However, the hydroxide complexes are formed in competition with the acetate complexes and therefore the tendency of forming hydroxide complexes must decrease when the acetate concentration is increased. Moreover, the hydrolytic reactions must be depressed if the hydrogen ion concentration of the complex solution is increased, *i.e.* if a more acid buffer solution is used.

From the investigation of the Yb^{3+}—Ac^-—system it is evident that the hydrolysis of the ytterbium ions is rather weak, as the $\bar{n}/[A]$-functions obtained with the different buffers approach each other rapidly when [A] is increased. Besides, the buffers with $\delta = 2$ and 5 give approximately the same $\bar{n}/[A]$-functions even at the lowest values of [A]. Therefore it seems certain that the formation of Yb^{3+}—OH^-—complexes by the addition of the buffer 2 HAc:1 NaAc is so slight that it can be neglected.

In the discussion above the possibility of complex formation between Yb^{3+} and unprotolyzed HAc has been excluded, as extinctiometric measurements have shown that two solutions with the composition
80 mM $Ho(ClO_4)_3$ + 100 mM $HClO_4$ + 1420 mM $NaClO_4$ + x mM HAc
and having $x = 0$ and 990, respectively, show the same extinction curve within the limits of the random errors.

THE SYSTEMS INVESTIGATED

The praseodymium acetate system. The E_A-values obtained experimentally and the values of [A] and $\bar{n}/[A]$, calculated by means of eqns. (2)—(4), are collected in Table 1. The coincidence between the two $\bar{n}/[A]$-functions is so good that formation of polynuclear complexes to a detectable amount can be excluded.

The complexity constants have been computed by means of eqns. (5), (7) and (8). The X-functions of the system are to be found in Table 3A.

Table 1. The corresponding values of [A] and $\bar{n}/[A]$ for the praseodymium acetate system.

$C_M = \overset{\circ}{C}_M (1 - \overset{'}{C}_A \times 10^{-3})$ mM							
$\overset{\circ}{C}_M = 20.2$ mM $\quad C_H = 3.27 \times 10^{-2} \times C_M$ mM $\quad \delta = 2$				$\overset{\circ}{C}_M = 40.2$ mM $\quad C_H = 1 \times 10^{-3} \times C_M$ mM $\quad \delta = 2$			
$\overset{'}{C}_A$ mM	$E_A - \Delta E_A$ mV	[A] mM	$\dfrac{\bar{n}}{[A]}$ M^{-1}	$\overset{''}{C}_A$ mM	$E_A - \Delta E_A$ mV	[A] mM	$\dfrac{\bar{n}}{[A]}$ M^{-1}
3.323	27.7	1.222	62.4	6.62	31.0−0.1	1.953	60.8
9.90	20.9−0.1	4.50	53.7	13.16	29.3−0.2	4.165	54.8
19.61	17.6−0.1	9.98	45.8	29.13	26.0−0.3	10.62	44.8
38.5	13.9−0.2	22.55	35.0	47.6	22.7−0.4	19.71	37.0
56.6	11.5−0.3	36.5	28.0	65.4	20.1−0.5	30.1	31.2
74.1	9.9−0.3	50.9	23.8	90.9	17.0−0.6	47.5	25.0
107.1	7.9−0.4	79.9	18.5	122.8	14.1−0.7	72.3	19.8
166.7	5.6−0.4	135.9	13.2	189.2	10.5−0.8	128.9	14.3
230.7	4.3−0.4	198.0	10.5	285.5	7.3−0.8	220.9	10.2
333	3.1−0.4	299.5	8.2	375	5.5−0.7	310	8.3
412	2.4−0.3	379	7.2	444	4.4−0.7	384	7.0
474	1.9−0.3	445	6.0	500	3.6−0.6	444	6.3
546	1.6−0.3	519	5.7	583	2.8−0.5	532	5.7

Table 2. The corresponding values of [A] and $\bar n/[A]$ for the samarium acetate system.

$C_M = C_M^\circ (1 - C_A' \times 10^{-3})$ mM										
$C_M^\circ = 25.0$ mM $C_H = 4.3 \times 10^{-3} \times C_M$ mM $\delta = \frac{1}{2}$				$C_M^\circ = 50.0$ mM $C_H = 4.3 \times 10^{-3} \times C_M$ mM $\delta = \frac{1}{2}$			$C_M^\circ = 75.0$ mM $C_H = 4.3 \times 10^{-3} \times C_M$ mM $\delta = 2$			
C_A' mM	$E_A - \Delta E_A$ mV	[A] mM	$\frac{\bar n}{[A]}$ M^{-1}	$E_A - \Delta E_A$ mV	[A] mM	$\frac{\bar n}{[A]}$ M^{-1}	C_A' mM	$E_A - \Delta E_A$ mV	[A] mM	$\frac{\bar n}{[A]}$ M^{-1}
9.90	29.3 − 0.1	3.18	84.1	45.1 − 0.1	1.729	93.6	9.90	53.3 − 0.2	1.220	95.2
19.61	26.0 − 0.2	7.13	70.8	41.8 − 0.2	3.85	82.6	19.61	51.3 − 0.3	2.617	87.9
29.13	23.1 − 0.2	11.85	59.7	39.3 − 0.4	6.33	73.8	38.5	47.3 − 0.5	6.05	74.1
47.6	18.7 − 0.3	23.09	44.5	34.5 − 0.5	12.49	58.8	56.6	43.6 − 0.7	10.38	62.7
74.1	14.6 − 0.4	42.3	32.3	28.8 − 0.7	24.48	43.6	74.1	40.1 − 0.9	15.72	53.3
107.1	11.2 − 0.5	70.3	23.5	23.2 − 0.9	44.5	31.5	90.9	36.8 − 1.0	22.07	45.6
137.9	9.2 − 0.5	97.9	18.9	19.4 − 1.0	66.8	24.7	122.8	31.2 − 1.2	37.5	34.5
166.7	7.9 − 0.5	124.5	16.3	16.7 − 1.0	89.7	20.5	152.5	26.9 − 1.3	55.4	27.5
230.7	5.8 − 0.5	187.2	12.0	12.4 − 1.0	147.1	14.7	193.5	22.2 − 1.4	85.0	21.1
333	4.0 − 0.5	290.4	8.9	8.3 − 1.0	249.9	10.0	285.5	14.9 − 1.4	167.5	13.1
412	3.0 − 0.4	372	7.3	6.2 − 0.9	334	7.9	375	10.6 − 1.3	259.6	9.5
500	2.3 − 0.4	464	6.2	4.7 − 0.7	427	6.8	444	8.4 − 1.2	334	7.9
546	2.0 − 0.3	510	6.1	4.0 − 0.7	479	6.1	546	5.9 − 1.0	449	6.3

The samarium acetate system. The results obtained for this complexity system are collected in Tables 2 and 3B. Also for this system the formation of polynuclear complexes can be excluded.

The dysprosium acetate system. As seen in Table 4 and Fig. 1 the $\bar n/[A]$-values increase with C_M at low [A]. This indicates the presence of polynuclear

Table 3. The X-functions of the praseodymium and the samarium acetate systems.

[A] mM	A Praseodymium acetate system					B Samarium acetate system				
	X ([A])	X_1 M^{-1}	X_2 M^{-2}	X_3 M^{-3}	X_4 M^{-4}	X ([A])	X_1 M^{-1}	X_2 M^{-2}	X_3 M^{-3}	X_4 M^{-4}
0	1	64.6	645	1 940	2 300	1	102.8	1 810	7 100	6 500
2	1.1325	66.2				1.2128	106.4			
6	1.411	68.6				1.683	113.9			
12	1.869	72.5				2.508	125.5	1 900		
20	2.567	78.3	685			3.845	142.2	1 970		
30	3.59	86.3	723			5.93	164	2 045		
50	6.15	103.0	768			11.64	212.5	2 200		
70	9.50	121.5	813			19.75	268	2 360		
100	16.33	153.5	887			37.3	363	2 600		
140	29.4	203	990			73.4	517	2 960	8 180	
200	59.5	292.5	1 140	2 475		162	805	3 510	8 460	6 800
300	150.3	498	1 445	2 665	2 380	440	1 460	4 530	9 050	6 500
400	316.5	789	1 810	2 915	2 410	960	2 400	5 730	9 800	6 800
500	590	1 178	2 225	3 160	2 420	1 820	3 650	7 090	10 560	6 900

Table 4. The corresponding values of [A] and $\bar{n}/[A]$ for the dysprosium acetate system.

$C_M = 25.0$ mM (constant) $C_H = 0.225$ mM $\delta = 2$. Sign ○				$C_M = 50.0$ mM (constant) $C_H = 0.485$ mM $\delta = 2$. Sign □			$C_M = 73.0$ mM (constant) $C_H = 0.723$ mM $\delta = 2$. Sign △			
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	C_A' mM	$E_A - \Delta E_A$ mV	[A] mM	$\dfrac{\bar{n}}{[A]}$ M⁻¹
3.98	21.5	1.753	47.5	34.8	1.063	48.1	3.88	44.6	0.720	49.8
9.90	20.2 — 0.1	4.52	46.2	32.4 — 0.1	2.82	47.5	9.65	41.0 — 0.1	1.978	49.2
19.61	19.2 — 0.2	9.30	43.7	31.2 — 0.2	5.82	46.1	28.4	38.7 — 0.3	6.29	46.9
38.5	17.9 — 0.3	19.23	39.7	29.9 — 0.4	12.04	43.3	46.4	37.7 — 0.6	10.77	44.6
56.6	16.6 — 0.4	29.9	35.6	28.7 — 0.6	18.69	40.1	63.8	36.6 — 0.8	15.55	42.0
90.9	14.2 — 0.5	52.9	28.6	26.4 — 0.8	33.1	34.7	88.6	35.3 — 1.0	22.9	39.0
122.8	12.3 — 0.6	77.3	23.4	24.0 — 1.0	49.5	29.4	134.5	32.4 — 1.3	39.4	32.9
166.7	10.4 — 0.6	113.2	18.9	21.1 — 1.2	76.0	23.8	188.7	28.8 — 1.7	64.7	26.1
230.7	8.4 — 0.6	169.5	14.4	17.6 — 1.3	121.2	18.1	325	21.8 — 2.0	148.6	16.2
333	6.6 — 0.7	264	10.5	13.8 — 1.4	204.2	12.6	365.5	20.1 — 2.1	179.5	14.1
412	5.7 — 0.7	338	8.7	11.9 — 1.4	271.9	10.3	433	17.7 — 2.1	234	11.6
500	4.9 — 0.7	424	7.2	10.3 — 1.5	353	8.3	532	15.1 — 2.2	319.5	9.1
583	4.4 — 0.8	506	6.1	9.2 — 1.5	430	7.1	600	13.9 — 2.2	378	8.0

complexes. When both mono- and dinuclear complexes are formed, the connection between $\bar{n}/[A]$ and [M] is given by the equation

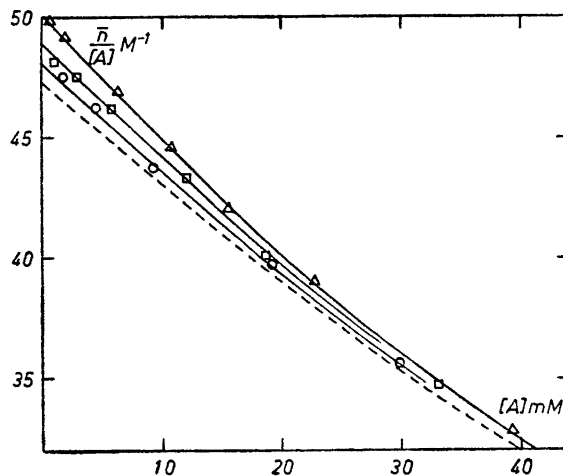$$\frac{\bar{n}}{[A]} = \frac{X' + [M] \cdot Y'}{X + 2[M] \cdot Y} \tag{9}$$

Fig. 1. The function $\dfrac{\bar{n}}{[A]} = f([A])$ of the dysprosium acetate system. The signs refer to the different values of C_M given in Table 4. The broken curve is the function obtained by extrapolation to $C_M = 0$.

(cf. eqn. I(8)). From the theory given by Fronæus [2] and confirmed experimentally, it appears that the $\bar{n}/[A]$-functions of series with different C_M will approach each other when [A] is increased. Finally the functions will meet at a point, and after that they will diverge again but in the reversed order. For the Dy^{3+}-Ac^--system the $\bar{n}/[A]$-curves meet at $[A] \approx 60$ mM, but the curves seem to coincide at higher [A]-values.

As [M] = 0 at $C_M = 0$ we can deduce from (9)

$$\lim_{C_M \to 0} \frac{\bar{n}}{[A]} = \left(\frac{\bar{n}}{[A]}\right)_{C_M = 0} = \frac{X'}{X} = \frac{\bar{n}_I}{[A]} \tag{10}$$

The function $(\bar{n}/[A])_{C_M=0} = f([A])$ is listed in Table 6A and represented by the broken curve in Fig. 1. The function has been used for the computation of the X-functions in Table 6A according to eqns. (7) and (8). In this way it is possible to calculate the complexity constants of the mononuclear complexes.

From eqn. (9) it can be deduced

$$\lim_{C_A \to 0} \frac{\bar{n}}{[A]} = \beta_1 + C_M \cdot \beta_1' \tag{11}$$

According to this formula $\beta_1' \approx 40$ M^{-2}.

The holmium acetate system. The results of the measurements on the Ho^{3+}-Ac^--system are shown in Tables 5 and 6B. Also for this system the series with $C_M = 40$ mM gives somewhat higher $\bar{n}/[A]$ at low [A] than the series with $C_M = 20$ mM. In calculating the X-functions in Table 6B the $\bar{n}/[A]$-curve was drawn in accordance to the values of $(\bar{n}/[A])_{C_M=0}$ given in Table 6B.

Table 5. The corresponding values of [A] and $\bar{n}/[A]$ for the holmium acetate system.

C_A' mM	$E_A-\Delta E_A$ mV	[A] mM	$\dfrac{\bar{n}}{[A]}$ M⁻¹	C_A' mM	$E_A-\Delta E_A$ mV	[A] mM	$\dfrac{\bar{n}}{[A]}$ M⁻¹
	C_M = 20.0 mM (constant) C_H = 0.225 mM δ = 2				C_M = 40.0 mM (constant) C_H = 0.450 mM δ = 2		
3.323	18.0	1.693	43.4	6.62	27.4	2.315	42.7
9.90	16.0−0.1	5.35	41.0	13.16	25.9−0.1	4.82	41.4
19.61	15.1−0.1	10.90	39.2	29.13	24.7−0.3	11.18	39.3
38.5	14.0−0.3	22.44	35.3	47.6	23.6−0.4	19.10	36.8
56.6	13.0−0.3	34.3	32.2	65.4	22.6−0.6	27.5	34.1
74.1	12.0−0.4	46.9	28.8	90.9	21.0−0.7	40.8	30.5
107.1	10.5−0.5	72.2	24.1	122.8	19.0−0.9	60.1	25.9
166.7	8.2−0.5	123.0	17.7	189.2	15.4−1.0	107.1	19.1
230.7	6.7−0.6	181.4	13.5	285.5	11.9−1.1	186.5	13.2
333	5.2−0.6	278	9.9	375	9.8−1.2	267	10.1
412	4.4−0.6	354	8.1	444	8.5−1.2	333	8.3
474	4.0−0.6	414	7.2	500	7.9−1.2	384	7.5
546	3.6−0.6	485	6.3	583	7.1−1.2	462	6.5
615	3.3−0.6	553	5.6	667	6.4−1.2	543	5.7

Table 6. The X-functions of the dysprosium and the holmium acetate systems.

[A] mM	A Dysprosium acetate system						B Holmium acetate system					
	$\left(\dfrac{\bar{n}}{[A]}\right)_{C_M=0}$	$X([A])$	X_1 M^{-1}	X_2 M^{-2}	X_3 M^{-3}	X_4 M^{-4}	$\left(\dfrac{\bar{n}}{[A]}\right)_{C_M=0}$	$X([A])$	X_1 M^{-1}	X_2 M^{-2}	X_3 M^{-3}	X_4 M^{-4}
0	*47.3*	1	*47.1*	*930*	*6 100*	*7 800*	*43.4*	1	*43.3*	*725*	*5 600*	*3 800*
2	46.4	1.0983	49.1				42.5	1.0898	44.9			
6	44.7	1.318	53.0				40.8	1.2875	47.9			
10	43.0	1.571	57.1	1 000			39.2	1.511	51.1	780		
20	39.0	2.367	68.4	1 065			35.9	2.200	60.0	835		
30	35.3	3.432	81.1	1 133			33.0	3.107	70.2	897		
50	29.1	6.52	110.5	1 265			28.0	5.71	94.3	1 020		
70	24.9	11.16	145	1 400			24.2	9.61	123.0	1 140	5 910	
100	20.4	21.9	209	1 620	6 900		20.1	18.60	176	1 325	6 020	
140	16.5	45.6	318.5	1 935	7 190		16.2	38.2	266	1 590	6 170	
200	12.9	108.5	538	2 455	7 630	7 650	12.5	89.6	443	2 000	6 370	3 830
300	9.5	326.5	1 085	3 460	8 430	7 760	9.2	261	866	2 740	6 730	3 760
400	7.6	763	1 905	4 640	9 280	7 950	7.4	593	1 480	3 590	7 170	3 930
500	6.2	1 510	3 020	5 940	10 020	7 840	6.1	1 165	2 330	4 570	7 700	4 200

The erbium acetate system. From the $\bar{n}/[A]$-values in Table 7 it must be inferred that polynuclear complexes are present also in this system. β_1' can be estimated to ≈ 30 M^{-2}. In the computation of the X-functions in Table 9A, the values of $(\bar{n}/[A])_{C_M=0}$ have been used.

Table 7. The corresponding values of [A] and $\bar{n}/[A]$ for the erbium acetate system.

C_A' mM	$C_M = 25.0$ mM (constant) $C_H = 0.295$ mM $\delta = 2$			$C_M = 50.0$ mM (constant) $C_H = 0.590$ mM $\delta = 2$			C_A' mM	$C_M = 75.2$ mM (constant) $C_H = 1.013$ mM $\delta = 2$		
	$E_A - \Delta E_A$ mV	[A] mM	$\dfrac{\bar{n}}{[A]}$M^{-1}	$E_A - \Delta E_A$ mV	[A] mM	$\dfrac{\bar{n}}{[A]}$M^{-1}		$E_A - \Delta E_A$ mV	[A] mM	$\dfrac{\bar{n}}{[A]}$M^{-1}
6.62	18.9	3.21	39.6	30.6	2.059	39.6	6.62	40.7	1.418	40.8
9.90	18.3 − 0.1	4.90	39.0	29.6 − 0.1	3.17	39.4	13.16	37.8 − 0.1	3.07	40.0
19.61	17.4 − 0.2	10.01	37.5	28.4 − 0.2	6.52	38.7	29.13	36.0 − 0.3	7.21	38.8
38.5	16.2 − 0.3	20.59	34.3	27.2 − 0.4	13.42	36.6	47.6	35.0 − 0.5	12.28	37.3
56.6	15.3 − 0.4	31.5	31.6	26.3 − 0.6	20.57	34.5	65.4	34.1 − 0.7	17.57	35.5
74.1	14.2 − 0.4	43.0	28.7	25.3 − 0.7	28.1	32.4	90.9	33.0 − 1.0	25.75	33.4
107.1	12.6 − 0.6	66.7	24.1	23.6 − 0.9	43.7	28.8	122.8	31.4 − 1.2	37.3	30.2
166.7	10.1 − 0.6	114.6	18.1	20.2 − 1.2	78.7	22.2	189.2	27.9 − 1.6	67.0	24.1
230.7	8.3 − 0.7	170.9	13.9	17.2 − 1.3	123.1	17.4	285.5	22.9 − 2.0	125.1	17.0
333	6.4 − 0.7	266.1	10.1	13.6 − 1.4	205.8	12.3	375	19.4 − 2.1	189.3	13.0
412	5.6 − 0.7	339	8.5	11.7 − 1.5	275.2	9.9	444	17.1 − 2.2	246.7	10.6
500	4.9 − 0.7	424	7.2	10.1 − 1.5	356	8.1	546	14.8 − 2.2	332	8.5
583	4.5 − 0.7	502	6.4	9.1 − 1.5	432	7.0	615	13.5 − 2.3	395	7.4

Table 8. The corresponding values of [A] and $\bar{n}$/[A] for the ytterbium acetate system.

C_A' mM	A $C_M = 25.0$ mM (constant) $C_H = 0.280$ mM $\delta = \frac{1}{2}$. Sign $+$			B $C_M = 25.0$ mM (constant) $C_H = 0.280$ mM $\delta = 2$. Sign ○			C $C_M = 25.0$ mM (constant) $C_H = 0.280$ mM $\delta = 5$. Sign ●		
	$E_A - \Delta E_A$ mV	[A] mM	$\frac{\bar{n}}{[A]}$ M⁻¹	$E_A - \Delta E_A$ mV	[A] mM	$\frac{\bar{n}}{[A]}$ M⁻¹	$E_A - \Delta E_A$ mV	[A] mM	$\frac{\bar{n}}{[A]}$ M⁻¹
3.323	25.1	1.433	45.5	21.5	1.494	43.5	20.4	1.534	43.8
6.62	21.8	3.025	44.1	19.9	3.082	43.2	19.5	3.115	43.6
13.16	19.7−0.1	6.31	41.7	18.5−0.1	6.43	40.6	18.4−0.1	6.43	41.1
29.1	17.6−0.2	14.91	37.4	17.0−0.2	15.06	36.8	17.0−0.2	15.04	37.1
47.6	15.9−0.3	26.0	32.9	15.5−0.3	26.2	32.4	15.6−0.3	26.05	32.9
65.4	14.6−0.4	37.6	29.3	14.4−0.4	37.7	29.2	14.5−0.4	37.5	29.6
90.9	13.1−0.5	55.6	25.3	12.9−0.5	55.7	25.1	12.9−0.5	55.7	25.1
122.8	11.5−0.6	80.2	21.2	11.4−0.6	80.2	21.1	11.4−0.6	80.2	21.2
189.2	9.1−0.7	136.1	15.5	9.0−0.7	136.4	15.4	9.0−0.7	136.3	15.5
285.5	7.1−0.7	222.2	11.4	7.0−0.7	222.8	11.3	7.0−0.7	222.7	11.3
375	5.8−0.7	307	8.8	5.8−0.7	307	8.9	5.8−0.7	307	8.9
444	5.2−0.7	372	7.7	5.2−0.7	372	7.8	5.2−0.7	372	7.8
546	4.6−0.7	468	6.6	4.6−0.7	468	6.6	4.6−0.7	468	6.7
615	4.2−0.7	536	5.9	4.2−0.7	536	5.9	4.3−0.7	534	6.1

C_A' mM	D $C_M = 50.0$ mM (constant) $C_H = 0.560$ mM $\delta = 2$. Sign □			E $C_M = 75.0$ mM (constant) $C_H = 0.840$ mM $\delta = 2$. Sign △		
	$E_A - \Delta E_A$ mV	[A] mM	$\frac{\bar{n}}{[A]}$ M⁻¹	$E_A - \Delta E_A$ mV	[A] mM	$\frac{\bar{n}}{[A]}$ M⁻¹
6.62	32.3	1.920	44.3	41.8	1.340	45.8
9.90	31.2−0.1	2.971	43.6	40.3−0.1	2.097	45.3
19.61	29.6−0.2	6.21	41.7	38.3−0.2	4.43	43.6
38.5	27.8−0.4	13.10	38.0	36.6−0.4	9.27	41.0
56.6	26.5−0.6	20.40	35.0	35.3−0.6	14.43	38.3
74.1	25.2−0.7	28.2	32.2	34.1−0.8	19.93	35.7
107.1	23.0−0.9	44.8	27.6	32.1−1.1	31.5	31.7
142.9	20.8−1.1	65.6	23.4	29.9−1.4	46.4	27.5
230.7	16.3−1.3	127.6	16.1	24.8−1.8	93.0	19.6
333	12.9−1.4	211.5	11.5	20.1−2.1	163.7	13.7
412	11.2−1.5	281	9.3	17.5−2.2	225	11.0
500	9.7−1.5	362	7.6	15.3−2.2	298	9.0
583	8.7−1.5	439	6.6	13.7−2.2	370	7.7
667	8.0−1.5	516	5.8	12.5−2.3	446	6.6

The ytterbium acetate system. As mentioned before the hydrolysis of Yb^{3+} has been examined by means of acetate buffers with different δ. Table 8A—C and Fig. 2 show that the hydrolysis can be neglected when the buffer 2 HAc: 1 NaAc is added.
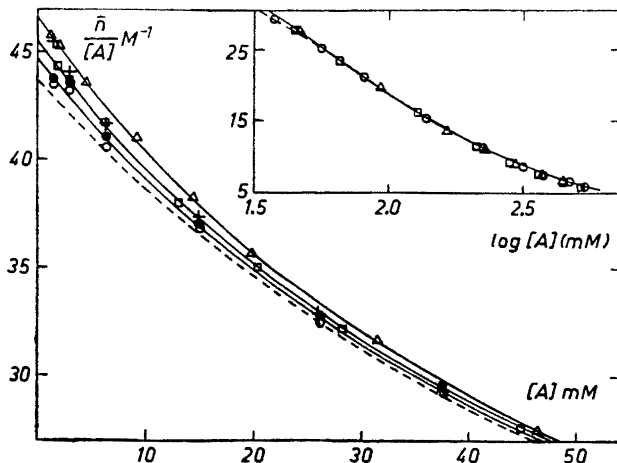
Fig. 2. $\dfrac{\bar{n}}{[A]}$ as a function of [A] for the ytterbium acetate system at different values of C_M and δ, according to the titration series in Table 8. The broken curve is obtained by extrapolation to $C_M = 0$.

It is seen from Table 8B, D, E and Fig. 2 that polynuclear complexes probably are formed. β_1' can be estimated to about 30 M^{-2}. The X-functions in Table 9B are computed from $(\bar{n}/[A])_{C_M = 0}$.

Table 9. The X-functions of the erbium and the ytterbium acetate systems.

[A] mM	A Erbium acetate system						B Ytterbium acetate system					
	$\left(\dfrac{\bar{n}}{[A]}\right)_{C_M=0}$	$X([A])$	X_1 M^{-1}	X_2 M^{-2}	X_3 M^{-3}	X_4 M^{-4}	$\left(\dfrac{\bar{n}}{[A]}\right)_{C_M=0}$	$X([A])$	X_1 M^{-1}	X_2 M^{-2}	X_3 M^{-3}	X_4 M^{-4}
0	40.1	1	40.1	678	4 520	4 300	43.8	1	43.7	680	3 500	4 200
2	39.5	1.0831	41.5				42.7	1.0904	45.2			
6	38.4	1.2665	44.4				40.5	1.288	48.0			
10	37.3	1.474	47.4	725			38.7	1.509	50.9	720		
20	34.4	2.110	55.5	770			34.6	2.175	58.8	752		
30	31.8	2.938	64.6	817			31.2	3.022	67.4	790		
50	27.2	5.29	85.8	915	4 740		26.2	5.345	86.9	864	3 680	
70	23.6	8.78	111.2	1 015	4 810		22.7	8.71	110.1	949	3 840	
100	19.7	16.75	157.5	1 175	4 970		18.8	16.17	151.7	1 080	4 000	
140	15.9	34.0	236	1 400	5 160		15.3	31.8	220	1 260	4 150	
200	12.5	79.3	391	1 760	5 400	4 380	12.1	71.9	354.5	1 555	4 380	4 400
300	9.4	232.5	771	2 440	5 870	4 500	9.1	205	680	2 120	4 810	4 350
400	7.6	540	1 350	3 270	6 480	4 890	7.4	464	1 160	2 790	5 260	4 400
500	6.5	1 098	2 195	4 310	7 260	5 480	6.4	920	1 840	3 590	5 810	4 600

B. THE EXTINCTIOMETRIC INVESTIGATION

In order to check the potentiometrically determined complexity constants of the acetate systems of the higher rare earths, an extinctiometric examination of the erbium acetate system has been performed. This method of investigation has been examined theoretically by Fronæus [2,p. 87], who has shown that only systems of exclusively mononuclear complexes are suitable for extinctiometric investigation. However, we can in favourable cases get an approximate value of at least β_1 also for systems with dinuclear complexes (cf. the extinctiometric investigation of the copper(II) acetate system performed by Fronæus [2]).

As to the erbium acetate system it is indicated by the potentiometric investigation that polynuclear complexes are probably formed ($\beta_1' \approx 30$ M^{-2}, if the presence of only mono- and dinuclear complexes is assumed). However, the concentration of the first dinuclear complex, calculated from β_1', is very low (cf. Table 10), and it might therefore be possible to get at least some idea of the constants of the mononuclear complexes by extinctiometric measurements.

Calculation of the complexity constants from extinctiometric data

In addition to the notations already given, it is denoted by

E the total extinction of the solution, measured with water in the reference cell,

d the thickness of the absorbing layer in cm,

e the quotient E/d,

$\varepsilon_M^\circ, \; \varepsilon_A^\circ$ the molar extinctions of M and A,

$\varepsilon_n, \; \varepsilon_n'$ the molar extinctions of the mononuclear complexes MA_n and the dinuclear complexes M_2A_n, respectively.

In the case where both mono- and dinuclear complexes are formed, the following is valid

$$e = \varepsilon_M^\circ \cdot [M] + \sum_{n=1}^{N} \varepsilon_n \cdot [MA_n] + \sum_{n=1}^{L} \varepsilon_n' \cdot [M_2A_n] + \varepsilon_A^\circ \cdot [A] \qquad (12)$$

Table 10. The concentrations of the first dinuclear (a) and the first mononuclear (b) erbium acetate complexes at some values of C_M and [A], chosen from the extinctiometric measurements. The potentiometrically obtained values of β_1 and β_1' have been used in the calculations.

C_M mM	37.3	36.6	35.8	14.9	14.8	14.6	7.5	7.4	7.3
[Ac$^-$] mM	2	10	20	2	10	20	2	10	20
a mM	0.07	0.18	0.17	0.011	0.03	0.03	0.003	0.008	0.007
b mM	2.8	9.9	13.6	1.1	4.0	5.6	0.56	2.0	2.8
$\frac{a}{b} \cdot 10^{+2}$	2.5	1.8	1.3	1.0	0.8	0.5	0.5	0.4	0.3

After having expressed $[MA_n]$ and $[M_2A_n]$ by means of $[A]$, β_n and β_n', and introduced the abbreviations

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

$$\xi = \sum_{n=1}^{N} (\varepsilon_n - \varepsilon_M^\circ - n \cdot \varepsilon_A^\circ)\, \beta_n [A]^n$$

$$\eta = \sum_{n=1}^{L} (\varepsilon_n' - 2\varepsilon_M^\circ - n\varepsilon_A^\circ)\, \beta_n' [A]^n$$

we get the expression

$$\varepsilon = \frac{\xi + [M] \cdot \eta}{X + 2[M] \cdot Y} \tag{13}$$

$\varepsilon = \xi/X$ in the case where *only mononuclear* complexes are formed, as $\eta = 0$ and $Y = 0$. Thus $\varepsilon = f([A])$, independent of $[M]$, and consequently solutions with the same value of ε must have the same value of $[A]$. In this case we have

$$\left(\frac{\partial C_A}{\partial C_M}\right)_\varepsilon = \bar{n}_I \text{ (Constant } \varepsilon) \tag{14}$$

By extrapolating the straight line $(C_A)_\varepsilon = [A] + \bar{n}_I \times (C_M)_\varepsilon$ obtained from eqn. (14) to $C_M = 0$, we get $[A]$ of all solutions with the same value of ε.

If *both mono- and dinuclear* complexes are present, eqn. (14) is not valid, as $\varepsilon = f([A], [M])$. However, using eqn. (13) (ε being constant) and the expressions of C_M and C_A at the bottom of page 167 in Part I, we can deduce for $C_M = 0$

$$\left(\frac{\partial C_A}{\partial C_M}\right)_\varepsilon = k_\varepsilon = \bar{n}_I + \frac{2\,Y \cdot \xi - X \cdot \eta}{X(X \cdot \xi' - X' \cdot \xi)} \tag{15}$$

$$C_M = 0$$

The determination of k_ε can be performed in the following way. The function $\varepsilon = f(C_A)$ is determined experimentally for some values of C_M. By cutting the curves with lines $\varepsilon = $ constant, we obtain the pairs of corresponding values $(C_A, C_M)_\varepsilon$. Then, k_ε for every value of ε is determined from the slope of the function $(C_A)_\varepsilon = f(C_M)_\varepsilon$ at $C_M = 0$. This function, however, is not necessarily a straight line as seen from eqn. (15), and therefore the calculation of k_ε can be rather uncertain.

For the Er^{3+}-Ac^--system, $[M_2A_n]$ is very low and decreases much more rapidly than $[MA_n]$ when $[M] \to 0$, as seen in Table 10 (calculated with the use of eqns. 1a, 1b, 5 and 5a). Therefore it is probable that the values of $(C_A)_{C_M=0} = [A]$, obtained by extrapolations of the function $(C_A)_\varepsilon = f(C_M)_\varepsilon$ to $C_M = 0$, represent approximately the concentration of free ligand also in solutions with low $C_M \neq 0$. Therefore, the function $(C_A)_\varepsilon = f(C_M)_\varepsilon$

ought to be a straight line at low values of C_M, indicating that $k_\varepsilon \approx \bar{n}_I$ at low C_M. Then, if the second term of eqn. (15) can be neglected, we can compute the complexity constants of the mononuclear complexes by use of $k_\varepsilon/[A]$ and eqn. (7). However, the constants may contain a systematic error that we cannot estimate.

From eqn. (15) it can be deduced

$$\lim_{[A]\to 0} \frac{k_\varepsilon}{[A]} = \beta_1 - \frac{\Delta\varepsilon_1' \cdot \beta_1'}{\Delta\varepsilon_1 \cdot \beta_1} \text{ , with } \begin{cases} \Delta\varepsilon_1' = \varepsilon_1' - 2\varepsilon_M^\circ - \varepsilon_A^\circ \\ \Delta\varepsilon_1 = \varepsilon_1 - \varepsilon_M^\circ - \varepsilon_A^\circ \end{cases} \tag{16}$$

Thus, we get directly an approximate value of β_1 if we can compute k_ε at so low [A] that it is possible to extrapolate $k_\varepsilon/[A]$ to $[A] = 0$, and if the last term of (16) can be neglected.

Measurements

The extinctiometric measurements have been carried out at 20°C with a Beckman Recording Quartz Spectrophotometer Model DK 1. Except in obtaining the survey in Fig. 3, the spectrophotometer was constantly adjusted to the wavelength 378 mμ. As the absorption bands are very narrow, it is necessary to use a very narrow band width. Therefore the apparatus was set at a high sensitivity (80), which resulted in a very narrow slit and an effective band width of only ≈ 5 Å.

According the Fronæus [2,p.95] the experimental error caused by the imperfect mono-chromaticity of the light is reduced if the measurements are carried out in a wavelength range where the extinction curve has a horizontal tangent. This is not possible in the case of the Er^{3+}-Ac$^-$-system, owing to the narrow peaks and to the fact that the positions of the peaks are shifted when the complexes are formed. At 378 mμ, however, the extinction curve has about the same slope at all values of [Ac$^-$].

Another systematic error is caused by the partial reflection of the light at the end plates of the absorption cells. This error is reduced if the corresponding solutions, used at the calculation of k_ε (*i.e.*, solutions with the same ε), have the same value of E. This condition is fulfilled approximately if solutions with the same value of C_A' also have the same value of $d.C_M$ (*cf.* Table 11).

The solutions measured have been prepared by mixing different volumes of two solutions,

$$S_1: \frac{75}{d} \text{ mM Er(ClO}_4)_3 + (2\ 000 - 6.\frac{75}{d}) \text{ mM NaClO}_4$$

$$S_2: 2\ 000 \text{ mM HAc} + 1\ 000 \text{ mM NaAc} + 1\ 000 \text{ mM NaClO}_4$$

Thus, the connection between C_M and C_A' is

$$C_M = \frac{75}{d}(1 - C_A' \times 10^{-3}),\ C_M \text{ and } C_A' \text{ in mM} \tag{17}$$

In the calculation of the true ligand concentration $C_A = C_A' + [\text{H}^+] - C_H$ of the complex solution, the potentiometrically obtained values of the correction terms [H$^+$] and C_H have been used.

As one absorption cell has been filled with the complex solution and the other with a buffer solution with the same C_A', the value of $E - d \cdot \varepsilon_A^\circ \cdot C_A'$ has been determined directly.

It was controlled that Beer's law is valid for erbium perchlorate solutions with low C_M. At 378 mμ it was found $\varepsilon_M^\circ = 2.15 \pm 0.03$ for $C_M \leq 40$ mM.
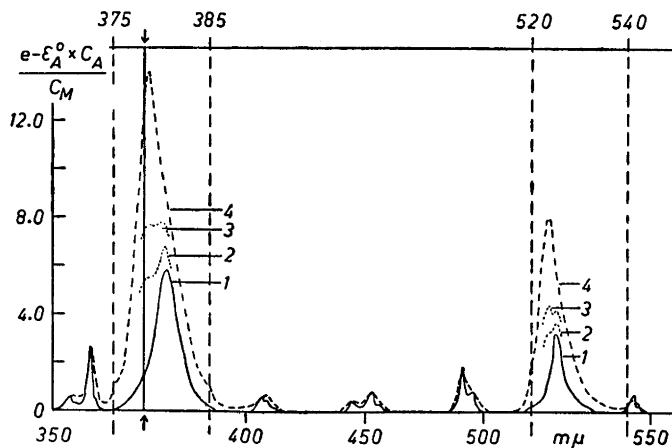
Fig. 3. Extinction curves of one erbium perchlorate solution (curve 1) and three erbium perchlorate solutions with various amounts of the buffer 2 HAc:1 NaAc; $\bar{n} \approx 0.9$ (curve 2), $\bar{n} \approx 1.4$ (curve 3) and $\bar{n} \approx 4$ (curve 4), $\bar{n}$ according to the potentiometric measurements. The arrows and the line indicate the wavelength 378 mμ at which the extinctiometric investigation has been performed. - - - - The erbium ion has still another absorption band in the visible range at about 660 mμ. The height of the peak is nearly independent of C_{Ac} ($\varepsilon_M^\circ \approx 1.5$). — — — The two ranges 375—385 mμ and 520—540 mμ have been enlarged.

Fig. 3 shows the extinction curves of one erbium perchlorate solution and three complex solutions with different values of [A]. The addition of acetate buffer results in the appearance of a new peak of somewhat shorter wavelength in the band at 380 mμ as also in the band at 525 mμ. At high acetate concentration the new peak dominates and incorporates the original peak. It is evident that ε of the new peak is a function of [A]. Otherwise, of course, the extinc-

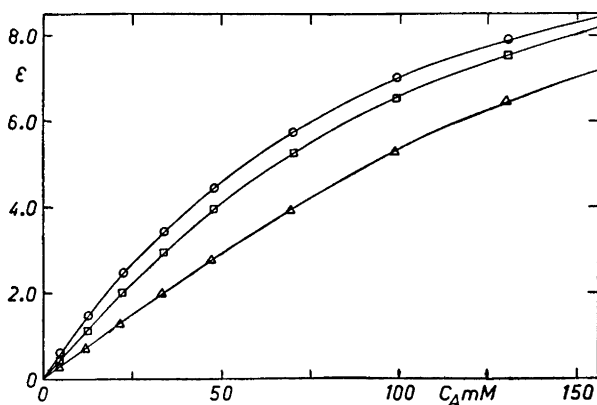*Fig. 4.* ε of the erbium acetate system as a function of C_{Ac} - for three different values of the factor $\dfrac{75}{d}$ of eqn. (17). $\bigcirc : d = 10$ cm; $\square : d = 5$ cm; $\triangle : d = 2$ cm.

Table 11. Determination of the corresponding values of [A] and k_ε for the erbium acetate system and a comparison between $k_\varepsilon/[A]$ and the potentiometrically obtained values of $\bar{n}_I/[A]$.

ε	$d = 2$ cm		$d = 5$ cm		$d = 10$ cm		$C_M = 0$ [A] mM	k_ε	$\dfrac{k_\varepsilon}{[A]}$	$\dfrac{\bar{n}_I}{[A]}$ pot.
	C_A mM	C_M mM	C_A mM	C_M mM	C_A mM	C_M mM				
1.5	25.6	36.6	16.6	14.8	13.0	7.4	10.2	0.42	41.5	37.5
2.0	33.8	36.2	22.3	14.7	17.8	7.4	14.0	0.55	39	36.5
2.5	42.4	35.9	28.2	14.6	23.0	7.3	18.2	0.68	37.5	35
3.0	51.5	35.6	34.4	14.5	28.6	7.3	22.8	0.81	35.5	34
3.5	60.5	35.2	40.8	14.4	34.6	7.2	28.0	0.93	33	32.5
4.0	70.0	34.8	48.5	14.3	41.0	7.2	33.5	1.05	31.5	31
4.5	80.5	34.5	56.0	14.2	48.0	7.1	39.5	1.18	30	29.5
5.0	91.5	34.1	65.0	14.0	56.0	7.1	46.5	1.32	28.5	28
5.5	103	33.6	74.5	13.9	65.0	7.0	55.0	1.45	26.5	26
6.0	116.5	33.1	85.5	13.7	75	6.9	64.0	1.59	25	24.5
6.5	131	32.6	98	13.5	86.5	6.8	74.5	1.73	23	23
7.0	148	32.0	112	13.3	99.5	6.8	86.5	1.92	22	21.5
7.5	167	31.2	129	13.1	115	6.6	102	2.1	20.5	19.5
8.0	190	30.4	148	12.8	134	6.5	120	2.2	18	17.5

tiometric method of investigation of the complexity system were not applicable. The peak at 380 mμ has been chosen for the measurements as solutions with lower C_M can be used.

Complex rare earth systems have been examined extinctiometrically before, *e.g.*, by Moeller and Brantley [3] and by Vickery [4], who have examined solutions of the EDTA-complexes. They, too, observed that in some cases the dominating bands of the rare earth were split when the complexing agent was added. However, no attempts of computing the complexity constants of the systems were made.

The function $\varepsilon = f(C_A)$ of three series with different C_M is shown in Fig. 4. Table 11 gives the corresponding values of C_A and C_M at some values of ε. The function $(C_A)_\varepsilon = f(C_M)_\varepsilon$ proves to be approximately linear for $\varepsilon > 2.0$. Thus it is possible to extrapolate the function to $C_M = 0$ and to calculate

Table 12. The X-functions of the erbium acetate system calculated from the extinctiometric measurements.

[A] mM	X ([A])	X_1 M^{-1}	X_2 M^{-2}	X_3 M^{-3}
0	1	*45*	*770*	*4 500*
10	1.535	53.5		
15	1.87	58		
25	2.69	67.5	900	
40	4.35	84	975	
60	7.57	110	1 080	5 100
80	12.2	140	1 200	5 300
100	18.7	177	1 320	5 500

Table 13. The complexity constants with the random errors of the systems investigated.

Systems	β_1 M⁻¹	β_2 M⁻²	β_3 M⁻³	β_4 M⁻⁴	β_1' M⁻²
A. Potentiometric investigation.					
Pr^{3+} —Ac⁻	65 ± 2	650 ± 60	1 900 ± 300	∼2 000	—
Sm^{3+} —Ac⁻	103 ± 3	1 810 ± 180	7 100 ± 1 200	∼7 000	—
Dy^{3+} —Ac⁻	47 ± 2	930 ± 90	6 100 ± 1 000	∼8 000	40 ± 20
Ho^{3+} —Ac⁻	43 ± 2	730 ± 70	5 600 ± 800	∼4 000	—
Er^{3+} —Ac⁻	40 ± 2	680 ± 70	4 500 ± 700	∼4 000	30 ± 20
Yb^{3+} —Ac⁻	44 ± 2	680 ± 70	3 500 ± 600	∼4 000	30 ± 20
B. Extinctiometric investigation.					
Er^{3+} —Ac⁻	45 ± 5	750 ± 150	∼5 000	—	—

the values of k_ε and [A] given in Table 11. As seen in the table the agreement between $k_\varepsilon/[A]$ and $\bar{n}_I/[A]$, potentiometrically obtained, is surprisingly good, especially for [A] > 25 mM.

The function $k_\varepsilon/[A] = f([A])$ has been extrapolated to [A] = 0 and after that the complexity constants have been computed in the same way as before (Table 12). The constants obtained extinctiometrically are in good agreement with those determined potentiometrically (Table 13). Therefore it seems plausible to assume that the approximations made are permissible, *i.e.*, that the concentration of polynuclear complexes in erbium acetate solutions with low C_M is so low that $k_\varepsilon \approx \bar{n}_I$.

Table 14. The stability constants of the rare earth acetate systems reported in Parts I and II, the ionic radii and the numbers of electrons in the 4f-orbitals of the tervalent rare earth ions.

Rare earth	Atomic number	Ionic radius* in A	Number of electrons in the 4f-orbitals	b_1 $= \beta_1$	b_2	b_3	b_4	$\dfrac{b_1}{b_2}$	$\dfrac{b_2}{b_3}$	$\dfrac{b_3}{b_4}$
La	57	1.06	0	36	8.3	3.2	0.9	4.3	2.6	4
Ce	58	1.03	1	48	10.2	2.8	1.1	4.7	3.6	3
Pr	59	1.01	2	65	10.0	2.9	1.0	6.5	3.5	3
Nd	60	1.00	3	80	12.8	2.8	1.2	6.3	4.6	2
Sm	62	0.96	5	103	17.6	3.9	1.0	5.9	4.5	4
Gd	64	0.94	7	69	19.1	3.9	1.0	3.6	4.9	4
Dy	66	0.91	9	47	19.8	6.6	1.3	2.4	3.0	5
Ho	67	0.89	10	43	17.0	7.7	0.7	2.5	2.2	11
Er	68	0.88	11	40	17.0	6.6	0.9	2.4	2.6	7
Yb	70	0.86	13	44	15.5	5.1	1.1	2.8	3.0	5

* Templeton, D. H. and Dauben, C. H. *J. Am. Chem. Soc.* **76** (1954) 5237.

At low [A], $k_\varepsilon/[A]$ seems to be somewhat higher than $\bar{n}_I/[A]$. As seen in eqn. (16) this is possible if $\varDelta\varepsilon_1 < 0$, or, perhaps more likely, if $\varDelta\varepsilon_1' < 0$. When [A] < 15 mM, [A] and k_ε will be very uncertain, as the values of $(C_A, C_M)_\varepsilon$ no longer represent a straight line.

DISCUSSION OF THE RESULTS

As seen in Table 14, the stability constant b_1 of the first mononuclear complex increase strongly from La to Sm. This increase is expected as the ionic radius decreases in the same direction. However, from Sm to Dy b_1 decreases strongly and then b_1 remains approximately constant at Dy, Ho, Er and Yb, although the ionic radius decreases incessantly. Thus it seems as if the possibility of forming the first acetate complex is rendered more difficult after the 4f-orbitals have been half-filled with electrons.

To begin with, the stability constant of the second complex increases when the ionic radius of the rare earth decreases, but from Dy to Yb also b_2 shows a decided tendency to decrease. The maximum stability of the third complex is reached at Ho. Thus the tendency to form higher complexes does not decrease as rapidly as the tendency to form the first complex.
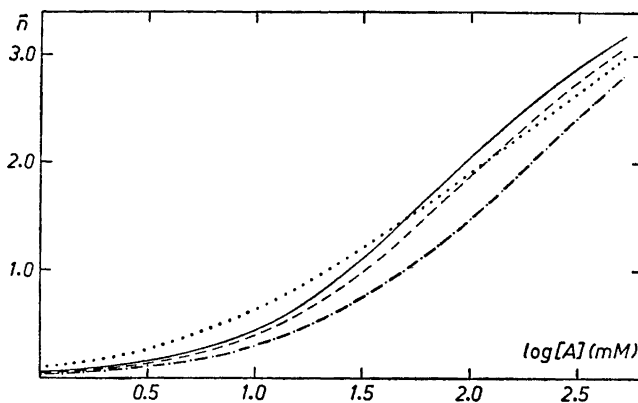

Fig. 5. The complex formation curves of some rare earth acetate systems: ———— the Dy^{3+}-Ac$^-$-system; — — — the Yb^{3+}-Ac$^-$-system; · · · · · the Sm^{3+}-Ac$^-$-system; — · — · — the La^{3+}-Ac$^-$-system.

Fig. 5 shows how the ligand number $\bar{n}_I$ of some rare earth acetate systems varies with the concentration of free ligand of the solution.

As was discussed in Part I, it is doubtful whether the fourth complexity constant has a real meaning, as anionic acetate complexes of the rare earths cannot be proved by anion exchange experiments (Fronæus [5]).

As to the formation of polynuclear complexes, β_1' is 30 à 40 M^{-2} for Gd, Dy, Er and Yb and probably also for Ho. For the acetate systems of the

lighter rare earths the presence of polynuclear complexes is not so evident (perhaps because the $\bar{n}/[A]$-curves are rather steep at the lowest values of [A]).

REFERENCES

1. Sonesson, A. *Acta Chem. Scand.* **12** (1958) 165.
2. Fronæus, S. *Komplexsystem hos koppar* (Diss.) Lund 1948.
3. Moeller, Th. and Brantley, J. C. *J. Am. Chem. Soc.* **72** (1950) 5447.
4. Vickery, R. C. *J. Chem. Soc.* **1952** 421.
5. Fronæus, S. *Svensk Kem. Tidskr.* **65** (1953) 19.