On the Complex Chemistry of the Tervalent Rare Earth Ions

I. The Acetate Systems of Lanthanum, Cerium, Neodymium, and Gadolinium

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The complexity constants of the acetate complexes of La^{3+}, Ce^{3+}, Nd^{3+}, and Gd^{3+} have been determined. The values of the complexity constants $\beta_n = \frac{[MA_n]}{[M] \cdot [A]^n}$ that are given in Table 8 have been found in perchlorate medium of ionic strength 2 M at 20°C. The fourth constant must be considered only as a quantity formally computed from the potentiometric measurements, as an ion exchange investigation (Fronæus [1,17]) has shown that the cerium acetate system most probably does not contain anionic complexes to a detectable amount at acetate concentrations <500 mM.

The value of β_1 increases from La^{3+} to Nd^{3+}, which is expected on account of the decreasing ionic radius. The gadolinium acetate system, however, has a smaller β_1 than the neodymium system.

THE fifteen elements with the atomic numbers 57 to 71 are called rare earths or lanthanons *. As all the terpositive rare earth ions have the same electron configuration $5s^2$ $5p^6$ of the outermost shell, they show great similarity with regard to their chemical properties. The decrease of the ionic radius from lanthanum to lutetium (cf. Herlinger [2]) leads, however, gradually to a slight change in the chemical properties. Thus, we can expect that the terpositive ions will form complexes of the same structure and of about the same strength, but that the strength of the complexes will increase from lanthanum to lutetium. Such a change has also been found by Schwarzenbach [3,4], Spedding [3,5], Vickery [6] and their coworkers. They have investigated the complex formation with some very strong complexing agents, such as ethylenediamine tetra-acetic acid and some of its derivatives, which all give chelates. These

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* Spectroscopists usually do not count lanthanum among the rare earths as it has no electrons in the 4f subshell. Chemically, however, lanthanum belongs to the rare earths.

investigations also show that the increase in the stability of the complexes is not quite uniform. If the complexity constants are plotted as a function of the atomic number or the ionic radius of the rare earth, the curve will show a distinct break at gadolinium.

So far the variation of the complexity constants in the rare earth series has been studied only for polydentates. For an examination of the different steps of the complex formation, a monodentate ligand must be chosen that gives complexes of at least moderate strength. The acetate ion has proved a suitable ligand, especially as the acetate complexes are easy to investigate by potentiometric measurements. The only rare earth acetate system that has been investigated so far is the cerium(III) acetate system, the complexity constants of which Fronæus [1] has determined by the cation exchange method. In the present investigation a series of rare earth acetate systems will be examined by potentiometric measurements. In some cases the potentiometrically obtained results will be controlled by other investigations.

Calculation of the complexity constants in measurements of the free ligand concentration

By the potentiometric measurements the concentration of free ligand ([A]) has been determined in solutions with a known total concentration of the central ion (C_M) and of the ligand (C_A). The calculations are performed according to the method elaborated by Fronæus [7] (earlier works by Bjerrum [8] and Leden [9]). In the present paper only definitions of the symbols and a summary of the equations used are given.

If only mononuclear complexes MA_1, MA_2, ... MA_N are formed, we have the following equilibrium for the formation of the complex MA_n

$$MA_{n-1} + A \rightleftharpoons MA_n$$
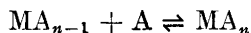
The corresponding complexity constant β_n is defined

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

With β_n we can express C_M and C_A as functions of [A] and [M].

$$C_M = [M] \cdot X \tag{1a}$$

$$C_A = [A] + [M] \cdot X' \cdot [A] \tag{1b}$$

where $X = X([A])$ is defined by the equation

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

and

$$X' = \frac{d\ X([A])}{d\ [A]}$$

The ligand number $\bar{n}$ is defined according to Bjerrum [8]

$$\bar{n} = \frac{C_A - [A]}{C_M} \tag{2}$$

By plotting $\bar{n}$ as a function of log [A] we get the complex formation curve. Combination of the eqns. (1) and (2) and elimination of [M] will give

$$\frac{\bar{n}}{[A]} = \frac{X'}{X} \qquad (3)$$

and after integration

$$\ln X([A]_j) = \int_0^{[A]_j} \frac{\bar{n}}{[A]} \cdot d[A] \qquad (4)$$

Thus, this integration gives us corresponding values of X and [A].

The complexity constants β_1, β_2, ... can now be calculated by successive extrapolation to [A] = 0 of the functions X_1, X_2, ...

$$X_1 = \frac{X - 1}{[A]} = \beta_1 + \beta_2 \cdot [A] + \beta_3 \cdot [A]^2 + \dots \\
X_2 = \frac{X_1 - \beta_1}{[A]} = \beta_2 + \beta_3 \cdot [A] + \dots \qquad (5)$$

and so on for the following constants.

The composition of the complex system at a known [A] can be computed from the following equations.

$$\alpha_0 = \frac{[M]}{C_M} = \frac{1}{1 + \beta_1 \cdot [A] + \beta_2 \cdot [A]^2 + \dots} \\
\alpha_n = \frac{[MA_n]}{C_M} = \frac{\beta_n \cdot [A]^n}{1 + \beta_1 \cdot [A] + \beta_2 \cdot [A]^2 + \dots} \qquad (6)$$

When the complexity constants are known we can check our calculations by computing the ligand number $\bar{n}_c$ at some values of [A].

$$\bar{n}_c = \sum_{n=1}^{N} \frac{n\beta_n [A]^n}{1 + \beta_n [A]^n} \qquad (7)$$

If polynuclear complexes are formed, we cannot directly use the $\bar{n}/[A]$-function for the computation of the constants of the mononuclear complexes. We assume here that the solution contains only mono- and dinuclear complexes. β_n' denotes the constant for the n:th dinuclear complex

$$\beta_n' = \frac{[M_2 A_n]}{[M]^2 \cdot [A]^n}$$

We mean by Y the following function (Fronæus [7 p. 14])

$$Y([A]) = \sum_{n=1}^{L} \beta_n' \cdot [A]^n$$

Then we get for the total concentration of central ion and ligand

$$C_M = [M] \cdot X + 2[M]^2 \cdot Y$$

and

$$C_A = [A] + [M] \cdot X' \cdot [A] + [M]^2 \cdot Y' \cdot [A]$$

The expression corresponding to eqn. (3) will now be

$$\frac{\bar{n}}{[A]} = \frac{X' + [M] \cdot Y'}{X + 2[M] \cdot Y} \tag{8}$$

Thus, for a system with both mono- and dinuclear complexes $\bar{n}/[A]$ is a function of both [A] and [M]. When $C_M \to 0$, we get

$$\lim_{C_M \to 0} \frac{\bar{n}}{[A]} = \frac{X'}{X} \tag{9a}$$

Consequently, it is possible to compute the constants of the mononuclear complexes in the ordinary way by the aid of (9a).

If $C_A \to 0$, eqn. (8) will give (as $[M] \to C_M$, when $C_A \to 0$)

$$\lim_{C_A \to 0} \frac{\bar{n}}{[A]} = \beta_1 + C_M \cdot \beta_1' \tag{9b}$$

Thus, the $\bar{n}/[A]$-values at low [A] must increase with C_M if the complex system contains both mono- and dinuclear complexes.

Calculation of [A] and $\bar{n}$ from experimental data

If C'_{HA} and C'_A signify the stoichiometric concentrations of acetic acid and sodium acetate, respectively, and $[H^+]'$ the hydrogen ion concentration in a buffer solution free from rare earth ions, the following equation is valid

$$K_c = \frac{[H^+]' \, (C'_A + [H^+]')}{C'_{HA} - [H^+]'} \tag{10}$$

For a solution with the concentration C_M of rare earth ions and with the same stoichiometric concentration of acetate buffer as above, we denote by $[H^+]$ the concentration of hydrogen ions, by [A] the concentration of free acetate ions and by [HA] the concentration of unprotolysed acetic acid. If the rare earth perchlorate contains some free acid, its concentration $C_H = \nu \cdot C_M$ must be accounted for. Then we get

$$[HA] = C'_{HA} + C_H - [H^+]$$

and

$$K_c = \frac{[H^+] \cdot [A]}{C'_{HA} + C_H - [H^+]} \tag{11}$$

[A], which is the concentration sought, can be derived from eqns. (10) and (11). If $C'_{HA}/C'_A = \delta$ we get

$$[A] = \frac{[H^+]'}{[H^+]} \cdot \frac{(C'_A + [H^+]') \, (\delta C'_A + C_H - [H^+])}{\delta C'_A - [H^+]'} \tag{12}$$

This expression can (Ahrland [10]) be simplified to

$$[A] = \frac{[H^+]'}{[H^+]} \left[C'_A + \frac{C_H - [H^+] + (1 + \delta) \cdot [H^+]'}{\delta} \right] \tag{13}$$

Eqn. (13) can be used for the computation of [A] except at the very lowest [A]-values.

As the total acetate concentration in the complex solution is $C_A = C'_A + [H^+] - C_H$, we get for the ligand number

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

The hydrogen ion concentration has been determined by a quinhydrone electrode. If E denotes the emf of the element in (15) and E' the emf of the same element when $C_M = 0$, we have at 20°C

$$E' - E = E_A = 58.16 \log \frac{[H^+]}{[H^+]'} \tag{14}$$

CHEMICALS USED

Rare earth perchlorates. The perchlorates were prepared from *perchloric acid* (Baker's analyzed) and lanthanum chloride *puriss.*, cerium(III) chloride *puriss.*, neodymium oxide (quality "Specpure" from Johnson, Matthey and Co, London) and gadolinium nitrate (from A. D. Mackay, New York), respectively. The nitrate and the chlorides were evaporated several times with perchloric acid until no nitrate or chloride ions could be detected. The oxide was dissolved by heating with the acid. The greatest part of the excess of perchloric acid was removed by evaporation and the residue was determined by a potentiometric pH-titration.

The stock solutions were examined in a Beckman DU Spectrophotometer. No foreign elements with absorption in the wavelength range 2 000—9 000 Å could be detected. Cerium(IV) ions could not be found in the cerium(III) perchlorate.

The concentrations of lanthanum, neodymium and gadolinium were determined according to Berl-Lunge [11] by precipitating the rare earth as oxalate, igniting the precipitate and weighing the residue as oxide. The concentrations of lanthanum and neodymium were controlled by precipitation with 8-hydroxychinoline according to Pirtea [12]. The agreement between the values obtained by the oxalate and the hydroxychinoline method was very good. The cerium content was determined volumetrically according to Weiss and Sieger [13].

Sodium perchlorate with less than 0.01 % Cl⁻ and ClO₃⁻ was prepared from the quality *purum* by two recrystallizations according to Fronæus [7, p. 31].

Calculated amounts of *acetic acid (p. a.)* and *sodium acetate* (Baker's analyzed) were used for preparation of the buffer solutions. The concentrations of acid and acetate were controlled.

Quinhydrone was prepared according to Biilman and Lund [14].

EXPERIMENTAL

By potentiometric measurements the emf of elements of the following composition was determined.

| Au | Quinhydrone 10.2 mM HClO₄ NaClO₄ to $I = 2.0$ M | 2.0 M NaClO₄ | Quinhydrone C_M mM Me(ClO₄)₃ $C_H = \nu \cdot C_M$ mM HClO₄ C'_A mM NaAc $C'_{HA} = \delta \cdot C'_A$ mM HAc NaClO₄ to $I = 2.0$ M | Au | (15) |

Here Me^{3+}, Ac^- and I denote, respectively, rare earth ions, acetate ions and the ionic strength of the solution. The concentration of perchloric acid in the left half-cell was not quite the same in all series, but the exact value did not differ very much from 10.2 mM.

The solution in the right half-cell was prepared by adding a known volume of a buffer solution S_2 to a known volume of a solution S_1 with rare earth perchlorate.

	Solution S_1	Solution S_2	
$Me(ClO_4)_3$	C_M^0	0	mM
$HClO_4$	$C_H^0 = v \cdot C_M^0$	0	mM
NaAc	0	$C_A^0 = 1\,000$	mM
HAc	0	$C_{HA}^0 = \delta \cdot C_A^0$	mM
$NaClO_4$	$2\,000 - 6\ C_M^0 - C_H^0$	$1\,000$	mM

The mixing of the solutions to be measured was brought about by a stream of nitrogen, free from oxygen but containing water vapour of the pressure prevailing over a 2 M solution of sodium perchlorate. During the experiments the solutions were kept in a thermostat at a constant temperature of 20°C. Every titration series was repeated at least once. For the potentiometric measurements a Leeds-Northrup »Students Potentiometer» was used. The emfs were stable and could be reproduced within 0.2 mV with very few exceptions. The uncertainty of the E_A-values is estimated to $\pm$ 0.2 mV.

MEASUREMENTS

As a check of the applicability of the quinhydrone electrode for pH-measurements in solutions with rare earth ions, a quinhydrone element with $C_H = 90$ mM ($HClO_4$) and $C_M = 0$ mM ($I = 2.0$ M) was mixed with different volumes of a neodymium perchlorate solution with very nearly the same content of acid as above ($I = 2.0$ M). A slight deviation, increasing with C_M, was found between the calculated and the measured emfs. At $C_M = 15$ mM the deviation was 0.3 mV and at $C_M = 100$ mM as high as 1.0 mV. The direction of the deviation was such that the hydrogen ion concentration of the neodymium solution became too high. This may indicate a slight complex formation between neodymium and hydroquinone. However, a positive conclusion cannot be drawn, because at least a part of the deviation may depend on a salt error of the quinhydrone electrode and on variations of f_{H^+} and the liquid junction potentials, caused by the medium changes.

In order to obtain another check of the E_A-values obtained by the quinhydrone electrode, two titration series were repeated using a hydrogen gas electrode. If hydroquinone complexes are formed, the hydrogen gas electrode should give lower E_A-values (E_A^H) than the quinhydrone electrode (E_A^Q). The difference $E_A^Q - E_A^H$ ought to be particularly significant at high C_M and low C_A. Tables 3 D and 5 E show that generally E_A^Q is greater than E_A^H, even at such high acetate concentrations that the hydroquinone complexes must have disappeared. This confirms that the formation of hydroquinone complexes is not the only reason for the disagreement between the two sets of E_A-values.

The plausible conclusion seems to be that if rare earth-hydroquinone complexes exist, they are so weak that they cannot cause serious errors in the complexity constants computed form E_A^Q.

In order to check the tendency of the unprotolyzed acetic acid to form complexes with the rare earth ions, the solutions I and II in the table below were examined extinctiometrically.

	Solution I	Solution II	
$Nd(ClO_4)_3$	50	50	mM
$HClO_4$	100	100	mM
$NaClO_4$	1 600	1 600	mM
HAc	0	2 500	mM

The two solutions gave extinction curves that were practically identical in the wave length range 3 000—9 000 Å. Therefore, complexes with the unprotolyzed acetic acid can be excluded.

The hydrated rare earth ions (at least up to gadolinium) have only a very slight tendency to give off protons at pH <5 as shown by Moeller [15] and Fronæus [16]. This conclusion must be drawn also from the investigations related to in the present paper. The concentration of acetic acid of the buffer solutions used in the titration series has been varied widely, but the $\bar{n}/[A]$-functions of the acetate systems show no tendency to depend on the pH of the complex solutions.

On account of the complex formation the ionic strength of the solutions we measure decreases considerably at higher C_M. This causes a certain error in E_A and then also in $\bar{n}/[A]$. We can eliminate this error by determining $\bar{n}/[A]$-functions for different C_M and extrapolating them to $C_M = 0$. This method, however, is rather time-consuming as it requires several series of measurement, and, moreover, it cannot be used if we want to determine complexity constants for dinuclear complexes. In the present investigation the decrease of ionic strength has been compensated by addition of a calculated amount of sodium perchlorate. The change of emf, ΔE_A, obtained in this way, has then been plotted in a diagram against ΔI, the decrease in ionic strength. The increase in volume caused by the added perchlorate requires only a slight correction of ΔE_A. Measurements of this kind have been carried out with some rare earth acetate systems at different C_M. They have given practically the same connection between ΔE_A and ΔI.

$$\Delta E_A = 5.0 \cdot \Delta I \qquad (16)$$

(ΔE_A in mV and ΔI in M). ΔI has been computed according to formula (17) from $\bar{n}$, calculated with the aid of uncorrected E_A-values.

$$\Delta I = 0.5 \ C_M \cdot \bar{n} \ (7 - \bar{n}) \qquad (17)$$

This formula is derived with the assumption that the solution contains only the complex $MA_{\bar{n}}^{3-\bar{n}}$ ($\bar{n}$ is the ligand number). However, assuming that four complexes are formed, the correct expression for ΔI is

$$\Delta I = C_M(3\alpha_1 + 5\alpha_2 + 6\alpha_3 + 6\alpha_4) \qquad (18)$$

α is the distribution of the central ions between the particular complexes (eqn. 6). In order to be able to use eqn. (18), we must know at least approximate values of the complexity constants. However, calculations have shown

Table 1. Determination of E' as a function of C'_A for the different acetate buffers used.

↓ Buffer	C'_AmM →	9.90	29.1	74.1	130.4	230.7	333	444	546	$K_c \times 10^{+5}$ at $C'_A \approx$ 100 mM
$\delta = 0.5$	E' mV →	180.2	180.1	180.0	180.0	179.9	179.9	179.9	179.9	1.64
$\delta = 2.0$	E' mV →	145.1	145.0	144.9	144.8	144.6	144.6	144.6	144.7	1.65
$\delta = 5.0$	E' mV →	121.8	121.6	121.3	121.1	120.9	120.8	120.9	121.0	1.68

that the eqns. (17) and (16) give ΔE_A-values, which at most are only 0.2 mV higher than ΔE_A computed with ΔI from eqn. (18). As there are probably other errors in E_A on account of the medium changes, which we have no possibility of making corrections for, eqn. (17) gives a value of ΔI that is accurate enough.

The emf E' in eqn. (14) has been determined at different C'_A by measuring the emf of the element (15) with $C_M = 0$. The E'-values for the buffers used are shown in Table 1. The measurements show that the emf varies slightly when the perchlorate is gradually exchanged for acetate buffer. Additions of the most acid buffer have an especially great influence. The reason for the change of emf may be that the medium changes cause variations of the liquid junction potentials and of the activity coefficients of the hydrogen ions and the quinhydrone components. Under the presumption that E' is changed in the same way when rare earth ions are present in the solution, the variation of E' does not affect the results, as only the E_A-values are used for the computations (except for determination of the correction terms of eqn. (12)).

1. The lanthanum acetate system

The experimentally obtained values of E_A and the values of [A] and $\bar{n}/[A]$ calculated from $E_A - \Delta E_A$ are collected in Tables 2A-D. The second term in the E_A-columns is the correction term ΔE_A in eqn. (16), which must be subtracted from the first term, the experimentally determined E_A-value to compensate for the reduction of the ionic strength.

Fig. 1 shows that the agreement between the $\bar{n}/[A]$-values from series with different C_M is so good that polynuclear complexes can be formed only to a very slight extent.

For the lanthanum acetate system, as for the following complex systems in this paper, the $\bar{n}/[A]$-values are independent of the ratio C'_{HA}/C'_A of the buffer solutions.

By graphical integration of the fulldrawn curve in Fig. 1, the function X in Table 4A has been computed and after that the functions $X_1...X_4$ and the complexity constants. As the lanthanum acetate system, like the other

Table 2. Determination of corresponding values of [A] and $\bar{n}$/[A] for the lanthanum acetate system.

$C_M = C_M^\circ(1 - C_A' \times 10^{-3})$ mM						
	A $C_M^\circ = 50.6$ mM $C_H = 4.25 \times 10^{-3} \times C_M$ mM Buffer $\frac{1}{2}:1$ Sign $\square$			**B** $C_M^\circ = 75.5$ mM $C_H = 2.12 \times 10^{-3} \times C_M$ mM Buffer $\frac{1}{2}:1$ Sign $\triangle$		
C_A' mM	E_A mV	[A] mM	$\dfrac{\bar{n}}{[A]}$ M^{-1}	E_A mV	[A] mM	$\dfrac{\bar{n}}{[A]}$ M^{-1}
9.90	26.9	3.55	34.6	33.3	2.73	34.6
19.61	24.9 − 0.1	7.50	32.0	31.8 − 0.2	5.69	32.7
38.5	22.4 − 0.3	16.21	27.9	29.5 − 0.4	12.24	29.4
56.6	20.5 − 0.4	25.7	25.0	27.7 − 0.6	19.46	26.7
90.9	17.6 − 0.6	46.6	20.6	24.6 − 0.8	35.5	22.7
122.8	15.4 − 0.7	68.9	17.6	22.0 − 1.0	53.6	19.5
152.5	13.7 − 0.8	91.8	15.4	19.9 − 1.1	72.6	17.2
200.0	11.5 − 0.9	131.7	12.8	17.0 − 1.2	107.1	14.3
285.7	8.6 − 0.9	210.9	9.8	12.9 − 1.3	180.6	10.8
375	6.5 − 0.8	299.5	8.0	9.8 − 1.2	267	8.6
500	4.5 − 0.7	430	6.4	6.7 − 1.0	399	6.7
	C $C_M^\circ = 50.6$ mM $C_H = 4.25 \times 10^{-3} \times C_M$ mM Buffer 2:1 Sign $\blacksquare$			**D** $C_M^\circ = 75.5$ mM $C_H = 2.12 \times 10^{-3} \times C_M$ mM Buffer 2:1 Sign $\blacktriangle$		
C_A' mM	E_A mV	[A] mM	$\dfrac{\bar{n}}{[A]}$ M^{-1}	E_A mV	[A] mM	$\dfrac{\bar{n}}{[A]}$ M^{-1}
9.90	25.7	3.62	34.0	32.7	2.73	34.8
29.13	23.0 − 0.2	11.86	29.5	30.5 − 0.3	8.84	31.2
47.6	21.2 − 0.3	20.85	26.5	28.4 − 0.5	15.81	27.9
74.1	18.8 − 0.5	36.0	22.5	26.1 − 0.7	27.1	24.7
107.1	16.4 − 0.6	57.4	19.1	23.2 − 0.9	44.4	21.0
166.7	12.9 − 0.8	103.3	14.5	18.8 − 1.2	83.1	16.0
230.7	10.3 − 0.9	159.1	11.6	15.3 − 1.3	132.6	12.7
333	7.3 − 0.8	258	8.7	11.1 − 1.3	226	9.4
444	5.2 − 0.7	372	6.9	7.9 − 1.1	340	7.4
546	3.8 − 0.6	481	5.9	5.8 − 0.9	449	6.2
583	3.4 − 0.5	520	5.8	—	—	—

systems of this paper, shows no tendency to stop its complex formation at $\bar{n} = 3$ (*cf.* Fig. 2), four constants have been computed.

In Table 9 the experimentally determined ligand number $\bar{n}_{exp}$, the computed ligand number $\bar{n}_c$ and the distribution of the central ion between the particular complexes are given for some values of [A].
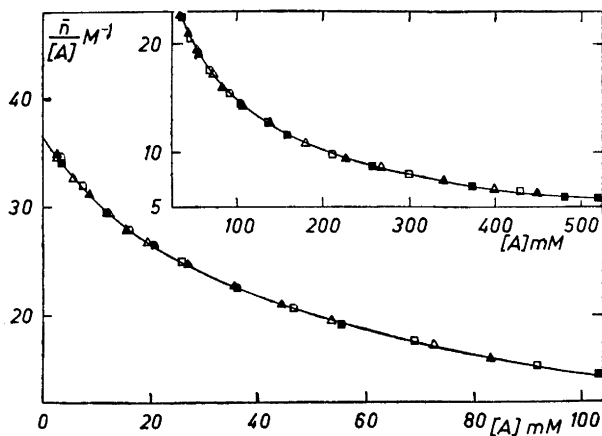
Fig. 1. $\bar{n}/[A]$ as a function of [A] for the lanthanum acetate system. The signs refer to the corresponding series in Table 2.

2. The cerium(III) acetate system

Experiments and calculations for the cerium acetate system were performed in the same way as for the preceding system. The results are to be found in Tables 3A—D and 4B. The complex formation curve is shown in Fig. 2.

Also for this system the coincidence between the $\bar{n}/[A]$-curves of the different series is so good that polynuclear complexes can be formed only to a very slight extent.

In order to check the applicability of the quinhydrone electrode, the quinhydrone series in 3D was repeated with a hydrogen gas electrode, which gave the E_A^H-values in the same table. The maximum discrepancy between uncorrected E_A^Q and E_A^H is 0.5 mV. A possible cause of this difference has been discussed on page 170.

3. The neodymium acetate system

The results obtained for this system are collected in Tables 5A-E and 7A. For this system, too, we can exclude formation of polynuclear complexes.

The series 5E was performed with both quinhydrone electrode and hydrogen gas electrode. The maximum difference $E_A^Q - E_A^H$ is + 0.8 mV.

4. The gadolinium acetate system

Measurements and calculations for this system were performed in the same way as in the foregoing systems. The results are shown in Tables 6A—D and 7B and in Fig. 3.

Table 3. Determination of corresponding values of [A] and $\bar{n}$/[A] for the cerium(III) acetate system.

$C_M = C^\circ_M(1 - C'_A \times 10^{-3})$ mM						
	A $C^\circ_M = 25.0$ mM $C_H = 5.24 \times 10^{-2} \times C_M$ mM Buffer 5 : 1 Sign O			**B** $C^\circ_M = 50.0$ mM $C_H = 5.24 \times 10^{-2} \times C_M$ mM Buffer 2 : 1 Sign ■		
C'_A mM	E_A mV	[A] mM	$\dfrac{\bar{n}}{[A]}$ M^{-1}	E_A mV	[A] mM	$\dfrac{\bar{n}}{[A]}$ M^{-1}
9.90	22.3	4.23	43.6	40.5	2.25	46.8
19.61	18.8 − 0.1	9.51	38.5	33.8 − 0.2	5.52	43.0
38.5	15.1 − 0.3	21.6	30.3	28.2 − 0.3	13.16	36.1
56.6	12.9 − 0.3	34.6	25.6	24.8 − 0.4	22.0	31.0
90.9	10.2 − 0.4	61.9	19.8	20.6 − 0.6	41.7	24.7
130.4	8.2 − 0.4	96.0	16.0	16.7 − 0.8	70.1	19.9
200.0	5.9 − 0.4	161.1	11.7	12.4 − 0.9	127.6	13.8
285.7	4.3 − 0.4	245.1	9.1	8.9 − 0.9	208.9	10.1
375	3.3 − 0.4	334.5	7.6	6.6 − 0.8	299	8.0
500	2.2 − 0.3	464	6.1	4.4 − 0.7	433	6.1
546	1.9 − 0.3	512	5.6	—	—	—
	C $C^\circ_M = 50.0$ mM $C_H = 5.24 \times 10^{-2} \times C_M$ mM Buffer $\frac{1}{2}$: 1 Sign □			**D** $C^\circ_M = 75.0$ mM $C_H = 5.24 \times 10^{-2} \times C_M$ mM Buffer 5 : 1 Sign △		
C'_A mV	E_A mV	[A] mM	$\dfrac{\bar{n}}{[A]}$ M^{-1}	E^Q_A mV	E^H_A mV	[A] mM	$\dfrac{\bar{n}}{[A]}$ M^{-1}
9.90	48.2	2.23	46.5	49.9	50.9	1.480	46.6
29.13	33.6 − 0.2	9.12	39.6	39.3 − 0.3	38.9	6.39	41.5
47.6	28.5 − 0.3	17.23	34.0	35.2 − 0.5	35.0	12.26	36.4
74.1	23.7 − 0.5	31.5	27.5	30.9 − 0.7	30.6	22.65	30.5
107.1	19.7 − 0.7	52.7	22.1	26.8 − 0.9	26.3	38.7	25.1
166.7	14.8 − 0.8	98.3	16.1	21.1 − 1.2	20.5	76.2	18.4
230.7	11.4 − 0.9	155.0	12.4	16.4 − 1.3	16.2	127.3	13.7
333	7.9 − 0.8	254	9.1	11.5 − 1.3	11.7	223	9.7
444	5.7 − 0.8	368	7.3	8.0 − 1.1	8.3	339	7.3
546	4.0 − 0.7	481	5.7	5.6 − 0.9	5.5	453	5.9
583	—	—	—	5.0 − 0.9	—	496	5.5

For this system the values of $\bar{n}$/[A] at low [A] show a slight tendency to increase with C_M. This may indicate a slight formation of polynuclear complexes. However, the value of β'_1 computed according to eqn. (9b) will be as low as 30 ± 20, and therefore the existence of dinuclear complexes must be considered as rather uncertain. The $\bar{n}$/[A]-function used for the computation of the complexity constants has been drawn in accordance to the lower $\bar{n}$/[A]-values at low [A].

Table 4. The X-functions of the lanthanum (A) and the cerium (B) acetate systems, obtained by graphical integrations of the $\bar{n}/[A]$-functions.

[A] mM	A The lanthanum acetate system					B The cerium 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	36.3	296	950	850	1	48.4	485	1 350	1 600
2	1.0740	37.0				1.0987	49.4			
6	1.230	38.2				1.310	51.6			
12	1.481	40.1				1.658	54.8			
20	1.853	42.7				2.178	58.9			
30	2.384	46.1	327			2.926	64.2	525		
50	3.688	53.8	350			4.81	76.2	556		
70	5.365	62.4	373			7.24	89.2	585		
100	8.67	76.7	404			12.14	111.4	630		
140	14.87	99.1	449			21.55	147	705		
200	29.2	141	523	1 135		43.4	212	820	1 670	1 600
300	71.1	234	655	1 200	840	108.8	359	1 040	1 840	1 630
400	144.9	360	810	1 280	830	226	563	1 290	2 000	1 620
500	266	529	985	1 380	860	414	826	1 560	2 140	1 580

DISCUSSION OF THE RESULTS

The complexity constants of the systems investigated are collected in Table 8. Table 9 gives for all four systems a comparison between determined and calculated ligand numbers ($\bar{n}_{exp}$ resp. $\bar{n}_c$) and information about the calculated distribution of the central ion between the particular complexes at some [A]-values (eqns. 6 and 7).

The limits of error given in Table 8 refer to the maximum random errors. For the four acetate systems so far examined, the potentiometric measurements have given a fourth complexity constant, the random error of which may be
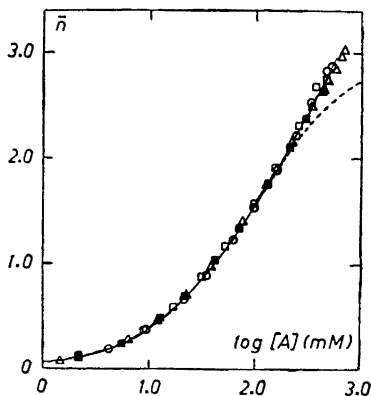

Fig. 2. The complex formation curve of the cerium acetate system. The fulldrawn curve is computed by use of $\beta_1-\beta_4$ and the broken curve by use of $\beta_1-\beta_3$ only.

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

$C_M = C^\circ_M \ (1-C'_A \times 10^{-3}) \ \text{mM}$									
	A $C^\circ_M = 25.0$ mM $C_H = 1.40 \times 10^{-2} \times C_M$ mM Buffer $\frac{1}{2}:1$			B $C^\circ_M = 50.0$ mM $C_H = 1.40 \times 10^{-2} \times C_M$ mM Buffer $\frac{1}{2}:1$			C $C^\circ_M = 75.5$ mM $C_H = 1.40 \times 10^{-2} \times C_M$ mM Buffer $\frac{1}{2}:1$		
C'_A mM	E_A mV	[A]mM	$\dfrac{\bar{n}}{[A]}$ M⁻¹	E_A mV	[A]mM	$\dfrac{\bar{n}}{[A]}$ M⁻¹	E_A mV	[A]mM	$\dfrac{\bar{n}}{[A]}$ M⁻¹
9.90	27.5 − 0.1	3.58	67.7	42.9 − 0.1	2.06	70.4	54.9 − 0.1	1.36	74.5
19.61	23.5 − 0.1	8.04	57.1	38.4 − 0.2	4.61	63.5	49.7 − 0.2	3.05	69.2
38.5	18.4 − 0.3	19.11	41.5	33.0 − 0.4	10.95	51.0	44.2 − 0.4	7.14	58.6
56.6	15.2 − 0.3	31.7	32.8	28.8 − 0.5	18.89	41.6	40.1 − 0.6	12.26	49.7
90.9	11.5 − 0.4	59.0	23.6	22.9 − 0.7	38.3	29.8	33.6 − 0.9	25.4	37.0
130.4	8.9 − 0.5	93.9	17.7	18.1 − 0.8	66.4	22.0	27.4 − 1.2	46.9	26.8
200.0	6.3 − 0.5	159.5	12.6	13.1 − 0.9	124.1	15.2	20.0 − 1.4	96.6	17.6
285.7	4.5 − 0.4	243.3	9.7	9.4 − 0.9	204.8	10.5	14.3 − 1.4	172.4	12.1
375	3.3 − 0.4	334.5	7.7	6.9 − 0.8	295	8.6	10.5 − 1.3	261	9.2
500	2.3 − 0.4	464	6.2	4.5 − 0.7	431	6.4	7.0 − 1.1	397	6.9
546	1.9 − 0.3	512	5.7	3.7 − 0.6	483	5.7	5.9 − 1.0	450	6.1

	D $C^\circ_M = 75.5$ mM $C_H = 1.40 \times 10^{-2} \times C_M$ mM Buffer $5:1$			E $C^\circ_M = 100.0$ mM $C_H = 1.40 \times 10^{-2} \times C_M$ mM Buffer $5:1$			
C'_A mM	E_A mV	[A] mM	$\dfrac{\bar{n}}{[A]}$ M⁻¹	E^Q_A mV	E^H_A mV	[A] mM	$\dfrac{\bar{n}}{[A]}$ M⁻¹
9.90	49.3 − 0.1	1.44	74.1	56.7 − 0.2	56.1	1.091	75.8
29.13	44.5 − 0.3	5.10	62.8	52.3 − 0.4	51.8	3.76	67.4
47.6	40.6 − 0.5	9.78	53.0	48.9 − 0.6	48.3	7.08	59.0
74.1	35.5 − 0.8	18.81	41.5	44.1 − 0.9	43.5	13.45	48.0
107.1	30.1 − 1.0	33.9	31.7	38.7 − 1.3	37.9	24.4	37.5
166.7	22.7 − 1.3	71.5	21.0	30.2 − 1.6	29.7	53.8	25.0
230.7	17.4 − 1.4	122.6	15.1	23.4 − 1.8	23.0	98.2	17.4
333	12.0 − 1.4	219.2	10.3	16.2 − 1.8	15.8	188.7	11.2
444	8.3 − 1.2	336	7.7	11.1 − 1.6	11.0	305	8.2
546	5.8 − 1.0	451	6.1	7.9 − 1.3	8.1	420	6.5
630	—	—	—	6.0 − 1.1	—	519	5.8

estimated to about 40 %. Thus, it seems to be possible to give at least the order of magnitude of the fourth constant.

As to the systematic errors, they apparently do not affect the determination of the lower constants, as the three first complexity constants of the cerium(III) acetate system found by Fronæus[1] in a cation exchange investigation are in good agreement with the constants obtained by the author. The two sets of constants are given in Table 10. The constants published by Fron-

Table 6. Determination of corresponding values of [A] and $\bar{n}$/[A] for the gadolinium acetate system.

$C_M = \overset{\circ}{C_M} (1 - C_A' \times 10^{-3})$ mM							
	A $\overset{\circ}{C_M} = 23.6$ mM $C_H = 8.30 \times 10^{-2} \times C_M$ mM Buffer $\frac{1}{2}:1$ Sign $\bigcirc$			B $\overset{\circ}{C_M} = 47.2$ mM $C_H = 6.37 \times 10^{-2} \times C_M$ mM Buffer $\frac{1}{2}:1$ Sign $\square$			
C_A' mM	E_A mV	[A] mM	$\dfrac{\bar{n}}{[A]}$ M^{-1}	E_A mV	[A] mM	$\dfrac{\bar{n}}{[A]}$ M^{-1}	
9.90	36.6	3.23	63.1	56.5−0.1	1.69	67.1	
19.61	28.2−0.1	7.74	55.6	45.2−0.2	4.29	62.6	
38.5	21.6−0.3	18.17	44.7	37.3−0.4	10.26	54.4	
56.6	17.9−0.4	30.2	36.6	32.8−0.6	17.68	45.8	
90.9	13.5−0.4	56.2	27.2	26.3−0.8	35.1	35.1	
122.8	10.8−0.5	83.9	21.4	21.6−0.9	56.5	27.2	
152.5	8.9−0.5	111.7	17.5	18.2−0.9	79.5	22.2	
200.0	7.0−0.5	157.0	14.0	14.3−1.0	121.0	16.7	
285.7	4.8−0.4	242.4	10.2	9.8−0.9	203.8	11.6	
375	3.5−0.4	334	8.1	6.9−0.8	298	8.6	
500	2.2−0.3	466	6.1	4.5−0.7	433	6.4	
	C $\overset{\circ}{C_M} = 23.6$ mM $C_H = 8.30 \times 10^{-2} \times C_M$ mM Buffer $5:1$ Sign $\bullet$			D $\overset{\circ}{C_M} = 47.2$ mM $C_H = 3 \times 10^{-5} \times C_M$ mM Buffer $5:1$ Sign $\blacksquare$			
C_A' mM	E_A mV	[A] mM	$\dfrac{\bar{n}}{[A]}$ M^{-1}	E_A mV	[A] mM	$\dfrac{\bar{n}}{[A]}$ M^{-1}	
9.90	28.9	3.29	63.9	34.9−0.1	2.51	65.9	
29.13	21.8−0.2	12.58	51.3	32.3−0.3	8.22	56.2	
47.6	17.9−0.3	23.9	40.8	29.4−0.5	15.18	47.9	
74.1	14.3−0.4	43.0	31.3	25.3−0.7	27.9	38.0	
107.1	11.2−0.5	70.4	23.6	21.2−0.8	47.8	29.5	
137.9	9.2−0.5	98.0	19.2	17.9−0.9	70.4	23.6	
166.7	7.8−0.5	125.2	16.2	15.4−1.0	94.3	19.6	
230.7	5.7−0.5	188.1	12.0	11.2−1.0	153.4	13.9	
333	3.9−0.4	290.5	9.1	7.6−0.9	255.5	9.7	
444	2.7−0.4	406	7.0	5.1−0.8	375	7.1	
546	1.9−0.3	512	5.9	3.6−0.6	485	5.9	

æus as obtained potentiometrically by the present author are those calculated without correction for the decrease of the ionic strength, and therefore they differ somewhat from the figures given below.

The fourth constant, however, seems to be rather dubious, as Fronæus found that anionic complexes are not formed to a detectable amount at acetate ion concentrations < 500 mM. This result is, moreover, supported by anion exchange measurements, Fronæus [17]. It is possible that the small
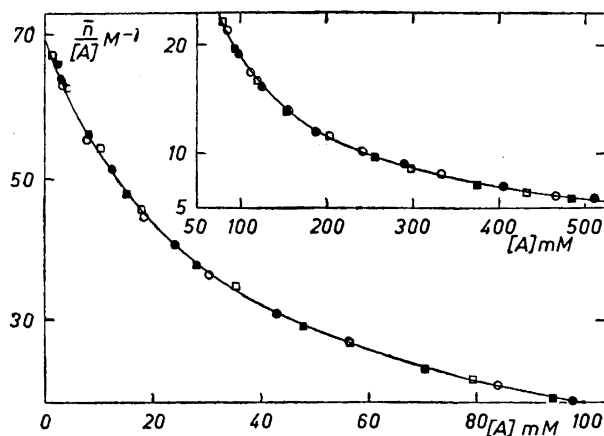
Fig. 3. The connection between $\bar{n}/[A]$ and $[A]$ for the gadolinium acetate system, according to the titration series in Table 6.

E_A-values at high ligand concentrations contain so great systematic errors that the fourth complexity constant is only imaginary. If so the complex formation curve for the cerium acetate system is represented by the broken curve in Fig. 2.

In order to exclude the dubious fourth complex, the composition of the complexity systems has been given in Table 9 only at low ligand concentrations.

Table 7. The X-functions of the neodymium (A) and the gadolinium (B) acetate systems.

[A] mM	A The neodymium acetate system					B The gadolinium 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*	*79.7*	*1 020*	*2 850*	*3 600*	*1*	*69.3*	*1 320*	*5 200*	*5 000*
2	1.1635	81.8				1.1439	72.0			
6	1.518	86.3				1.465	77.5			
12	2.112	92.6				2.036	86.3			
20	3.028	101.4	1 085			2.972	98.6	1 460		
30	4.395	113.2	1 115			4.440	114.7	1 510		
50	7.92	138.5	1 170			8.53	150.7	1 630		
70	12.65	166.5	1 240			14.43	191.8	1 750		
100	22.45	214.5	1 350			27.3	263	1 940		
140	41.6	290	1 500			53.6	376	2 190		
200	86.5	428	1 740	3 600		118.2	586	2 580	6 300	
300	223	740	2 200	3 930	3 600	322	1 070	3 330	6 700	5 000
400	471	1 175	2 740	4 300	3 630	700	1 750	4 200	7 200	5 000
500	882	1 760	3 360	4 690	3 680	1 32ɉ	2 640	5 130	7 650	4 900

Table 8. The complexity constants of the systems investigated.

System	β_1 M^{-1}	β_2 M^{-2}	β_3 M^{-3}	β_4 M^{-4}
La^{3+} — Ac$^-$	36 ± 1	300 ± 30	950 ± 200	~ 900
Ce^{3+} — Ac$^-$	48 ± 1	490 ± 50	$1\ 350 \pm 250$	$\sim 1\ 500$
Nd^{3+} — Ac$^-$	80 ± 3	$1\ 020 \pm 100$	$2\ 900 \pm 500$	$\sim 3\ 500$
Gd^{3+} — Ac$^-$	69 ± 2	$1\ 320 \pm 150$	$5\ 200 \pm 1\ 000$	$\sim 5\ 000$

Table 9. Experimentally determined ligand numbers ($\bar{n}_{exp}$), calculated ligand numbers ($\bar{n}_c$), and the composition of the acetate systems with the assumption that only three complexes are formed.

[A] mM	Rare earth	$\bar{n}_{exp}$	$\bar{n}_c$	100 a_0	100 a_1	100 a_2	100 a_3
	La^{3+}	0.30	0.30	72.0	25.9	2.1	—
	Ce^{3+}	0.39	0.38	65.4	31.4	3.2	—
10	Nd^{3+}	0.53	0.53	52.5	42.0	5.4	0.1
	Gd^{3+}	0.54	0.53	54.7	37.8	7.2	0.3
	La^{3+}	1.00	1.00	27.3	49.1	20.4	3.2
	Ce^{3+}	1.12	1.12	20.8	50.1	25.6	3.5
50	Nd^{3+}	1.29	1.27	12.5	49.9	33.1	4.5
	Gd^{3+}	1.46	1.43	11.9	41.1	39.3	7.7
	La^{3+}	1.48	1.46	11.7	42.1	35.1	11.1
	Ce^{3+}	1.57	1.55	8.3	39.8	40.7	11.2
100	Nd^{3+}	1.72	1.68	4.5	36.2	46.2	13.1
	Gd^{3+}	1.92	1.86	3.8	26.2	50.2	19.8

Table 10. The complexity constants of the cerium(III) acetate system determined by

	the potentiometric method	the cation exchange method
β_1	48 ± 1 M^{-1}	48 ± 2 M^{-1}
β_2	490 ± 50 M^{-2}	450 ± 80 M^{-2}
β_3	$1\ 350 \pm 250$ M^{-3}	$1\ 700 \pm 500$ M^{-3}
β_4	$1\ 600 \pm 600$ M^{-4}	—

At $[A] = 100$ mM β_4 would give $100 \cdot a_4 = 1.0$ and 1.6 for the lanthanum and the gadolinium systems, respectively.

Table 8 shows that the stability of the first complex increases from lanthanum to neodymium, as is to be expected from the decreasing ionic radius, whereas gadolinium gives a considerably weaker first complex than neodymium. The gadolinium complexes number two and three, however, are stronger than the corresponding neodymium complexes.

A more detailed discussion must be postponed until other acetate systems have been examined.

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