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Kinetic Studies of Lanthanoid Carboxylate Complexes

III. The Dissociation Rates of Praseodymium, Neodymium, Europium, and Erbium EDTA Complexes

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The dissociation rates of praseodymium, neodymium, europium, and erbium EDTA complexes in a slightly acid medium have been investigated. The rate constants of these dissociations were determined from reactions in which the ligand is exchanged between two different metal ions. The measurements were made at 25.0°C and at an ionic strength of 0.5 M, using potassium chloride as neutral salt. The solutions were buffered with 12.5 mM sodium acetate and varying amounts of acetic acid. The dissociation was found to be catalyzed by hydrogen ions, according to the equation $f = k_0 + \bar{k}_1[H^+] + \bar{k}_2[H^+]^2$ for the rate constant f.

In a preceding paper [1] rate constants for the dissociation of lanthanum, erbium, ytterbium, and copper EDTA complexes in a slightly acid medium were reported. The dissociation rate of the lanthanum EDTA complex in a slightly alkaline medium and measurements of the labilities of the coordinative bonds in lanthanoid EDTA complexes were published in a second paper.[2] The present work is an investigation of the dissociation rates of the praseodymium, neodymium, europium, and erbium EDTA complexes by means of exchange reactions in a slightly acid medium: $LA + M \rightleftharpoons L + MA$.

EXPERIMENTAL

Chemicals. All chemicals were of analytical grade. Standard solutions of $PrCl_3$, $NdCl_3$, $EuCl_3$, $ErCl_3$, and $CuCl_2$ were prepared by dissolving the corresponding oxides (from Potash & Chemical Corp.) in hydrochloric acid. The solutions were standardized as previously described.[1] Solutions of EDTA, potassium chloride, and acetate buffer were prepared as described in Ref. 1.

Measurements. All measurements were made at 25.0 ± 0.1°C and at the ionic strength 0.5 M. The solutions were buffered with 12.5 mM sodium acetate and varying amounts of acetic acid. The ionic strength for each of the solutions S and T (see below) was adjusted to 0.5 M by potassium chloride.

The reactions were performed by mixing two solutions, and the hydrogen ion concentration of the resulting solution was measured as described in Ref. 1.

The praseodymium and neodymium systems. Copper was used as the second metal, M, for both these systems. The reaction rates were studied by a Durrum-Gibson stopped-flow spectrophotometer, using a wavelength range of 600 – 820 nm. To verify the absence of photochemical effects, some of the solutions were studied at different wavelengths and slitwidths. No differences in the observed rate constants could be detected.

The two solutions, S and T, which were mixed in equal volumes, had the following compositions:

S: $2\,C_L^\circ$ $PrCl_3$ or $NdCl_3$; $2\,C_A^\circ$ Na_2H_2EDTA; buffer; $I = 0.5$ M (KCl)

T: $2\,C_M^\circ$ $CuCl_2$; buffer; $I = 0.5$ M (KCl)

To remove dissolved air, the solutions were boiled at decreased pressure at room temperature for 2 min before mixing.

The reactions were followed during approximately three half-lives. The data in Tables 1 and 2 are averages of three independent measurements.

The europium system. In the aforementioned exchange reactions, copper was used together with one of the lanthanoids. In the europium system, however, ytterbium was used as the second metal, M, in order to investigate if the over-all reaction proceeds to a measurable extent with direct substitution, path II (see Ref. 1), when both the metals are lanthanoids.

Because of the small absorption coefficients of the *f-f* spectra and the nearly identical UV spectra for different lanthanoid complexes containing the same ligand, the reaction between ytterbium ions and the europium EDTA complex is difficult to follow by spectrophotometric methods. Therefore the system was studied polarographically.

The polarographic half-wave potentials of the free europium ion and its EDTA complex are well separated both from one another and from the corresponding potentials of the other lanthanoid ions.[3] Hence, it is possible to follow the exchange reaction by measuring the diffusion current of the free europium ion when the reaction rate is suitable.

Table 1. Rate data for the praseodymium system. L = Pr and M = Cu.

$[H^+] \times 10^5$/M, $k_{obs} \times 10$/s^{-1}, $100(k_{obs} - k_{calc})/k_{calc}$, $f_{LA,exp} \times 10$/s^{-1};

$C_L^\circ = 6.20 \times 10^{-4}$ M, $C_A^\circ = 6.00 \times 10^{-4}$ M, $C_M^\circ = 1.50 \times 10^{-3}$ M: 9.00, 1.43, 5.5, 1.68; 12.9, 2.11, 8.6, 2.49; 24.6, 4.12, 7.0, 4.89; 32.8, 5.54, 5.0, 6.64;

$C_L^\circ = 3.10 \times 10^{-4}$ M, $C_A^\circ = 3.00 \times 10^{-4}$ M, $C_M^\circ = 4.99 \times 10^{-3}$ M: 6.60, 1.08, −4.3, 1.12; 21.2, 3.73, 3.8, 4.01;

$C_L^\circ = 3.10 \times 10^{-4}$ M, $C_A^\circ = 3.00 \times 10^{-4}$ M, $C_M^\circ = 9.98 \times 10^{-3}$ M: 3.21, 0.616, 4.0, 0.626; 4.34, 0.759, −1.8, 0.774; 16.5, 2.88, 3.2, 3.04; 20.0, 3.51, 3.2, 3.74; 29.6, 5.03, −1.8, 5.50; 40.1, 7.61, 7.4, 8.56;

$C_L^\circ = 3.10 \times 10^{-4}$ M, $C_A^\circ = 3.00 \times 10^{-4}$ M, $C_M^\circ = 1.50 \times 10^{-2}$ M: 4.81, 0.850, 0.0, 0.866; 8.09, 1.32, −4.5, 1.36; 11.9, 1.98, −2.0, 2.06; 14.6, 2.41, −2.2, 2.52; 17.9, 2.96, −2.5, 3.13; 20.2, 3.56, 3.3, 3.79; 23.7, 4.18, 2.9, 4.49; 27.4, 4.63, −1.9, 5.02; 31.5, 5.38, −1.7, 5.90; 37.5, 6.45, 2.3, 7.19; 46.1, 8.23, −0.4, 9.39; 53.7, 9.66, −1.1, 11.2; 60.7, 10.9, −2.6, 12.9;

$C_L^\circ = 3.10 \times 10^{-4}$ M, $C_A^\circ = 3.00 \times 10^{-4}$ M, $C_M^\circ = 2.00 \times 10^{-2}$ M: 10.3, 1.62, −7.5, 1.68; 26.5, 4.47, −2.1, 4.84;

$C_L^\circ = 6.20 \times 10^{-4}$ M, $C_A^\circ = 3.00 \times 10^{-4}$ M, $C_M^\circ = 2.00 \times 10^{-2}$ M: 3.97, 0.727, 1.8, 0.741; 11.9, 1.98, −1.9, 2.06; 19.9, 3.40, 0.6, 3.62; 27.9, 4.81, 0.1, 5.23; 35.8, 5.99, −4.6, 6.66.

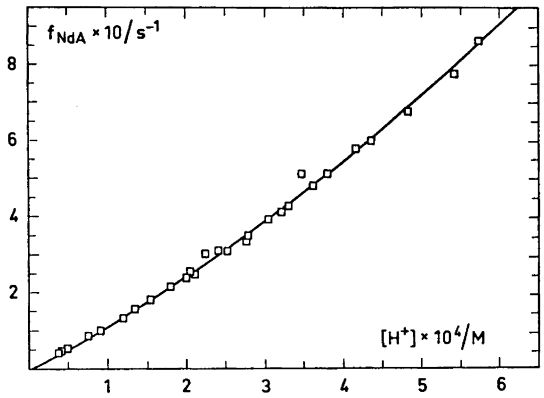


Fig. 1. The dissociation rate constant of the neodymium EDTA complex, f_{NdA}, as a function of the hydrogen ion concentration. The fulldrawn curve has been calculated from the rate constants obtained in this work.

Table 2. Rate data for the neodymium system. L = Nd and M = Cu.

$[H^+] \times 10^5/M$, $k_{obs} \times 10/s^{-1}$, $100(k_{obs} - k_{calc})/k_{calc}$, $f_{I,A,exp} \times 10/s^{-1}$;

$C_L^\circ = 6.78 \times 10^{-4}$ M, $C_A^\circ = 6.40 \times 10^{-4}$ M, $C_M^\circ = 4.99 \times 10^{-3}$ M: 22.4, 2.77, 9.8, 3.07;

$C_L^\circ = 6.78 \times 10^{-4}$ M, $C_A^\circ = 6.40 \times 10^{-4}$ M, $C_M^\circ = 9.98 \times 10^{-3}$ M: 4.11, 0.445, −0.1, 0.459; 7.57, 0.862, 3.9, 0.865; 20.5, 2.40, 2.5, 2.59; 34.7, 4.58, 11.3, 5.15; 41.6, 5.07, 1.1, 5.80; 57.4, 7.22, 0.6, 8.61;

$C_L^\circ = 3.39 \times 10^{-4}$ M, $C_A^\circ = 3.20 \times 10^{-4}$ M, $C_M^\circ = 1.50 \times 10^{-2}$ M: 4.90, 0.539, 0.1, 0.551; 9.06, 0.983, −2.0, 1.02; 12.1, 1.31, −3.6, 1.37; 13.4, 1.51, 0.2, 1.59; 15.5, 1.73, −1.2, 1.83; 18.0, 2.06, 0.3, 2.20; 21.0, 2.36, −2.6, 2.53; 25.2, 2.86, −2.4, 3.11; 27.9, 3.24, −1.2, 3.54; 33.0, 3.87, −1.1, 4.31; 38.0, 4.58, −0.1, 5.15; 43.6, 5.26, −1.2, 6.01; 48.3, 5.83, −1.9, 6.76; 54.3, 6.60, −2.7, 7.76; 60.8, 7.88, 2.7, 9.45;

$C_L^\circ = 6.78 \times 10^{-4}$ M, $C_A^\circ = 3.20 \times 10^{-4}$ M, $C_M^\circ = 1.50 \times 10^{-2}$ M: 3.78, 0.423, 2.6, 0.433; 11.9, 1.30, −2.5, 1.36; 20.0, 2.25, −1.5, 2.42; 24.0, 2.89, 3.7, 3.14; 32.1, 3.74, −1.7, 4.15; 36.2, 4.30, −0.7, 4.83;

$C_L^\circ = 6.78 \times 10^{-4}$ M, $C_A^\circ = 6.40 \times 10^{-4}$ M, $C_M^\circ = 2.00 \times 10^{-2}$ M: 27.7, 3.08, −5.1, 3.37; 30.5, 3.59, −0.4, 3.96.

Fig. 2 shows the waves of three different solutions, recorded by a Radiometer P04 polarograph with a dropping mercury electrode (dropping time 2.7 s and flow rate 3.39 mg/s) against a saturated calomer electrode, S.C.E., as reference. The half-wave potential *vs.* S.C.E. in the medium used was found to be −0.72 V for free europium ions and −1.03 V for europium EDTA.

The polarograph was equipped with a fast recorder, type Servogor Re 511, in order to record concentration *vs.* time curves. The concentration of uncomplexed europium was followed at a constant voltage of −0.85 V.

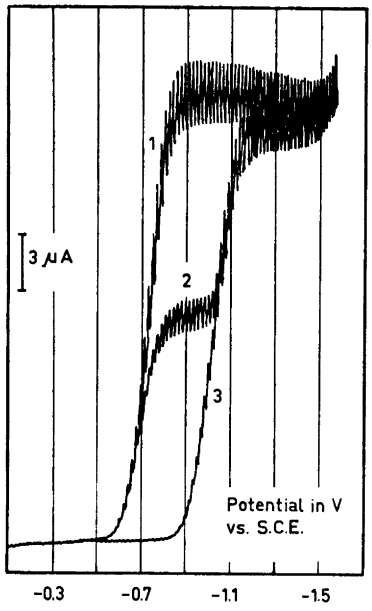


Fig. 2. Polarographic waves for (1) 5.89 mM Eu^{3+}; (2) 5.89 mM Eu^{3+} and 2.9 mM EDTA; and (3) 5.89 mM Eu^{3+} and ~10 mM EDTA. Medium: pH = 4, [NaAc] = 12.5 mM, 0.01 % gelatin, and I = 0.5 M (KCl).

3.00 ml of the thermostated solution S was injected by a syringe into 17.0 ml of solution T, which was thermostated in the reaction vessel. The solutions S and T had the following compositions:

$$\text{S:}\begin{cases} 6.67\ C_L^\circ\ EuCl_3 \\ 6.67\ C_A^\circ\ Na_2EDTA \\ I = 0.5\ M\ (KCl) \end{cases} \qquad \text{T:}\begin{cases} 1.18\ C_M^\circ\ YbCl_3 \\ 1.18 \times 12.5\ mM\ NaAc \\ \text{var. HAc} \\ 1.18 \times 0.01\ \%\ \text{gelatin} \\ I = 0.5\ M\ (KCl) \end{cases}$$

The mixing time was less than 3 s. Before mixing, dissolved oxygen was removed by bubbling nitrogen through the solutions. The reaction was followed during at least three half-lives.

It was not possible to vary the hydrogen ion concentration more than by a factor of 5. Precipitation of hydroxo complexes occurred at low hydrogen ion concentrations. In more acid solutions the reactions became too fast for this method, which is limited to reactions with half-lives longer than 15 s.[4]

From some experiments it was found that moderate changes in the gelatin concentration did not affect the observed rate constants. The data in Table 3 are averages of at least three independent measurements.

The erbium system. The erbium system was investigated with copper as the second metal, M. Two solutions, S and T, were mixed rapidly (mixing time less than 5 s) in a reaction vessel. Samples from this vessel were then taken at different time intervals and measured by a Zeiss PMQ II spectrophotometer, equipped with a Solatron digital voltmeter LM 142.02, from which the transmittance of the copper EDTA complex was read.

Because of the small total concentrations, it was necessary to perform the measurements in the UV region (wave length 280 – 300 nm), where the molar light absorptivity is high. Because of photochemical effects it was necessary to use this sampling technique (see Ref. 1).

Table 3. Rate data for the europium system. L = Eu and M = Yb.

$[H^+] \times 10^5$/M, $k_{obs} \times 10^2/s^{-1}$, $100(k_{obs} - k_{calc})/k_{calc}$, $f_{L,A,exp} \times 10^2/s^{-1}$;

$C_L^\circ = 4.56 \times 10^{-4}$ M, $C_A^\circ = 2.00 \times 10^{-4}$ M, $C_M^\circ = 5.02 \times 10^{-3}$ M: 1.88, 0.701, −6.3, 0.842; 3.59, 1.49, −6.2, 1.77; 5.30, 2.24, −12.9, 2.62; 7.01, 3.65, −1.4, 4.33;

$C_L^\circ = 2.94 \times 10^{-4}$ M, $C_A^\circ = 2.00 \times 10^{-4}$ M, $C_M^\circ = 7.47 \times 10^{-3}$ M: 2.74, 1.28, 3.9, 1.46; 5.73, 3.32, 6.9, 3.65; 7.81, 4.86, 5.1, 5.36;

$C_L^\circ = 2.94 \times 10^{-4}$ M, $C_A^\circ = 2.00 \times 10^{-4}$ M, $C_M^\circ = 1.01 \times 10^{-2}$ M: 2.38, 1.25, 12.6, 1.35; 3.08, 1.59, 6.6, 1.71; 3.38, 1.84, 11.0, 1.99; 4.36, 2.21, −1.8, 2.37; 4.99, 2.75, 3.5, 2.96; 5.37, 3.32, 13.8, 3.59; 5.83, 3.21, −0.6, 3.45; 6.51, 3.64, −2.0, 3.92; 7.24, 4.28, 0.5, 4.62; 8.59, 5.21, −2.4, 5.63;

$C_L^\circ = 2.94 \times 10^{-4}$M, $C_A^\circ = 1.02 \times 10^{-4}$ M, $C_M^\circ = 1.01 \times 10^{-2}$ M: 1.82, 0.801, −2.6, 0.858; 3.42, 1.52, −9.9, 1.62; 5.02, 2.61, −2.7, 2.80; 6.62, 3.80, 0.1, 4.09.

The solutions S and T had the following compositions:

S: $2\ C_L^\circ$ $ErCl_3$; $2\ C_A^\circ$ Na_2H_2EDTA; buffer; $I = 0.5$ M (KCl)

T: $2\ C_M^\circ$ $CuCl_2$; buffer; $I = 0.5$ M (KCl)

Equal volumes of the solutions S and T were mixed. The reactions were followed during approximately three half-lives. The data in Table 4 are averages of three independent measurements.

Table 4. Rate data for the erbium system. L = Er and M = Cu.

$[H]^+ \times 10^5$/M, $k_{obs} \times 10^3/s^{-1}$, $100(k_{obs} - k_{calc})/k_{calc}$, $f_{L,A,exp} \times 10^3/s^{-1}$;

$C_L^\circ = 2.00 \times 10^{-4}$ M, $C_A^\circ = 1.94 \times 10^{-4}$ M, $C_M^\circ = 4.99 \times 10^{-3}$ M: 1.21, 0.126, 4.5, 0.124; 1.67, 0.160, −7.2, 0.157; 2.45, 0.268, 1.1, 0.267; 3.16, 0.368, 3.0, 0.369; 4.68, 0.560, −3.0, 0.568; 6.17, 0.777, −5.5, 0.796; 7.67, 1.17, 6.9, 1.22; 9.22, 1.45, 2.5, 1.52; 10.7, 1.72, −0.9, 1.82; 12.2, 2.10, 0.6, 2.25; 14.0, 2.52, −1.5, 2.72; 15.1, 2.92, 2.1, 3.18; 16.4, 3.20, −0.8, 3.52; 18.0, 3.65, −1.9, 4.05;

$C_L^\circ = 3.19 \times 10^{-4}$ M, $C_A^\circ = 3.12 \times 10^{-4}$ M, $C_M^\circ = 4.99 \times 10^{-3}$ M: 5.44, 0.682, −3.2, 0.689; 6.51, 0.893, 0.7, 0.913; 9.55, 1.50, 1.0, 1.57;

$C_L^\circ = 7.02 \times 10^{-4}$ M, $C_A^\circ = 3.12 \times 10^{-4}$ M, $C_M^\circ = 4.99 \times 10^{-3}$ M: 2.03, 0.208, −4.6, 0.202; 6.12, 0.831, 2.7, 0.859; 10.2, 1.54, −3.9, 1.64; 14.3, 2.45, −5.1, 2.70; 18.5, 4.05, 7.5, 4.66;

$C_L^\circ = 2.00 \times 10^{-4}$ M, $C_A^\circ = 1.94 \times 10^{-4}$ M, $C_M^\circ = 7.48 \times 10^{-3}$ M: 3.38, 0.420, 9.0, 0.425; 7.04, 0.988, 1.6, 1.03; 8.22, 1.16, −3.3, 1.21; 11.4, 1.90, −0.1, 2.03; 13.2, 2.33, 0.1, 2.52; 16.6, 3.32, 0.9, 3.66;

$C_L^\circ = 2.00 \times 10^{-4}$ M, $C_A^\circ = 1.94 \times 10^{-4}$ M, $C_M^\circ = 9.97 \times 10^{-3}$ M: 2.80, 0.322, 4.8, 0.325; 4.00, 0.472, 0.1, 0.480.

CALCULATIONS AND RESULTS

The maximum errors in the observed rate constants were approximately ± 5 % except for the europium system, where they were around ± 8 %. The hydrogen ion concentration was determined with an error of about 1 %.

Table 5. Stability constants used in the calculations.

System	log β	Ref.	log K_{LAH}	Ref.
Pr	15.76	5	2.5	7
Nd	16.05	5	2.5	7
Eu	16.66	5	2.6	7
Er	18.37	5	2.8	7
Yb	18.99	5	2.7	7
Cu	18.68	6	3.0	6

All the k_{obs}-values were calculated from a simple first order equation (see Ref. 1). The stability constants for the lanthanoid EDTA complexes determined by Betts and Dahlinger [5] in 0.1 M potassium chloride were used in the calculations. The stability constant for the copper EDTA complex determined by Schwarzenbach *et al.*[6] was adjusted to 25°C by means of the enthalpy value given by Case and Stavely.[8] The constants for formation of the acid complexes were those of Kolat and Powell [7] for the lanthanoids, and of Schwarzenbach *et al.*[6] for copper. The constants valid in 0.1 M medium have been shown to be good approximations for the values in the 0.5 M medium used.[1] The constants used are given in Table 5.

The observed rate constant, k_{obs}, for the exchange reaction is related to the dissociation rate constants f_{LA} and f_{MA} of the complexes LA and MA according to eqn. (1):

$$k_{obs} = \left(\frac{f_{LA}}{1 + (f_{LA}/f_{MA})\delta_1} + f_D \frac{C_M}{\alpha_M} \right) \delta_2 \quad (1)$$

All notations are defined in Ref. 1.

Copper was used as the second metal, M, in the praseodymium, neodymium, and erbium systems. The dissociation rate constant for the copper EDTA complex f_{MA} is [1]

$$f_{CuA} = [(9.0 \pm 5.1)10^{-5} + (6.5 \pm 1.0)[H^+] + (3.5 \pm 0.3)[H^+]^2/s^{-1}$$

In the europium system, ytterbium was used as the second metal, M. The rate constant for the dissociation of the ytterbium EDTA complex f_{MA} is [1]

$$f_{YbA} = [(0.76 \pm 0.08)[H^+] + (1.43 \pm 0.07)10^4[H^+]^2/s^{-1}$$

The parameters in the expression for the rate constant f in the above systems were computed by a data program written by Ekström and Ryhl.[9] Eqn. (2) described the results from all four systems:

$$f = \bar{k}_0 + \bar{k}_1[H^+] + \bar{k}_2[H^+]^2 \quad (2)$$

Here each $\bar{k}_i$ is a product of the true rate constant and the corresponding equilibrium constant for the association of protons to the lanthanoid EDTA

Table 6. The obtained rate constants of dissociation of lanthanoid EDTA complexes together with the values of other authors. The constants $\bar{k}_{01}$, $\bar{k}_1$, and $\bar{k}_2$ contain the equilibrium constants for the corresponding complexes. The errors given are the confidence limits on the 99 % level.

Ln	k_0/s^{-1}	$\bar{k}_1/s^{-1}\,M^{-1}$	$\bar{k}_2/s^{-1}\,M^{-2}$	t°C	Ref.
La	$(2.0 \pm 1.0)10^{-2}$	$(3.7 \pm 0.3)10^3$	$(1.9 \pm 0.7)10^6$	25	1
	–	7.0×10^3	–	25	22
Ce	–	1.6×10^3	–	20	14
	–	1.8×10^3	–	20	17
	–	3.5×10^3	–	25	23
Pr	$(9.0 \pm 7.5)10^{-3}$	$(1.6 \pm 0.1)10^3$	$(1.0 \pm 0.4)10^6$	25	This work
	–	1.7×10^3	–	25	23
Nd	–	$(1.09 \pm 0.04)10^3$	$(7.0 \pm 1.5)10^5$	25	This work
		6.6×10^2	–	20	17
		1.08×10^3	–	25	22
Eu	–	$(4.3 \pm 0.7)10^2$	$(2.8 \pm 1.5)10^6$	25	This work
		6.0×10^2	–	22	10
Gd	–	87	6.0×10^6	20	17
Tb	–	31	9.5×10^6	20	17
Dy	–	12.3	5.8×10^5	25	22
Ho	–	12.8	–	24	24
Er	–	8.9 ± 0.5	$7.7 \pm 0.7)10^4$	25	This work
Yb	–	0.76 ± 0.08	$(1.43 \pm 0.07)10^4$	25	1
	–	0.70	2.3×10^4	25	22
Lu	–	0.52	5.4×10^3	20	17
	–	0.23	–	25	13
La	$\bar{k}_{01} = (2.0 \pm 0.4)10^8$ $s^{-1}\,M^{-1}$			45	2

complex. f_D, *i.e.* the rate constant for direct substitution, path II, was found to be zero for all these systems. The results are given in Table 6.

DISCUSSION

The following discussion of the dissociation of the lanthanoid EDTA complexes is based on the results from this and two previous papers.[1,2]

The rate law of exchange reactions. The rate law for the gross reaction

$$LA + M \rightleftharpoons L + MA \qquad (3)$$

can be described fairly well by the proposed model.[1] The gross reaction is considered to consist of two parallel sets of reactions, *viz.* (i) path I, a primary dissociation of the complex LA, followed by an association of the ligand A to the metal ion M, and (ii) path II, a direct substitution between M and the complex LA to give the products L and MA.

The expression for the observed rate constant [1] can be rearranged in two different ways:

(i) If the dissociation of LA is rate determining, which is the case for $f_{LA}C_L/\alpha_L \ll (f_{MA}\beta_M/\beta_L)C_M/\alpha_M$

$$k_{obs} = \left(\frac{f_{LA}}{(1 + (f_{LA}/f_{MA})\delta_1} + f_D \frac{C_M}{\alpha_M} \right) \delta_2 \quad (4)$$

$$\delta_1 = \frac{\beta_L C_L \alpha_M}{\beta_M C_M \alpha_L}$$

$$\delta_2 = \frac{1}{\alpha_{LA}} \left(1 + \frac{C_{LA}}{C_M} + \frac{\beta_L}{\beta_M} \cdot \frac{C_L + C_{MA}}{C_M} \cdot \frac{\alpha_M \alpha_{LA}}{\alpha_L \alpha_{MA}} \right)$$

In this case, f_{LA} can be determined from eqn. (4).

(ii) If the association of A to M is rate determining, which is the case for $f_{LA} C_L/\alpha_L \gg (f_M \beta_M/\beta_L) C_M/\alpha_M$

$$k_{obs} = \left(\frac{f_{MA}}{(1 + (f_{MA}/f_{LA})\delta_1'} + \frac{\beta_L}{\beta_M} f_D \frac{C_L}{\alpha_L} \right) \delta_2'$$

$$\delta_1' = \frac{\beta_M C_M \alpha_L}{\beta_L C_L \alpha_M}$$

$$\delta_2' = \frac{1}{\alpha_{MA}} \left(1 + \frac{C_{MA}}{C_L} + \frac{\beta_M}{\beta_L} \cdot \frac{C_M + C_{LA}}{C_L} \cdot \frac{\alpha_L \alpha_{MA}}{\alpha_M \alpha_{LA}} \right)$$

Here the dissociation rate of the MA complexes, f_{MA}, can be determined from eqn. (5).

If f_{LA} and f_{MA} β_M/β_L are of the same order of magnitude, either f_{LA} or f_{MA} can be determined from reaction (3), depending on the relative values of C_M/α_M and C_L/α_L.

D'Olieslager and Choppin [10] have used a large excess of both lanthanum ions and lanthanum EDTA complex over europium ions in the reaction

$$\text{LaEDTA} + \text{Eu} \rightleftharpoons \text{La} + \text{EuEDTA}$$

which obeys the experimental rate law

$$-\frac{\text{d[Eu]}}{\text{d}t} = k \frac{[\text{H}^+][\text{LaEDTA}]}{[\text{La}]} [\text{Eu}]$$

This is just a special case of the rate law discussed earlier. By dividing their rate constant by the quotient β_{Eu}/β_{La}, almost the same value of the dissociation rate constant of the europium complex is obtained as in the present paper (Table 6).

The rate law has also been checked by the following two experiments: (i) By using large concentrations of both lanthanum ions and lanthanum EDTA complex together with a small concentration of copper ions; and (ii) by using a large excess of ytterbium ions over both copper ions and the copper complex. The rate constants of the dissociation of the copper EDTA complex obtained from the two experiments were in agreement.[1]

The mechanism of dissociation. The dissociation of EDTA from the lanthanoid EDTA complexes is catalyzed both by hydrogen ions and hydroxide ions.[2] The hydrogen ion catalysis proceeds through two parallel path-ways,

viz. via complexes, containing a monoprotonated and a diprotonated ligand, whereas the path catalysed by hydroxide ions proceeds through the hydroxo complex.

$$\mathrm{Ln(OH)EDTA} \xrightarrow{k_{01}} \mathrm{Ln(OH)} + \mathrm{EDTA}$$

$$\mathrm{LnEDTA} \xrightarrow{k_0} \mathrm{Ln} + \mathrm{EDTA}$$

$$\mathrm{Ln(EDTA)H} \xrightarrow{k_1} \mathrm{Ln} + \mathrm{H(EDTA)}$$

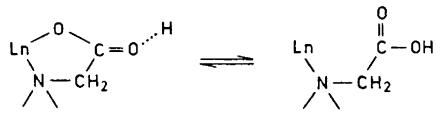
$$\mathrm{Ln(EDTA)H_2} \xrightarrow{k_2} \mathrm{Ln} + \mathrm{H_2(EDTA)}$$

The acid and hydroxo complexes are all in rapid equilibria with each other (see below).

According to Lind *et al.*[11] the proton in La(EDTA)H is bound to one of the four non-coordinating carboxylate oxygens. The configuration of the complex makes it impossible for any of the nitrogen atoms to bind a proton. Presumably, this is also the case for the second proton in the diprotonated complex, where both the protons are then bound to carboxylate groups.

The PMR spectra [2] show that the metal-oxygen bonds have short lifetimes both in the rapidly dissociating lanthanum complex and in the much more slowly dissociating lutetium complex. The metal-nitrogen bond has a long lifetime in the lutetium complex, but is labile in the lanthanum complex. Hence, the rate-determining factor of the dissociation seems to be the cleavage of the metal-nitrogen bond. The same conclusion has been drawn by Margerum [12] from exchange reactions of copper and nickel with EDTA and with hydroxyethylethylenediaminetriacetate.

The formation of a protonated complex in solution presumably proceeds *via* the primary association of a proton to the non-coordinated oxygen atom of a carboxylate oxygen, which is probably a very rapid process, followed by a cleavage of the coordinative bond between the metal and the other oxygen atom in the same carboxylate group.



Since the PMR data may be interpreted in support of the view that the cleavage of the metal-nitrogen bond is the rate-determining step of the dissociation, the cleavage of the metal-oxygen bond described above must also be a fast part of the multistep dissociation. One reason for the slower cleavage of the metal-nitrogen bond might be that the nitrogen atom in EDTA is not available for proton attack of the type possible on a carboxylate group, because of its second oxygen atom.

On the other hand, the metal-nitrogen bond is also labilized when the ligand becomes protonated, which is of course the reason why hydrogen ions act as catalyst for the dissociation.

Some authors [10,13,14] have proposed a mechanism in which the association of protons to the complex is a slow process followed by a rapid dissociation of the ligand. This mechanism does not seem to be very probable for reasons given above.

In the hydroxo complex, formed by dispelling one proton from one of the coordinated water molecules, the hydroxide ion is bound directly to the lanthanoid ion. The effective charge of the metal ion is thus reduced which would lead to a labilization of the coordinative bonds. In accordance with this, the rate constant [2] for the path catalysed by hydroxide ions is several orders of magnitude greater than that for the reaction catalysed by hydrogen ions *via* the monoprotonated species.

By substitution of water molecules in the lanthanoid EDTA complex, it is possible to coordinate a second ligand, thus forming a mixed complex. Acetate ions accelerate the dissociation of the EDTA complex to a small extent.[1,14] Brucher and Szilagyi [15] found from exchange reactions with copper that glycolate ions increase the dissociation rate of the terbium EDTA complex to a considerable extent. The affinity of acetate ions for lanthanoid ions is much greater than that of glycolate ions. The concentration of the mixed acetate complex is much smaller than that of the mixed glycolate complex at similar concentrations of acetate and glycolate. Both these ligands are presumably bound directly to the metal ion in the mixed lanthanoid complexes. Their ability to increase the dissociation rates may then be due to a labilization of the metal-nitrogen bonds in the EDTA complex, *i.e.* an effect similar to, but weaker than that of the hydroxide ion.

Variations of the dissociation rates with the ionic radii of the lanthanoid ions. In Table 6, the rate constants from this investigation have been collected together with the values from other authors. The constants given for the pathways catalysed by hydrogen ions and hydroxide ions are products of the constant $K_{\mathrm{LnAH_n}}{}^{1}$ and $K_{\mathrm{LnA(OH)}}{}^{2}$ for the corresponding complex and the true rate constant. Kolat and Powell have reported such constants for almost all the monoprotonated lanthanoid complexes. The logarithm of these constants have values between 2.5 and 2.8. Some tentative values of the stepwise constants $K_{\mathrm{LnAH_2}}/K_{\mathrm{LnAH}}$ for the diprotonated complexes have been reported by Brucher and Szarvas [16,17] to be in the range $(0.1-0.2)$ $\mathrm{M^{-1}}$. It is likely that the constants $K_{\mathrm{LnAH_2}}$ for the diprotonated complexes do not change more than those for the monoprotonated complexes along the lanthanoid series. The constant, $K_{\mathrm{LaA(OH)}}$, for the hydroxo EDTA complex of lanthanum is estimated to be less than 1000 $\mathrm{M^{-1}}$.[18] Because of the lack of accurate values of these constants, no calculations of the true rate constants have been done.

In Fig. 3, $\log \bar{k}_1$ and $\log \bar{k}_2$ have been plotted *vs.* the inverse ionic radius of the lanthanoid ions. In this graph the rate constants valid at 20 or 24°C have been adjusted to 25°C by means of a value of the activation energy, 12 kcal/mol, for the protonated cerium complex, determined by Glentworth *et al.*[14]

Both curves show an irregularity, *viz.* for $\bar{k}_1$ in the region dysprosium to

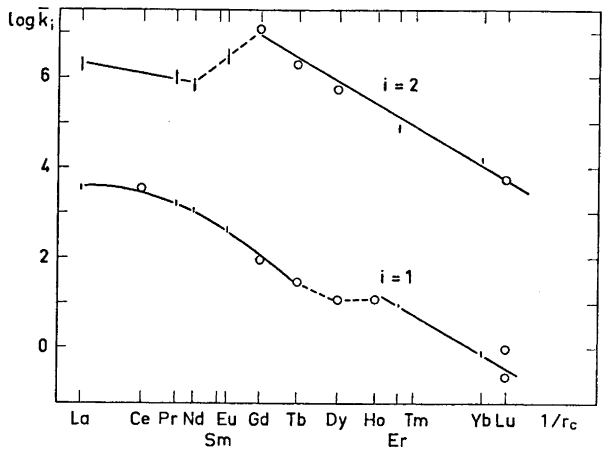


Fig. 3. The logarithm of the dissociation rate constants for the paths with first and second order dependence of the hydrogen ion concentration, as a function of the inverse ionic radius of the lanthanoid ions.

erbium and for $\bar{k}_2$ between neodymium and gadolinium. Geier and Karlen [19] found a corresponding behaviour of the rate constant for the nonprotonated complexes reacting with oxyquinoline-5-sulfonate in the region of samarium to terbium. They have also carried out some spectrophotometric measurements on europium EDTA complexes at varying temperatures.[20] They claim that the temperature dependence of the spectra is due to the existence of two kinds of complexes, *viz.* $Ln(EDTA)(H_2O)_3^-$ and $Ln(EDTA)(H_2O)_2^-$, which are in equilibrium with each other. The one with three water molecules predominates in the beginning of the series, whereas the dihydrated complex is favoured at the end of the series. Ots [21] has found clear evidence for this reaction from calorimetric measurements of the enthalpy of formation of the lanthanoid EDTA complexes at different temperatures. Lind *et al.*[11] have found four water molecules coordinating to the lanthanum ion in the solid $LaH(EDTA)(H_2O)_4$.

On the grounds given above, one may conclude that the two regions with monotonous changes of the rate constants in each of the two curves correspond to complexes with different numbers of coordinated water molecules. Thus, the monoprotonated complexes might have four coordinated water molecules in the beginning of the series and three water molecules at the end.

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