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The Dissociation Kinetics of Rare Earths–N-methylethylenediamine-N,N′,N′-triacetate Complexes

M. DE JONGHE and W. D'OLIESLAGER*

University of Leuven, Laboratory of Radiochemistry, Celestijnenlaan 200G, 3030 Heverlee, Belgium

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Abstract

The dissociation kinetics of lanthanide–N-methylethylenediamine-N,N′,N′-triacetate (MEDTA) complexes have been studied in aqueous acetic acid/sodium acetate solutions using Cu^{2+} ions as sequestring agent. The reaction mechanism involves a fast protonation equilibrium (K_H) of a mixed complex Ln–MEDTA–OAc$^-$, followed by a slow rate determining internal proton transfer (k_s)

$$\text{Rate} = \frac{k_sK_HK_MK_a[H^+]\,C_{LnMEDTA}[\text{Buffer}]}{K_a + K_MK_a[\text{Buffer}] + [H^+]}$$

where K_a is the acid dissociation constant of acetic acid and K_M the stability constant of the mixed complexes Ln–MEDTA–OAc. K_M values increase and the product k_sK_H decreases with decreasing ionic radii of the trivalent rare earths. Formal rate constants for the formation reaction are calculated from the dissociation rate and the stability of the mixed complex; however, this reaction is too fast to be followed by the stopped-flow spectrometer.

Introduction

The kinetics of the exchange and dissociation of lanthanide–polyaminopolycarboxylate complexes is of considerable interest not only from the point of view of the coordination chemistry of these elements, but also because of their effect on the widening and overlapping of the elution bands in chromatographic and ion exchange separation methods. There is general agreement that the exchange of lanthanide (or actinide) ions and the EDTA, HEDTA and DCTA complexes in dilute acid medium (pH 3.5–6), as measured by radioisotope techniques, proceeds mainly by a mechanism involving the acid catalyzed dissociation of the metal chelate [1–10]. The rate constants thus obtained are in good agreement with the data obtained for the dissociation rate by a spectrophotometric method using Cu^{2+} ions as scavenger for the free ligand [12, 13]. The rate constants for the dissociation of these chelates decrease from La to Lu by several orders of magnitude in the opposite direction to their stability constants.

Most of these studies indicate that mechanisms involving a direct attack of free lanthanide ions on the complex (associative paths) contribute little to the overall exchange rate of Ln–EDTA, HEDTA and DCTA complexes. However, there is ample evidence that, for other analogous ligands (*e.g.* DTPA, EGTA ...), the bimolecular associative mechanism becomes the more important pathway, especially in less acidic solutions and at higher free lanthanide concentrations [13–17].

The influence of buffer anions (*e.g.* acetate, benzoate, glycolate ...) on the rate of both dissociative and associative pathways has been reported by several authors [1, 6, 8, 9, 15]. However, this effect has not been studied systematically and there is no general consensus concerning its importance or interpretation (the formation of mixed ligand complexes).

In this paper we report the results of a kinetic study of the dissociation of Ln–MEDTA (N-methylethylenediamine-N,N′,N′-triacetate). This ligand was first synthesized and isolated by Powell and coworkers, who also measured the stability constants of its complexes with the lanthanide ions [18, 19]; they suggested its potential use as a complexing eluent for ion exchange separations because the non-dissociated acid (H_3MEDTA) is substantially more soluble in water than its analogue (H_4EDTA). As the dissociation rates of Ln–MEDTA complexes are much faster than those of other aminopolycarboxylate complexes, the kinetics of the reaction were monitored using a stopped-flow spectrometer with Cu^{2+} ions as scavenger.

Experimental

Synthesis MEDTA

N-methylethylenediamine-N,N′,N′-triacetic acid (H_3MEDTA) was synthesized by carboxymethyla-

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*Author to whom correspondence should be addressed.

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tion of N-methylethylenediamine with formaldehyde and sodium cyanide. The product was isolated on a cation exchange column and purified by crystallisation from an alcohol–water mixture as described by Powell [18]. The purity of the product was checked by elemental analysis: H_3-MEDTA = $C_9H_{16}O_6N_2$, found C = 43.45%, H = 6.4%, O = 38.81% and N = 11.25% (calculated: C = 43.55%, H = 6.5%, O = 38.67%, N = 11.28%). The proton NMR spectrum, the melting point (T_{mp} = 190 °C) and the acid dissociation constants (pK_1 = 1.72 ± 0.003, pK_2 = 2.46 ± 0.01, pK_3 = 5.46 ± 0.01 and pK_4 = 10.14 ± 0.01 at 0.5 M ionic strength ($NaClO_4$)) correspond well with published data.

Solutions

All solutions were made using commercially available analytical grade reagents and de-ionized, twice distilled water. Stock solutions of lanthanide perchlorates, copper perchlorate, acetate buffer solutions and solutions of sodium perchlorate, used to maintain constant ionic strength, were prepared and analyzed as described earlier [9].

Stock solutions of the disodium salt of MEDTA were prepared by dissolving the required amount of the acid H_3MEDTA and two equivalents of sodium hydroxide. The concentration of the ligand was determined by a complexometric titration with zinc sulphate titrisol (Merck *p.a.*) in an ammonia buffer (pH = 10) with Eriochrome black T as the indicator.

Kinetic Runs

The reaction kinetics were measured by spectrophotometry (using a stopped-flow spectrometer built at the University) at λ = 285 nm. At this wavelength the difference in the extinction of $CuMEDTA^-$ and $Cu(acetate)_x^{2-x}$ is maximal, and neither the lanthanide ions nor their MEDTA complexes absorb appreciably.

·The solutions in the two syringes of the stopped-flow spectrometer (one containing the required amount of the Ln–MEDTA complex – formed by mixing appropriate amounts of the stock solutions of $Ln(ClO_4)_3$ and $Na_2HMEDTA$ – in acetate buffer at 0.5 M ionic strength ($NaClO_4$), and the other containing $CuSO_4$ in acetate buffer at the same pH and ionic strength) were pre-equilibrated at the required temperature.

The output signal from the spectrometer was fed into a logarithmic amplifier, digitized and stored in a quarter of the memory of a 1024 multichannel analyzer (Tracor Northern NS 710). Thus, four consecutive experiments could be stored in the buffer memory. The multichannel analyzer was interfaced to a PDP 11/05 minicomputer for data processing and the rate constants were calculated using a least squares program.

TABLE I. Independence of EuMEDTA Dissociation Kinetics on the Cu(II) Concentration at 5 × 10^{-5} M EuMEDTA, 0.02 M Acetate Buffer, pcH = 4.71, 0.5 M Ionic Strength and T = 25 °C.

10^4 × [Cu(II)] M	k_{1exp} s^{-1}
1.0	4.81 ± 0.10
2.0	4.68 ± 0.10
3.0	4.70 ± 0.10
5.0	4.70 ± 0.10
10.7	4.84 ± 0.10

The tabulated values of the rate constants represent the mean of at least four experiments; the errors are the standard deviations (σ) on the mean and are used as weighting factors in least squares calculations.

The hydrogen ion concentration of the reaction mixture was measured using a Beckman model 4500 digital pH meter (a glass electrode and a NaCl-saturated calomel electrode). The mV-reading was converted to pcH using a calibration plot pcH–mV made with a set of solutions with known concentration of perchloric acid at 0.5 M total ionic strength.

Results and Discussion

Since the stability constants of the rare earth–MEDTA complexes (log K varies from 11.50 for LaMEDTA to 14.51 for LuMEDTA [19]) are much smaller than for CuMEDTA (log K =17.65*), the exchange reaction:

$$LnMEDTA + Cu^{2+} \rightleftharpoons CuMEDTA^- + Ln^{3+} \qquad (1)$$

will be complete in the conditions studied (a large excess of Cu^{2+} ions).

The experimental data fit a pseudo first order kinetics with respect to the LnMEDTA complex, and as can be seen from the data in Table I (for EuMEDTA), are independent of the concentration of Cu^{2+} ions. This result is similar to data for the

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*The stability constant of CuMEDTA has not been previously reported in the literature. From the titration curves of the acid, with and without an equimolar amount of copper nitrate, Powell [18] estimated that the value of $K_{CuMEDTA}$ is close to the stability of copper–N-benzylethylenediamine-N,N',N'-triacetate (log $K_{CuBEDTA}$ = 16.8). The value reported in this work was estimated from the shift of the half wave potential on the dropping mercury electrode of copper due to the complexation by MEDTA; as the electron transfer is not reversible, this value is an upper limit.

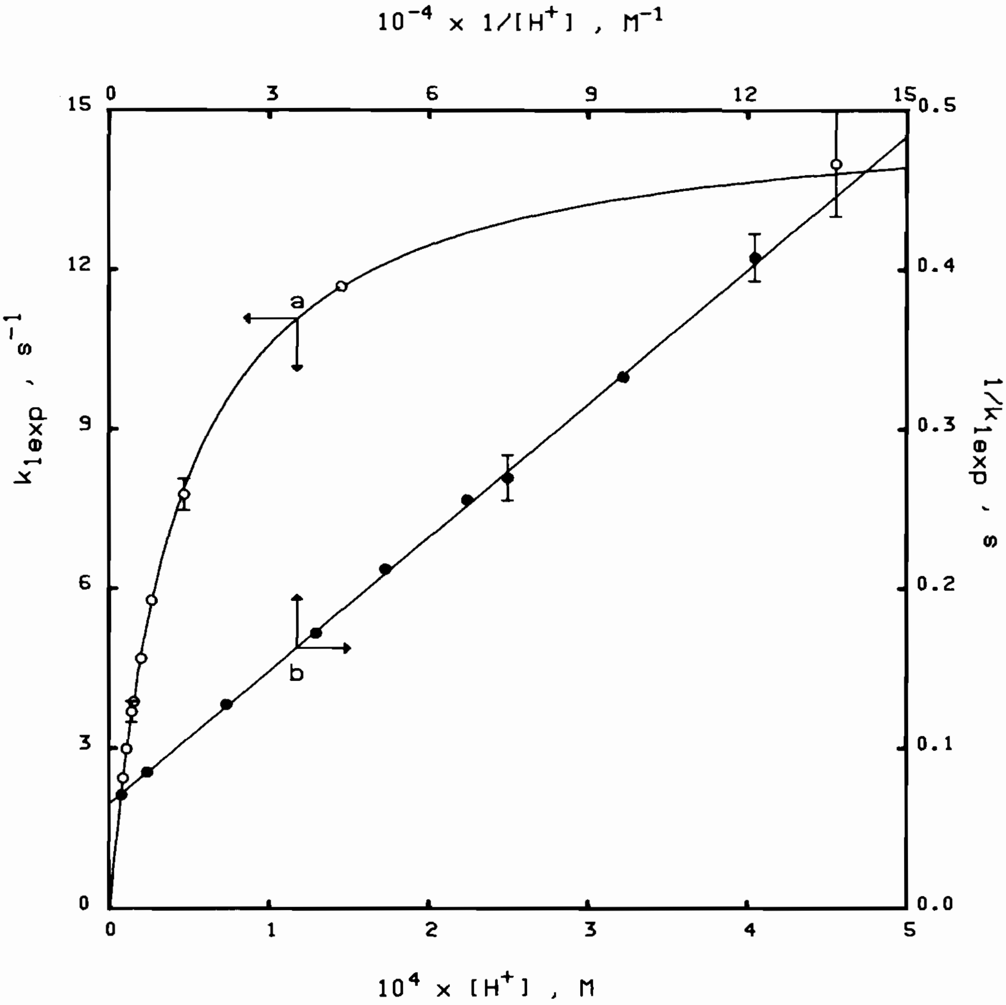

Fig. 1. The dependence of the pseudo first order rate constant ($k_{1\,exp}$) of the dissociation of EuMEDTA on the hydrogen ion concentration; [EuMEDTA] = 5 × 10^{-5} M, [Cu(II)] = 5 × 10^{-4} M at 0.02 M acetate buffer, μ = 0.5 M and T = 25 °C.

exchange of LnDCTA with copper [18, 19] and is consistent with a dissociative mechanism:

$$\mathrm{EuMEDTA} \rightleftharpoons \mathrm{Eu^{3+} + MEDTA}$$

$$\mathrm{MEDTA + Cu^{2+} \longrightarrow CuMEDTA^-} \qquad (2)$$

The dependence of the pseudo first order rate constants on the hydrogen ion concentration (at different constant total buffer concentrations) is tabulated in Table II. As shown in Fig. 1a $k_{1\,exp}$ increases considerably at low acidity but becomes almost independent of it at pcH < 4. On the contrary a plot of $1/k_{1exp}$ *versus* $1/[H^+]$ fits the experimental data on a straight line (see Fig. 1b). Thus the hydrogen ion dependence of the pseudo first order rate constant can be written as:

$$k_{1exp} = \frac{k'[H^+]}{a + b[H^+]} \qquad (3)$$

The values of the slope (a/k') and the intercept (b/k') of the straight lines (as in Fig. 1b) are both inversely proportional to the total acetate buffer concentration corrected for the formation of copper acetate complexes ([Buffer]) as shown in Fig. 2. For all LnMEDTA complexes it was found that the plots b/k' *versus* 1/[Buffer] have a zero intercept within the experimental error limits and that the straight lines a/k' *versus* 1/[Buffer] have a non-zero intercept. Thus, the pseudo first order rate constant can be written formally to include the influence of both the hydrogen ion concentration and the acetate buffer:

$$k_{1exp} = \frac{k[H^+][\mathrm{Buffer}]}{\alpha + \beta[H^+] + \gamma[\mathrm{Buffer}]} \qquad (4)$$

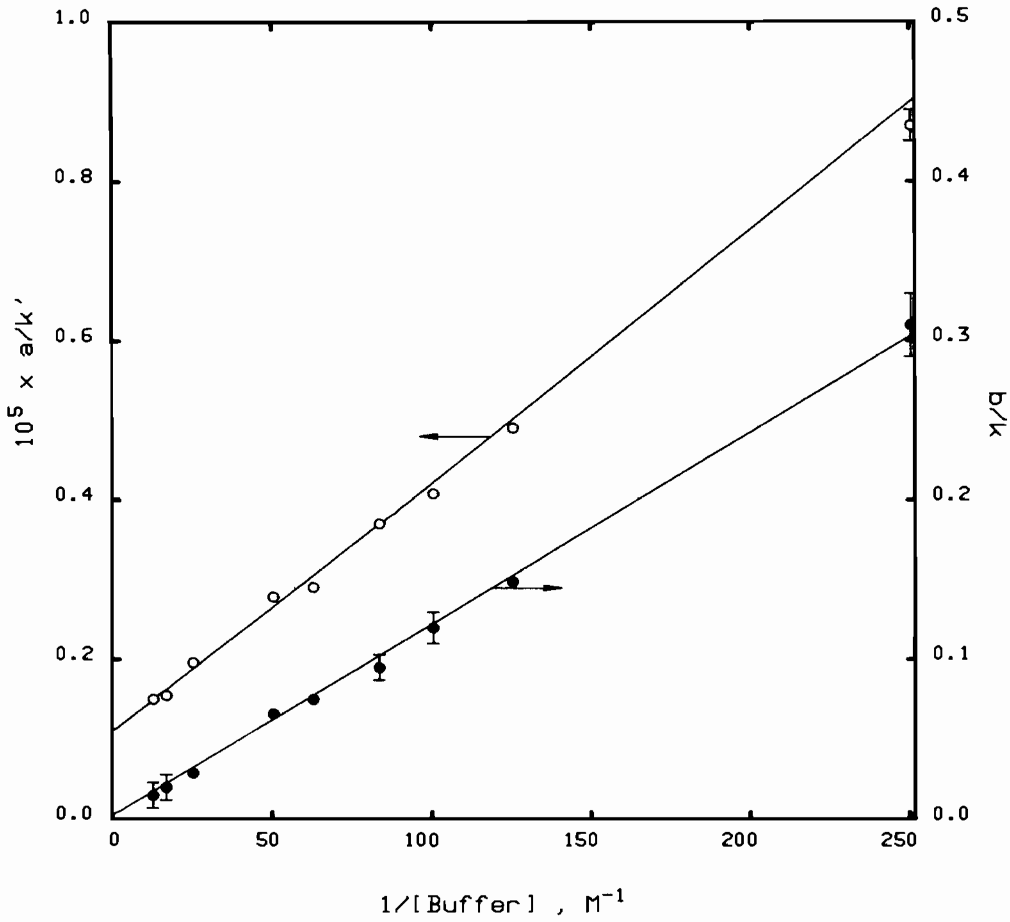

Fig. 2. The dependence of the slope (a/k') and the intercept (b/k') of the curves $1/k_{1\mathrm{exp}}$ *versus* $1/[\mathrm{H}^+]$ on the total acetate buffer concentration; [EuMEDTA] = 5×10^{-5} M, [Cu(II)] = 5×10^{-4} M at μ = 0.5 M and T = 25 °C.

TABLE II. Dependence of the Pseudo First Order Rate Constant ($k_{1\mathrm{exp}}$) for EuMEDTA on the Concentration of Hydrogen Ions at Different Total Buffer Concentration at 5×10^{-5} M EuMEDTA, 5×10^{-4} M Cu(II), 0.5 M Ionic Strength and 25 °C.

C_{buffer} M	$10^5 \times [\mathrm{H}^+]$ M	$k_{1\mathrm{exp}}$ s^{-1}	C_{buffer} M	$10^5 \times [\mathrm{H}^+]$ M	$k_{1\mathrm{exp}}$ s^{-1}
0.004	0.68	0.63 ± 0.04	0.016	4.33	7.02 ± 0.02
	0.91	0.79 ± 0.02		7.62	9.05 ± 0.31
	1.84	1.29 ± 0.02			
	4.26	1.93 ± 0.03	0.020	0.82	2.45 ± 0.09
	5.21	2.26 ± 0.13		1.04	3.00 ± 0.04
				1.34	3.74 ± 0.23
0.008	0.92	1.46 ± 0.03		1.49	3.90 ± 0.09
	1.64	2.26 ± 0.08		1.93	4.69 ± 0.12
	6.03	4.21 ± 0.36		2.59	5.81 ± 0.10
	11.1	5.50 ± 0.36		4.60	7.81 ± 0.32
	67.0	6.30 ± 0.27		14.46	11.69 ± 0.14
				45.49	14.13 ± 1.23
0.010	0.30	0.65 ± 0.03			
	0.40	0.92 ± 0.02	0.040	0.58	2.73 ± 0.01
	0.61	1.26 ± 0.03		0.96	4.24 ± 0.15
	0.76	1.58 ± 0.04		2.32	8.60 ± 0.27

(continued on facing page)

TABLE II. *(continued)*

C_{buffer} M	$10^5 \times [H^+]$ M	k_{1exp} s^{-1}
	1.00	1.89 ± 0.02
	1.55	2.57 ± 0.05
	2.02	3.10 ± 0.12
	2.46	3.42 ± 0.06
	3.51	4.60 ± 0.01
	5.65	5.22 ± 0.21
0.012	0.85	1.84 ± 0.03
	2.84	4.52 ± 0.06
	5.07	5.90 ± 0.13
	14.1	7.10 ± 0.45
	50.0	10.09 ± 0.70
0.016	0.42	1.31 ± 0.03
	0.84	2.30 ± 0.05
	1.47	3.62 ± 0.05
	2.57	5.49 ± 0.06
	2.71	10.44 ± 0.55
	3.67	11.97 ± 0.22
0.060	0.09	0.57 ± 0.01
	0.16	1.03 ± 0.02
	0.25	1.54 ± 0.01
	1.36	7.41 ± 0.15
	2.11	10.55 ± 0.41
	3.06	13.61 ± 1.00
0.080	0.17	1.10 ± 0.01
	0.27	1.75 ± 0.02
	0.46	3.14 ± 0.04
	0.98	5.27 ± 0.05
	1.35	8.01 ± 0.32
	2.16	11.93 ± 0.45
	2.71	14.18 ± 0.13

with

$$[\text{Buffer}] = [CH_3COOH] + [CH_3COO^-] =$$

$$= C_{\text{Buffer}} - i\Sigma[Cu(CH_3COO)_i{}^{2-i}] \qquad (5)$$

Thus, although the exchange reaction proceeds through a dissociative mechanism similar to that for other lanthanide–polyaminopolycarboxylate complexes (*e.g.* EDTA, HEDTA and DCTA), the formal pseudo first order rate constant depends, in a very different way, on the concentration of hydrogen ions and of the acetate buffer. The influence of both these parameters on the reaction rate decreases with their increasing concentration. Eventually the reaction rate becomes almost independent of their influence (approximately at $[H^+] > 2 \times 10^{-4}$ M or [Buffer] > 0.06 M).

Although a reaction scheme involving a fast protonation equilibrium shifted to the formation of a large amount of protonated intermediate complex and preceding the rate determining dissociation step would explain a hydrogen ion dependence as shown in eqn. (3), this cannot account for the effect of the acetate buffer as expressed in eqn. (4). Since the concentration of free acetate ions depends on the acidity, this would result in quadratic terms with respect to the hydrogen ion concentration. However, eqn. (4) can be explained assuming the formation of appreciable amounts of LnMEDTA–acetate mixed complex as reactive intermediate.

Since curves of k_{1exp} *versus* [Buffer] at constant pcH show a zero intercept within error limits, thus indicating that the LnMEDTA complexes are much less reactive than the mixed acetate complexes, the reaction scheme can be formulated as:

$$\text{LnMEDTA} + \text{OAc}^- \overset{K_M}{\rightleftharpoons} \text{Ln(MEDTA)(OAc)}^- \qquad (6)$$

$$\text{Ln(MEDTA)(OAc)}^- + H^+ \overset{K_H}{\rightleftharpoons} \text{LnH(MEDTA)(OAc)} \qquad (7)$$

$$\text{LnH(MEDTA)(OAc)} \xrightarrow[\text{slow}]{k_s} \text{Ln(HMEDTA)(OAc)} \qquad (8)$$

$$\text{Ln(HMEDTA)(OAc)} + (x-1)H^+ \xrightarrow[\text{fast}]{} \text{LnOAc}^{2+} + H_x\text{MEDTA}^{(3-x)-} \qquad (9)$$

$$H_x\text{MEDTA}^{(3-x)-} + \text{Cu(OAc)}_i{}^{(2-i)+} \xrightarrow[\text{fast}]{} \text{CuMEDTA}^- + i\text{OAc}^- + xH^+ \qquad (10)$$

Since the exchange reaction goes to completion, the reverse reactions are not included in this scheme. Assuming that K_M is rather large, so that under the conditions studied a relatively large amount of mixed complexes Ln(MEDTA)(OAc)$^-$ exists in the solution, the following rate equation can be deduced:

$$\text{Rate} = \frac{k_s K_M K_H [H^+][\text{OAc}^-] C_{\text{LnY}}}{1 + K_M[\text{OAc}^-]} \qquad (11)$$

where C_{LnY} stands for the concentration of both LnMEDTA and Ln(MEDTA)(OAc)$^-$ complexes. The concentration of free acetate ions can be written as a function of the total buffer (taking into account the formation of Cu^{2+} acetate complexes) and the hydrogen ion concentration, so that eqn. (11) can be transformed to:

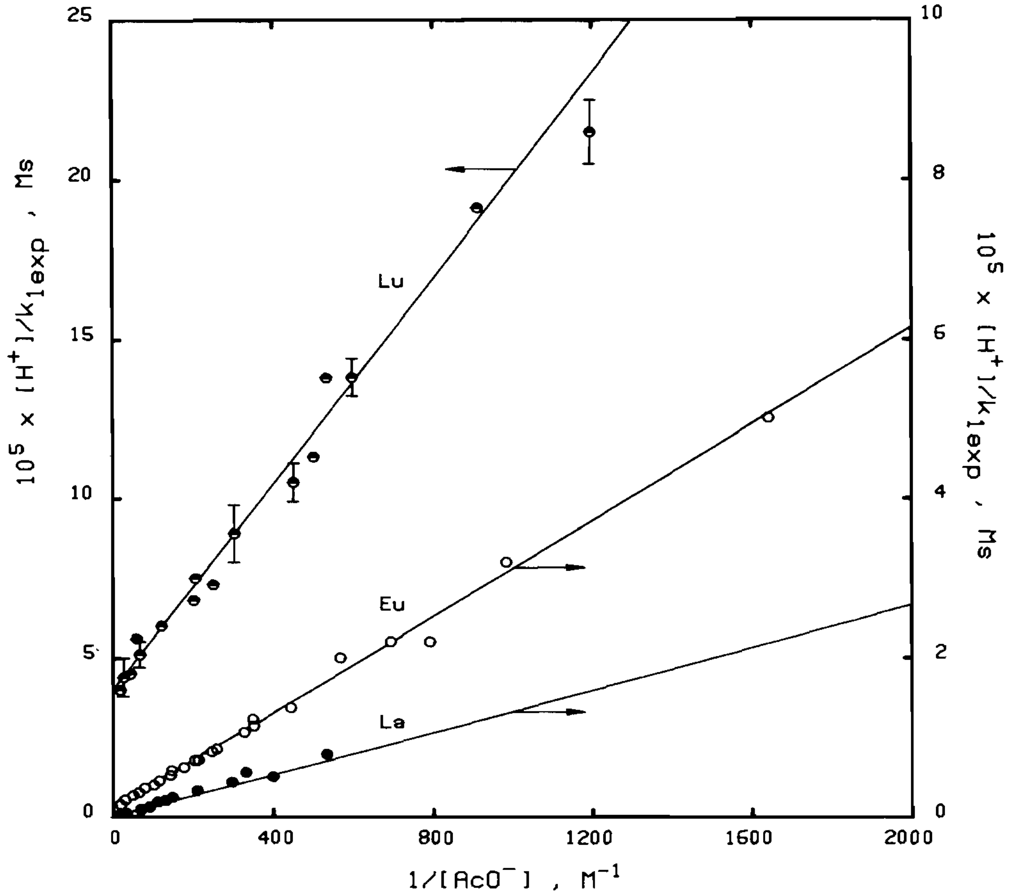

Fig. 3. Plot of $[H^+]/k_{1\mathrm{exp}}$ *versus* the concentration of free acetate anions for LaMEDTA. EuMEDTA and LuMEDTA; [LnMEDTA] = 5 × 10^{-5} M, [Cu(II)] = 5 × 10^{-4} M at μ = 0.5 M and T = 25 °C.

TABLE III. Variation of the Stability Constant (K_M) of the Mixed LnMEDTA–Acetate Complexes, the Dissociation Rate Constant (k_s K_M) and the Calculated Formation Rate Constant for the Lanthanides (except Pm) and Yttrium at 0.5 M Ionic Strength, T = 25 °C.

Ln	r Å	K_M M^{-1}	$10^{-6} \times k_s K_H$ M^{-1} s^{-1}	$10^{-10} \times k_{\mathrm{Form}}$ M^{-2} s^{-1}
La	1.061	10 ± 1	7.9 ± 1.4	0.183
Ce	1.034	7 ± 1	7.0 ± 1.0	0.267
Pr	1.013	10 ± 1	4.8 ± 0.7	0.714
Nd	0.995	9 ± 2	3.2 ± 0.7	0.633
Sm	0.964	42 ± 8	0.82 ± 0.19	1.76
Eu	0.950	36 ± 2	0.86 ± 0.38	2.14
Gd	0.938	29 ± 3	1.02 ± 0.14	2.01
Tb	0.923	33 ± 4	0.69 ± 0.11	3.75
Dy	0.908	38 ± 4	0.50 ± 0.06	5.61
Ho	0.894	58 ± 10	0.252 ± 0.050	6.78
Er	0.881	75 ± 23	0.124 ± 0.043	7.15
Tm	0.869	85 ± 23	0.092 ± 0.027	11.3
Yb	0.858	152 ± 31	0.042 ± 0.009	11.9
Lu	0.848	255 ± 12	0.024 ± 0.002	14.3
Y	0.93	37 ± 6	0.7 ± 0.2	4.20

$$\frac{\text{Rate}}{C_{\mathrm{LnY}}} = k_{1\mathrm{exp}} = \frac{k_s K_H K_M K_a [H^+] [\text{Buffer}]}{K_a + K_M K_a [\text{Buffer}] + [H^+]} \qquad (12)$$

with K_a the acid dissociation constant of acetic acid and [Buffer] as defined by eqn. (5).

Equation (12) is equivalent to the experimental rate eqn. (4) with $k = k_s\ K_H\ K_M\ K_a$, $\alpha = K_a$, $\beta = 1$ and $\gamma = K_M K_a$. It is also obvious from eqn. (11) that a plot of $[H^+]/k_{1\mathrm{exp}}$ *versus* $1/[\mathrm{AcO}^-]$ should be a straight line for each of the LnMEDTA complexes, as is shown in Fig. 3 for the complexes of lanthanum, europium and lutetium (for clarity, only a limited number of data are plotted). The value of the stability constant for the mixed complex (K_M) and the product k_s K_H can be calculated from the slope and intercepts of the straight lines as in Fig. 3 or from the plots of $1/k_{\mathrm{exp}}$ *versus* $1/[H^+]$ at constant total buffer concentration as can be deduced from eqn. (12). The values thus obtained are summarized in Table III for all lanthanides (except Pm) and yttrium.

The main difference between the reaction mechanism for the dissociation of LnMEDTA complexes

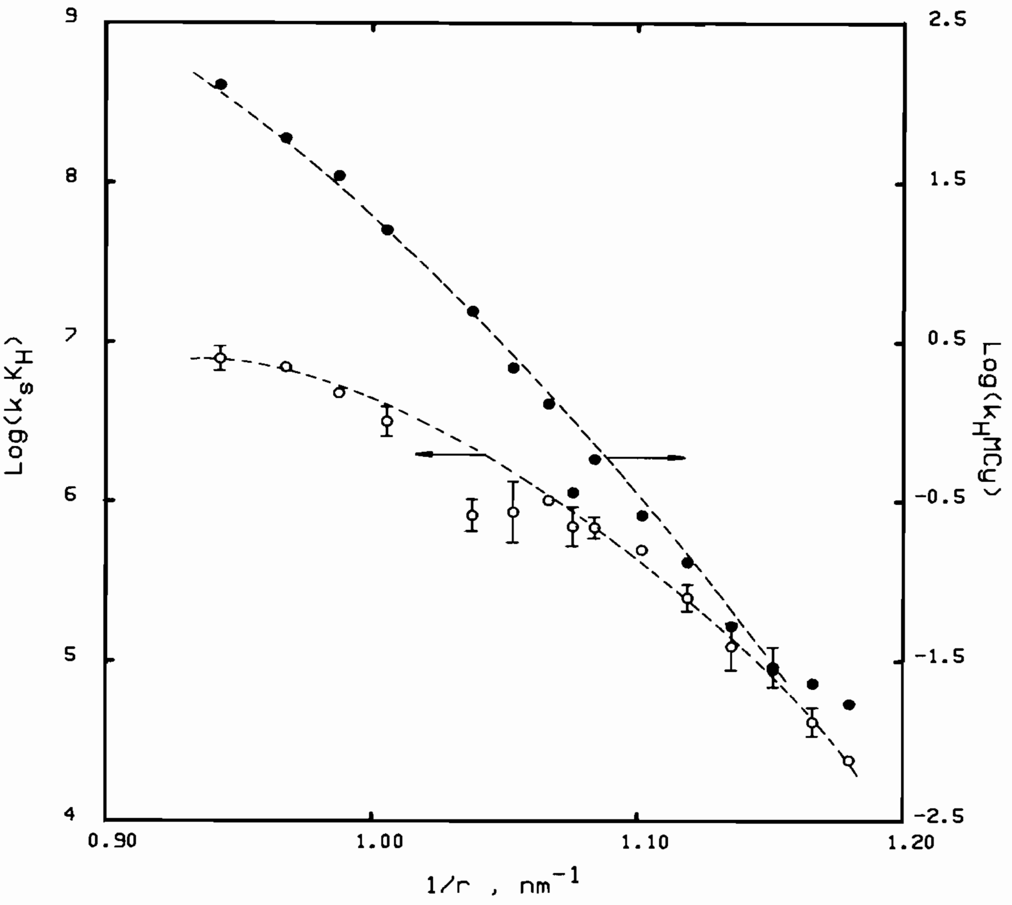

Fig. 4. Variation of the dissociation rate constant ($k_s\ K_H$) of the mixed complexes Ln(MEDTA)(OAc)$^-$ and of LnDCTA$^-$ (taken from ref. 11, k_H^{Mcy}) *versus* the reciprocal ionic radii of the rare earth ions. ○ Ln(MEDTA)(OAc)$^-$, this work. ● LnDCTA$^-$, data from ref. 11.

proposed herein and that for the acid catalyzed dissociation of LnEDTA or analogous complexes proposed in the literature, is in the formation and the role of mixed chelate–acetate complexes. The existence of such species was reported by Elgavish and Reuben [20]. The stability constants obtained from PMR shift for the mixed complexes of Pr(III), Gd(III) and Yb(III) are small (between 1 and 10); this would explain that the formation of these mixed complexes does not show up in the kinetics of dissociation or exchange of LnEDTA chelates. Contrary to the hexadentate EDTA ligand, MEDTA has one less coordinating acetate group and, as such, forms uncharged chelates with Ln^{3+} ions. This results in a lower electrostatic barrier compared to LnEDTA$^-$ anions which may inhibit or preclude the binding of the acetate anion. Furthermore, the values of K_M increase with increasing atomic number for the heavier lanthanides in accordance with decreasing ionic radii, but are almost independent of it for the first members of the series (La–Nd). This trend contrasts somewhat with the variation observed for lanthanide mono-acetate complexes where K values increase from La(III) to Eu(III), then show a decreasing trend through Ho(III) and finally show a slightly rising trend throughout the remainder of the series [21].

The product $k_s\ K_H$ (the rate constant of the slow intramolecular hydrogen transfer multiplied by the protonation constant of the mixed ligand complex) decreases with increasing atomic number of the lanthanide ion and thus varies in an opposite way to their stability constants. This evolution, shown in Fig. 3 as log k_sK_H *versus* $1/r$, is almost identical to the variation of the acid dependent rate constants for the dissociation of lanthanide–diaminocyclohexane-N,N,N′,N′-tetraacetate complexes as reported by Nyssen and Margerum [11]. The rate constants for the dissociation of LnDCTA complexes are, however, five to six orders of magnitude smaller than those of the corresponding LnMEDTA–OAc complexes and the range of the variation (from La to Lu) is much larger; this clearly illustrates the role of the structure of the ligand, which is much more rigid for DCTA than for MEDTA, on the dissociation kinetics.

Since values for the dissociation reaction are known, the 'formal' rate constants for the formation of LnMEDTA complexes can be calculated from the scheme:

$$\mathrm{Ln(MEDTA)(OAc)^- + H^+} \underset{k_{\mathrm{Form}}}{\overset{k_{\mathrm{Diss}}}{\rightleftharpoons}} \mathrm{Ln^{3+} + OAc^- + HMEDTA^{2-}} \xrightarrow[\text{fast}]{\mathrm{Cu^{2+}}} \text{Products} \tag{13}$$

where $k_{\mathrm{Diss}} = k_s K_H$. In the pH range studied both $\mathrm{HMEDTA^{2-}}$ and $\mathrm{H_2MEDTA^-}$ are the predominant forms of the free ligand; assuming that the monoprotonated dianion is the more reactive species the formal formation rate constant can be expressed as:

$$k_{\mathrm{Form}} = k_s K_H K_M K_4 K_c \tag{14}$$

where K_4 is the acid dissociation constant of $\mathrm{HMEDTA^{2-}}$, ($\mathrm{p}K_4 = 10.14$), K_c the stability constant of LnMEDTA (values are taken from ref. 19) and k_s, K_H and K_M were defined previously. The values of k_{Form} thus obtained are listed in Table III; they show a steady increase with increasing atomic number. Owing to the complex nature of k_{Form}, which involves the formation of the mixed ligand complex, no direct comparison with the values reported for the formation of the LnDCTA complexes [11] is possible. A direct measurement of the rate of formation of these complexes was attempted; however, the reaction was too fast and was completed within the mixing time of the stopped-flow spectrometer.

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