

Spectroscopy and Structure of Heavy Lanthanide Complexes with EDTA

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(Received December 23, 1986)

Abstract

The electronic absorption method has been used to study the equilibria and structure of Ho^{3+} and Er^{3+} complexes with EDTA. Spectral properties of these systems are investigated for different Ln^{3+} concentrations at M:L ratios of 1:1 and 1:2 within a broad pH range. Analysis of the 'hypersensitive' transition band shapes and intensities and of the Judd–Ofelt intensity parameters τ_λ allows us to investigate the formation and the type of bonding of Ln^{3+} –EDTA species occurring in solution. Comparison of the results for Ho^{3+} and Er^{3+} with Nd^{3+} –EDTA [1] complexes shows a significant difference between EDTA complexes of heavy and light lanthanides.

Introduction

In a recent paper [1], we discussed the spectral properties of Nd^{3+} –EDTA complexes in solution considered in terms of intensity changes of f–f transitions. Particularly, the changes of 'hypersensitive' transitions oscillator strengths and τ_λ Judd–Ofelt parameter values have been discussed. These results show that electronic spectroscopy data can be considered as quite a sensitive proof of the solution coordination state. This is true even for other lanthanide complexes [2–4] with different ligand atoms present in the inner coordination sphere of the lanthanide ion. Moreover, our results for NTA complexes of light and heavy lanthanide ions [2, 3] show that even differences between these systems could be observed by the absorption spectroscopy method.

It was therefore interesting to see how these differences are revealed in the more complicated EDTA system, where both a higher number of donor groups and stronger entropy effects obscure the direct interaction between the Ln^{3+} ion and ligand donor atoms.

Experimental

Reagents

Stock solutions of Ho^{3+} and Er^{3+} perchlorates were prepared from 99.9% lanthanide oxides (Merck). The

concentrations of the Ln^{3+} ions were determined gravimetrically. Commercial EDTA was used as the sodium salt ($\text{Na}_2\text{H}_2\text{EDTA}$). A carbonate-free NaOH solution was used to adjust the pH of the ligand solutions to appropriate values.

Measurements and Calculations

All spectral measurements were made on a Cary 14 spectrophotometer within the region 10 000–41 000 cm^{-1} . All the measured solutions were prepared with the same ionic strength (0.5 M NaClO_4). The pH values of the solutions investigated spectroscopically were measured on a Radelkis pH-meter (with an accuracy of ± 0.05 pH unit). Experimental oscillator strength values were obtained by a graphic integration of the area under the absorption curves, after appropriate correction for the base line.

τ_λ parameters were calculated from the experimental oscillator strengths and the Judd–Ofelt equation written in the following modified form:

$$P = \sum \sigma \tau_\lambda (f^N \psi_J || U^{(\lambda)} || f^N \psi_{J'})^2 / (2J + 1) \quad (1)$$

$$\lambda = 2, 4, 6$$

where σ is the wave number (cm^{-1}), $U^{(\lambda)}$ is the matrix element of the unit tensor calculated by Carnall *et al.* [5] in the intermediate coupling scheme, $f^N \psi_J$, $f^N \psi_{J'}$ are the initial and final states of electronic transitions, respectively, and J is the total quantum number. τ_λ parameter values were fitted to the experimental oscillator strength values of the absorption bands: 11 for the Ho^{3+} ion and 9 for the Er^{3+} ion within the absorption region 15 000–30 000 cm^{-1} . The identifications of the electronic levels and wave number values are listed in ref. 6.

Results and Discussion

The absorption spectra of Ho^{3+} and Er^{3+} ions in strongly acid solutions with an M:L ratio lower than one changed significantly with the amount of ligand added. This is presented in Fig. 1 for the Ho^{3+} –EDTA system, where distinct changes, in comparison with the aqua-ion, are observed, especially for the 'hypersensitive' transition (${}^5\text{G}_6 \leftarrow {}^5\text{I}_8$).

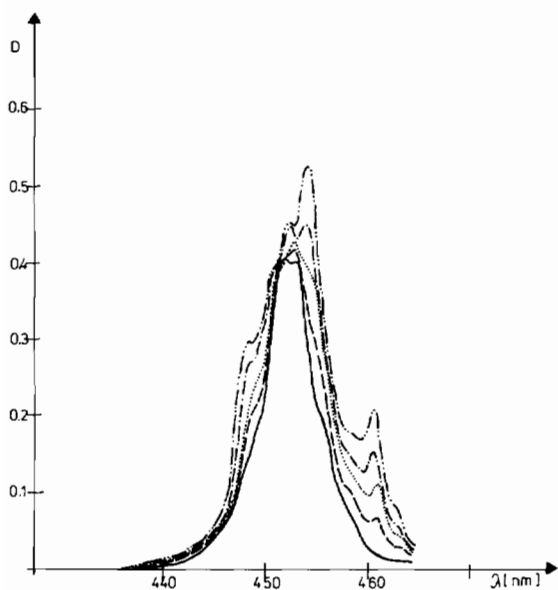
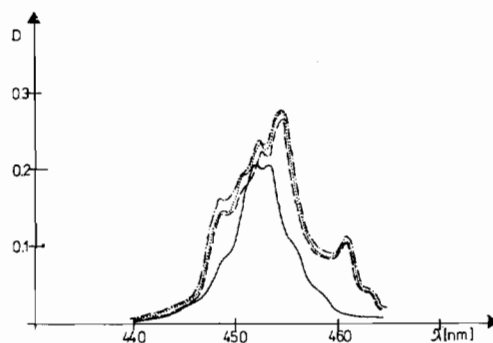
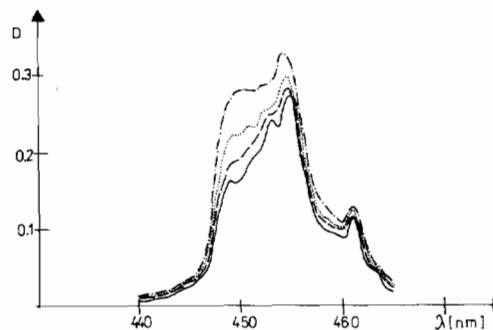


Fig. 1. Effect of the EDTA concentration on the 'hypersensitive' transition ${}^5G_6 \leftarrow {}^5I_8$ in the absorption spectrum of Ho^{3+} ion for $\text{Ho}^{3+}:\text{EDTA}$ ratios of $1:n$ ($c_{\text{Ho}^{3+}} = 2.002 \times 10^{-2}$ M). 1:0, — (pH = 2.65); 1:0.25, --- (pH = 1.48); 1:0.5, (pH = 1.17); 1:0.75, -.- (pH = 1.02); 1:1.5, -.- (pH = 1.25).

Above M:L concentration ratio = 1, further increase of the ligand concentration does not change either the intensities or shapes even of the 'hypersensitive' transition. There are significant differences between EDTA complexes of heavy and light lanthanides. For the Nd^{3+} -EDTA system, distinct differences both in shape and intensities of the 'hypersensitive' transition were observed when M:L ratios varied, even at low pH values. This means that for Ho^{3+} and Er^{3+} EDTA systems at very low pH values only one 1:1 species exists. Moreover, detailed inspection of the systems with M:L ratio = 1:1 over a large pH range (1–13) proves that the same shape is preserved up to $\text{pH} \approx 11$ with intensities slightly increasing in different ways. At very high pH values ($\text{pH} > 11$) both for Ho^{3+} and Er^{3+} significant changes of 'hypersensitive' transition shapes and intensities were observed for 1:1 systems. In Figs. 2–4 these results are presented for the Ho^{3+} and Er^{3+} -EDTA systems, respectively. For Ho^{3+} and Er^{3+} -EDTA systems with M:L ratio = 1:2, different spectral behaviour of the 'hypersensitive' transitions was observed (Figs. 3–5). At the acidic pH values (up to 4.5 for Ho^{3+} and 5.0 for Er^{3+}) the same shape and no intensity changes of the 'hypersensitive' transitions as for the 1:1 complex were observed. This suggests that the same species exists under these conditions. Above these pH values systematic changes in the 'hypersensitive' band shape and intensity are



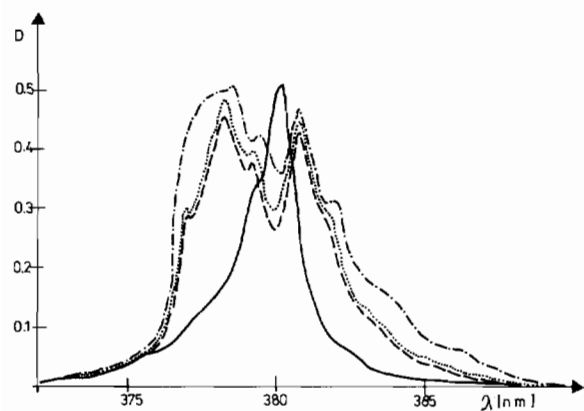
(a)



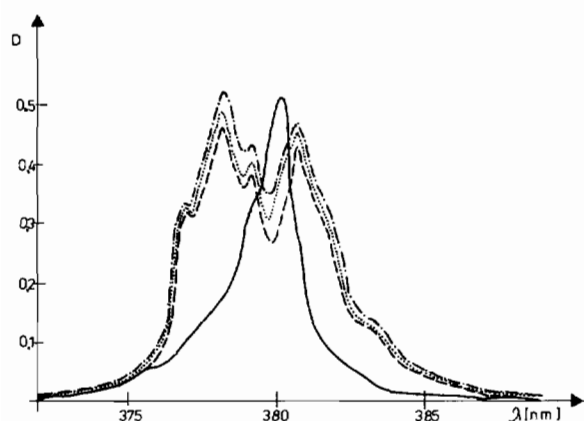
(b)

Fig. 2. Effect of pH on the 'hypersensitive' transition ${}^5G_6 \leftarrow {}^5I_8$ in the absorption spectrum of Ho^{3+} ion for a $\text{Ho}^{3+}:\text{EDTA}$ ratio of 1:1 ($c_{\text{Ho}^{3+}} = 1.001 \times 10^{-2}$ M, $c_{\text{EDTA}} = 1 \times 10^{-2}$ M). (a) $\text{Ho}(\text{ClO}_4)_3$, — (pH = 3.16); $\text{Ho}(\text{ClO}_4)_3 + \text{EDTA}$, --- (pH = 2.26); $\text{Ho}(\text{ClO}_4)_3 + \text{EDTA}$, (pH = 6.82); $\text{Ho}(\text{ClO}_4)_3 + \text{EDTA}$, -.- (pH = 11.00). (b) $\text{Ho}(\text{ClO}_4)_3 + \text{EDTA}$, — (pH = 11.00); $\text{Ho}(\text{ClO}_4)_3 + \text{EDTA}$, --- (pH = 11.33); $\text{Ho}(\text{ClO}_4)_3 + \text{EDTA}$, (pH = 11.92); $\text{Ho}(\text{ClO}_4)_3 + \text{EDTA}$, -.- (pH = 12.59).

observed. At extremely high pH values the shape is changed and the intensities distinctly increase. These results suggest the necessity of more detailed study of intensity changes. We express them as both directly calculated experimental oscillator strength values of 'hypersensitive' transitions and as Judd-Ofelt parameters τ_λ , evaluated from the experimental oscillator strength values of f-f transitions appearing in the measured absorption region. The evaluation of Judd-Ofelt parameters was necessary for the comparison of how other than 'hypersensitive' transitions are effected by the process of complexation. Some values for oscillator strengths of 'hypersensitive' transitions and Judd-Ofelt parameters are presented in Tables I and II for Ho^{3+} and Er^{3+} -EDTA systems, respectively. As in our previous papers [1–4], the oscillator strength values of the 'hypersensitive' transitions seem to be the most sensitive parameter describing the complexation process. On the other hand, τ_λ



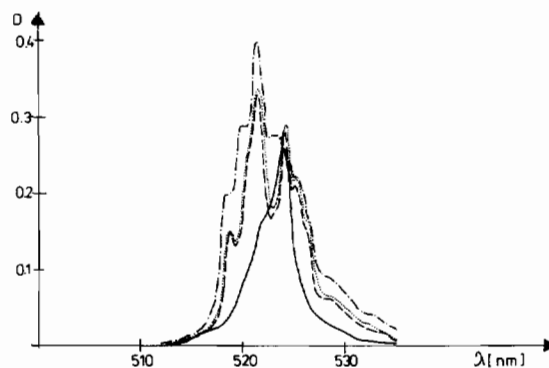
(a)



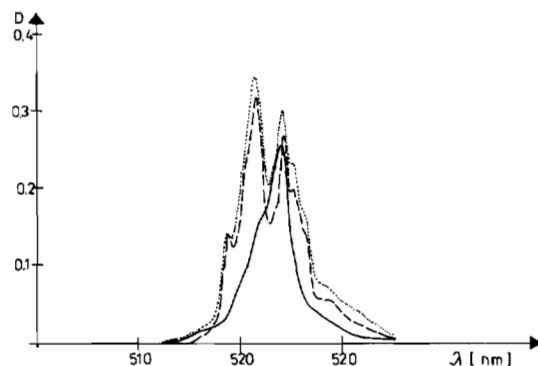
(b)

Fig. 3. Effect of pH on the 'hypersensitive' transition ${}^4G_{11/2} \leftarrow {}^4I_{13/2}$ in the absorption spectrum of Er^{3+} ion for: (a) $\text{Er}^{3+}:\text{EDTA} = 1:1$ ($c_{\text{Er}^{3+}} = 1.496 \times 10^{-2}$ M, $c_{\text{EDTA}} = 1.5 \times 10^{-2}$ M). $\text{Er}(\text{ClO}_4)_3$, — (pH = 1.61); $\text{Er}(\text{ClO}_4)_3 + \text{EDTA}$, --- (pH = 2.05); $\text{Er}(\text{ClO}_4)_3 + \text{EDTA}$, (pH = 9.27); $\text{Er}(\text{ClO}_4)_3 + \text{EDTA}$, -.- (pH = 12.38). (b) $\text{Er}^{3+}:\text{EDTA} = 1:2$ ($c_{\text{Er}^{3+}} = 1.496 \times 10^{-2}$ M, $c_{\text{EDTA}} = 3 \times 10^{-2}$ M). $\text{Er}(\text{ClO}_4)_3$, — (pH = 1.61); $\text{Er}(\text{ClO}_4)_3 + \text{EDTA}$, --- (pH = 2.17); $\text{Er}(\text{ClO}_4)_3 + \text{EDTA}$, (pH = 7.30); $\text{Er}(\text{ClO}_4)_3 + \text{EDTA}$, -.- (pH = 9.35).

parameter values from the Judd–Ofelt eqn. (1) give a better insight into the whole spectrum changes, because in many cases intensity changes are not limited to the 'hypersensitive' transition (whose intensity depends mainly on $U^{(2)}$ and τ_2 values) only. The results (Tables I and II) indicate clearly that for the spectra of heavy lanthanide–EDTA complexes significant intensity changes are connected mainly with changes in the τ_2 parameter values. The τ_4 and τ_6 parameter values remain almost constant for all measurements within the whole pH range investigated with different M:L ratios.



(a)



(b)

Fig. 4. Effect of pH on the 'hypersensitive' transition ${}^2H_{11/2} \leftarrow {}^4I_{13/2}$ in the absorption spectrum of Er^{3+} ion for: (a) $\text{Er}^{3+}:\text{EDTA} = 1:1$ ($c_{\text{Er}^{3+}} = 1.496 \times 10^{-2}$ M, $c_{\text{EDTA}} = 1.5 \times 10^{-2}$ M). $\text{Er}(\text{ClO}_4)_3$, — (pH = 1.61); $\text{Er}(\text{ClO}_4)_3 + \text{EDTA}$, --- (pH = 2.05); $\text{Er}(\text{ClO}_4)_3 + \text{EDTA}$, (pH = 9.27); $\text{Er}(\text{ClO}_4)_3 + \text{EDTA}$, -.- (pH = 12.38). (b) $\text{Er}^{3+}:\text{EDTA} = 1:2$ ($c_{\text{Er}^{3+}} = 1.496 \times 10^{-2}$ M, $c_{\text{EDTA}} = 3 \times 10^{-2}$ M). $\text{Er}(\text{ClO}_4)_3$, — (pH = 1.61); $\text{Er}(\text{ClO}_4)_3 + \text{EDTA}$, --- (pH = 2.17); $\text{Er}(\text{ClO}_4)_3 + \text{EDTA}$, (pH = 9.35).

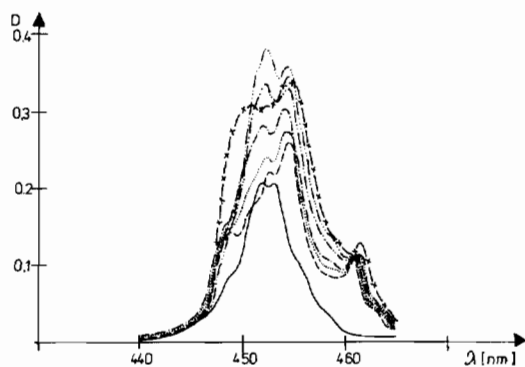
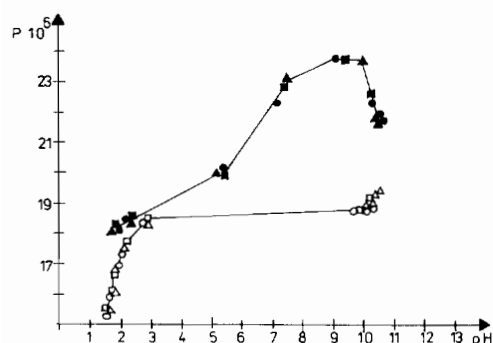


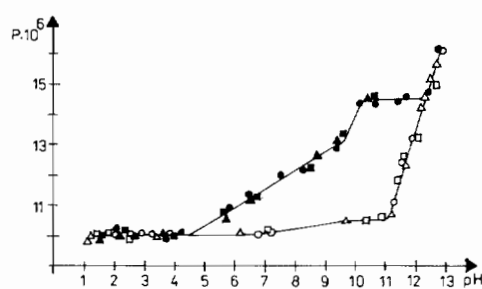
Fig. 5. Effect of pH on the 'hypersensitive' transition ${}^5G_6 \leftarrow {}^5I_8$ in the absorption spectrum of Ho^{3+} ion for a $\text{Ho}^{3+}:\text{EDTA}$ ratio of 1:2 ($c_{\text{Ho}^{3+}} = 1.001 \times 10^{-2}$ M, $c_{\text{EDTA}} = 2 \times 10^{-2}$ M). $\text{Ho}(\text{ClO}_4)_3$, — (pH = 3.16); $\text{Ho}(\text{ClO}_4)_3 + \text{EDTA}$, --- (pH = 2.52); $\text{Ho}(\text{ClO}_4)_3 + \text{EDTA}$, (pH = 5.77); $\text{Ho}(\text{ClO}_4)_3 + \text{EDTA}$, -.- (pH = 7.48); $\text{Ho}(\text{ClO}_4)_3 + \text{EDTA}$, -.-.- (pH = 9.46); $\text{Ho}(\text{ClO}_4)_3 + \text{EDTA}$, -.-.-.- (pH = 10.67); $\text{Ho}(\text{ClO}_4)_3 + \text{EDTA}$, -x- (pH = 12.78).

TABLE I. Oscillator Strength Values (P) of the ${}^5G_6 \leftarrow {}^5I_8$ 'Hypersensitive' Transition and the Judd–Ofelt Parameter Values (τ_λ) of Ho^{3+} for $\text{Ho}^{3+}:\text{EDTA}$ Ratios of 1:1 and 1:2 at Different pH Values ($c_{\text{Ho}^{3+}} = 2.002 \times 10^{-2}$ M; $c_{\text{EDTA}} = 2 \times 10^{-2}$ M, 4×10^{-2} M)

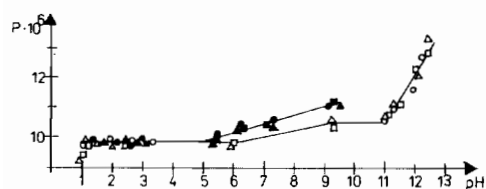
$\text{Ho}^{3+}:\text{EDTA}$	pH	$P \times 10^6$	$\tau_2 \times 10^9$	$\tau_4 \times 10^9$	$\tau_6 \times 10^9$
1:0	2.65	6.1975	0.46 ± 0.25	4.24 ± 0.37	3.99 ± 0.26
1:1	1.06	9.7720	2.21 ± 0.35	4.30 ± 0.52	4.77 ± 0.36
	1.24	9.9928	2.45 ± 0.33	4.03 ± 0.48	4.93 ± 0.34
	2.05	9.9787			
	2.90	10.0469			
	3.36	9.9660	2.27 ± 0.35	4.36 ± 0.52	4.95 ± 0.36
	6.19	10.5239	2.49 ± 0.31	4.43 ± 0.46	5.02 ± 0.32
	9.73	10.4920			
	10.97	10.5543			
	11.20	10.5984	2.90 ± 0.34	3.77 ± 0.50	4.94 ± 0.35
	11.33	11.3218	3.22 ± 0.40	3.94 ± 0.59	4.89 ± 0.42
	11.71	12.2749	3.37 ± 0.37	4.49 ± 0.54	4.80 ± 0.38
	12.19	14.2174	4.58 ± 0.35	4.17 ± 0.51	4.33 ± 0.36
	12.34	14.6345	4.87 ± 0.36	4.03 ± 0.53	4.42 ± 0.37
	12.51	15.2360	5.19 ± 0.35	4.00 ± 0.51	4.25 ± 0.36
12.72	15.7707	5.33 ± 0.33	4.25 ± 0.49	4.33 ± 0.34	
1:2	1.46	9.8342	2.31 ± 0.31	4.16 ± 0.46	4.76 ± 0.32
	2.15	10.0192			
	2.65	10.0157			
	3.61	10.1150	2.35 ± 0.31	4.31 ± 0.46	4.97 ± 0.32
	5.73	10.5417	2.55 ± 0.40	4.41 ± 0.59	5.00 ± 0.41
	6.49	11.1718	2.87 ± 0.42	4.38 ± 0.61	5.04 ± 0.43
	8.75	12.5360	3.48 ± 0.31	4.53 ± 0.38	5.06 ± 0.38
	9.38	13.0746	3.61 ± 0.38	4.73 ± 0.33	5.02 ± 0.39
	10.37	14.4913	4.11 ± 0.41	5.10 ± 0.60	5.03 ± 0.42



(a)



(b)



(c)

Fig. 6. Oscillator strength values of the 'hypersensitive' transition (a) ${}^2G_{7/2}, {}^4G_{5/2} \leftarrow {}^4I_{9/2}$ of Nd^{3+} ion, (b) ${}^5G_6 \leftarrow {}^5I_8$ of Ho^{3+} ion, (c) ${}^4G_{11/2} \leftarrow {}^4I_{13/2}$ of Er^{3+} ion, as a function of pH values for $\text{Ln}^{3+}:\text{EDTA}$ ratios of 1:1/ $\circ, \square, \triangle$ / and 1:2/ $\bullet, \blacksquare, \blacktriangle$ /: $c_{\text{Nd}^{3+}} = 9.96 \times 10^{-3}$ M, \circ, \bullet ; 1.494×10^{-2} M, \square, \blacksquare ; 1.993×10^{-2} M, $\triangle, \blacktriangle$; $c_{\text{Ho}^{3+}} = 1.001 \times 10^{-2}$ M, \circ, \bullet ; 1.489×10^{-2} M, \square, \blacksquare ; 2.002×10^{-2} M, $\triangle, \blacktriangle$; $c_{\text{Er}^{3+}} = 1.004 \times 10^{-3}$ M, \circ, \bullet ; 1.496×10^{-2} M, \square, \blacksquare ; 2.007×10^{-2} M, $\triangle, \blacktriangle$.

In Ln^{3+} –EDTA systems it seems reasonable to look at the changes of $P_{\text{hyp}} = f(\text{pH})$ (free ligand concentration) and to interpret them in terms of complex equilibria and the structures of particular

species existing in solution (Fig. 6). For a better comparison of heavy and light lanthanide–EDTA complexes, our data for the Nd^{3+} –EDTA system [1] are also included in Fig. 6.

TABLE II. Oscillator Strength Values (P_1) of the ${}^4G_{11/2} \leftarrow {}^4I_{13/2}$ and (P_2) of the ${}^2H_{11/2} \leftarrow {}^4I_{13/2}$ 'Hypersensitive' Transitions and the Judd-Ofelt Parameter Values (τ_λ) of Er^{3+} for Er^{3+} : EDTA Ratios of 1:1 and 1:2 at Different pH Values ($c_{Er^{3+}} = 2.007 \times 10^{-2} M$; $c_{EDTA} = 2 \times 10^{-2} M, 4 \times 10^{-2} M$)

Er^{3+} :EDTA	pH	$P_1 \times 10^6$	$P_2 \times 10^6$	$\tau_2 \times 10^9$	$\tau_4 \times 10^9$	$\tau_6 \times 10^9$
1:0	1.45	6.0791	2.7684	1.97 ± 0.33	2.74 ± 0.54	2.28 ± 0.31
1:1	0.89	9.2479	4.2425	3.91 ± 0.44	2.73 ± 0.71	2.67 ± 0.41
	0.97	9.7251	4.3279			
	1.09	9.5041	4.3018	4.00 ± 0.48	2.84 ± 0.77	2.68 ± 0.44
	1.45	9.8006	4.4262			
	2.00	9.7064	4.5013	4.37 ± 0.42	2.41 ± 0.68	2.73 ± 0.39
	2.16	9.6818	4.4586			
	5.93	9.6893	4.5637	4.24 ± 0.42	2.69 ± 0.68	2.73 ± 0.39
	9.18	10.6478	4.9492			
	10.97	10.7014	5.1099	4.84 ± 0.42	2.80 ± 0.68	2.70 ± 0.39
	11.31	11.1035	5.0330	4.84 ± 0.54	3.11 ± 0.87	2.72 ± 0.50
	12.08	12.0676	5.6788			
	12.44	13.2695	6.4250	6.26 ± 0.49	3.18 ± 0.78	2.68 ± 0.45
1:2	1.45	9.7908	4.5974	4.35 ± 0.40	2.55 ± 0.64	2.72 ± 0.37
	1.69	9.7721	4.5356			
	2.01	9.7456	4.5851			
	2.42	9.9067	4.5117	4.40 ± 0.49	2.54 ± 0.79	2.76 ± 0.45
	2.83	9.8043	4.6129			
	5.33	9.8492	4.5800	4.27 ± 0.42	2.73 ± 0.68	2.83 ± 0.39
	6.14	10.2581	4.6850			
	7.28	10.3251	4.7976			
	9.45	10.9185	5.0031	5.01 ± 0.52	2.60 ± 0.83	2.79 ± 0.48

Solutions of Ho^{3+} and Er^{3+} with M:L Ratio = 1:1

Some intensity changes are observed for the Ho^{3+} and Er^{3+} -EDTA solutions at very low pH values, when a significant deficit of deprotonated ligand is present. It should be pointed out, however, that above pH = 1.25 for both these heavy lanthanide ions, oscillator strength values are constant up to pH = 6.75 for Ho^{3+} and 6.0 for Er^{3+} . Above these pH values, intensities slightly increase up to pH = 9.75 for Ho^{3+} and 9.0 for Er^{3+} and then again remain constant up to pH \approx 11 for both these heavy lanthanide ions. Above this pH value a strong intensity increase is observed. This means that for heavy lanthanides in very acidic pH range with a deficit of deprotonated ligand there can exist species bonded by carboxylic groups only. Above pH = 1.25 for both these heavy lanthanide ions only one species bonded through O and N donor atoms exists up to pH \approx 11. Small intensity changes at pH = 6–11 can be caused by some polynuclear species. Above pH = 11, the hydrolysis of these complexes occurs. This feature of intensity changes is in good agreement with the results of Spaulding and Brittain [7] who investigated intermolecular energy transfer between Tb^{3+} and Eu^{3+} aminopolycarboxylic complexes using a luminescence spectroscopy method.

The data of Nd^{3+} -EDTA fit very well to such an interpretation. The region of pH where species

bonded by carboxylic groups exist is significantly larger (1.5–2.9) and even some equilibria between them could be observed. Even in this case a 1:1 species bonded both by N and O exists over quite a large pH range (2.9–10.3). It is unexpected that a significant intensity increase, resulting from hydrolysis, occurs at higher pH values in heavy lanthanides (pH > 11) and not in Nd^{3+} (pH > 10), as can be seen in Fig. 6. However, stability constants [8] of 1:1 species for Ho^{3+} (pK = 17.13) and Er^{3+} (pK = 17.45) are distinctly higher than for Nd^{3+} (pK = 15.75).

Solutions of Ho^{3+} and Er^{3+} with M:L Ratio = 1:2

For solutions of Ho^{3+} and Er^{3+} with M:L ratio = 1:2 a different character of the $P_{hyp} = f(pH)$ is observed. In this case a significant difference between the relation for Nd^{3+} and that for heavy lanthanide ions can be seen.

For Ho^{3+} and Er^{3+} , it is noticeable that there is good correspondence of the P_{hyp} values for the systems with M:L ratios of 1:1 and 1:2 in the acidic pH range. It is clear that under these conditions the same species exists in both solutions, namely species 1:1, bonded by both carboxylic and N-ethylene donor groups. The increase of intensities which is observed above pH = 4.5 and 5.0 for Ho^{3+} and Er^{3+} , respectively, can be explained by an equilibrium between the 1:1 and 1:2 species. At the range of

higher pH values (4.5 for Ho^{3+}) species 1:2 exist predominantly, which hydrolyse above $\text{pH} \approx 12$.

These results enable us to explain better the properties of the Nd^{3+} -EDTA system with M:L ratio = 1:2. The most interesting feature of behaviour in this system is the lack of an intensity plateau which is observed for both Ho^{3+} and Er^{3+} -EDTA. This plateau for heavy lanthanides is obviously related to the formation of a 1:1 species bonded both by ethylenediamine and carboxylic groups. For Nd^{3+} -EDTA a systematic increase of intensities is observed. No full correspondence of the oscillator strength values between the Nd^{3+} -EDTA systems of 1:1 and 1:2 ratios exists in acidic solution. The increase in the oscillator strength values over the pH region of 1.5–7.5 suggests the existence of some equilibria.

Southwood-Jones and Merbach [9] also observed such equilibria in the ^1H NMR spectra and explained them by assuming additional interactions between the $[\text{Pr}(\text{EDTA})]^-$ complex and the iminodiacetic group of the second EDTA molecule. Elgavish and Reuben [10], who investigated the formation of ionic pairs by EDTA lanthanide chelates with organic cations, assumed that light lanthanides form penta-coordinated chelates with one free acetate group. In this case some association by acetate bridges should be observed in solution.

In a recent paper [1], we assumed some equilibria at the same pH range between species differently bonded by acetate groups; however, the results for heavy lanthanides show that Nd^{3+} -EDTA with a 1:2 ratio is bonded by the nitrogen atoms as well. The $P_{\text{hyp}} = f(\text{pH})$ dependence at the range 7.5–10.3 for Nd^{3+} -EDTA should then be related to a 1:1 and 1:2 species equilibrium. Above $\text{pH} = 9$, however, a species of 1:2 ratio predominantly exists in solution. For very high pH values, above 10.3, the Nd^{3+} -EDTA

system also hydrolyses. Similarly to the 1:1 species, this occurs also at lower pH values for Nd^{3+} than for heavy lanthanides.

All methods and all investigations of these systems lead to the same conclusions. However, determination of the mechanism for the light lanthanides is still impossible.

Generally, NMR, luminescence and absorption spectroscopy are a further step towards the understanding of polyamino acid chelate structure and formation. Electronic absorption spectroscopy, however, demonstrates quite clearly a significant difference between EDTA complexes of heavy and light lanthanides. In some cases this method is more sensitive than NMR and luminescence measurements, even if we consider the equilibria which can exist for particular lanthanide–ligand systems in solution.

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