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The Formation of Mixed Complexes of NdMEDTA and NdHyEDTA with Acetate*

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The formation of stable mixed ligand complexes (LnYA) of lanthanide diaminopolycarboxylate chelates (LnY; Y = EDTA, CyDTA, HyDTA, etc.) with di- and polydentate ligands (e.g. acetylacetone, oxalate, citrate, IMDA, mercapto acids, etc.) is well known from studies by potentiometric and various spectroscopic techniques [1–6]. Although the existence of analogous complexes with monofunctional ligands (e.g. acetate) has been postulated in kinetic studies to explain the dependence of the dissociation rate of LnY chelates on the acetate buffer concentration, the formation of such species has been much less studied by direct methods. The stability constants of the complexes of some LnEDTA chelates (Ln is Pr, Gd and Yb) with acetate, estimated from the PMR shift, are of the order of 1 to 10 [7]; the rather small values of these constants explain the difficulties in studying these mixed ligand complexes.

Recently we reported data on the dissociation kinetics of LnMEDTA (MEDTA = *N*-methylethylenediamine-*N*,*N'*,*N'*-triacetate) [8] and LnHyEDTA (HyEDTA = *N*-hydroxyethylethylenediamine-*N*,*N'*,*N'*-triacetate) [9] that unambiguously indicate that a mixed ligand complex with acetate is the main reactive species; the stability constants (K_m) and the kinetic parameters were calculated from the dependence of the dissociation rate on the free acetate and proton concentration. The values of K_m increase from approximately 5 to 250 with increasing atomic number of the lanthanide ion. In this paper we report the results of an independent study by absorption spectrometry to obtain more direct evidence for the existence of the complexes of NdMEDTA and NdHyEDTA with acetate ions.

Experimental

The synthesis and purification of *N*-methylethylenediamine-*N*,*N'*,*N'*-triacetic acid and the experimental procedures to prepare and analyse stock solutions of $Nd(ClO_4)_3$, ligands, etc. have been described elsewhere [8, 9]. $NaClO_4$ was used to adjust the ionic strength to a constant value (I = 0.5 M).

UV–Vis absorption spectra (in 4 or 5 cm quartz supracil cells) were measured with a Pye-Unicam Model 8800 spectrometer interfaced to a Hewlett Packard HP 86 microcomputer; all spectra were recorded at 25 ± 0.5 C.

Results and Discussion

The absorption spectra of NdMEDTA and NdHyEDTA in acetate-free $NaClO_4$ solutions are very similar to each other and to the spectrum of NdEDTA reported by Moeller and Brantley [10]. The sharp absorption bands are shifted to longer wavelengths compared to the spectrum of aqueous Nd^{3+} as a consequence of the electric field imposed on the metal ion by the surrounding ligand groups. The most significant changes in the spectra on adding acetate ions to the solution of these chelates are related to the band at 580 nm ($^4I_{9/2} \rightarrow {}^2G_{7/2}, {}^4G_{5/2}$), as is shown in Fig. 1 for NdMEDTA, and to a smaller extent to the band at 800 nm ($^4I_{9/2} \rightarrow {}^2H_{9/2}, {}^4F_{5/2}$) (not shown in the Figure). These observations are in agreement with the conclusions by Choppin *et al.* [11] that the hypersensitive band at 580 nm is very sensitive to an increase in the number of coordinating acetate ligands. Similar results are obtained for NdHyEDTA–acetate solutions, as shown in Fig.

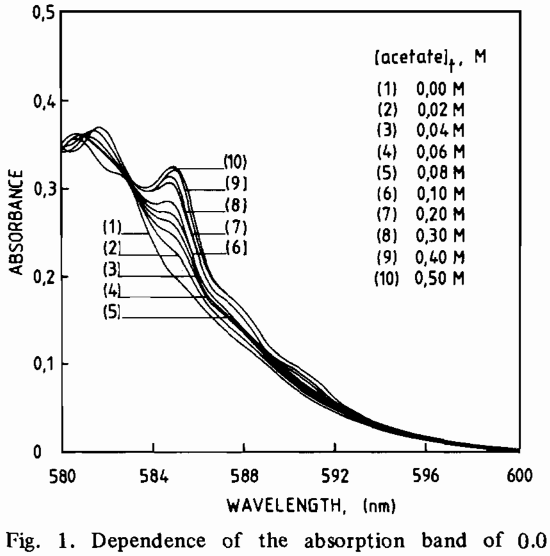

Fig. 1. Dependence of the absorption band of 0.01 M NdMEDTA at 580 nm on the acetate buffer concentration: pcH = 5.00, 4 cm cells, scan speed = 0.1 nm/s and bandwidth = 0.5 nm.

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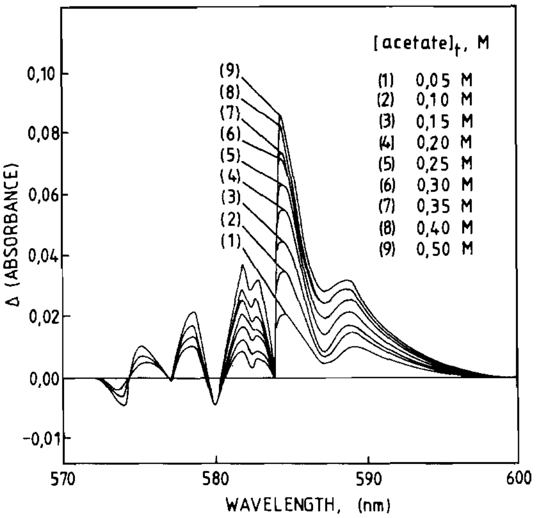

Fig. 2. Difference spectra of 0.01 M NdHyEDTA in the presence and absence of acetate buffer (band at 580 nm): pcH = 5.00, 5 cm cells, scan speed = 0.1 nm/s and bandwidth = 0.5 nm.

2: in this Figure the difference spectra between NdHyEDTA–acetate and NdHyEDTA are plotted for different buffer concentrations. Since the absorbance at the maximum still increases for the largest excess of acetate (0.5 M), it must be concluded that the formation of the mixed ligand complex is not yet complete.

The equilibrium constant for the mixed complex formation:

$$\mathrm{NdY} + \mathrm{Ac}^- \rightleftharpoons \mathrm{NdY(Ac)}^- \tag{1}$$

$$K_\mathrm{m} = \frac{[\mathrm{NdY(Ac)}^-]}{[\mathrm{NdY}][\mathrm{Ac}^-]} \tag{2}$$

can be obtained by the following procedure: the absorbance of NdY–acetate solutions is

$$A = \epsilon_1[\mathrm{NdY}]d + \epsilon_2[\mathrm{NdY(Ac)}^-]d \tag{3}$$

where ϵ_1 = molar absorptivity of either NdMEDTA or NdHyEDTA (NdY); ϵ_2 = molar absorptivity of either NdMEDTA(Ac)$^-$ or NdHyEDTA(Ac)$^-$ (NdY(Ac$^-$)); and d = optical path length.

From the mass balance of the Nd species ($[\mathrm{NdY}]_t$ = [NdY] + [NdY(Ac)$^-$]) and eqn. (2) one obtains:

$$[\mathrm{NdY}] = \frac{[\mathrm{NdY}]_t}{1 + K_\mathrm{m}[\mathrm{Ac}^-]} \quad \text{and}$$
$$[\mathrm{NdY(Ac)}^-] = \frac{K_\mathrm{m}[\mathrm{NdY}]_t[\mathrm{Ac}^-]}{1 + K_\mathrm{m}[\mathrm{Ac}^-]} \tag{4}$$

Substitution of both these concentrations in eqn. (3) results in:

$$\Phi = K_\mathrm{m}[\mathrm{Ac}^-] = \frac{(A/[\mathrm{NdY}]_t d) - \epsilon_1}{\epsilon_2 - (A/[\mathrm{NdY}]_t d)} \tag{5}$$

The concentration of 'free' acetate ions can be derived from the mass balance ($[\mathrm{acetate}]_t$ = [HAc] + [Ac$^-$] + [NdY(Ac)$^-$]), the mass balance of neodymium and eqn. (4):

$$[\mathrm{Ac}^-] = \frac{[\mathrm{acetate}]_t - [\mathrm{NdY}]_t + [\mathrm{NdY}]_t/(1 + K_\mathrm{m}[\mathrm{Ac}^-])}{1 + [\mathrm{H}^+]/K_\mathrm{a}} \tag{6}$$

It can be shown from eqns. (5) and (6) after some easy rearrangements that:

$$K_\mathrm{m} = \frac{\Phi(1 + [\mathrm{H}^+]/K_\mathrm{a})}{[\mathrm{acetate}]_t - [\mathrm{NdY}]_t\Phi/(\Phi + 1)} \tag{7}$$

The values of ϵ_1 of the LnY chelates are obtained from measurements in the absence of acetate buffer: ϵ_1^{585} = 5.05 (NdMEDTA) and 4.80 M^{-1} cm^{-1} (NdHyEDTA). The only unknown on the right-hand side of eqn. (7) is ϵ_2 (the molar absorptivity of the mixed complex) that is used as a parameter which is varied so as to make K_m independent of the buffer concentration. Results of such parametric calculations are shown in Figs. 3 and 4; a constant value of K_m is indeed obtained in agreement with the proposed model: $K_\mathrm{m} = 14 \pm 2$, $\epsilon_2^{585} = 9.2$ (NdMEDTA(Ac)$^-$) and $K_\mathrm{m} = 4.3 \pm 0.3$, $\epsilon_2^{585} = 7.8$ (NdHyEDTA(Ac)$^-$). These values agree well with the results obtained from the dissociation kinetics of NdMEDTA ($K_\mathrm{m} = 9 \pm 1$) and NdHyEDTA' ($K_\mathrm{m} = 5 \pm 4$) in acetate-buffered solutions.

The fact that the stability constant of the mixed ligand complex of NdMEDTA with acetate is substantially larger than for NdHyEDTA can be attri-

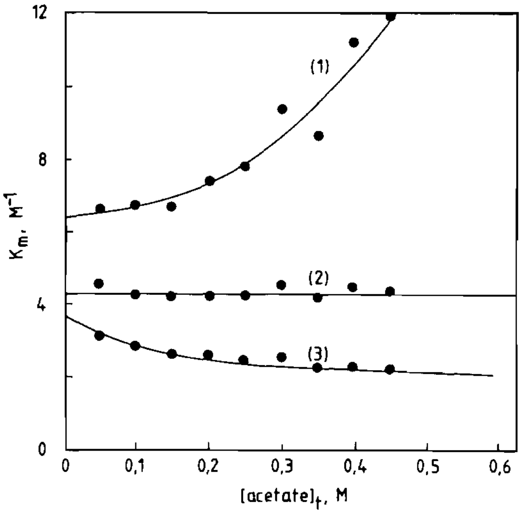

Fig. 3. Dependence of K_m of NdMEDTA(Ac)$^-$, calculated from eqn. (7), on the acetate concentration using different values of the parameter ϵ_2^{585}: (1) 8.8; (2) 9.2; (3) 10.0.

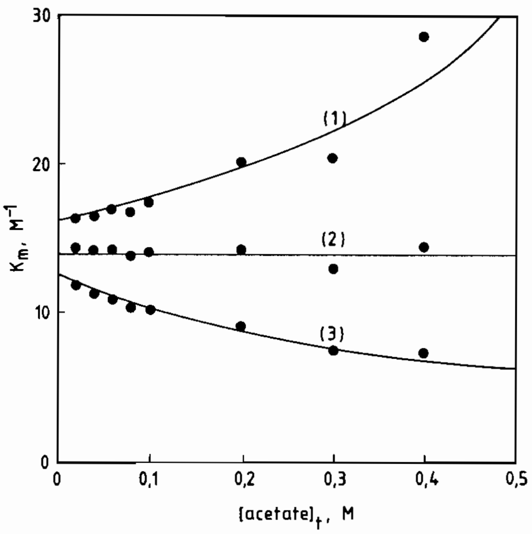

Fig. 4. Dependence of K_m of NdHyEDTA(Ac)$^-$, calculated from eqn. (7), on the acetate concentration using different values of the parameter ϵ_2^{585}: (1) 7.0; (2) 7.8; (3) 9.0.

buted to a steric effect in the latter case. Indeed, because of its structure MEDTA is a pentadentate ligand; on the contrary, in complexes with HyEDTA it is possible that the hydroxyethyl group of this ligand is coordinated to the lanthanide ion (through a water molecule), thus resulting in an extra chelate ring. (This also would explain the fact that the stability constants of LnHyEDTA complexes are up to two orders of magnitude larger than those of the corresponding MEDTA complexes.) The hexadentate coordination with HyEDTA will result in a larger steric hindrance for the incoming extra 'free' acetate ligand in the coordination sphere of the metal ion.

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