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On the Role of the Ground State Tb(III)/Acetylacetone Complex in Sensitized Emission of Tb(III) in Ethanol Solution

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Summary. The Tb(III)-acetylacetone system in ethanol solution has been studied by spectroscopic methods. The formation of a Tb(III)/acetylacetone (1 : 1) complex in the ground state has been proved and its stability constant determined, $K = (0.97 \pm 0.06) \cdot 10^4\,\mathrm{dm^3\,mol^{-1}}$. The role of this complex in the spectrofluorimetric determination of *Ln*(III) ions in the presence of acetylacetone has been discussed.

Keywords. Tb(III)/acetylacetone complex in ground state; Energy transfer; Quenching; Sensitized emission; Stability constant of complexes.

Über die Rolle eines Tb(III)-Acetylaceton-Komplexes im Grundzustand in der sensibilisierten Emission von Tb(III) in Ethanol-Lösung

Zusammenfassung. Das Tb(III)-Acetylaceton-System in Ethanol-Lösung wurde mit spektroskopischen Methoden untersucht. Die Bildung eines Tb(III)-Acetylaceton(1 : 1)-Komplexes im Grundzustand wurde bestätigt und seine Stabilitätskonstante bestimmt, $K = (0.97 \pm 0.06) \cdot 10^4\,\mathrm{dm^3\,mol^{-1}}$. Die Rolle dieses Komplexes in der spektrofluorimetrischen Bestimmung von *Ln*(III)-Ionen in Gegenwart von Acetylaceton wurde erörtert.

Introduction

In our previous investigations we have shown that an energy transfer process from the acetylacetone molecule (*acac*H) to the lanthanide ions (*Ln*) may be used for spectrofluorimetric determination of these ions [1–3]. After excitation of the *Ln*(III)—*acac*H system in ethanol solution at a wavelength of $\lambda \sim 300\,\mathrm{nm}$, a fluorescence characteristic for *Ln*(III) ions has been observed and interpreted as a result of an energy transfer from the excited acetylacetone molecule (donor) to the lanthanide ion, according to Eq. (1),

$$\begin{aligned} acac\mathrm{H} + h\nu &\rightarrow (acac\mathrm{H})^*, \\ (acac\mathrm{H})^* + Ln(\mathrm{III}) &\rightarrow acac\mathrm{H} + Ln(\mathrm{III})^*, \\ Ln(\mathrm{III})^* &\rightarrow Ln(\mathrm{III}) + h\nu_f. \end{aligned} \tag{1}$$

Our present investigations are concerned with the mechanism responsible for a high sensitivity of the method of spectrofluorimetric determination of *Ln*(III). It seems advisable to examine the possibility of complex formation between *Ln*(III) and *acac*H in the ground state and its influence on the absorbance of the system as well as the participation in the energy transfer process. The system containing Tb(III), showing the most intensive fluorescence among the examined lanthanides in our experimental conditions, has been chosen for these experiments.

Experimental

Acetylacetone (pure, Riedel-de-Haen A.G.) was purified according to Pope and co-workers [4] and 1,1,1,5,5,5-hexafluoroacetylacetone (Aldrich) by distillation. Ethanol solutions of $Tb(ClO_4)_3$ and Tb(*acac*)$_3$ were prepared by dissolving spectroscopically pure compounds in ethanol for fluorescence. Tb(*acac*)$_3$ was prepared according to Stities et al. [5]. Absorption spectra were recorded by means of Specord M-40 and Shimadzu UV-VIS 160 spectrophotometers and emission spectra using a Perkin-Elmer MPF-3 spectrofluorimeter.

Results and Discussion

In our experiments solutions of $Tb(ClO_4)_3$ served as the uncomplexed Tb(III) system whereas Tb(*acac*)$_3$ is a stable chelate in ethanol solution [6]. On the grounds of the recorded UV absorption spectra of the Tb(III)—*acac*H system in different molar ratios, the formation of a Tb(III)/*acac*H complex has been detected. The normalized absorption spectra of the systems studied are shown in Fig. 1.

Figure 1 shows that in the Tb(III)—*acac*H system a complex is formed. It is characterized by the absorption maximum at $\lambda = 300$ nm (curve 4), different from

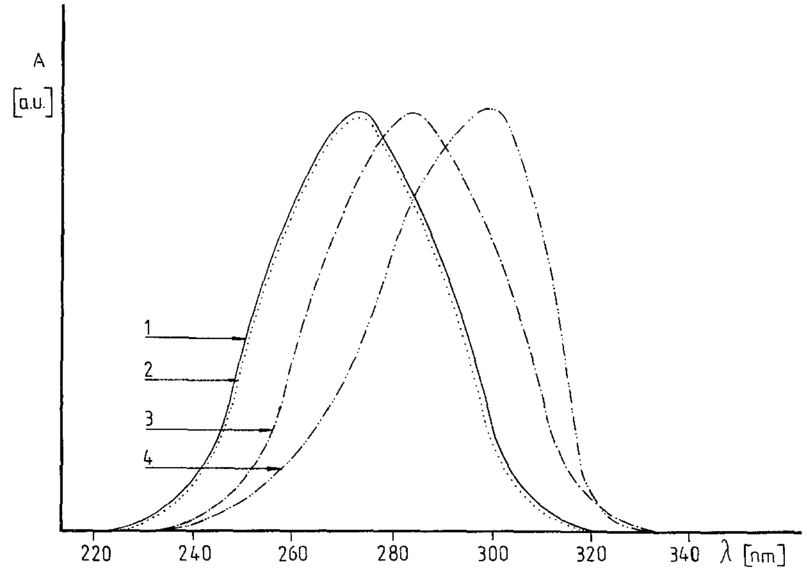

Fig. 1. Normalized absorption spectra in ethanol solution: *1*: *acac*H ($1 \cdot 10^{-4}$ mol dm^{-3}); *2*: *acac*H ($1 \cdot 10^{-4}$ mol dm^{-3}) + $NaClO_4$ ($3 \cdot 10^{-4}$ mol dm^{-3}); *3*: Tb(*acac*)$_3$ ($1 \cdot 10^{-4}$ mol dm^{-3}); *4*: $Tb(ClO_4)_3$ ($1 \cdot 10^{-4}$ mol dm^{-3}) + *acac*H ($1 \cdot 10^{-4}$ mol dm^{-3})

those of acetylacetone and Na(I)—*acac*H, $\lambda = 274\,\text{nm}$ (curves 1 and 2), and Tb($acac$)$_3$ chelate with an absorption maximum appearing at $\lambda = 288\,\text{nm}$ (curve 3). The absorption spectra recorded for the Tb(III)—*acac*H system, with a constant concentration of *acac*H ($1 \cdot 10^{-4}\,\text{mol dm}^{-3}$) and increasing concentration of Tb(III) in the range $1 \cdot 10^{-7} - 1 \cdot 10^{-3}\,\text{mol dm}^{-3}$, are shown in Fig. 2.

The observed typical changes in the absorption spectra confirm the formation of a Tb(III)/*acac*H complex: vanishing of the band due to *acac*H (274 nm), and appearance of a new band (300 nm) together with the isosbestic point at $\lambda = 283\,\text{nm}$. Changes in the absorption spectra shown in Fig. 2 [increasing Tb(III) concentration at constant *acac*H concentration] and results obtained for increasing *acac*H concentrations at a constant Tb(III) concentration ($1 \cdot 10^{-4}\,\text{mol dm}^{-3}$) suggest the molar ratio Tb(III):*acac*H to be equal to 1:1 in the Tb(III)/*acac*H complex. Considering this fact and using Eq. (2) (see [7]) one obtains

$$\frac{1}{\varepsilon - \varepsilon_D} = \frac{1}{K(\varepsilon_C - \varepsilon_D)}\,\frac{1}{[A]} + \frac{1}{\varepsilon_C - \varepsilon_D}, \tag{2}$$

where $[A]$ is the molar concentration of Tb(III), $\varepsilon = A/[D]$, A is the absorbance of the system at $\lambda = 300\,\text{nm}$ ($l = 1\,\text{cm}$), $[D]$ is the molar concentration of the donor

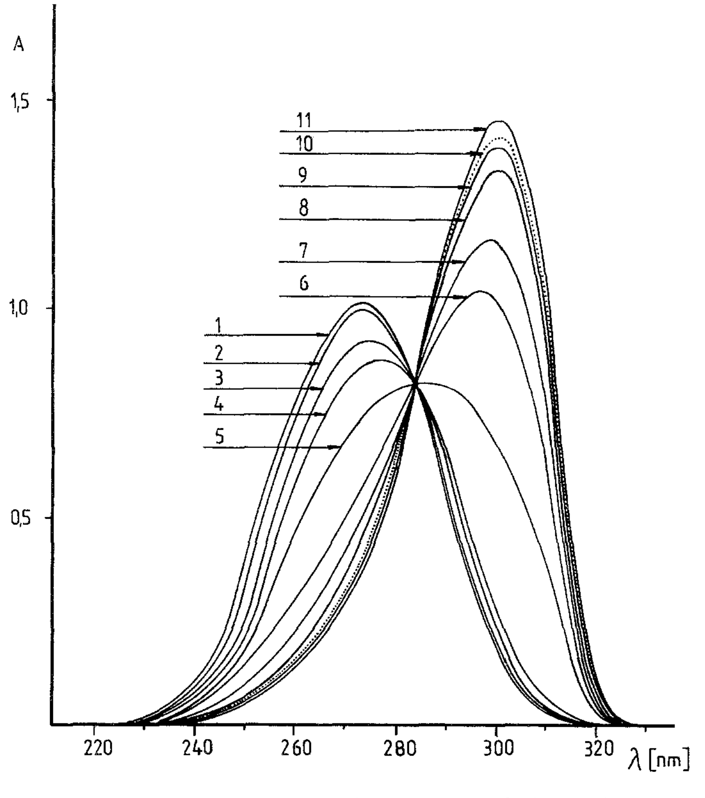

Fig. 2. Changes in the absorption spectra of the Tb(III)—*acac*H system in ethanol solution (concentration of *acac*H equal to $1 \cdot 10^{-4}\,\text{mol dm}^{-3}$ in each sample): *1*: without Tb(III); *2*: $1 \cdot 10^{-7}\,\text{mol dm}^{-3}$ Tb(III); *3*: $1 \cdot 10^{-6}\,\text{mol dm}^{-3}$ Tb(III); *4*: $6 \cdot 10^{-6}\,\text{mol dm}^{-3}$ Tb(III); *5*: $1 \cdot 10^{-5}\,\text{mol dm}^{-3}$ Tb(III); *6*: $2 \cdot 10^{-5}\,\text{mol dm}^{-3}$ Tb(III); *7*: $4 \cdot 10^{-5}\,\text{mol dm}^{-3}$ Tb(III); *8*: $6 \cdot 10^{-5}\,\text{mol dm}^{-3}$ Tb(III); *9*: $8 \cdot 10^{-5}\,\text{mol dm}^{-3}$ Tb(III); *10*: $1 \cdot 10^{-4}\,\text{mol dm}^{-3}$ Tb(III); *11*: $1 \cdot 10^{-3}\,\text{mol dm}^{-3}$ Tb(III)

(*acac*H), ε_D is the molar absorption coefficient of the donor at $\lambda = 300\,\text{nm}$, ε_C is the molar absorption coefficient of the complex at $\lambda = 300\,\text{nm}$. The formation constant of the Tb(III)/*acac*H complex has been determined as $K = (0.97 \pm 0.06) \cdot 10^4\,\text{dm}^3\,\text{mol}^{-1}$. Thus, the formed ground state complex, Tb(III)/*acac*H, is characterized by an intensive absorption band $\lambda_{\max} = 300\,\text{nm}$, $\varepsilon_{\max} = 1.5 \cdot 10^4\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1}$ and a stability constant of the range $1 \cdot 10^4\,\text{dm}^3\,\text{mol}^{-1}$. The latter value is by ten orders of magnitude smaller than the stability constant of the Tb(*acac*)$_3$ chelate ($\log K = 14.04$ [8]).

Fluorescence spectra of ethanol solutions of Tb(ClO$_4$)$_3$ [Tb(III) uncomplexed], Tb(III)/*acac*H (complex of the ratio 1 : 1) and Tb(*acac*)$_3$ show a similar line-like structure due to f-f transitions in the Tb(III) ion. But they differ in the fluorescence quantum yield (Φ_f) determined by using quinine sulphate as a standard [9] according to the procedure described in [10]. The results are collected in Table 1.

The obtained results of fluorescence quantum yield are compatible with the previously determined values for Tb(III) in complexes with aminopolycarboxylic acids [10]. The Φ_f values increase with an increasing stability constant of the complex (K). It seems to confirm the fact that the Tb(III)/*acac*H (1 : 1) complex is much less stable than the Tb(*acac*)$_3$ chelate.

Addition of small quantities of Gd(ClO$_4$)$_3$ [as uncomplexed Gd(III)] to the solution of Tb(III)/*acac*H (1 : 1), results in a quenching of Tb(III) emission sensitized by Tb(III)/*acac*H complex, as shown in Table 2.

In the case of Gd(III) ions as quencher, an energy transfer from the emission ff level of Tb(III) to that of Gd(III) is impossible due to energy reasons [11]. Further,

Table 1. Fluorescence quantum yield of the Tb(III) ($1 \cdot 10^{-4}$ mol dm^{-3}) in solution at room temperature

Compound	Solvent	Φ_f	λ_{ex} (nm)
Tb(ClO$_4$)$_3$	C_2H_5OH	0.021	368
Tb(III)/*acac*H (1 : 1)	C_2H_5OH	0.027	310
Tb(*acac*)$_3$	C_2H_5OH	0.065	310
Tb(*acac*)$_3$	CH_3CN	0.071	310

Table 2. Quenching of fluorescence of the Tb(III)-acetylacetone system by Gd(III) ions in ethanol ($\lambda_{ex} = 300\,\text{nm}$, concentration of Tb(III) and *acac*H equal to $1 \cdot 10^{-4}\,\text{mol}\,\text{dm}^{-3}$)

Quencher concentration (mol dm^{-3})	F ($\lambda = 545\,\text{nm}$)	$\frac{F_0}{F} - 1$
0	212 (F_0)	0
$1 \cdot 10^{-5}$	196	0.08
$4 \cdot 10^{-5}$	163	0.30
$8 \cdot 10^{-5}$	113	0.88
$1 \cdot 10^{-4}$	94	1.26
$4 \cdot 10^{-4}$	41	4.17

for the used Gd(III) concentrations, the absorption of exciting radiation ($\lambda_{ex} \sim 300$ nm) by these ions, i.e. the inner filter effect, may be neglected. However, because of very similar chemical properties of Gd(III) and Tb(III) ions it can be stated that the quenching of Tb(III) fluorescence results from the formation of the Gd(III)/*acac*H complex in the ground state as the competitive process for the formation of the Tb(III)/*acac*H complex (i.e. the static quenching process [12]). The data presented in Table 2 may then be analysed using the standard Stern-Volmer equation for intensity quenching,

$$\frac{F_0}{F} - 1 = K_{eq}[Q], \tag{3}$$

where K_{eq} is the quenching constant ($\mathrm{dm^3\,mol^{-1}}$) for the static quenching [12]. The constant K_{eq} determined from the results of Table 2 and Eq. (3) is equal to $(1.05 \pm 0.06) \cdot 10^4\,\mathrm{dm^3\,mol^{-1}}$. This value is consistent with the previously determined formation constant of the Tb(III)/*acac*H complex and confirms the fundamental role of this ground state complex in the mechanism of Tb(III) emission for the Tb(III)—*acac*H system in solution. Thus, after absorption of radiation by the Tb(III)/*acac*H complex ($\lambda_{ex} \sim 300$ nm) and an efficient energy transfer within the complex, Tb(III) emission has been observed. It seems that this mechanism can explain the very high sensitivity of the spectrofluorimetric determination of Tb(III) by means of *acac*H as a sensitizer [1, 2],

$$\mathrm{Tb(III)}/acac\mathrm{H} \xrightarrow[(\sim 300\,\mathrm{nm})]{h\nu} [\mathrm{Tb(III)}/acac\mathrm{H}]^* \rightarrow \mathrm{Tb(III)}^* \rightarrow \mathrm{Tb(III)} + h\nu_f. \tag{4}$$

The mechanism of sensitized emission of Tb(III), proposed in Eq. (1), should therefore be completed with the process of Tb(III)/*acac*H complex formation according to Eq. (4).

The structure of the examined Tb(III)/*acac*H complex has not been fully explained till now. Additional studies performed with the use of hexafluoroacetylacetone (*hfac*H) instead of *acac*H, enabled to observe the Tb(III)/*hfac*H complex in the absorption spectra ($\lambda_{max} = 311$ nm, $\varepsilon_{max} = 2.2 \cdot 10^3\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$) and to estimate its stability constant ($K \sim 10^3\,\mathrm{dm^3\,mol^{-1}}$). Similarly as in the case of Cu(II) complexes, namely Cu(*acac*)$_2$ and trifluoro- and hexafluoroderivatives [6], also in the case of Tb(III)/1,3-diketone complexes the values of complex stability constants are remarkably decreasing after the introduction of strongly electron-withdrawing CF_3-groups to the ligand. Thus, the change of the electron density on the oxygen atoms of the 1,3-diketone affects the value of the stability constant of the complex.

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