Fluorescence of Lanthanide(III) Complexes in Aqueous Solutions

The Influence of *pH* and Solution Composition

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The fluorescence of lanthanide ions and of their complexes with *EDTA*, *NTA* and *AA* in aqueous solutions was investigated. It has been shown that the fluorescence band intensities of Sm(III), Eu(III), Gd(III), Tb(III) and Dy(III) complexes depend on the *pH* and the complexing agent concentration. Fluorescence measurements were used to characterise the lanthanide complexes formed and an attempt was made to interpret the results theoretically.

[Keywords: Acetic acid; Complexes of Dy(III), Eu(III), Gd(III), Sm(III), Tb(III); *Ethylenediaminetetraacetic acid; Fluorescence; Hypersensitive bands; Nitrilotriacetic acid; Transition dipole moment method]*

Untersuchung der Fluoreszenz von Lösungen einiger Lanthaniden (III)-Komplexe in Abhängigkeit von pH und Zusammenhang der Lösung

Die Fluoreszenz von wäßrigen Lösungen der Ionen und Komplexe einiger Lanthaniden mit Ethylendiamintetraessigsäure, Nitrilotriessigsäure und Essigsäure wurde untersucht. Der Einfluß von *pH* und Konzentration der Komplexbildner auf die Intensität der Fluoreszenzbanden von Sm(III), Eu(III), Gd(III), Tb(III) und Dy(III) wurde bewiesen. Die Fluoreszenzmessungen wurden für die Charakterisierung von Lösungen der Lanthanidenkomplexe genützt und ein Versuch der theoretischen Interpretation der beobachteten Änderungen im Spektrum wurde unternommen.

Introduction

The spectra (absorption and fluorescence) of aqueous solutions containing lathanide ions consist of sharp, spectrally narrow bands.

From the point of view of luminescence in aqueous solutions lanthanides(III) can be divided into three groups. The first one consists of elements in the middle of the lanthanide series, Sm, Eu, Gd, Tb and Dy, which exhibit the strongest fluorescence. The elements in the second group, comprising Pr, Nd, Ho, Er and Tm give low fluorescence intensities. Ce, Yb and Lu, which make up the third group, give no fluorescence in the visible or ultraviolet part of the spectrum.

Recent papers concerned with the fluorescence of lanthanide ions and of lanthanide complexes describe results on a number of different complexes under chosen conditions[1—8]. In 1982 two publications appeared devoted to the emission spectra of Gd(III) in solution[9,10]. There have also been a number of papers discussing the problem of hypersensitive transitions observed with some of the lanthanides[2,5,8,11—13].

Previous work on the fluorescence of lanthanide complexes with ethylenediaminetetraacetic acid (*EDTA*) and nitrilotriacetic acid (*NTA*) in aqueous solution was concerned mainly with investigating the physico-chemical properties of the solutions (the composition of the complexes formed, intermolecular energy transfer between complexes, the use of complex solutions as aqueous shift reagents for NMR). The work was therefore confined to a narrow range of experimental variables, in particular the *pH* range and complexing agent concentration[11—16].

A theoretical discussion of the absorption and fluorescence bands and the corresponding transitions has been given before[17—21].

The present paper is a continuation of the work on the fluorescence of lanthanide ions and of lanthanide complexes in aqueous solution[22,23]. It has been shown on the basis of experiments carried out over a wide range of *pH* values and complexing agent concentrations that these factors influence the fluorescence intensity. The measurements were carried out on solutions of lanthanide complexes with *EDTA*, *NTA* and *AA* (acetic acid), using the lanthanides of the first group: Sm(III), Eu(III), Gd(III), Tb(III) and Dy(III) and of the second group: Pr(III), Nd(III), Ho(III), Er(III) and Tm(III). The complexing agent solutions used in this investigations are well known as eluents in an ion-exchange method of separating the lanthanides and exhibiting different complexing tendencies. Fluorescence measurements were used to characterise solutions containing lanthanide complexes and an attempt was made to interpret the results theoretically.

Experimental

The method was the same as that used previously[22,23]. The concentration of *Ln*(III) ions in solution was kept constant in all experiments, at 0.01 mol/dm^3. Solutions with the following molar ratios of *Ln*(III) to complexone (*EDTA* or

NTA) were employed: 1 : 1, 1 : 2, 1 : 3, 1 : 4 and 1 : 5. The *pH* values were: 3.0, 5.5, 7.5 and 11.5. For *Ln*(III)—*AA* complexes the molar ratios were from 1 : 1 to 1 : 10, with *pH* values at 3.0, 5.5 and 7.5.

The recording system for the corrected fluorescence band intensities was identical to that used in earlier studies[22,23], but the excitation wavelengths and amplification of emission used were different for each lanthanide: Sm –402 nm (100-fold), Eu –394 nm (10-fold), Gd –274 nm (unit), Tb –372 nm (3-fold), Dy – 350 nm (30-fold), Pr –444 and 468 nm (100-fold), Nd –353 and 428 nm (100-fold), Ho –451 and 361 nm (100-fold), Er-379 and 255 nm (100-fold) and Tm –361 and 272 nm (100-fold).

Results and Discussion

Aqueous solutions of complexes of the lathanides in the second group (Pr, Nd, Ho, Er and Tm) give very low fluorescence emission intensities, similarly to chloride aqueous solutions and the corresponding transitions are hard to identify. The results are also not fully reproducible and this makes it impossible to interpret the fluorescence spectra quantitatively. In this case it might be better to use a laser source, which would make it possible to excite a given electronic level in the lanthanide ion.

For the elements in the first group, i.e. Sm(III), Eu(III), Gd(III), Tb(III) and Dy(III) the fluorescence intensity increases after complexing the ions with *EDTA, NTA* or *AA*. The positions of the most intense bands are listed in Table 1, together with the corresponding allowed and hypersensitive ($\Delta J = \pm 2$) transitions.

For complexes of Eu(III)[22], Sm(III)[23], Tb(III)[23] and Dy(III) with *EDTA* and *NTA*, the fluorescence band intensities increase with increasing *pH* values for the solutions (over the *pH* range 3 to 10) and with increasing concentration of the complexone. Typical results illustrating the de-

Table 1. *The positions of the most intense fluorescence bands (λ_{max}) for the lanthanides, together with the corresponding transitions*

| Ion	Band, λ_{max} (nm)	Transition	
Sm(III)	596	$^4G_{5/2}$—$^6H_{7/2}$	
	640	$^4G_{5/2}$—$^6H_{9/2}$	$\Delta J = 2$
Eu(III)	590	$^5D_0$—$^7F_1$	
	615	$^5D_0$—$^7F_2$	$\Delta J = 2$
Gd(III)	312	$^6P_{7/2}$—$^8S_{7/2}$	
Tb(III)	491	$^5D_4$—$^7F_6$	$\Delta J = 2$
	545	$^5D_4$—$^7F_5$	
Dy(III)	479	$^4F_{9/2}$—$^6H_{15/2}$	
	577	$^4F_{9/2}$—$^6H_{13/2}$	$\Delta J = 2$
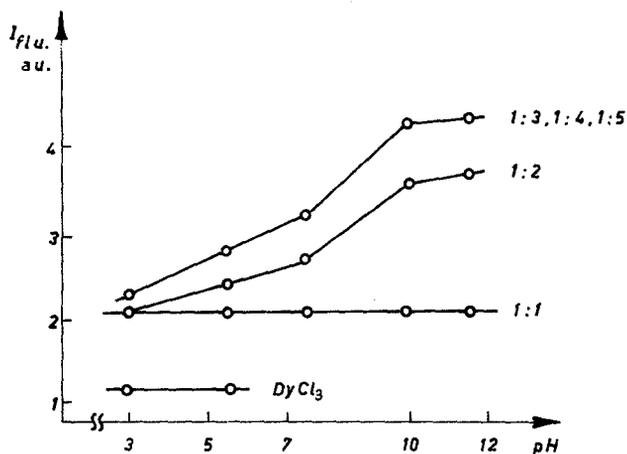
Fig. 1. The intensity of the fluorescence band at $\lambda = 577$ nm for Dy(III): *EDTA* molar ratios 1:1, 1:2, 1:3, 1:4 and 1:5 as a function of the *pH*
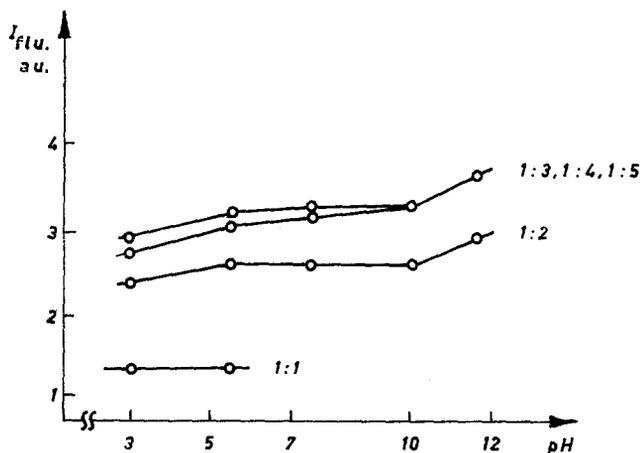

Fig. 2. The intensity of the fluorescence band at $\lambda = 577$ nm for Dy(III): *NTA* molar ratios 1:1, 1:2, 1:3, 1:4 and 1:5 as a function of the *pH*

pendence of the fluorescence intensity on these two parameters are shown in Figs. 1 and 2 for complexes of Dy(III) with *EDTA* and *NTA*.

For Sm(III)[23], Tb(III)[23] and Dy(III) complexes with *EDTA* and *NTA* the intensities of the allowed and the hypersensitive bands increase proportionately as the *pH* value and the complexone concentration
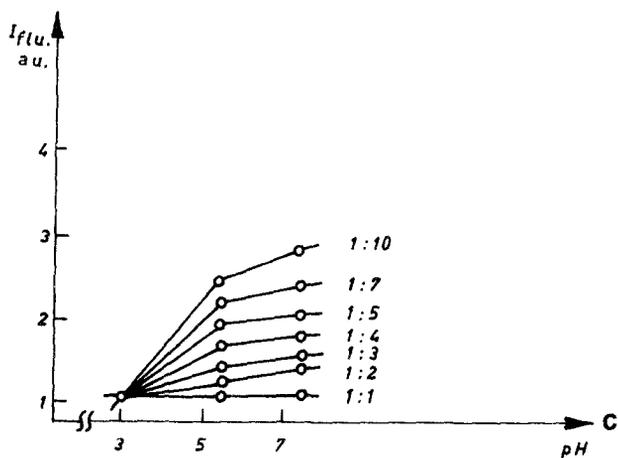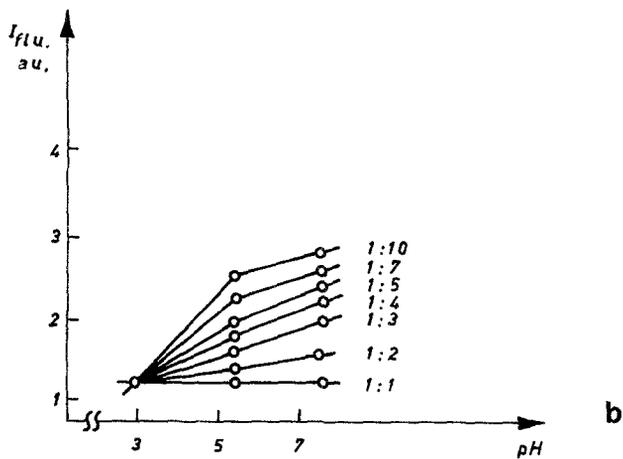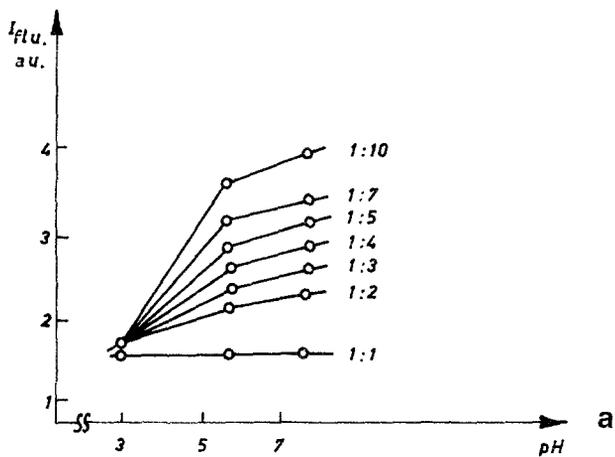
Fig. 3. The intensity of the fluorescence bands of Gd, Tb and Dy complexes with acetic acid as a function of the *pH*: *a* at $\lambda = 312$ nm for Gd : *AA* = 1 : 1—1 : 10; *b* at $\lambda = 545$ nm for Tb : *AA* = 1 : 1—1 : 10; *c* at $\lambda = 577$ nm for Dy : *AA* = 1 : 1—1 : 10

increase. With Eu/*EDTA* complexes[22], however, the intensity of the hypersensitive band (λ_{max} = 615 nm) increases more rapidly (under the same experimental conditions) than that of the allowed band (λ_{max} = 590 nm). With Eu/*NTA* complexes[22], the band at λ_{max} = 590 nm increases in intensity to a greater extent than the λ_{max} = 615 nm band.

In the case of Gd complexes with *EDTA* and *NTA*[23] the dependence of the fluorescence intensity on the *pH* of the solution and on the complexone concentration is different. As the complexone concentration excess
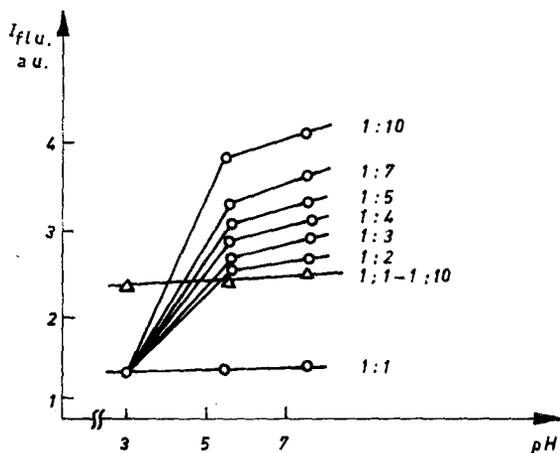

Fig. 4. The intensity of the fluorescence bands at λ = 590 and 615 nm for Eu : *AA* = 1 : 1—1 : 10 as a function of the *pH*

increases, the fluorescence intensity decreases. Maximum intensities are observed for *pH* values in the range 5.5–7.5.

Complexes of Sm(III), Eu(III), Gd(III), Tb(III) and Dy(III) with acetic acid (*AA*) were also investigated. The formation of such complexes leads to relatively slight fluorescence intensity increase with respect to aqueous solutions of lanthanide chlorides. This is particularly true for Sm—in this case the increase is hardly measurable. These complexes are weak, with stability constants in the range of 10^2–10^3. Changes in the fluorescence intensity could be followed only up to *pH* = 7.5 because of the precipitation of lanthanide hydroxides. The fluorescence of acetate complexes of the lanthanides in this group is considerably lower than that shown by solutions of their complexes with *EDTA* or *NTA*. For acetate complexes of Gd, Tb and Dy, the intensity of the fluorescence bands increases with increasing *pH* and with acetic acid excess. This is illustrated in Figs. 3 a–c.

The Eu/AA complex gives an increase in the intensity of the hypersensitive band ($\lambda_{max} = 615$ nm), with that of the allowed band remaining unchanged. This is shown in Fig. 4.

In the most strongly acid solution ($pH = 3$) the fluorescence intensity for all the solutions investigated were the same as for solutions without acetic acid, which indicates that the formation of acetate complexes does not occur under these conditions.

All these observations lead to some inferences about the correlations between certain properties of the lanthanide complexes and changes in the intensities of their characteristic fluorescence bands:

1. at constant lanthanide concentration, the higher the stability constant for the complex, the higher the observed fluorescence intensity;

2. when the composition of the solution corresponds to the stoich-iometry of a stable complex ($Ln : EDTA = 1 : 1, Ln : NTA = 1 : 1$ and $1 : 2$), i.e. without an excess of the complexone being present, the fluorescence intensity is constant over the whole pH range;

3. the presence of an excess of complexing agent causes an increase in the fluorescence intensity of lanthanide complex, with the only exception of Gd complexes.

A problem in the interpretation of the experimental results is the lack of a distinct shift of the maxima in the emission spectra at simultaneous essential intensity changes.

In order to explain the change in transition intensity (its dependence on the macroscopic parameters, such as the pH or the dielectric constant, and on the microscopic parameters, such as the molar ratio of the lanthanide ion to the complexing agent), the following model is tentatively proposed.

The intensity of a transition depends on the distribution of the electronic cloud which describes a transition dipole moment decisive for the oscillator strength of a given transition. The latter quantity is defined by the equation:

$$f^{\circ}_{OK} = \frac{8\,\pi^2\,m\,c\,\nu_{OK}}{3\,h\,e^2}\,\mu^{\circ}_{OK}$$

where m = electronic mass, c = velocity of light, h = *Planck*'s constant, e = electronic charge, ν_{OK} = emitted/absorbed frequency, μ°_{OK} = transition dipole moment defined by:

$$\mu^{\circ}_{OK} = \int \psi^{\circ}\,\mu^{\circ}\,\psi^{K}\,d\,\tau$$

ψ°, ψ^{K} are the wave functions of the initial and final state, respectively.

Since the spectrum considered is that of the lanthanide ion in a complex, the equations refer to the whole complex molecule, and the wave functions are the wave functions for the complex. Thus μ°_{OK} is the

transition dipole moment for the complex (without an excess of the complexing agent being present).

In the proposed model, the change in the transition intensity for the complex—observed when an excess of the complexing agent is present—is attributed to a change in the dipole moment for the transition as a result of its modification by the ions' dipole moment of the complexing agent. Therefore the intensity of the transition, and thus also the oscillator strength are determined by the resultant transition moment for the whole system—i.e. the complex molecule and the surrounding complexing agent molecules. Such a situation does not affect, or hardly affects the energy associated with the transition, but affects the transition intensity. This is supported by the following argument. Let $\vec{\mu}_0$ and $\vec{\mu}_1$ represent the temporary dipole moments of the complex when there is not and there is complexing agent excess, respectively. Then the dipole moment for the transition will be given by:

$$\mu_{OK}^{\circ} = \int \psi^{\circ} (\vec{\mu}_0 + \vec{\mu}_1) \psi^{K} d\tau$$

If $\vec{\mu}_e$ is the resultant dipole moment for the system: complex—excess of complexing agent, so

$$\vec{\mu}_{OK}^{e} = \int \psi^{\circ} \vec{\mu}_e \psi^{K} d\tau$$

the resultant dipole moment $\vec{\mu}_e$ for the transition will be either greater or smaller than $\vec{\mu}_0$ depending on the orientation of the two dipole moments. Thus the observed intensity of the transition for the complex will be either increased or decreased by the presence of an excess of the complexing agent.

The above model can be used to explain the influence of *pH* on the change of the transition intensity for the complex solutions in the presence of an excess of the complexing agent.

In solutions containing the complex alone, without an excess of the complexing agent being present, i.e. for $Ln:EDTA = 1:1$, $Ln:NTA = 1:1$ and for $pH \geqslant 5.5$ for $Ln:NTA = 1:2$ the fluorescence intensity is practically constant over the whole *pH* range. For $Ln:NTA = 1:2$, in solutions with $pH = 3$, the fluorescence intensity is much lower than at $pH > 5.5$ which can be explained if under these conditions the $1:1$ complex is dominant.

If the solution contains additionally the complexing agent which is not combined with lanthanide ions, then, as the solution becomes less acidic, the concentration of the anionic form of the complexing agent increases, the magnitude of the effect depending on its dissociation constant. Thus in *EDTA* solutions H_4Y, H_3Y^-, H_2Y^{2-}, HY^{3-} and Y^{4-} will be present, in *NTA* solutions H_3X, H_2X^-, HX^{2-} and X^{3-}, and in *AA* solutions, HA and A^-.

In those solutions which contain an excess of the complexing agent, its molecules and ions surround the complex molecules and modify its effective electric charge and thus also change the resultant dipole moment. At higher pH values the more highly charged anions dominate and influence the resultant dipole moment—this is observed in solutions containing lanthanide complexes with $EDTA$, $(LnY)^-$ and an excess of $EDTA$ ions. In solutions containing lanthanide complexes with NTA, $(LnX)^\circ$ and $(LnX_2)^{3-}$ and an excess of NTA, the influence of NTA molecules is observed under acidic conditions ($pH = 3$, Figs. 1 and 2).

The interactions just described lead to an increase in the resultant dipole moment, and hence to the observed increase in the intensity of the transition in the complex (Figs. 1 and 2). This intensity increase of fluorescence slows down in solutions where the complexing agent excess is considerable with respect to the complex ($Ln : EDTA$ and $Ln : NTA = 1 : 4$ and $1 : 5$). This effect is explained by the influence of steric factors which are particularly important when the complexing agent molecules are large ($EDTA$, NTA). The complexes of europium[22], samarium[23], terbium[23] and dysprosium (Figs. 1 and 2) with $EDTA$ and NTA can be cited as examples.

When the complexing agent molecules are small (AA), there is no saturation effect even when the complexing agent excess is large ($Ln : AA = 1 : 10$) and the fluorescence intensity increases continuously with increasing complexing agent concentration. This is found for AA complexes with gadolinium, terbium and dysprosium as well as europium (the $\lambda_{max} = 615\,nm$) (Figs. 3 a–c and 4).

In the case when the resultant dipole moment is smaller than the dipole moment for the complex, which indicates that the dipole momenta of the complex and the complexing agent excess must be opposed, one should expect the opposite effect, i.e. a decrease in the transition intensity with increasing complexing agent concentration and with increasing pH of the solution. This is seen in solutions containing Gd/$EDTA$ and Gd/NTA complexes[23]. The reason why gadolinium complexes with $EDTA$ and NTA behave differently lies in the peculiar electronic structure of the gadolinium ion, exemplified by its very high excitation energy.

Summarising, we can state that a simple model connecting the intensity of a transition for a lanthanide ion with the resultant transition dipole moment of the system: complex—excess of the complexing agent, is capable of explaining the observations in a qualitative manner.

Attention must, however, be drawn to the fact that the resultant dipole moment $\tilde{\mu}_e$ which appears in the expression for the dipole moment depends, strictly speaking, on the distance between the ion and the complexing agent molecule. Because this distance is not constant, but changes as a result of vibrational motions, one can expect changes in the resultant dipole moment when the energy of vibration changes, i.e. when

there is a temperature change. It means that temperature by excitation of the vibrational levels leads to a change of the average distances between the ion and the complexing agent. This will bring about a modification in the resultant dipole moment. Such an effect has been observed by us for dysprosium complexes, and will be the subject of another communication.

In analysing the luminescence spectra of lanthanides, the hypersensitive transitions are important ($\Delta J = \pm 2$). For Eu(III)[22], Sm(III)[23], Tb(III)[23] and Dy(III) the ratio of the hypersensitive band intensity to the allowed band intensity has been calculated. This value, denoted by η, has been investigated for Sm, Tb and Dy ions. In all complex solution investigated, as well as for the uncomplexed ions, the η values are low, between 0.4 and 0.8.

For Eu(III) ions, the η values for complex solutions with *NTA* are similar to above. For Eu(III) complexes with *EDTA* the η values are between 0.9 and 1.8. For Eu(III)/*AA* complexes they increase from 0.4 to 2.3 as the excess of *AA* increases. There is a distinct difference in the η values for uncomplexed Eu(III) ($\eta_{EuCl_3} = 0.1$) and for Eu(III) complexes with *EDTA, NTA* and *AA*. This problem will be the subject of another publication.

Acknowledgement

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