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Fluorescence of Lanthanide(III) Complexes with Aminopolyacetic Acids in Aqueous Solutions

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The fluorescence of Eu(III), Gd(III), Tb(III) and Dy(III) ions complexed with aminopolyacetic acids was investigated. The influence of temperature and the dimensions of the ligand molecules and of their electric charge on the intensity of the emission bands is discussed as well as the ratio of the hypersensitive (forbidden) band to the allowed band intensity. On the basis of the fluorescence measurements a simple theoretical model is discussed and certain generalizations concerning the fluorescence of the lanthanides group are derived.

[Keywords: Aminopolyacetic acids; Complexes of Dy(III), Eu(III), Gd(III), Tb(III); *Fluorescence; Hypersensitive transitions; Transition dipole moment method, temperature influence]*

Fluoreszenz von Lanthaniden(III)-Komplexen mit Aminopolyessigsäuren in wäßrigen Lösungen

Die Fluoreszenz von mit Aminopolyessigsäuren komplexierten Eu(III), Gd(III), Tb(III) und Dy(III) Ionen wurde untersucht. Der Einfluß von Temperatur und Größe der Ligandenmoleküle und von deren elektrischer Ladung auf die Intensität der Emissionsbanden wird diskutiert, ebenso das Verhältnis der Intensitäten der hyperempfindlichen und erlaubten Banden. Auf der Basis von Fluoreszenzmessungen wird ein einfaches theoretisches Modell diskutiert und Verallgemeinerungen betreffend der Fluoreszenz der Lanthanidengruppe getroffen.

Introduction

Among the literature on the fluorescence of the lanthanides, papers concerned with the fluorescence exhibited by lanthanide complexes with aminopolyacetic acids and amino acids occupy an important position. Much of this work has been concerned primarily with the dependence of the fluorescence intensity on the *pH* of the medium, the molar lanthanide/complexing agent ratio and on the composition and stability of the complexes formed [1–5]. Fluorescence studies of lanthanide complexes serve as the basis for the discussion of energy transfer processes, both intramolecular [6–8] and intermolecular [9–12]. Selected fluorescence bands of a number of lanthanide complexes in solution are utilised in analytical work, which constitutes a very sensitive and highly selective method of determining trace amounts of these metals [13–16]. The hypersensitivity of the lanthanide fluorescence bands has also been investigated. The calculated ratio of the intensity of the hypersensitive to the allowed transitions, η, is used to assess the composition, stability and other physico-chemical properties of the complexes [2, 3, 17]. The influence of temperature on the intensity of transitions and temperature quenching have also been discussed [18, 19].

Our previous work [20–22] has been devoted to study the dependence of the fluorescence bands intensity of Sm(III), Eu(III), Gd(III), Tb(III) and Dy(III) over a wide range of *pH* values and complexing agent concentrations. The studies were carried out in chloride solutions and in solutions of lanthanide complexes with ethylenediaminetetraacetic acid (*EDTA*), nitrilotriacetic acid (*NTA*) and acetic acid (*AA*).

In this paper, results are presented on the fluorescence of Eu(III), Gd(III), Tb(III) and Dy(III) ions, complexed with aminoacetic acid (*AAA*) and iminodiacetic acid (*IDA*), under the same conditions as those used previously [20–22]. Sm(III) complexes were not studied, because of very low fluorescence bands intensity. The effect of temperature on the intensity of the observed bands was also examined. Following earlier remarks [22] more care has been devoted to demonstrate the relationship between the intensity of fluorescence bands and the stability constants of the complexes studied. The values of η, the ratio of the hypersensitive (forbidden) band to the allowed band, have been calculated. The influence of the dimensions of the ligand molecules and of their electric charge on the intensity of the emission bands is discussed.

On the basis of our studies of lanthanide complexes with acetic, aminoacetic, iminodiacetic, nitrilotriacetic and ethylenediaminetetraacetic acid as ligands we have been able to derive some generalizations concerning the fluorescence of the lanthanides group in aqueous solutions.

Experimental

The aminoacetic acid, analytical grade, produced by POCh Gliwice—Poland, was used without any additional purification. The iminodiacetic acid, pure, made by Reachim—U.S.S.R., was recrystallised twice from ethanol.

The solutions whose fluorescence spectra were investigated were characterised by the following molar *Ln*(III): complexing agent ratios, for *AAA*: 1 : 1, 1 : 2, 1 : 3, 1 : 4, 1 : 5, 1 : 8, and 1 : 10 at *pH* values of 3.0, 5.5, and 7.5 and for IDA: 1 : 1, 1 : 2, 1 : 3, 1 : 4, and 1 : 5 at *pH* values of 3.0, 5.5, 7.5, 10.0, and 11.5. The *Ln*(III) concentration was kept constant in all experiments, and was equal to $1 \cdot 10^{-2}\,M$. The measurements were carried out at two temperatures, 291 K and 351 K (± 1 K).

The apparatus used, the means employed to excite and to register the fluorescence bands, and to measure their intensity were all described in earlier publications. The spectral characteristics of the transitions involved for each lanthanide were also given [20–22].

Results and Discussion

The intensity of the fluorescence bands for Eu(III), Gd(III), Tb(III) or Dy(III) ions complexed by *AAA* or *IDA* is higher than with the corresponding chloride solutions. A similar phenomenon had previously been observed with *EDTA*, *NTA*, and *AA* complexes [20–22].

The dependence of the fluorescence band intensity on the *pH* and on the composition of the solution [the molar ratios *Ln*(III) : *AA* and *Ln*(III) : IDA] is illustrated in Figs. 1–8.

It can be seen that over the *pH* range 5.5–10.0, for Ln(III)/*IDA* complexes (Figs. 1, 2, 3 and 4), the fluorescence band intensity increases markedly with rising *pH* of the solutions, by as much as 45-fold. For strongly alkaline solutions, however, for $pH > 10$, the intensity falls again. The intensity of the fluorescence band increases also with increasing *IDA* concentration, the effect being greatest for *Ln*(III) : *IDA* ratios up to 1 : 4. Higher complexing agent concentrations have little effect.

The intensity of the fluorescence bands of the solutions of *Ln*(III)/*AAA* complexes increase with increasing *pH*, particularly over the range of *pH* values 5.5–7.5, and with increasing *AAA* concentration up to *Ln*(III) : *AAA* = 1 : 10 (Figs. 5, 6, 7 and 8). *pH* values above 7.5 could not be realized, because of the precipitation of $Ln(OH)_3$. However, the increases in the intensities of the fluorescence bands are much smaller than those for the complexes with *IDA*.

Data pertaining to the fluorescence of the solutions of lanthanide complexes with *AAA* and *IDA* (this paper) and *EDTA*, *NTA*, and *AA* (previous publications [20–22]) are summarized in Table 1. The following quantities are listed: the stability constant (as $\log \beta$), the wavelength corresponding to the maximum fluorescence band intensity (λ_{max}), the relative fluorescence band intensity denoted by *I* at two temperature

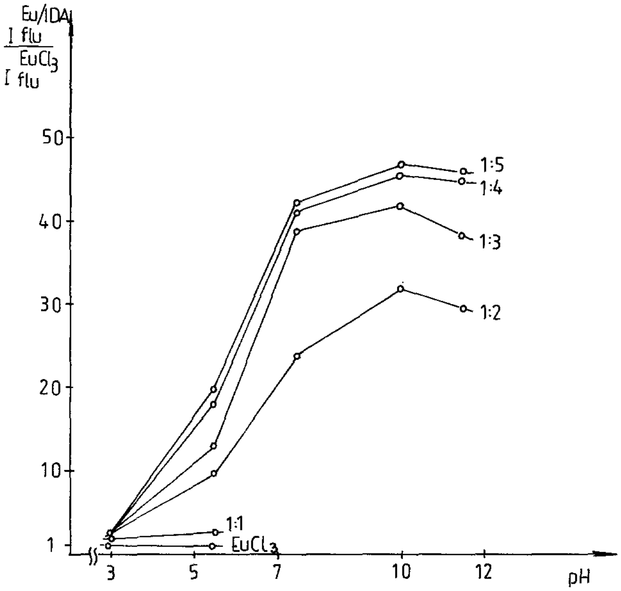

Fig. 1. The intensity of the fluorescence band at $\lambda = 615\,\mathrm{nm}$ for Eu(III) : *IDA* molar ratios 1 : 1, 1 : 2, 1 : 3, 1 : 4, and 1 : 5 as a function of the *pH*

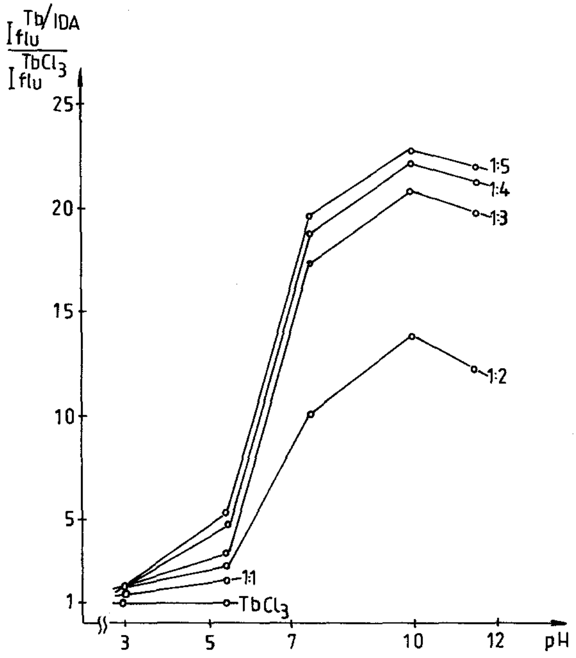

Fig. 2. The intensity of the fluorescence band at $\lambda = 545\,\mathrm{nm}$ for Tb(III) : *IDA* molar ratios 1 : 1, 1 : 2, 1 : 3, 1 : 4, and 1 : 5 as a function of the *pH*

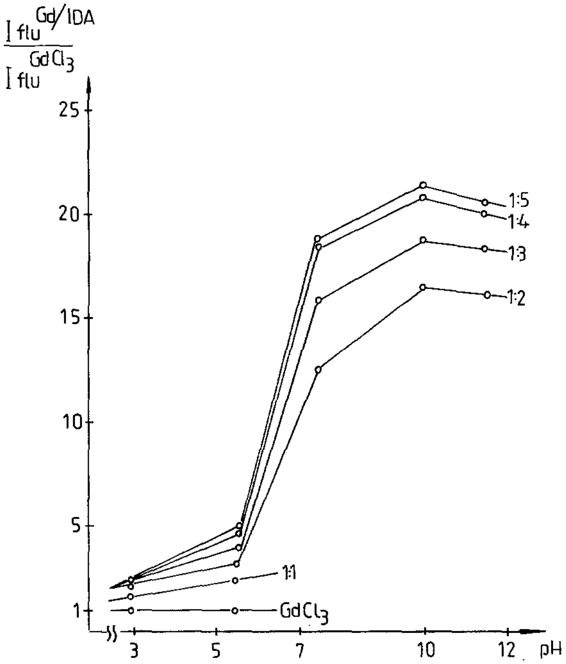

Fig. 3. The intensity of the fluorescence band at $\lambda = 312\,\mathrm{nm}$ for Gd(III) : *IDA* molar ratios 1 : 1, 1 : 2, 1 : 3, 1 : 4, and 1 : 5 as a function of the *pH*

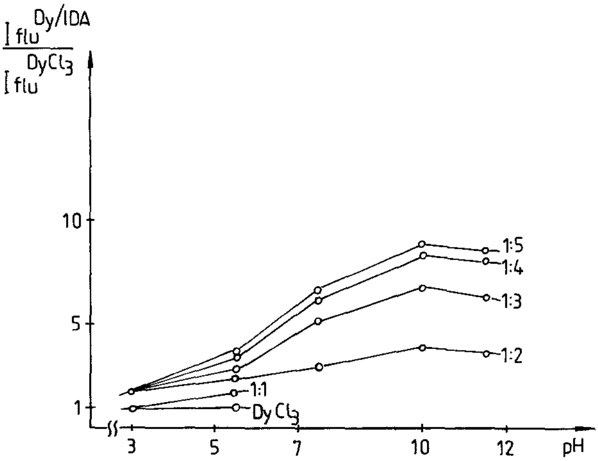

Fig. 4. The intensity of the fluorescence band at $\lambda = 577\,\mathrm{nm}$ for Dy(III) : *IDA* molar ratios 1 : 1, 1 : 2, 1 : 3, 1 : 4, and 1 : 5 as a function of the *pH*

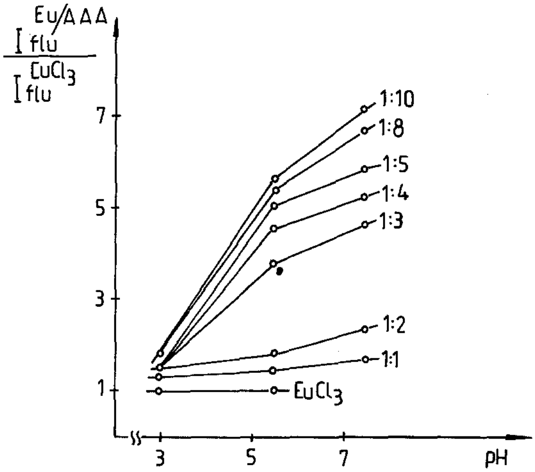

Fig. 5. The intensity of the fluorescence band at $\lambda = 615$ nm for Eu(III) : *AAA* molar ratios 1 : 1, 1 : 2, 1 : 3, 1 : 4, 1 : 5, 1 : 8, and 1 : 10 as a function of the *pH*

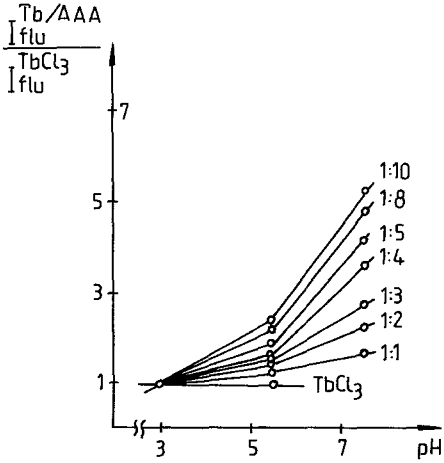

Fig. 6. The intensity of the fluorescence band at $\lambda = 545$ nm for Tb(III) : *AAA* molar ratios 1 : 1, 1 : 2, 1 : 3, 1 : 4, 1 : 5, 1 : 8, and 1 : 10 as a function of the *pH*

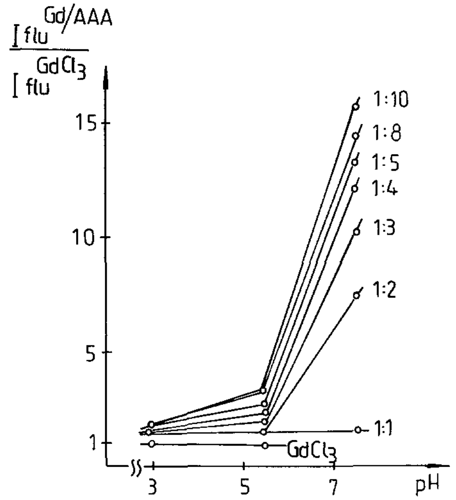

Fig. 7. The intensity of the fluorescence band at $\lambda = 312$ nm for Gd(III) : *AAA* molar ratios 1 : 1, 1 : 2, 1 : 3, 1 : 4, 1 : 5, 1 : 8, and 1 : 10 as a function of the *pH*

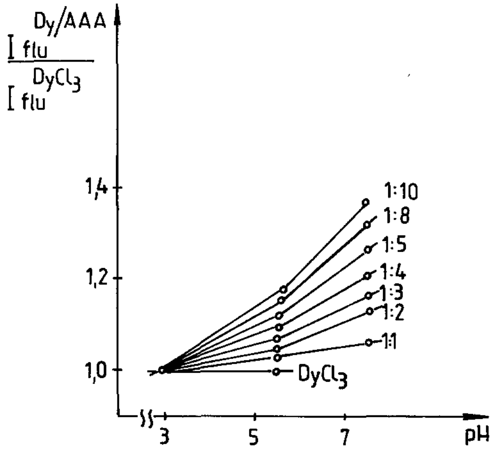

Fig. 8. The intensity of the fluorescence band at $\lambda = 577$ nm for Dy(III) : *AAA* molar ratios 1 : 1, 1 : 2, 1 : 3, 1 : 4, 1 : 5, 1 : 8, and 1 : 10 as a function of the *pH*

Table 1. *Fluorescence band intensities and related data for solutions of lanthanide complexes, at Ln(III) : L = 1 : 3 and at pH = 7.5*

Ligand	Complex	$\log\beta$ [Ref.]	Emission band λ_{max}	I 291 K	I 351 K	$\frac{I^{291}-I^{351}}{I^{291}}\cdot 100\%$	$\frac{I_{LnL}}{I_{LnCl_3}}$
Acetic- acid H*L* (*AA*)	EuL_2	3.91 [23]	615	40	26	35.0	3.4
	GdL_2	3.76	312	132	88	33.3	2.2
	TbL_2	3.66	545	206	144	30.1	1.4
	DyL_2	3.64	577	50	33	34.0	1.1
Amino- acetic acid H*L* (*AAA*)	EuL_2	6.7 [24]	615	47	32	31.9	3.9
	GdL_2	6.5	312	612	410	33.0	10.2
	TbL_2	6.5	545	406	280	31.0	2.8
	DyL_2	6.5	577	54	35	35.2	1.2
Iminodi- acetic acid H_2L (*IDA*)	EuL_2	12.11 [23]	615	470	324	31.0	38.8
	GdL_2	12.07	312	1 170	819	30.0	19.5
	TbL_2	12.24	545	2 498	1 756	29.7	17.4
	DyL_2	12.30	577	249	170	31.7	5.5
Nitrilo- triacetic acid H_3L (*NTA*)	EuL_2	20.70 [23]	615	680	503	26.1	65.7
	GdL_2	20.80	312	1 880	1 335	29.0	31.5
	TbL_2	20.97	545	5 253	3 671	30.1	36.5
	DyL_2	21.15	577	420	303	27.9	9.3
Ethylene- diamine- tetraace- tic acid H_4L (*EDTA*)	Eu*L*	17.35 [23]	615	1 620	1 166	28.0	135.0
	Gd*L*	17.37	312	1 640	1 196	26.9	27.3
	Tb*L*	17.90	545	5 100	3 662	28.2	35.4
	Dy*L*	18.30	577	356	253	28.9	7.8

values (291 and 351 K), the percentage change of band intensity on increasing the temperature from 291 K to 351 K ($I^{291} - I^{351}/I^{291} \cdot 100\%$), and the ratio between the observed fluorescence band intensity for the given solution of lanthanide complex and the registered one for a corresponding lanthanide chloride solution (I_{LnL}/I_{LnCl_3}).

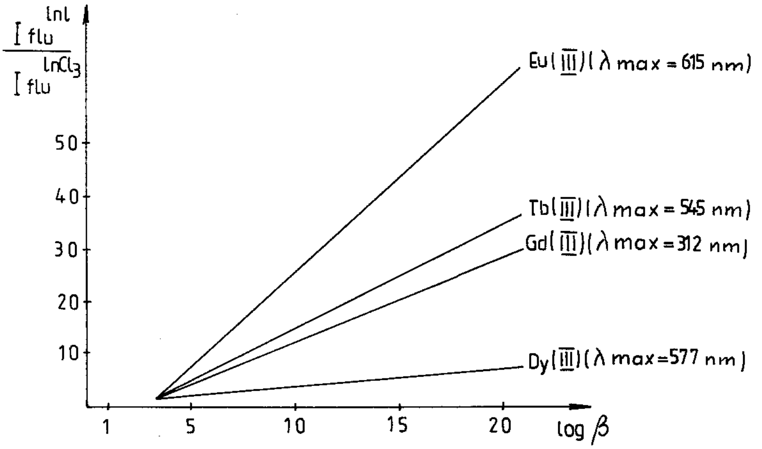

Fig. 9. The dependence of the fluorescence band intensities of Eu(III), Gd(III), Tb(III), and Dy(III) complexes with aminopolyacetic acids on the values of stability constants (log β)

The present data, combined with those obtained previously [20–22] indicate that the intensities of the fluorescence bands of the solutions of *Ln*(III) complexes depend on:

— the type of complex formed and its stability,

— the *pH* of the solution, which determines the anion types of the ligand and their charge,

— the size of the ligand molecules or ions,

— the electronic structure of the lanthanide ion,

— the temperature of the solution studied.

The values of the ratio I_{LnL}/I_{LnCl_3}, given in the last column of Table 1, tend to increase with the stability of the complex formed, as reflected in the value of log β. The nature of the ligand is thus a very important factor in determining the fluorescence band intensity. This correlation is represented graphically in Fig. 9 (I_{LnL}/I_{LnCl_3} v. log β). The effect is most marked for the hypersensitive fluorescence band of Eu(III), $\lambda_{max} = 615$ nm.

The intensity of the fluorescence bands always increases as the acidity of the solution is reduced. At high *pH* values, in consequence of dissociation, in the solution with an excess of the complexing agent (in relation to the complex created) various anionic forms of the ligand molecules appear, depending on the appropriate dissociation constants K[25]. In *EDTA* (H_4L) solutions the H_3L^-, H_2L^{2-}, HL^{3-} and L^{4-} ions are present (the respective pK values are 1.99, 2.67, 6.16 and 10.26). *NTA* (H_3L) gives rise to H_2L^-, HL^{2-} and L^{3-} ions (with pK 1.89, 2.49 and 9.73 respectively). The dibasic acid *IDA* (H_2L) dissociates to give HL^- and L^{2-} (pK 2.65 and 9.38 respectively). In *AAA* and *AA* solutions only L^- ions can be present, as both acids are monobasic (HL), with pK values 2.54 and 4.64.

These data indicate that even at pH as low as 3.0 lanthanide complexes with *EDTA* and *NTA* can be formed—which is reflected in a marked increase in the fluorescence band intensity as compared to that obtained for the corresponding chloride solution. Such acidic solutions containing a lanthanide ion in the presence of *IDA*, *AAA* or *AA* give practically the same fluorescence intensity as the corresponding chloride solutions. Complexes cannot be formed, because the degree of dissociation of the ligand molecules is too low. At pH values where the degree of dissociation of the ligand molecules (present in the solution of complex as an excess) becomes sufficient for complex formation, a large increase in the fluorescence intensity is observed (Figs. 1–8).

The fluorescence band intensity also depends on the size of the ligand molecules. With the largest molecules, *EDTA* and *NTA*, the intensity reaches a constant level for molar ratios *Ln*(III) : *EDTA* (or *NTA*) $= 1:3$. When the ligand molecules are smaller, as with *IDA*, the effect of such "saturation" is observed for *Ln*(III) : *IDA* $= 1:4$. With *AAA* and *AA* i.e. with the smallest molecules a constant level of fluorescence band intensity is not attained even for *Ln*(III) : *AAA* (or *AA*) $= 1:10$.

The fluorescence band intensity depends on the electronic structure of the lanthanide ions. The Gd(III) ion, with a large excitation energy (about $36\,600\,\mathrm{cm}^{-1}$), when complexed by *EDTA* or *NTA*, behaves differently from the other lanthanides—the fluorescence intensity actually decreases when the complexone concentration is increased beyond $1:2$ for *EDTA* and beyond $1:3$ for *NTA* [21].

Eu(III) ions give two close-lying emission bands, $\lambda_{max} = 615\,\mathrm{nm}$ hypersensitive band and $\lambda_{max} = 590\,\mathrm{nm}$ allowed one. The ratio of the intensity of the hypersensitive to the allowed bands (denoted by η and defined as the degree of the intensity "borrowing") has different values for solutions of different complexes of Eu(III), whereas for other lanthanides the η values are very similar to one another [21]. The values of η for the Eu(III) ion in various solutions are given in Table 2 together with the ratios of I_{EuL}/I_{EuCl_3} for the two bands.

Table 2. *The values of the parameter* $\eta = I_{^5D_0-^7F_2}/I_{^5D_0-^7F_1}$ *and the ratios of Eu(III) complex fluorescence band intensities to those obtained for* $EuCl_3$ *(*Eu*:* $L = 1:3$, *pH = 7.5), 291 K*

Solution	η	I_{EuL}/I_{EuCl_3}	
		$\lambda_{max} = 590$ nm ($^5D_0-^7F_1$)	$\lambda_{max} = 615$ nm ($^5D_0-^7F_2$)
$EuCl_3$	0.17	1	1
Eu/*AA*	0.57	1	3.4
Eu/*AAA*	0.61	1.1	3.9
Eu/*IDA*	1.53	4.3	38.8
Eu/*NTA*	0.91	12.3	65.7
Eu/*EDTA*	2.46	9.3	135

The numerical values of the borrowing coefficient η indicate clearly that the nature of the ligand is very important in determining the fluorescence band intensity for a lanthanide ion. Because there is no displacement of the band positions for the complexed ions, no explanation of the observed effects can be expected in terms of vibronic coupling, which can, under other circumstances, account for the intensity borrowing in a clear and convincing model. The problem requires taking into account other effects occurring in the system—and this will be the subject of further investigations.

In our previous publication [22] we tried to use our data in order to explain the observed effects in terms of a simple theoretical model. An attempt will now be made to develop this model further, taking into account additional results.

Using the dipole approximation, the intensity of a given electronic transitions depends on the dipole moment for the transition, and this is in turn determined by the value of the electric charges and their separation. The distance between the effective electric charges in an ion-ligand complex depends on the oscillations of the ion-ligand bond, hence one can write

$$\mu = \mu_0 + \sum_i \left(\frac{\partial \mu}{\partial Q_i}\right)_0 (Q_i - Q_i^0) + \cdots \tag{1}$$

The dipole moment for the transition can then be described by

$$\mu_{0K} = \int \psi^0 \varphi_P^0 \left[\mu_0 + \sum_i \left(\frac{\partial \mu}{\partial Q_i}\right)_0 (Q_i - Q_i^0)\right] \psi^K \varphi_r^K \, d\tau \tag{2}$$

where μ_0, μ are the dipole moments of the complex, assuming a rigid structure (i.e. fixed ion-ligand distance) and for the oscillating complex, respectively, Q_i is the vibration co-ordinate, describing the oscillatory motion of the complex, ψ^0, ψ^K are the electronic wave functions for the complex in the ground and in the excited electronic states of the ion, respectively, φ^0_p, φ^K_r are the vibrational wave functions for the ground and for the excited electronic states, respectively.

Equation (2) can be rewritten in the form

$$\mu_{0K} = S_{pr} \int \psi^0 \mu_0 \psi^K \mathrm{d}\, q + \int \psi^0 \sum_i \left(\frac{\partial \mu}{\partial Q_i}\right)_0 \varphi^0_p (Q_i - Q^0_i)\, \varphi^K_r \psi^K \mathrm{d}\, \tau \tag{3}$$

$$\mu_{0K} = S_{pr}\, \mu^0_{0K} + \Delta \mu_{0K} \tag{4}$$

where S_{pr} is the overlap integral for the vibrational wave functions of the ground and excited electronic states. This is equal to the *Kronecker* delta or to function S_{pr} of vibrational parameters if the two vibration states are different (for example they have different vibrational frequencies), d q and d τ are volume elements of the space containing the electrons and of the space containing both the electrons and the nuclei, respectively.

The first term in Eq. (3) gives the dipole moment for an electronic transition of a ion in a rigid complex in which the distance between the ion and the ligand is constant. This term does not depend on the temperature. The second term gives the change in the dipole moment for the transition which is caused by the non-rigidity of the complex and is strongly temperature dependent. A rise in temperature brings about an increase in the populations of the higher vibrational states—and so the vibrational wave functions which should be used in the calculations [cf. Eq. (4)] are no longer the same as for a rigid model. As a consequence the oscillator strength for the transition consists of the following components:

$$f_{0K} = f^0_{0K} + f^{(1)}_{0K} + f^{(2)}_{0K} \tag{5}$$

where

$$f^0_{0K} = \frac{8\pi^2 mc}{3h} \omega_{0K} |\mu_{0K}|^2 \tag{6}$$

$$f^{(1)}_{0K} = \frac{8\pi^2 mc}{3h} \omega_{0K} |\Delta \mu_{0K}|^2 \tag{7}$$

$$f^{(2)}_{0K} = \frac{8\pi^2 mc}{3h} 2\, \omega_{0K} \mu_{0K} \Delta \mu_{0K} \tag{8}$$

The first component [Eq. (6)] depending on the dipole moment for the transition is independent of temperature, while the second and third, given by Eq. (7) and (8), vary with the temperature as a result of the changes in the dipole moment brought about by the non-rigid character of the complex.

The macroscopic factors affecting f^0_{0K} such as the *pH* of the medium and the ligand excess were discussed previously [22]. The effects observed were accounted for in terms of changes in the dipole moments for the transitions.

At present we are concerned with the second and third component (both temperature-dependent) and their effects on the spectroscopic properties of the lanthanide complexes.

I. The form of $\Delta \mu_{0K}$ appearing in the above equations indicates that changes in the band positions of the electronic transition of the lanthanide ion in the complex should not be expected, since the electronic wave functions remain unchanged.

II. Changes in the fluorescence band intensity should depend on the dimensions of the ligand molecules—the bigger the complex molecule, the lower the vibration frequency of the central ion-ligand bond. The lower the vibration frequency, the lesser will be the effect of the temperature on the system. This implies that the temperature effect should be most prominent for complexes with *AA* and least for those with *EDTA*. The intensities of all fluorescence bands observed in the spectrum of a given lanthanide ion in the complex should be affected to a similar extent. This is in accord with the data of Table 1.

On the basis of the above model the observed effects can be interpreted as follows:

The Influence of the pH and of the Complexing Agent Concentration

The important point to note here is that a decrease in the acidity of the solution and the introduction of an excess of the complexing agent modifies the own dipole moment of the lanthanide in the complex. Then the value of the dipole moment for the transition is higher. The effect depends on the dimensions of the ligand molecule. The larger the ligand molecule, the lower the excess concentration of the ligand at which the fluorescence band intensity reaches a plateau. This is attributed to stronger complex molecule—free ligand (in excess) interactions [22].

The Influence of Temperature

The change in the fluorescence intensity should depend on the number of vibrations affecting the dipole moment for the transition and on the magnitude of $\partial \mu / \partial Q_i$. The lower the ligand—central (lanthanide) ion oscillation frequency, the lower the value of $\partial \mu / \partial Q_i$ and thus the lesser the effect of temperature on the fluorescence band intensity. Two cases can be considered here:

1. The electronic excitation of the central ion does not lead to changes in the central ion—ligand vibration frequency. The mixed term $f_{0K}^{(2)}$ then disappears, since $S_{pr} = \delta_{pr}$. For transitions with the conservation of vibrational quantum numbers for ground ("0") and excited ("K") electronic states $\Delta\,\mu_{0K} = 0$ [since $\int \varphi_p^0 (Q_i - Q_i^0)\, \varphi_r^K \,\mathrm{d}\,Q$ is equal to zero for $p = r$]. If in the electronic transition considered there is a change in vibration quantum numbers for ground and excited electronic states, $\delta_{pr} = 0$. Now the intensity of the transition considered will depend on $|\Delta\,\mu_{0K}|^2$ i.e. the fluorescence intensity should increase.

2. Excitation of the central ion leads to a change in the central ion—ligand bond vibration frequency. Then $S_{pr} \neq 0$ and $f_{0K}^{(2)}$ does not disappear in Equ. (5). This term can be negative when $\partial\,\mu/\partial\,Q_i < 0$, which implies that the ion—ligand vibration brings about a decrease in the dipole moment of the system. A rise in the temperature now causes a decrease in the fluorescence band intensity. This is the phenomenon that actually has been observed.

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