

## Quantum Efficiency of the Luminescence of Eu(III), Tb(III) and Dy(III) in Aqueous Solutions

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**Summary.** The luminescence quantum efficiency of Eu(III), Tb(III) and Dy(III) in chloride solutions as well as complexed by aminopolyacetic acids was determined. An interpretation of the observed dependences in the system investigated has been proposed.

**Keywords.** Quantum efficiency of Eu(III), Tb(III) and Dy(III) luminescence; Total and transition dipole moment.

### Die Lumineszenz-Quantenausbeute von Eu(III), Tb(III) und Dy(III) in wässrigen Lösungen

**Zusammenfassung.** Die Lumineszenz-Quantenausbeute von Eu(III), Tb(III) und Dy(III) in Chloridlösung und in Komplexen mit Aminopolyessigsäuren wurde bestimmt. Eine Interpretation der beobachteten Abhängigkeiten im untersuchten System wurde vorgeschlagen.

### Introduction

In the course of investigating the luminescence of lanthanide complexes with aminopolyacetic acids (APA) in aqueous solutions it was established that the emission intensity depends on the experimental conditions, reflected in such parameters as the *pH* of the solution, the excess of complexing agent, the size and charge of the ligand molecules and the temperature [1–7]. The intensity of the luminescence bands appearing in the luminescence spectra of the complexes [particularly Eu(III)] does not change with these parameters in any regular manner. For Eu(III) the hypersensitive (forbidden,  $\Delta J = \pm 2$ ) band, at  $\lambda_{\text{max}} = 615$  nm is much more affected by complexing than the allowed band at  $\lambda_{\text{max}} = 590$  nm. This implies that the ratio of the intensities of these two bands (hypersensitive to allowed) is not constant. This ratio, denoted by  $\eta$ , is different for different complexes [1, 2, 8–10]. Hence the luminescence properties of the lanthanide ions and their complexes cannot always be judged on the basis of the emission band intensity. The quantum efficiency of the emission is a more suitable quantity for this purpose. The quantum efficiency of the luminescence of Tb(III) and Eu(III) in chelate-type complexes with certain  $\beta$ -diketones was given by Dawson et al. [11]. Napier and coworkers [12] determined the quantum efficiency of the emission of Tb(III) chelate with

acetylacetone in the presence of other lanthanides(III) which quenched the emission. Recently, quantum efficiency of the luminescence of Eu(III) [13, 14] and Tb(III) [15] complexes with crown ethers has been determined.

This paper presents an account of the determination of the luminescence quantum efficiency of Eu(III), Tb(III) and Dy(III) in chloride solutions and when the ions are complexed by aminopolyacetic acids (*APA*). The method used was that described by Parker [16] and by Meech and Phillips [17]. An interpretation of the observed dependences in the system investigated has been proposed.

## Experimental

Lanthanide chloride solutions at  $pH = 5$  and solutions containing the complexes with *APA*, with  $Ln:APA = 1:3$  at  $pH = 7.5$ , were used. The complexing agents employed were ethylenediaminetetraacetic acid (*EDTA*), nitrilotriacetic acid (*NTA*), iminodiacetic acid (*IDA*) and aminoacetic acid (*AAA*). The lanthanide concentration was kept constant at  $1 \cdot 10^{-2} \text{ mol dm}^{-3}$  for all solutions used.  $1.4 \cdot 10^{-5} \text{ mol dm}^{-3}$  quinine sulphate (*SQ*) solution in  $0.1 \text{ N H}_2\text{SO}_4$  was employed as the luminescence standard with  $\Phi_{SQ} = 0.53$  [16, 17]. The measurements were carried out at  $291 (\pm 1) \text{ K}$ .

The absorption spectrum of the standard (*SQ*) and those of the solutions of lanthanide chlorides and of lanthanide complexes with *APA* were recorded on a Beckman Type 25 spectrophotometer. Corrected emission spectra of all the solutions were measured at  $90^\circ$  to the exciting beam using the Perkin-Elmer spectrofluorimeter MPF-44A. The measuring slit width of the spectrophotometer and the excitation slit width of the spectrofluorimeter were kept identical throughout the experiments.

The quantum efficiency of the  $Ln(\text{III})$  luminescence, relative to that of *SQ*, was calculated from the formula

$$\Phi_{Ln} = \frac{\int I_{Ln}(\tilde{\nu}) d\tilde{\nu} A_{SQ} n_{Ln}^2}{\int I_{SQ}(\tilde{\nu}) d\tilde{\nu} A_{Ln} n_{SQ}^2} \Phi_{SQ},$$

where the integration of intensities is carried out over all emission bands of the multiplet;  $A_{Ln}$ ,  $A_{SQ}$  are the absorbances of the lanthanide and of the standard, respectively, both at  $\lambda_{\text{max}}$  of  $Ln(\text{III})$ ;  $n_{Ln}$ ,  $n_{SQ}$  are the refractive indices of the lanthanide and of the *SQ* solution, respectively.

## Results and Discussion

The quantum efficiencies of the lanthanides(III) luminescence were estimated for the Tb(III), Eu(III) and Dy(III) chlorides and the complexes with *EDTA*, *NTA*, *IDA*, and *AAA*. In Figs. 1 a, b, c the emission spectra of the investigated lanthanide ions are presented. The *APA* solutions did not show any emission under the experimental conditions used. The results are summarized in Table 1 and in Fig. 2.

Figure 2 shows an almost linear dependence of lanthanide(III) emission quantum efficiency versus stability constants ( $\log \beta$ ) of the lanthanide complexes. The higher  $\log \beta$  values, the higher are the luminescence quantum efficiencies of the lanthanides(III). Higher values of the luminescence quantum efficiency in the instance of stable complexes result from a less important participation of the radiationless processes which deactivate the excited electronic state of the lanthanide(III) ions. This fact is observed for different kinds of the ligands employed.

The ions of Tb(III) show higher values of the luminescence quantum efficiency than Eu(III) and Dy(III) as a result of the differences of the energy gap between the ground and excited states of the lanthanide ions.

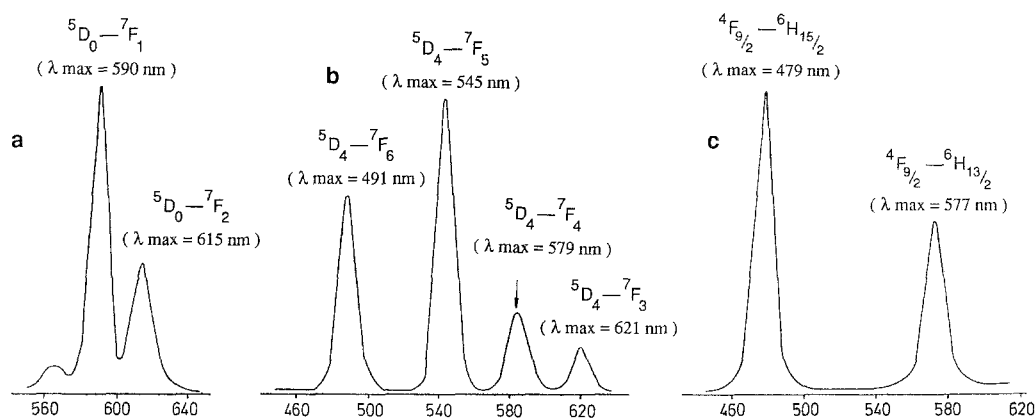


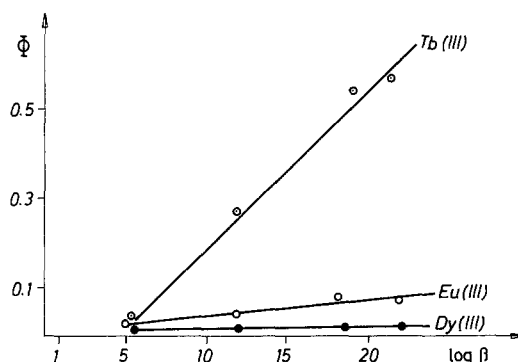
Fig. 1. Emission spectra of the lanthanide(III),  $c_{L_{III}} = 1 \cdot 10^{-2} \text{ mol dm}^{-3}$ ; a:  $\text{EuCl}_3$ , b:  $\text{TbCl}_3$ , c:  $\text{DyCl}_3$

Table 1. Experimental data and the luminescence quantum efficiencies ( $\Phi$ ) obtained for Eu(III), Tb(III) and Dy(III)

Compound	Absorption and excitation wavelength (nm)	Absorbance	$\Phi$	$\log \beta^a$
<i>SQ</i>	394	0.011	0.53 <sup>b</sup>	
<i>SQ</i>	368	0.075	0.53	
<i>SQ</i>	350	0.137	0.53	
$\text{EuCl}_3$	394	0.011	$6.5 \cdot 10^{-3}$	
$\text{EuEDTA}$	394	0.016	$9.9 \cdot 10^{-2}$	17.35
$\text{Eu(NTA)}_2$	394	0.016	$8.3 \cdot 10^{-2}$	20.70
$\text{Eu(IDA)}_2$	394	0.017	$4.9 \cdot 10^{-2}$	12.11
$\text{Eu(AAA)}_2$	394	0.012	$7.9 \cdot 10^{-3}$	6.7
$\text{TbCl}_3$	368	0.010	$2.9 \cdot 10^{-2}$	
$\text{TbEDTA}$	368	0.017	$5.4 \cdot 10^{-1}$	17.90
$\text{Tb(NTA)}_2$	368	0.018	$5.6 \cdot 10^{-1}$	20.97
$\text{Tb(IDA)}_2$	368	0.017	$2.7 \cdot 10^{-1}$	12.24
$\text{Tb(AAA)}_2$	368	0.011	$3.3 \cdot 10^{-2}$	6.5
$\text{DyCl}_3$	350	0.016	$6.4 \cdot 10^{-4}$	
$\text{DyEDTA}$	350	0.017	$3.5 \cdot 10^{-3}$	18.30
$\text{Dy(NTA)}_2$	350	0.017	$4.0 \cdot 10^{-3}$	21.15
$\text{Dy(IDA)}_2$	350	0.016	$2.5 \cdot 10^{-3}$	12.30
$\text{Dy(AAA)}_2$	350	0.017	$6.7 \cdot 10^{-4}$	6.5

<sup>a</sup> The values of  $\log \beta$  for *Ln* complexes with *EDTA*, *NTA*, and *IDA* were taken from [18], and for *Ln* complexes with *AAA* from [19]

<sup>b</sup> The values of  $\Phi$  for *SQ* were taken from [17]



**Fig. 2.** The dependence of the luminescence quantum efficiency of the lanthanides ( $\Phi$ ) vs. stability constants ( $\log \beta$ ) of the lanthanide(III) complexes with *EDTA*, *NTA*, *IDA*, and *AAA*

These results allow to draw several conclusions. The luminescence quantum efficiency of Eu(III), Tb(III) and Dy(III) is in the order:  $\Phi_{\text{Tb}} > \Phi_{\text{Eu}} \gg \Phi_{\text{Dy}}$ , irrespective of the nature of the ligand; it is always higher for complexes than that for chloride solution and is also highest for those lanthanide complexes which have the highest stability constants (for any of the three lanthanides studied):  $\Phi_{\text{LnNTA}} \geq \Phi_{\text{LnEDTA}} > \Phi_{\text{LnIDA}} > \Phi_{\text{LnAAA}} > \Phi_{\text{LnCl}_3}$ .

The emission intensity was determined by the total dipole moment of the central ion. On the basis of the previously proposed description of the luminescence phenomenon occurring in the rare earth complexes [2] the transition dipole moment given by the equation

$$\mu_{lk} = \int \Psi_l^0 \mu_0 \Psi_k^0 d\tau \quad (1)$$

(where  $\Psi_l^0$  is the electronic wave function of the ground state of the ion and  $\Psi_k^0$  is the electronic wave function of the excited state of the ion) plays a main role in the present discussion. The dipole moment of the central ion of the complex is defined by the equation

$$\mu_0 = - \sum_l e_l r_l, \quad (2)$$

where  $e_l$  is a charge distant  $r_l$  from the centre of the system where the atom is described and the summation runs over all the electrons of the system considered [20]. Since

$$e_l = e \int (\Psi_l^0)^2 d\nu, \quad (3)$$

where  $e$  is an elementary charge and  $\Psi_l^0$  is an electron wave function of the  $l$ -th electron, hence for the electrons participating in the bond between ion and ligand one can write

$$\Psi_l = N(\Psi_l^0 + \lambda \Psi), \quad (4)$$

where  $N$  is a normalization constant and  $\lambda$  is a parameter describing the participation of the ligand orbital  $\Psi$  in the molecular orbital of the complex.

Introducing Eq. (4) into Eq. (3) one can see that the effective charge of the  $l$ -centre depends on the ligand wave functions, i.e. on the ligand electron cloud in the bond. On the other hand from Eq. (2) one can conclude that with greater  $\lambda$  the effective charge and hence also the dipole moment is increased.

The excited lanthanide ion undergoes a radiationless deactivation to an emission level. This process is promoted by the vibration of the CH and the CH<sub>2</sub> bonds. The luminescence intensity from the emission level is determined by the total dipole moment of the central ion. The greater this dipole moment, the greater is the luminescence quantum efficiency. Increase of the strength of the complex bonding, i.e. of  $\log \beta$ , is connected with a greater total dipole moment due to a greater participation of the additional electron cloud which depends on  $\lambda$ . Hence, the stronger the bond of the complex, the greater is  $\lambda$  and the greater is the effective dipole moment, i.e. with increasing probability of emission the quantum efficiency of the lanthanide luminescence is increased as well.

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