

# Influence of adding rare earth ions on Tb(III) fluorescence in Tb(III)-salicylic acid complexes

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## Abstract

The influence of Ce(III) on the fluorescence of Tb(III) and the ligand as well as the enhanced fluorescence of Tb(III) by Ln(III) (Ln = Y, La, Gd, Lu) in Tb(III)-SA (SA, salicylic acid) complex solutions was observed. It was found that the Ce(III) ion quenched the SA ligand fluorescence and increased the fluorescence of Tb(III) in ethanol solutions of the complexes and that Ln(III) ions increased the Tb(III) fluorescence intensively as well.

## 1. Introduction

Recently two important applications of fluorescent complex systems of rare earths with organic compounds were developed, i.e. rare earth ions were used as fluorescence probes in biomolecular structures [1, 2] and as fluorimmunoassays in clinical diagnostics [3, 4]. These interesting applications have intensively promoted the investigation of luminescence in solution complexes of rare earths with aromatic carboxylic acids. The influence of other rare earth (RE) ions on the fluorescence properties of Eu(III) and Tb(III) ions in their complex systems has been studied by our group [5-8].

In this paper the effect of Ce(III) and Ln(III) ions (Ln = Y, La, Gd, Lu) on the fluorescence of Tb(III)-salicylic acid (SA)-ethanol complexes was studied.

## 2. Experimental details

### 2.1. Materials and procedures

The SA (AR grade) was not purified before use. The preparation of ethanol solutions of Tb(III) and Ln(III) has been described previously [5]. The ethanol solution of Ce(III) was prepared by dissolving CeCl<sub>3</sub>·6H<sub>2</sub>O (99.95%) in ethanol. The initial concentrations of Tb(III), Ce(III), Ln(III) and SA ligand were 1 × 10<sup>-3</sup>, 5 × 10<sup>-4</sup> and 1 × 10<sup>-2</sup> M, 5 × 10<sup>-3</sup> M respectively. In order to elucidate the interaction between RE ions and Tb(III) ions, various Ce(III) and Ln(III) ion concentrations were used, but the Tb(III):SA ratio was kept fixed at 1:8 and 1:20 for the Tb(III)-Ce(III)-SA and Tb(III)-Ln(III)-SA solution systems respectively.

That is, typical solutions were adjusted to 5 × 10<sup>-4</sup> and 4 × 10<sup>-3</sup> M and 1.25 × 10<sup>-5</sup> and 2.5 × 10<sup>-4</sup> M in Tb(III) and SA for the Tb(III)-Ce(III)-SA and Tb(III)-Ln(III)-SA systems respectively. All the complex solutions were adjusted to pH 6.

### 2.2. Apparatus

The fluorescence excitation, fluorescence emission and absorption spectra of the complexes were measured by the method described previously [5, 6]. The pH values of the solutions were determined with a pH-25 pH meter.

## 3. Results and discussion

### 3.1. Effect of Ce(III) ion on fluorescence of Tb(III)-SA solution complex systems

The energy transfer from Ce(III) to Tb(III) in their inorganic phosphors has been intensively studied [9]. Thus the interaction between Ce(III) and Tb(III) in organic complexes was given attention in our group, although the Ce(III) fluorescence of only a single Ce(III) complex has so far been investigated [10]. In the Ce(III)-containing complexes no Ce(III) fluorescence was observed, but the Tb(III) fluorescence was increased. Figure 1 shows the dependence of the fluorescence intensities at 405 nm of SA and at 545 nm of Tb(III) on the concentration of Ce(III) ions in Tb(III)-Ce(III)-SA solutions. It is found from Fig. 1 that the luminescence colour of the complex solutions changed with increasing Ce(III) concentration. That is, the luminescence colour of the solution at low Ce(III) content was bluish white, while a green luminescence

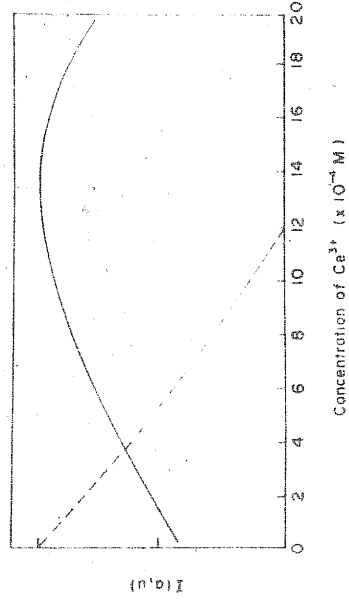


Fig. 1. Dependence of emission intensities of SA ligand (—) and Tb(III) (---) on Ce(III) concentration of Tb(III)-Ce(III)-SA in ethanol solutions. Tb(III),  $5 \times 10^{-4}$  M; pH 6.

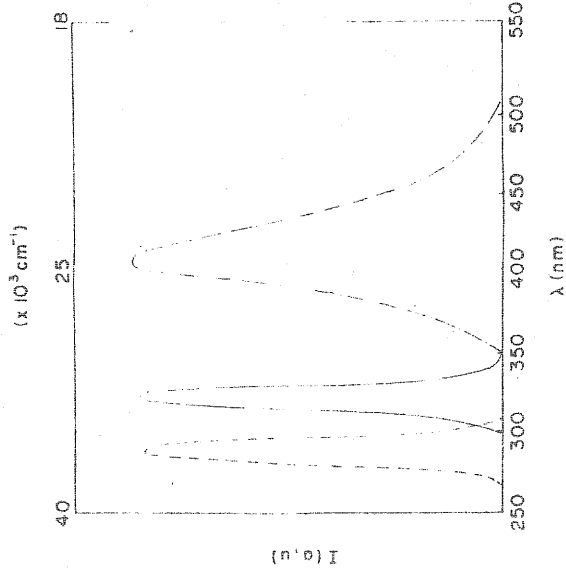


Fig. 2. Absorption (---), excitation (—) and emission (---) spectra of SA ligand in ethanol solutions.

colour became gradually brighter and brighter and the purplish blue colour of SA was not observed with increasing Ce(III) content. The excitation and emission spectra of the SA ligand are shown in Fig. 2. From the excitation and emission bands it was demonstrated that the lowest singlet state  $S_1$  should be at  $24 \times 10^3$   $\text{cm}^{-1}$ . Kleinerman has reported that the lowest triplet state  $T_1$  is situated at  $24.8 \times 10^3$   $\text{cm}^{-1}$  [11] and that the  $T_1$  level is considerably higher than the  $^5D_4$  level of Tb(III). It is well known that there should be an optimum difference between the  $T_1$  and  $^5D_4$  levels for efficient energy transfer from the ligand to Tb(III) [12, 13]. It is seen that the distance between the  $T_1$  and  $^5D_4$  levels is too large for energy transfer from the  $S_1$  to the  $^5D_4$  level via the  $T_1$  level to take place easily. It is known that 4f-5d transitions of Ce(III) are allowed for the absorption of electric dipole radiation [14]. However, the Ce(III) fluorescence was not measured under our experimental conditions. Thus we can suppose

that the 5d level of the Ce(III) ion in Tb(III)-Ce(III)-SA complex systems played only an intermediate role in the energy transfer from the  $S_1$  to the  $^5D_4$  level. It was assumed that the 5d level of the complexed Ce(III) must be lower than the  $T_1$  level and higher than the  $^5D_4$  level of Tb(III). That is, it seems that the 5d level should be situated at a more appropriate state between the  $T_1$  and  $^5D_4$  levels in order for energy transfer from  $S_1$  to  $^5D_4$  to occur efficiently. Therefore the luminescence phenomenon in Fig. 1 can be explained in terms of the emissions of the SA ligand and Tb(III) fluorescence being quenched and sensitized by the Ce(III) ion. The transfer process is shown in Fig. 3.

The solution colour (no fluorescence colour) of Tb(III)-Ce(III)-SA complexes changed from colourless to dark brown, which is similar to that of isolated  $\text{Ce}(\text{NO}_3)_4 \cdot (\text{B}_2\text{H}_6 \cdot 18 \cdot \text{C} \cdot 6) \cdot \text{MeON}$  crystals, which is also a dark brown crystalline complex and the body colour should be caused by the Ce(IV) [15], when the solutions were allowed to stand for 3 h, and even for Tb(III)-free Ce(III)-SA the colour change was observed. The Tb(III) fluorescence decreased when the solution colour changed to dark brown in Tb(III)-Ce(III)-SA complex systems. This can be explained as follows: the colour change was caused by oxidation from Ce(III) to Ce(IV) and is due to a charge transfer transition from the SA ligand to the Ce(IV) ion, because the Ce(III) ion in the complex solutions was not stable enough to prevent slow oxidation by air and/or oxygen-containing ligand.

### 3.2. Enhancement effect of Ln(III) ( $\text{Ln} = \text{Y}, \text{La}, \text{Gd}, \text{Lu}$ ) on Tb(III) emission in Tb(III)-Ln(III)-SA systems

Figure 4 shows the dependence of the fluorescence intensity of the Tb(III) ion on the Ln(III) ion content in Tb(III)-Ln(III)-SA systems. It is seen that the Tb(III) emission increased with increasing Ln(III) concentra-

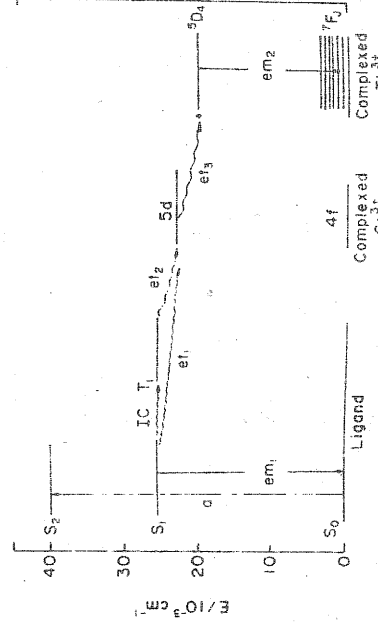


Fig. 3. Schematic representation of energy transfer processes for Tb(III)-Ce(III)-SA system in ethanol solutions: a,  $S_0$ - $S_2$  absorption; IC, intersystem crossing;  $em_1$ ,  $S_1 \rightarrow S_0$  transition;  $em_2$ ,  $^5D_4 \rightarrow ^7F_3$  ( $f=4-5$ ) transition;  $et_1$ , energy transfer from  $S_1$  to  $5d$  level;  $et_2$ , energy transfer from  $T_1$  to  $5d$  level;  $et_3$ , energy transfer from  $5d$  to  $^5D_4$  level of Tb(III) ion.

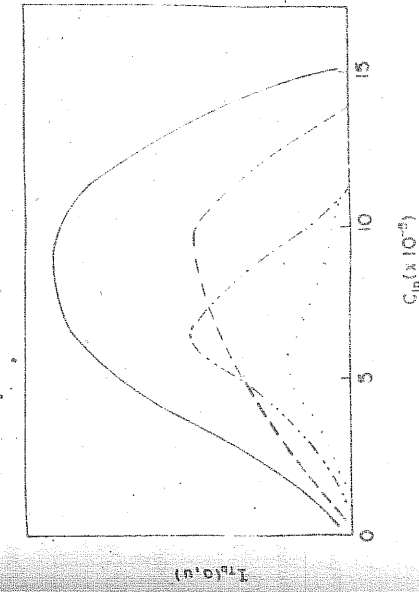


Fig. 4. Dependence of emission intensity of Tb(III) ion on Ln(III) (Ln = La, Y, Gd, Lu) concentration in —, La; ---, Y; ····, Gd; ·····, Lu.

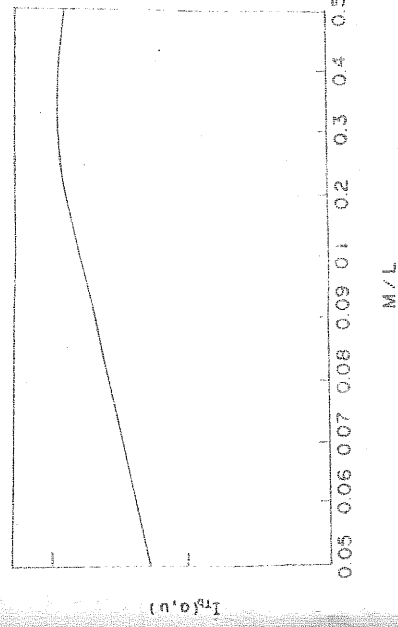


Fig. 5. Dependence of fluorescence intensity of Tb(III) on metal-to-ligand ratio in Tb(III)-SA system. Tb(III),  $2.5 \times 10^{-5}$  M; pH 6.

tion. Figure 5 shows the dependence of the Tb(III) emission intensity on the molar ratio in the Tb(III)-SA complex system. From Figs. 4 and 5 it is concluded that the increased Tb(III) emission did not result from a change in the Tb(III):SA ratio but was caused by the addition of Ln(III) ions. It is also noticed that the maximum enhancement of the Tb(III) emission resulted from the addition of La(III). The enhancement of the Tb(III) fluorescence upon adding Ln(III) can also be considered in terms of an energy transfer from the Ln(III)-SA complex to the complexed Tb(III) ion, because the environment of the Tb(III) ion was changed

from an irregular state of the free SA ligand to a regular state of the Ln(III)-SA complex. In other words, the electron-conjugated surface was larger for the Ln(III)-SA complex than for the free SA ligand. A more detailed explanation of the enhancement mechanism for Tb(III)-Ln(III)-SA systems is similar to the description given in Ref. 5. The fact that the enhancement effect of Tb(III) fluorescence was larger by La(III) than other Ln(III) ions was due to an optimum match of the SA ligand with the La(III) ion radius.

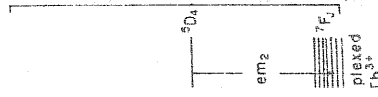
In addition to the solution complex systems, isolated powder crystalline complexes of Tb(III)-Ln(III)-SA were prepared and it was also found that the Tb(III) fluorescence of these was enhanced by adding Ln(III). The detailed mechanism of fluorescence enhancement of Tb(III) by Ln(III) ions is being studied in our group.

## References

- 1 J.-C.G. Bunzli and G.R. Choppin (eds.), *Lanthanide Probes in Life, Chemical and Earth Sciences*, Elsevier, Amsterdam, 1989, Chap. 7, pp. 272-281.
- 2 F. Srichadson, *Chem. Rev.*, **82** (1982) 541.
- 3 E. Soini and I. Hamila, *Clin. Chem.*, **25** (1979) 253.
- 4 E. Soini, I. Hamila, J. Marniemi, P.N. Jorgenson, J. Zevthen and T. Lovgren, *Clin. Chem.*, **32** (1986) 637.
- 5 W.-L. Li, G. Yu and S. Huang, *J. Alloys Comp.*, **194** (1993) 19.
- 6 W.-L. Li, W. Li, G. Yu, Q. Wang and R. Jin, *J. Alloys Comp.*, **192** (1993) 34.
- 7 W.-L. Li, W. Li, G. Yu, Q. Wang and R. Jin, *J. Alloys Comp.*, **191** (1993) 107.
- 8 W. Li, W.-L. Li and D. Tang, *J. Chinese Rare Earth Soc.*, **7** (1989) 27.
- 9 A. Bril, G. Blasse, A.H. Gomes de Mesquita and J.A. de Poorter, *Philips Tech. Rev.*, **32** (1971) 125.
- 10 W.-L. Li, T. Mishima, G.-Y. Adachi and J. Shiohawa, *Inorg. Chim. Acta*, **130** (1987) 277.
- 11 M. Kleiderman, *J. Chem. Phys.*, **51** (1969) 2370.
- 12 S. Sato and M. Wada, *Bull. Chem. Soc. Jpn.*, **43** (1970) 1955.
- 13 W.-L. Li, T. Mishima, G.-Y. Adachi and J. Shiohawa, *Inorg. Chim. Acta*, **121** (1986) 97.
- 14 G. Blasse, Chemistry and physics of R-activated phosphors, in K.A. Gschneidner Jr. and L. Eyring (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, North-Holland, Amsterdam, 1979, p. 242.
- 15 J.-C.G. Bunzli, Complexes with synthetic ionophores, in K.A. Gschneidner Jr. and L. Eyring (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, Elsevier, Amsterdam, 1987, p. 385.

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