

# DUAL MECHANISM OF ENERGY TRANSFER IN BENZOATE SENSITIZED LUMINESCENCE OF $\text{Eu}^{3+}$ AND $\text{Tb}^{3+}$

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Benzoate has been studied as a sensitizer of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  luminescence in aqueous and methanolic solution. In solutions with low concentrations of the lanthanide ions the mechanism is dynamic involving free benzoate triplets. At higher concentrations a switchover to a static mechanism involving complexed benzoate occurs. In the case of  $\text{Eu}^{3+}$  the dynamic sensitization is 3 times as efficient as the static one, which is explained by CT-quenching of singlet benzoate in the complex. The emission quantum yield of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  benzoate complexes increases with the number of benzoate ligands.

KEY WORDS: electronic energy transfer, luminescence, rare earth ion complexes.

## 1. INTRODUCTION

The long-lived luminescence of trivalent lanthanoid ions resulting from f-electron transitions has attracted recent interest because of its application potential e.g. in biochemical assays [1] or in functions of supramolecular assemblies [2]. Typically, in such situations the ions are coordinated by strongly binding multidentate  $\pi$ -electron ligands acting as absorption antennas and sensitizers for the lanthanoid ions whose absorption cross sections for direct excitation are very small. On the other hand, in the less recent literature there are many studies of energy transfer to lanthanoid ions using non-coordinating triplet sensitizers [3]. Whereas the energy transfer mechanism in the first type of cases where sensitizer and energy acceptor are already in contact when excitation occurs, may be termed a *static* one, the second type of mechanism is *dynamic* in that it requires diffusional encounters of energy acceptor and excited donor during the life time of the latter. In this paper we report on a situation where benzoate, a weakly coordinating ligand, is used as a sensitizer. This allowed us to study, in direct comparison, the peculiarities of dynamic and static pathways of sensitization. With regard to the dynamic pathway, it must be pointed out that, to the best of our knowledge, the existence of long lived triplet states for benzoate and benzoic acid in room temperature liquid solution has not yet been documented in the literature.

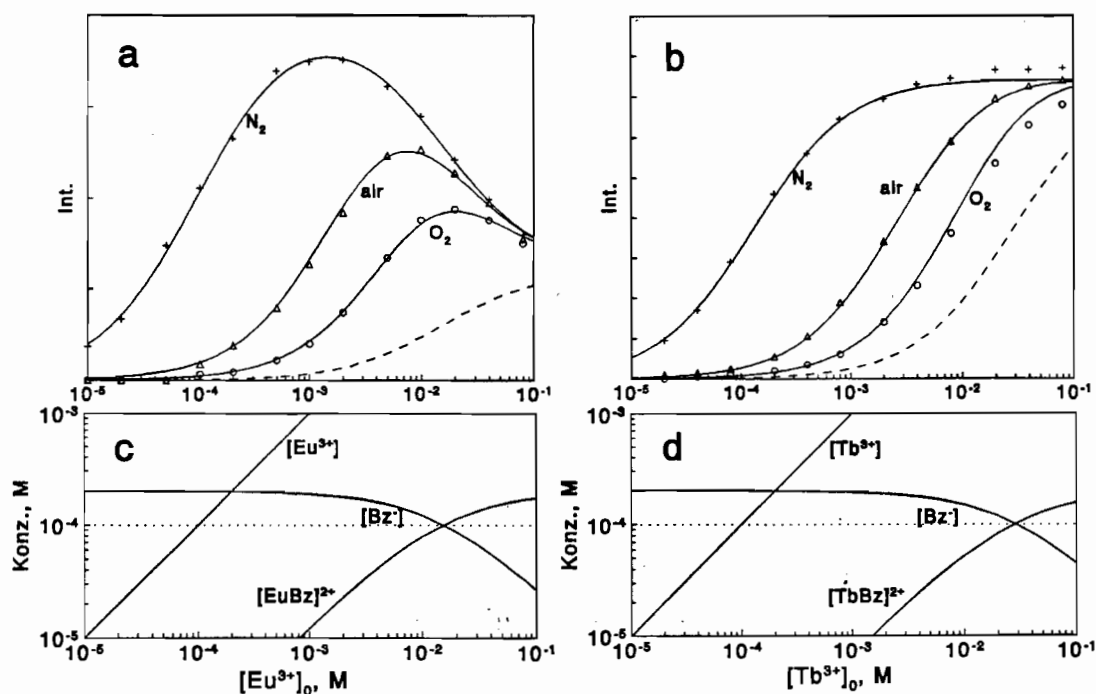
## 2. RESULTS AND DISCUSSION

### 2.1. Aqueous solutions

$\text{Eu}^{3+}$ : In solutions containing  $\text{Eu}^{3+}$  and benzoate the relative concentrations of free and coordinated benzoate are determined by the overall concentrations of ligand

and metal and by the complex formation constant. In aqueous solution with an ionic strength of 0.5 M we determined the stability constant of the 1:1 complex as  $65 \text{ M}^{-1}$ . Higher coordination does not occur under the conditions applied here. In Figure 1c the calculated concentrations of free and complexed benzoate are shown as a function of the overall concentration of  $\text{Eu}^{3+}$  ions in a typical luminescence titration run. For values of  $[\text{Eu}^{3+}]_0$  below  $10^{-3} \text{ M}$  the concentration of complexed benzoate is negligible.

Stationary luminescence spectra of  $\text{Eu}^{3+}$  were recorded in aqueous solutions with fixed concentration of benzoate and increasing concentration of  $\text{Eu}^{3+}$ . Excitation was effected in the first benzoate band at 262 nm, whereby it must be noted that the absorption of this band is enhanced by a factor of 1.5 when benzoate is coordinated to  $\text{Eu}^{3+}$ . The emission intensity resulting from corresponding solutions without benzoate is negligible. Thus all the luminescence described here is benzoate-sensitized. The luminescence intensity recorded for a  $\text{Eu}^{3+}$  concentration series is shown in Figure 1a for solutions saturated with nitrogen, air and oxygen, respectively. A comparison of the luminescence titration curves with the concentration profiles of free benzoate and 1:1 complex clearly shows that in oxygen free solutions the emission intensity reaches a maximum before a notable fraction of benzoate is complexed. This is clear indication of a dynamic pathway of energy transfer, occurring during diffusional encounters of excited free benzoate and  $\text{Eu}^{3+}$  ions. From the quenching



**Fig. 1** (a) Intensity of  $\text{Eu}^{3+}$  ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ ) emission at 593 nm sensitized through benzoate excitation at 262 nm in aqueous solutions with  $[\text{Bz}^-]_0 = 2 \times 10^{-4} \text{ M}$  and variable  $[\text{Eu}^{3+}]_0$ . Solutions were saturated with nitrogen, air, or oxygen, respectively. The curves shown are results of simulations (for details cf. text). The dashed curve is an extrapolation to infinite concentration of oxygen. (b) analogous diagram for the  $\text{Tb}^{3+}$ /benzoate system ( $\lambda_{\text{exc}} = 250 \text{ nm}$ ,  $\lambda_{\text{em}} = 545 \text{ nm}$ , corresponding to the  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$  transition). (c) calculated concentration profiles of  $\text{Bz}^-$ ,  $\text{Eu}^{3+}$  and  $(\text{EuBz})^{2+}$ . (d) analogous concentration profiles with  $\text{Tb}^{3+}$ .

effect of increasing concentrations of oxygen it must be concluded that sensitization at  $[\text{Eu}^{3+}]_0$  lower than  $10^{-3}$  M occurs via the lowest benzoate triplet state.

We note here that observations of the benzoate triplet in liquid solution at room temperature have not been reported so far. In laser flash experiments with benzoate solutions we were able to detect a transient absorption with a maximum at 310 nm that can be assigned to the benzoate triplet. In oxygen free solution this transient has a life time of 50  $\mu\text{s}$ . Its quenching by  $\text{Eu}^{3+}$  ions could be directly observed. The rate constant is in the range of  $2\text{--}10 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ , showing a marked decrease with increasing ionic strength.

The intensity of benzoate sensitized  $\text{Eu}^{3+}$  luminescence decreases at higher  $\text{Eu}^{3+}$  concentrations. At the same time, the susceptibility to oxygen quenching decreases. At concentrations higher than about  $10^{-1}$  M of  $\text{Eu}^{3+}$  where all benzoate is coordinated to  $\text{Eu}^{3+}$  the luminescence is no longer quenched by oxygen. This behaviour is consistent with fast 'static' energy transfer from the benzoate ligand to the central ion. Once the excitation has been transferred to  $\text{Eu}^{3+}$  it is no longer quenched by oxygen as can be shown in experiments with direct photoexcitation of  $\text{Eu}^{3+}$ . The pronounced decrease of luminescence going along with the switchover from dynamic to static energy transfer indicates the surprising fact that the static route of energy transfer is less effective than the dynamic one. The observations can be quantitatively accounted for by a simulation based on the following model:

- light absorption by free benzoate produces benzoate triplet  ${}^3\text{B}_z^-$  (quantum yield  $\phi_B$ , decay rate constant  $k_0$ ) which may be quenched by oxygen with rate constant  $K_{\text{O}_2}$  or transfer energy to  $\text{Eu}^{3+}$  with rate constant  $k_{\text{et}}$ , whereafter emission follows with quantum yield  $\phi_{f,0}$ .
- light absorption by benzoate bound as  $(\text{EuBz})^{2+}$  produces the emissive state of  $\text{Eu}^{3+}$  with a quantum yield of  $\phi_{K,1}$ . Subsequent emission of the  $(\text{EuBz})^{2+}$  complex has a quantum yield  $\phi_{f,1}$ , and is unquenched by oxygen.

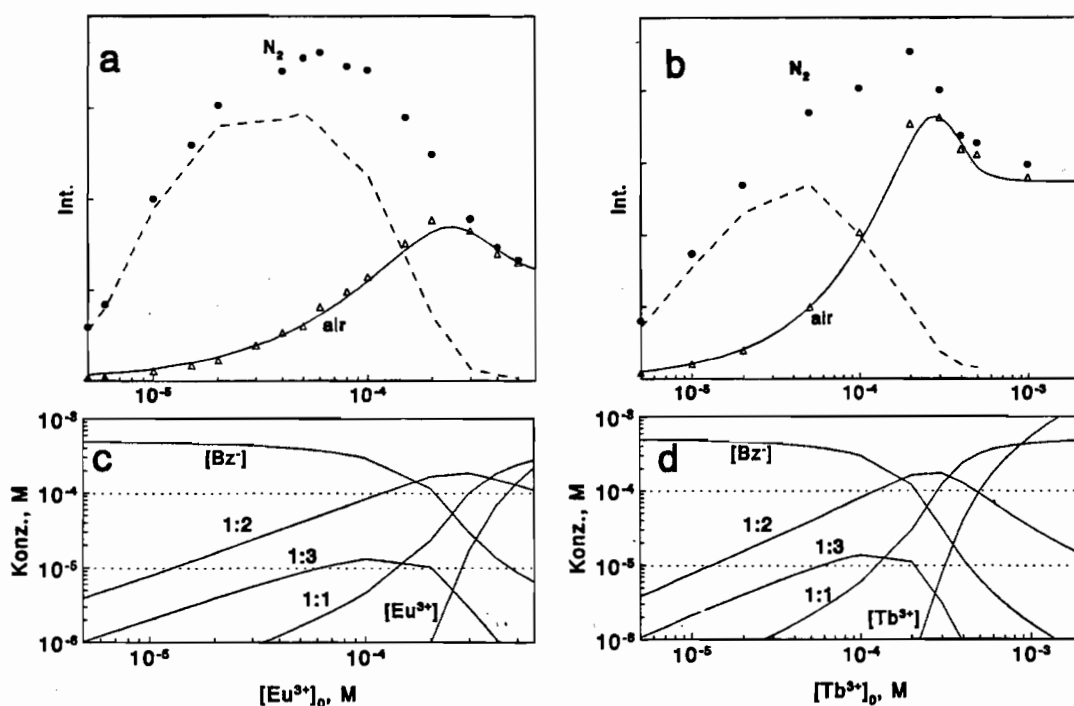
The curves shown in Figure 1a were obtained on the basis of this model with the following parameters:  $k_{\text{et}}/k_0 = 10^4 \text{ M}^{-1}$ ,  $K_{\text{O}_2}/k_0 = 7 \times 10^4 \text{ M}^{-1}$ ,  $(\phi_B\phi_{f,0})/(\phi_{K,1}\phi_{f,1}) = 3$ . The value of  $k_{\text{et}}/k_0$  is in fair agreement with the values determined by laser flash photolysis. The value of 3 for the ratio  $(\phi_B\phi_{f,0})/(\phi_{K,1}\phi_{f,1})$  indicates that the dynamic sensitization is much more efficient than the static one. Since it follows from arguments provided below, that the values of  $\phi_{f,0}$  and  $\phi_{f,1}$  are probably very similar, the main cause for the detected difference in the two pathways of sensitization lies in the difference of  $\phi_B$  and  $\phi_{K,1}$  that can be identified with the triplet formation yields of benzoate in free and complexed state. We suggest that the lower triplet yield of benzoate in the complexed state is due to CT-quenching of excited benzoate singlet in contact with  $\text{Eu}^{3+}$ . Indeed, as evidenced from its redoxpotential ( $E_{\text{Eu}^{2+}/\text{Eu}^{3+}}^0 = -0.43 \text{ V}$ ) and LMCT absorption bands observed even for the  $\text{Eu}^{3+}$ -aquo complex,  $\text{Eu}^{3+}$  has sufficient oxidation power. Moreover, as we could show by the excitation spectrum of directly excited  $\text{Eu}^{3+}$ -emission, excitations of the LMCT transitions do not lead in their deactivation pathway to a population of the emissive  $\text{Eu}^{3+}$  states.

$\text{Tb}^{3+}$ :  $\text{Tb}^{3+}$  is very similar to  $\text{Eu}^{3+}$  in its complex forming properties. In water we found a value of  $35 \text{ M}^{-1}$  for the stability constant of the 1:1 complex with benzoate.

With  $Tb^{3+}$  the analogous experiments as with  $Eu^{3+}$  led to the results shown in Figure 1b. Again, effective sensitization is already observed in regions of  $[Tb^{3+}]_0$  where no benzoate complexation takes place, and this luminescence, too, is quenched by oxygen. However, in the region of  $[Tb^{3+}]_0$  where complexation of benzoate occurs, no reduction of luminescence intensity is found. Again, the observed behaviour can be quantitatively modeled by the processes described for  $Eu^{3+}$ . The essential difference to  $Eu^{3+}$  is that for  $Tb^{3+}$  *the dynamic and the static pathway of sensitization are exactly equal*. Because  $Tb^{3+}$  is not an oxidant, this finding supports our above given explanation of CT-quenching as the reason for reduced efficiency of static sensitization in the case of  $(EuBz)^{2+}$ . The rate constant for dynamic triplet energy transfer from free benzoate triplets to  $Tb^{3+}$  is of the same order of magnitude as with  $Eu^{3+}$ .

## 2.2 Methanol solutions

Since the stability of benzoate and lanthanoid ion complexes is largely determined by electrostatic interactions, their stability is considerably higher in a less polar solvent such as methanol. In this solvent not only 1:1 complexes are readily formed but also 1:2 and 1:3 complexes. Their relative contributions as functions of  $[Eu^{3+}]_0$  and  $[Tb^{3+}]_0$  are represented in Figures 2c and 2d. The values are based on calculations using the equilibrium constants given in ref. [4]. For the given concentration of benzoate, the 1:2 complex is the most stable at low concentrations of the metal ion. As the metal concentration increases the concentration of the 1:2 complex passes



**Fig. 2** (a) Luminescence titration with  $Eu^{3+}$  in methanol. The curve drawn through the points for air saturated solution was obtained by a simulation of static energy transfer only, accounting for the relative concentrations of the various complexes. The dashed curve obtained as the difference between the results for oxygen free and air saturated solution represents the fraction of dynamic energy transfer. (b) analogous diagram for  $Tb^{3+}$ . (c) Concentration profiles of benzoate,  $Eu^{3+}$  and various complexes, calculated with the equilibrium constants given in ref. [4]. (d) analogous diagram for  $Tb^{3+}$ .

through a maximum after which the 1:1 complex takes over the dominating role. It is important to note that in methanol the metal concentration where complexation of free benzoate sets on, is by about 2 orders of magnitude lower than in water. This means that in methanol the switchover from dynamic to static energy transfer occurs at much lower metal concentrations, where oxygen can compete much more effectively with the metal ions for the free benzoate triplet. This behaviour is clearly borne out by the luminescence titration curves in methanol (cf. Figs. 2a,b). We note that the limit of the quenching effect of oxygen is already reached with air saturated solutions because not only is the metal concentration where complexation starts much lower than in water, but also the solubility of oxygen is higher by a factor of 7.5 in methanol [5] than in water. The solid curves signify energy transfer being exclusively due to the static transfer mechanism. It is noteworthy that the efficiency of static energy transfer passes through a maximum for both  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$ . Comparing this with the change of concentrations of the respective forms of the complexes, the qualitative conclusion is that exciting benzoate in the 1:2 complex leads to a higher emission yield than in case of the 1:1 complex. Relative values of the products  $(\phi_{B,i}\phi_{f,i})$ , where the index  $i$  refers to the number of benzoate ligands, could be estimated by a pertinent quantitative simulation accounting for the absorptions of the three variants of complexes. This simulation resulted in relative values for  $(\phi_{B,i}\phi_{f,i})$  of 1:2:(5) for  $i=1,2,3$  in the case of  $\text{Eu}^{3+}$  and 1:1.7:(3.3) in the case of  $\text{Tb}^{3+}$ . The values in parentheses referring to the 1:3 complexes must be considered as very rough estimates. Nevertheless, it is a clear trend that the relative values for the product  $(\phi_{B,i}\phi_{f,i})$  increase with the number of benzoate ligands at one center. We assume that it is not so much the triplet formation yield that is sensitive to the number of ligands, but rather that the quantum yield  $\phi_{f,i}$  of  $\text{Eu}^{3+}$ - emission in a complex increases with the number of benzoate ligands. This explanation refers to the well known role of OH vibrations of coordinated solvent molecules in the radiationless deactivation of the emissive states of the lanthanoid ions [6]. The more solvent molecules are replaced by other ligands, the more the radiationless decay should be disfavoured.

The dynamic part of sensitization in methanol is represented by the dashed curves in Figures 2 a, b. In the case of  $\text{Eu}^{3+}$  the maximum of the dynamic part clearly exceeds that of the static one, meaning that the CT-quenching of bound benzoate by  $\text{Eu}^{3+}$  suggested to account for the behaviour in water is also active in methanol, which does not seem surprising. In the case of  $\text{Tb}^{3+}$  the maximum of the dynamic contribution stays somewhat below the value that can be assigned to the 1:1 complex (cf.  $[\text{Tb}^{3+}] \geq 10^{-3}$  M in Fig. 2b). However, accounting for the fact that for a  $\text{Tb}^{3+}$  concentration where the maximum of the dynamic curve is reached there is already some competence by the static mechanism, one can estimate that the  $(\phi_{B,i}\phi_{f,i})$  products for  $i=0$  (i.e. the dynamic mechanism) and  $i=1$  (static mechanism in the 1:1 complex) are about the same, just like in water.

### 3. CONCLUSION

We have shown that studies of energy transfer from weakly complexing ligands to luminescing lanthanoid ions provide an interesting possibility to differentiate several

pathways of luminescence sensitization and yield valuable insights into the conditions determining their efficiency. Of particular interest is the case of  $\text{Eu}^{3+}$  where it is more favorable to excite the uncoordinated energy donor than the coordinated one. The likely possibility of CT-quenching of the excited coordinated donor has been pointed out. However, this effect is partially made up for by higher fluorescence quantum yields in higher coordinated complexes.

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