

photoexcitation with a uranyl nitrate flash filter solution<sup>10</sup> (which transmitted throughout the bromine absorption band and thus led to both  $^2P_{3/2}$  and  $^2P_{1/2}$  atoms) and with a potassium chromate-dichromate flash filter solution which transmitted only above the 511-nm convergence limit for bromine<sup>41</sup> (1% at 516 nm, 4% at 520 nm, 55% at 540 nm), so that only ground-state bromine atoms were produced. Within the rather large experimental errors, the two quantum yields were identical (0.31 vs. 0.38). Although some reactions involving only  $^2P_{1/2}$  halogen atoms have been observed with photolysis above the convergence limit,<sup>42</sup> the effect

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is strongly wavelength dependent and extends only a few kilojoules into the banded region. It is thus concluded that photobromination of benzene resulting in this work is not initiated solely by excited bromine atoms.

Although the gas-phase formation constant is not known for either the molecular or atomic bromine complex with benzene, it is highly unlikely that either complex could be present in sufficiently high concentration to participate in the bromination reactions to the extent observed, again unless a very efficient chain process results. The fact that good second-order kinetic plots result from assuming that all of the bromine loss occurs during the flash ( $<75 \mu\text{sec}$ ), with all third bodies used and under all flash conditions, suggests, however, that some species other than  $^2P_{3/2}$  bromine atoms initiate the irreversible photobromination.

## Fluorescence Studies of Europium(III) and *o*-Benzoylbenzoate in Ethanol-Water Solution

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**Abstract:** Fluorescence measurements on ethanol-water solutions of europium(III) and *o*-benzoylbenzoate (*o*-BB) have shown that energy transfer takes place from the organic ligand to the europium ion followed by narrow line emission characteristic of the lanthanide ion. From the intensities of the emission line at 590 nm, stability constants for the Eu(*o*-BB) complex have been calculated, and these constants are in agreement with those determined by potentiometry. The results are interpreted to indicate that energy transfer takes place only when a complex is formed between the ligand and lanthanide ion. No energy transfer is observed in strongly acid solution, conditions in which complex formation is negligible.

Since the first observance of energy transfer from an organic absorber to a rare-earth ion with subsequent narrow line emission,<sup>1</sup> extensive investigation has been carried out on such systems, stimulated by the interest in liquid laser devices. Evidence for both intermolecular and intramolecular energy transfer has been obtained. The investigation of energy transfer within rare-earth chelates has established that intramolecular energy transfer takes place between the excited triplet state of the ligand and a resonance level of the metal ion.<sup>2-4</sup> Actinide chelates show a similar behavior.<sup>5</sup> Several groups have observed transfer of energy between aromatic ketones and lanthanide ions in organic liquid solutions.<sup>6-8</sup> Heller and Wasserman<sup>6</sup> suggested that in these cases the energy transfer takes place *via* a second-order diffusion-controlled mechanism, *i.e.*, an intermolecular transfer process. Energy transfer from

benzophenone to tris(hexafluoroacetylacetonato)europium(III) was shown to take place through an intermolecular mechanism from ketone to ligand followed by an intramolecular energy transfer from ligand to metal ion.<sup>9</sup> Both intermolecular energy transfer<sup>10</sup> and intramolecular energy<sup>11,12</sup> transfer have been utilized in the analysis of low concentrations of luminescent rare-earth ions.

Relatively few investigations have been carried out on aqueous systems. A study of the fluorescence of europium(III) in aqueous solution in the presence of potential ligands such as  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , ethylenediaminetetraacetate (EDTA), and diethylenetriaminepentaacetate (DTPA) showed that complexation caused a general intensification of the spectra, a shift to longer wavelengths, and increased crystal field splitting.<sup>13</sup> This effect was particularly marked for strongly chelating ligands such as EDTA and DTPA. In these cases, however, no energy transfer from ligand to the europium ion was observed. In aqueous solutions containing

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*p*-benzoylbenzoate and ethylenediaminetetraacetatoeuropium(III), energy absorbed by the *p*-benzoylbenzoate was transferred to an appreciable extent to the europium complex followed by luminescence characteristic of the complex.<sup>14</sup> It was suggested that the fluorescence resulted from an intermolecular energy transfer from *p*-benzoylbenzoate to Eu(EDTA)<sup>-</sup> ions. In the same investigation energy transfer was found not to take place when *o*- or *m*-benzoylbenzoates replaced the *p*-benzoylbenzoate. Energy transfer has also been demonstrated between the uranyl ion and europium(III) in D<sub>2</sub>O solution.<sup>15</sup> Again, the mechanism suggested involved intermolecular energy transfer on collision. In a study of the use of rare-earth ions as probes for excited molecules in aqueous solution, Lamola and Eisinger<sup>16</sup> found energy transfer from acetophenone, thymidylic acid, guanidylic acid, and orotic acid to Eu<sup>3+</sup>. They proposed intermolecular transfer and a diffusion-controlled mechanism.

This paper presents the results of a study of energy transfer from *o*-benzoylbenzoate to europium(III) in ethanol-water solution. Since europium forms a complex with the anion, the possibility that energy transfer takes place only in the complex was investigated. The stability constants for the Eu(*o*-BB) complexes were determined by potentiometry, and these values were used in conjunction with the results of the luminescence studies to provide information concerning the energy-transfer mechanism and the application of fluorimetry to the determination of stability constants in such systems.

## Experimental Section

**Preparation of Solutions. Europium Perchlorate.** Eu<sub>2</sub>O<sub>3</sub> (99.99% from Michigan Chemical Co.) was dissolved in a minimum of concentrated HClO<sub>4</sub>. To remove the excess acid the solution was repeatedly evaporated to a paste and rediluted with distilled water. The final solution of pH ~5 was standardized by passing a sample through an ion-exchange column and titrating with NaOH.

**Sodium Perchlorate.** NaOH was titrated with perchloric acid to neutrality to produce a stock solution of [NaClO<sub>4</sub>] ~6 M. The solution was standardized as above.

**Sodium *o*-Benzoylbenzoate and *o*-Benzoylbenzoic Acid.** The reagent grade acid, obtained from K & K laboratories, was dissolved in dilute aqueous NaOH and precipitated with HCl. The procedure was repeated and the final product recrystallized from ethanol-water. Melting point determination indicated a pure compound and hence solutions were prepared by accurately weighing samples of the acid and bringing to a known volume.

**Buffer Solutions for pH Titration and Fluorescence Measurements.** Buffer solutions were prepared by partially neutralizing the *o*-benzoylbenzoic acid with sodium hydroxide and bringing the solutions to ionic strength 1.0 by addition of sodium perchlorate. Measurements were made on solutions of two different solvent compositions, ethanol-water = 1:1 and 2:1 by volume. All solutions were carefully adjusted to the appropriate solvent composition.

**Solutions for Fluorescence Measurements.** These solutions contained a total [*o*-benzoylbenzoic acid] + [sodium *o*-benzoylbenzoate] of 0.00300 M, and the concentrations of the acid and the salt were approximately equal. The [Eu(ClO<sub>4</sub>)<sub>3</sub>] varied from 0.00156 to 0.0472 M. For each series of solutions the pH was carefully checked and brought to a constant value close to the pK of the *o*-benzoylbenzoic acid. The pK of the acid in each solvent composition was determined by pH titration. In ethanol-water = 1:1 pK<sub>A</sub> = 4.48, and in ethanol-water = 2:1 pK<sub>A</sub> = 4.65. These values were used to calculate the exact ratio of the concentrations of *o*-benzoylbenzoic acid and its salt for each series of measurements.

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**Fluorescence Measurements.** All fluorescence measurements are made on an Aminco Bowman spectrophotofluorometer with thermostated cell compartment at a temperature of 25.0 ± 0.2°. Slits were adjusted to provide the optimum signal strength and resolution, and a photomultiplier tube with an S-20 response was used to detect the signal.

It was found that bubbling nitrogen (saturated with the solvent) through the solution had little effect on the emission intensity. In preliminary measurements, it was noted that when the sample was exposed to the light source in the instrument the emission intensities gradually decreased. In subsequent experiments the cell was placed in the path of the uv excitation beam only long enough to measure the spectrum. Under these circumstances the decrease in intensity was negligible.

**pH Measurements.** All pH measurements were made on a Corning Model 12 pH research pH meter. The KCl solution of the calomel reference electrode was replaced by saturated sodium chloride solution since precipitation of KClO<sub>4</sub> at the electrode junction resulted in unstable readings. This produced stable, reproducible readings. All pH measurements were made at 25.0 ± 0.2°.

**Determination of Stability Constants.** Stability constants for the europium *o*-benzoylbenzoate complexes were determined using the method described by Choppin and Chopoorian.<sup>17</sup> The concentration of uncomplexed *o*-benzoylbenzoate ion in the equilibrium solutions was calculated from pH measurements using the equation

$$L = \frac{[H]'}{[H]} \left( C_L' + \frac{C_H - [H] + (1 + \delta)[H]'}{\delta} \right)$$

$C_L'$  = stoichiometric concentration of the sodium salt of the ligand,  $C_{HL}'$  = stoichiometric concentration of the protolyzed ligand,  $[H]'$  = is the hydrogen ion concentration in the buffer solution,  $[H]$  = is the hydrogen ion concentration in the presence of the europium ions,  $C_H$  = is a correction to account for any free HClO<sub>4</sub> introduced into the buffer solution along with the europium ions,  $C_{HL}'/C_L' = \delta$ .

$\bar{n}$ , the average number of ligands bound to a metal ion in the equilibrium mixture, is calculated from

$$\bar{n} = \frac{C_L' + [H] - C_H - [L]}{C_M}$$

where  $C_M$  is the total metal concentration.

The formation constants are calculated using the equation

$$\frac{\bar{n}}{[L]} = \frac{\sum_{n=1}^N n\beta_n[L]^{n-1}}{1 + \sum_{n=1}^N \beta_n[L]^n}$$

where

$$\beta_N = \frac{[ML_N]}{[M][L]^N}$$

The values of the constants were calculated by a nonlinear general least-squares program on an IBM 360-40 computer. The method of calculation was checked by using published data and the procedure was checked by determination of stability constants for complexes for which extensive literature data were available.

For each determination 50 ml of 1.0 M NaClO<sub>4</sub> solution at the particular solvent composition was titrated with 10 ml of buffer solution. After the addition of each increment of buffer solution the pH was measured. The procedure was repeated except that the solution titrated contained Eu(ClO<sub>4</sub>)<sub>3</sub> ~ 0.04 M at ionic strength 1.0 at the same solvent composition. The overall procedure was repeated several times. Values quoted in Table I are an average of several determinations.

## Results and Discussion

**Fluorescence Measurements.** The emission and excitation spectra of Eu(ClO<sub>4</sub>)<sub>3</sub> in EtOH-H<sub>2</sub>O solution are shown in Figure 1 and the corresponding spectra for *o*-benzoylbenzoate-*o*-benzoylbenzoic acid in Figure 2. Typical excitation and emission spectra of a mixture of

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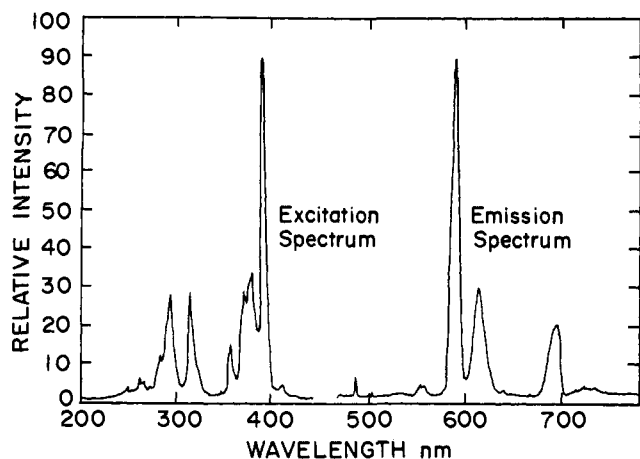


Figure 1. Emission and excitation spectra of  $\text{Eu}(\text{ClO}_4)_3$  in a 1:1 ethanol-water solution.  $[\text{Eu}(\text{ClO}_4)_3] = 0.1 \text{ M}$ .

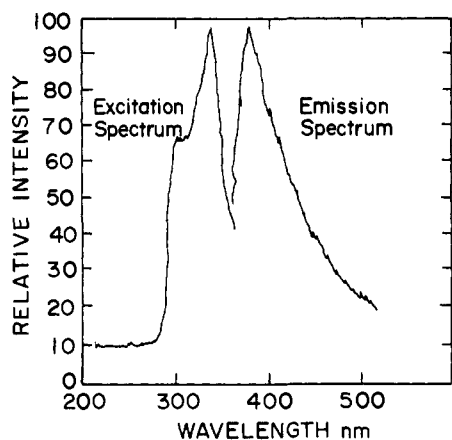


Figure 2. Emission and excitation spectra of a mixture of *o*-benzoylbenzoate (0.0015 M) and *o*-benzoylbenzoic acid (0.0015 M) in a 1:1 ethanol-water solution.

Table I. Stability Constants

Solvent	Fluorescence data $K_1, \text{l. mol}^{-1}$	pH titration	
		$K_1, \text{l. mol}^{-1}$	$K_2, \text{l. mol}^{-1}$
50% $\text{H}_2\text{O}$ -50% EtOH	$143 \pm 10$	$147 \pm 10$	$80 \pm 15$
33.3% $\text{H}_2\text{O}$ -66.7% EtOH	$334 \pm 20$	$336 \pm 9$	$119 \pm 13$

$\text{Eu}(\text{ClO}_4)_3$  and the *o*-benzoylbenzoate buffer are given in Figure 3. In this figure the excitation spectra is for the europium emission at 590 nm, while the emission spectra was measured with the excitation wavelength set at  $\lambda$  320 nm, the maximum in the excitation spectra. Figure 1 indicates that at this excitation wavelength the emission intensity of  $\text{Eu}^{3+}$  itself is small, while Figure 2 indicates that 320 nm is an effective wavelength for the excitation of *o*-benzoylbenzoate. The excitation spectrum of  $\text{Eu}^{3+}$  in the mixture is essentially the same as that of *o*-benzoylbenzoate except for the small peak at 390 nm which is for the direct excitation of  $\text{Eu}(\text{III})$ . Thus, it can be concluded that energy transfer is taking place between the absorbing benzoylbenzoate and the emitting europium(III). In Figure 3 there is no evidence of emission from the organic absorber itself. This cannot be taken as evidence for quenching by the metal ion, since even if quenching did not take place, the weak

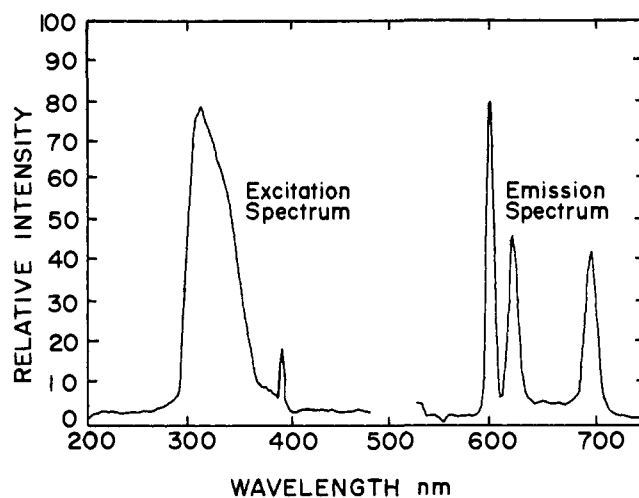


Figure 3. Emission and excitation spectra of a mixture of *o*-benzoylbenzoate (0.0015 M) and  $\text{Eu}(\text{ClO}_4)_3$  (0.00625 M) in a 1:1 ethanol-water solution.

emission of *o*-benzoylbenzoate would not be detected with instrumental settings employed in these measurements.

Another feature of importance in Figure 3 is the emission spectrum of the europium. Compared to the emission spectrum of Figure 1, in the presence of the benzoylbenzoate the intensity of the emission peak of 615 nm is considerably increased relative to the intensity of peak at 590 nm. Electrical dipole transitions are more sensitive to changes in the symmetry of the ion than are magnetic dipole transitions,<sup>13</sup> and hence the change in relative intensity indicates that the symmetry of the environment of the  $\text{Eu}^{3+}$  is affected by the presence of the ligand. As the concentration of the ligand is increased, the spectral changes become more pronounced. These efforts suggest that the *o*-benzoylbenzoate is complexing with the metal ion.

If energy is transferred only when the europium is complexed, then it can be assumed that the intensity of emission is proportional to the concentration of the complex providing that the excitation wavelength is such that no direct excitation of europium takes place; i.e.,  $I = \alpha[\text{complex}]$ . Concentrations were adjusted so that  $[\text{o-benzoylbenzoate}]$  was always less than  $[\text{Eu}^{3+}]$  and the concentration of  $\text{Eu}(\text{o-BB})_2^+$  was negligible.

Under these circumstances

$$\frac{1}{I} = \frac{1}{\alpha[\text{o-BB}]_T} \left( \frac{1}{K_1[\text{Eu}^{3+}]} + 1 \right) \quad (1)$$

where  $K$  is the equilibrium constant

$$K = \frac{[\text{Eu}(\text{o-BB})_2^+]}{[\text{Eu}^{3+}][\text{o-BB}^-]}$$

$[\text{o-BB}]_T$  is the stoichiometric concentration of the anionic ligand and  $[\text{Eu}^{3+}]$  is the concentration of uncomplexed europium.

The concentration of *o*-benzoylbenzoate was held constant while the europium concentration was varied. In each case the emission intensity  $I$  at  $\lambda$  590 nm was measured while the system was excited at  $\lambda$  320 nm.

$1/I$  was plotted against  $1/[\text{Eu}^{3+}]_{\text{total}}$  (see Figure 4) and approximate values of  $\alpha$  and  $k$  were determined. Corrections were then made to account for the fraction

of europium(III) which was in the form of the complex and a new set of values was calculated. After three corrections, no further refinements were necessary and the final values were obtained.

The whole series of measurements was repeated using new solutions and at the different solvent compositions. The values quoted in Table I are an average of three separate determinations.

The correlation between the two sets of values supports the suggestion that the energy transfer takes place through complex formation between the ligand and the metal ion.

When a mixture of *o*-benzoylbenzoate and  $\text{Eu}^{3+}$  is acidified, energy transfer ceases, and the excitation and emission spectra of  $\text{Eu}^{3+}$  are identical with that of a  $\text{Eu}(\text{ClO}_4)_3$  solution. The protonation of the ligand reduces complex formation and at the same time reduces energy transfer.

It must be pointed out that the fluorescence data are not inconsistent with eq 2 which is derived without consideration of complex formation<sup>15,18</sup>

$$\frac{1}{I} = \frac{1}{G[\text{o-BB}^-]} \left( 1 + \frac{1}{\gamma_0 k_2 [\text{Eu}^{3+}]} \right) \quad (2)$$

where  $k_2$  is the collision rate,  $\gamma_0$  is the lifetime of the excited state of *o*-benzoylbenzoate, and  $G$  is a factor depending on geometry and fluorescence yield.

However, even for systems for which a diffusion-controlled mechanism has been suggested, the experimental value of  $k_2$  is often less than the diffusion rate constant. Although the concentration dependence indicated by eq 2 is obeyed, a simple collision mechanism may be only an approximation and other factors may be important. For example, in acetone solution, energy transfer between  $\text{Tb}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Eu}^{3+}$ , and substituted organic molecules shows a dependence on the presence of a group with an unshared electron pair.<sup>19</sup> A different study in acetone solution showed that efficiency of energy transfer from organic carbonyl compounds to  $\text{Eu}^{3+}$  depends on the electron density of the

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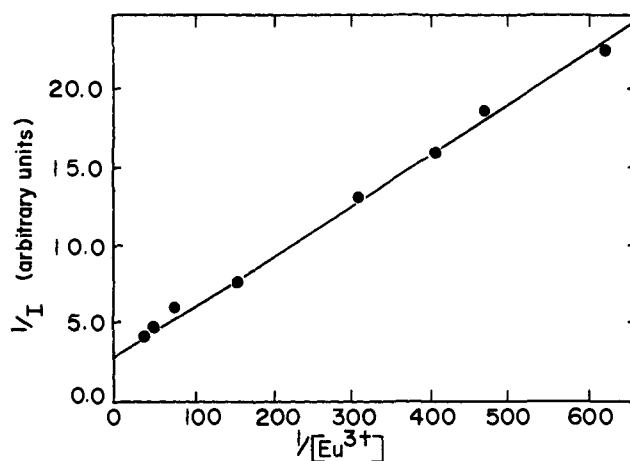


Figure 4.  $1/I$  vs.  $1/[\text{Eu}^{3+}]_{\text{total}}$ : [*o*-benzoylbenzoate] = 0.0165 M; [*o*-benzoylbenzoic acid] = 0.0135 M; solvent = 1:1 ethanol-water.

carbonyl group.<sup>20</sup> Recently, Morina<sup>21</sup> demonstrated that the rate constant for energy transfer between benzophenone and derivatives and  $\text{Eu}^{3+}$  in acetone and methanol depended on the overlap of orbitals of the donor and acceptor.

In the transfer of energy from *o*-benzoylbenzoate to europium(III) in ethanol-water solution, the important factor is the formation of a complex between the ligand donor and the metal ion acceptor. The ability of the *o*-benzoylbenzoate to transfer energy to  $\text{Eu}^{3+}$  contrasts with its failure to transfer energy to  $\text{EuEDTA}$ .<sup>14</sup> We feel that this is indicative of the inability of the *o*-benzoylbenzoate to form a complex with  $\text{EuEDTA}$  rather than its tendency to dissipate energy to the solution.

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