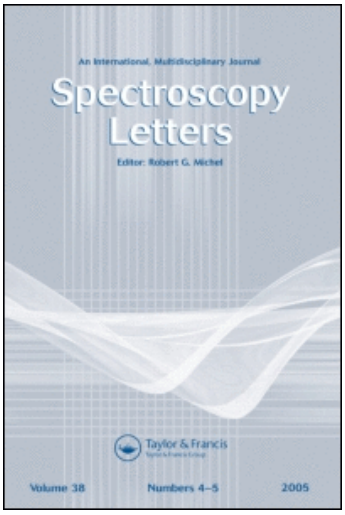

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TIME-RESOLVED LUMINESCENCE OF EU(III)/THENOYLTRIFLUOROACETONE/SURFACTANT SYSTEMS IN AQUEOUS SOLUTIONS

Keywords : Energy Transfer, Time-Resolved Luminescence, Europium Complex, Micelle

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ABSTRACT

Temporal developing of photoemission of Europium(III)-Thenoyltrifluoroacetone complex in micelle solutions was investigated. From steady-state fluorescence and phosphorescence excitation, steady-state and time-resolved emission spectra and decay curves it was found that not only $^5D_0$ triplet level but $^5D_1$ triplet level of Europium(III) also plays role in the energy transfer from the ligand to the Europium(III) ion.

INTRODUCTION

The Eu(III)- β-dichetone chelates has been studied since energy transfer in these systems was reported by Weissman [1]. These complexes are in the front of interest nowadays also. Detection of ultratrace amounts of materials has fundamental importance in clinical diagnostics and

environmental researches. Eu(III) is one of the most frequently used lanthanide ion in the fluoroimmunoassays [2, 3, 4, 5]. In chelates it has decay times in the sub-millisecond region, thus the phosphorescence of Eu(III) can be separated well in time from the luminescence of conventional fluorophores (fluorescein, rhodamine etc.) using time-resolution. The separation in time and spectral domain make the detection of extremely low amount of Eu(III) possible from solutions containing other lanthanides (Tb(III), Sm(III)) [6, 7, 8, 9, 10, 11, 12]. Numerous applications support the investigations of luminescence properties of Eu(III)-complexes.

In this work luminescence of Eu/Thenoyltrifluoroacetone/Triton X-100 (Eu/TTA/TX-100) and Eu/TTA/Sodium Dodecyl Sulphate (Eu/TTA/SDS) systems are studied. We chose these compounds because: (1) among β-dichetones TTA can produce one of the highest energy transfer yield; (2) TX-100 is a frequently used non-ionic detergent in the investigations of Eu(III)- β-dichetone complexes, because the luminescence intensity of Eu(III) emission is usually higher than in the case of other detergents [7, 11, 13]; (3) SDS is also an often used ionic detergent in the study Eu(III)- β-dichetone systems.

EXPERIMENTAL DETAILS

Reagents and Procedures. $Eu_2(SO_4)_3$, TTA, TX-100 and SLS were purchased from Fluka and used without any further purification. The concentrations of stock solutions were as follows : Eu(III), $1x10^{-3}$M; TTA, $1x10^{-3}$M; TX-100, $5x10^{-2}$M; SDS, $5x10^{-2}$M. The stock solutions of Eu(III) and the detergents were made by dissolving the appropriate amount of reagents in bidistilled, deionized water. The TTA was dissolved first in ethanol ($1x10^{-2}$M) then this solution was diluted with water to $1x10^{-3}$M concentration.

To a 10-ml test tube solutions were added in the following order : Eu(III) ion, TTA, detergent and bidistilled water. The measuring solutions were thoroughly shaken and left for one day before taking measurements. They contained : $1x10^{-5}$M Eu(III) (if present), $1x10^{-4}$M TTA, $5x10^{-3}$M TX-100 (or $1.5x10^{-2}$M SDS). The pH values were between 5.8 and 6.5 without any further buffering. We used the least chemical components in

the investigations, thus we neglected adding buffer which was not necessary because of the proper pH values. It is known from [11] that in the 5.5-7.0 pH region the luminescence intensity of Eu(III)/TTA/TX-100 system is nearly constant. On the other hand, the type of buffer has great influence on the luminescence [11]. In some cases it is quenched completely (e.g. citrate or phosphate buffers). The presence of metal ions (e.g. in NaOH) influences the measures and thus the inner structure of micelles [14]. It was advisable to neglect adding buffer in order to be able to identify clearly the spectral and temporal components.

The extremely wide range of the quality and quantity of the buffers used is one of the main reasons that in the literature there are differences in the published absorption, excitation and emission spectra [6, 7, 8, 9, 11, 12, 13]. This fact also induced us to use as few components as possible.

Apparatus. The steady-state excitation and emission spectra were measured on a HITACHI 650-60 spectrofluorimeter at room temperature. The decay curves and the time-resolved emission spectra were obtained by a boxcar-based laser-luminescence spectrometer developed in our laboratory (Figure 1.). The excitation source was a TEA N_2 laser. Its operating parameters are: wavelength=337.1nm, pulse duration=1.0ns, energy/pulse=150 μJ, repetition rate=10-25 Hz. Photoemission was dispersed by a grating monochromator and detected by an RCA 1P28 photomultiplier. Signal processing was achieved by an SRS boxcar integrator, which consisted of the following units : SR250 gated integrator, SR255 fast sampler, SR235 analog processor, SR245 computer interface and SR280 system mainframe. Boxcar integrator and the stepping motor of the monochromator was controlled by a personal computer. In this configuration the system is capable to determine decay times between 0.5ns and 10ms.

Both time-resolved and steady-state measurements were carried out at relatively narrow slit positions to have proper resolution spectra, because the main purpose was a spectroscopic one (to follow up processes in the Eu/TTA system) and not an analytical (to determine ultratrace amount of Eu(III)). Despite this fact the time-resolved spectrometer detected 10^{-15} mol Eu(III) in the active sample volume. It is not the detection limit of course. In an optimized solution (containing - among others - Tb(III), phenanthroline) the limit is under 10^{-18} mol Eu(III) for this setup.

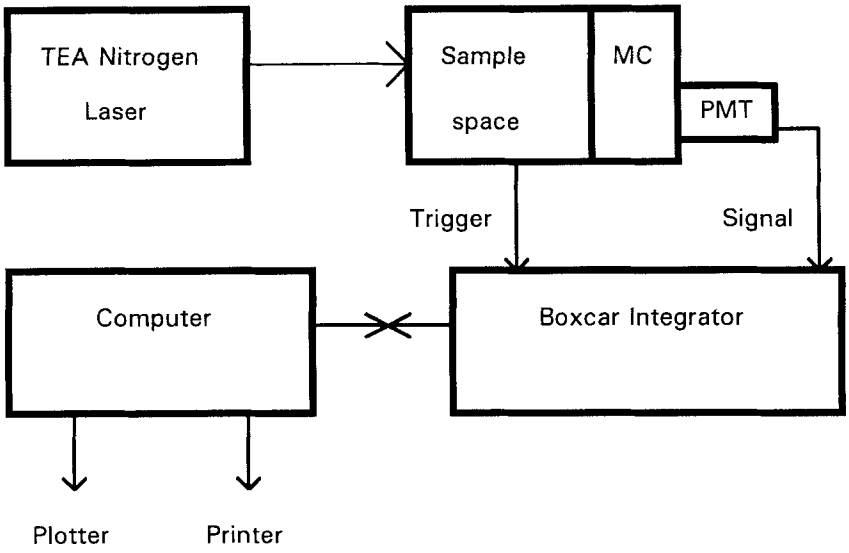


Fig. 1. Schematic diagram of the laser luminescence spectrometer used for time-resolved measurements. MC = monochromator, PMT = photomultiplier tube, TEA = transversally excited atmospheric pressure.

RESULTS AND DISCUSSION

Figure 2. shows the excitation spectra of Eu(III)/TTA/TX-100 and Eu(III)/TTA/SDS at the emission wavelength of 615nm. Not taking into account some small differences the two spectra are very similar.

These spectra belong - almost in 100% - to the Eu(III)/TTA complex. (Not in 100%, because TTA molecules being next to the Eu(III)/TTA complex can transfer some energy towards Eu(III), thus they contribute to the excitation spectra in a few percent.) In the case of the two detergents the emission intensities at 615nm emission of Eu(III) relative to the emission intensity of TTA differ significantly (Table 1.).

There are two main reasons of this fact: (1) in SDS the deactivation of T_1 triplet level of TTA by the O-H vibrations of the H_2O solvent molecules is stronger, thus the yield of energy transfer towards the Eu(III) is lower; (2) in SDS there are fewer TTA molecules surrounding the Eu(III) atoms

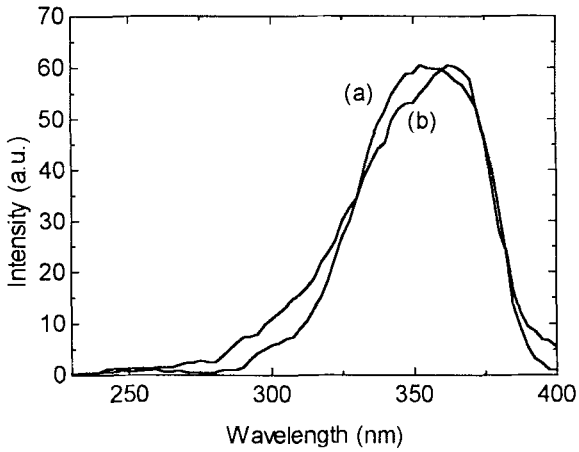


Fig. 2. Excitation spectra of (a) Eu(III)/TTA/TX-100 and (b) Eu(III)/TTA/SDS. Eu(III) $1x10^{-5}$ M, TTA $1x10^{-4}$ M. λ_{em}= 615 nm. The spectra are normalized to the same value to show the difference of their shape.

TABLE 1.
Relative Intensities of Emission of TTA and Eu(III) in Steady-State Emission Spectra.

	Eu(III)/TTA/TX-100	Eu(III)/TTA/SDS
I_{410}	1	34.8
I_{615}	7.3	1

beyond the Eu(III)/TTA complex. These conclusions are supported by the decay time data of the phosphorescence of Eu(III).

The main excitation band (360nm) comes from the chelating rings and a conjugated complex system [13]. There is an other, weaker excitation band at 295nm. Figure 3. shows the excitation spectra of Eu(III)/TTA/TX-100 and Eu(III)/TTA/SDS systems observing at 410nm emission wavelength of TTA.

Both the 360nm and the 295nm bands can be found but the ratio of them is different then in the case of 615nm emission wavelength. There are

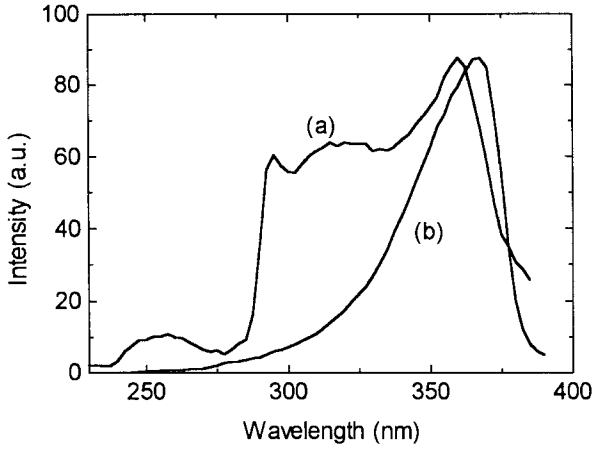


Fig. 3. Excitation spectra of (a) Eu(III)/TTA/TX-100 and (b) Eu(III)/TTA/SDS. Eu(III) $1x10^{-5}$ M, TTA $1x10^{-4}$ M. λ_{em}= 410 nm. The spectra are normalized to the same value to show the difference of their shape.

two main reasons of the difference of the excitation spectra observed at 410nm and 615nm. First, both Eu(III)/TTA and TTA have contributions to the emission at 410nm (mainly the TTA has). Secondly, the yield of energy transfer towards Eu(III) is different from the band at 295nm and from the band at 360nm (and in the case of TX-100 or SDS detergents).

The details of excitation spectra and TTA emission will be reported in a next paper. From the excitation spectra it can be seen that the 337.1nm of N_2 laser light is a good choice for "preparing" TTA for the energy transfer.[9, 12, 13, 15].

Figure 4. shows the time-resolved emission spectra of TTA/TX-100 and Eu(III)/TTA/TX-100 systems. On the series (a) let us focus to the emission characteristics of TTA.

The emission occurs mainly between 360nm and 550nm and there are two well-defined maxima at 380nm and 410nm. In the spectrum of (0-60ns) the bands at 380nm and 410nm can hardly be seen. Later the band at 410nm

decreases the less. The FWHM of the whole spectrum decreases by 20 %. The explanation of this effect needs further investigations.

On the series (b) the presence of Eu(III) can not be seen in the spectrum of (0-60)ns at all. After the first few ten ns a new maximum at 400nm is formed instead of 380nm and 410nm and does not change in time. In the spectrum of (200-300ns) certain emission lines of Eu(III) already appear. In the spectrum of (1-16μs) the emission intensities of Eu(III) and TTA are nearly the same. In the spectrum of (10-25μs) the emission of TTA disappears and the emission of Eu(III) remains detectable.

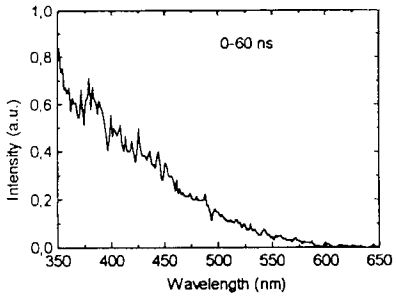
Comparing the steady-state spectrum of Figure 5. to the time-resolved series of Figure 4. the integral value and the temporal change of the emission of TTA and Eu(III) can be seen well. The luminescence of Eu(III) can be entirely discriminated from the emission of TTA using proper delay and gate times in time-resolved technique.

Table 2. reports the emission lines of Eu(III) which can be identified in the time-resolved and steady-state emission spectra. These numbers agree with the data in the literature [9].

Now let us study the emission bands of Eu(III). The relative change of the emission intensities of TTA and Eu(III) can easily be followed in the spectra of both Figure 4.b. and Figure 6. series. The spectral evolution in time is the same in these two detergents.

The emission of Eu(III) appears in the spectra measured between 200 and 300 ns after the excitation. The first appearing wavelengths are : 540, 558 and 580nm. Their relative intensities are : 8:3:3 in TX-100 detergent. In the spectrum of (1-16μs) the ratio of the Eu(III) lines are quite different. The lines centered at 540nm and 558nm disappeared, the line at 580nm remained and the lines at 592nm and 615nm appeared. These three lines also exist in the spectrum of (10-25μs) where the emission of TTA already disappeared totally. The spectral lines mentioned can be identified as the following transitions of Eu(III) (Table 2.). In the spectra of Figure 4.b/3 and b/4 the change of relative intensities of the lines of Eu(III) emission can be observed, especially the temporal developing of line at 615nm.

From the temporal developing of emission lines of Eu(III) it can be concluded that the energy transfer from TTA towards Eu(III) occurs to the



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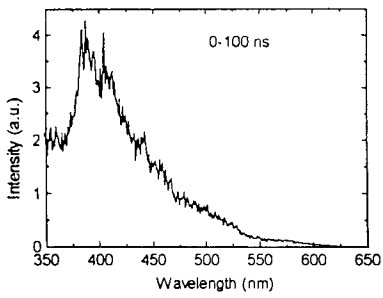

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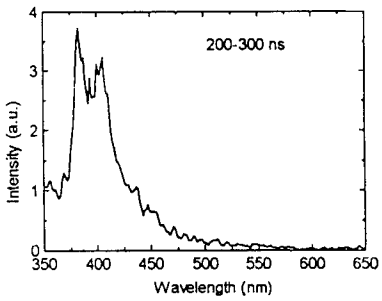

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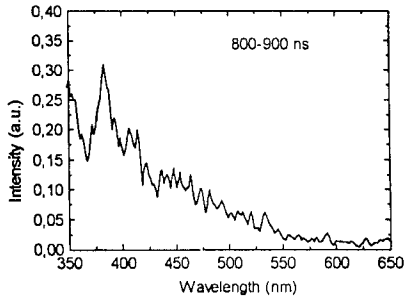

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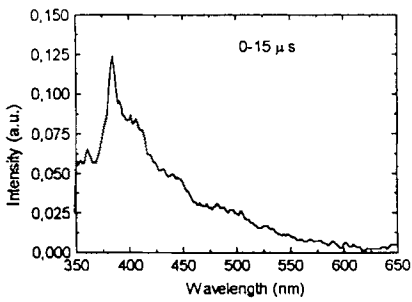

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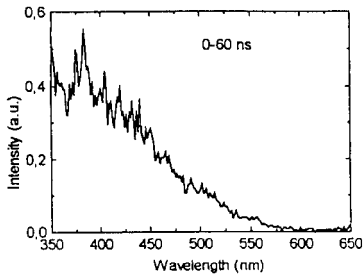
Fig. 4.a. 1-5. Time-resolved emission spectra of TTA/TX-100. TTA $1x10^{-4}$ M.



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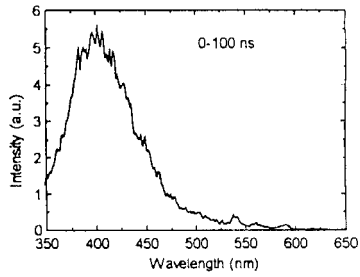

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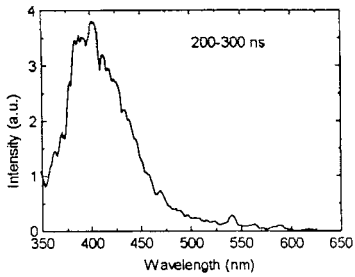

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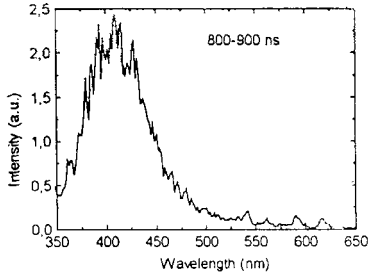

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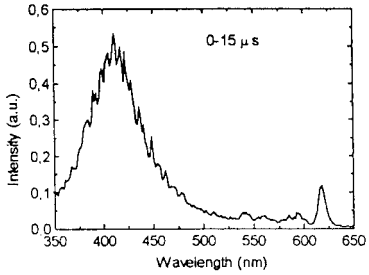

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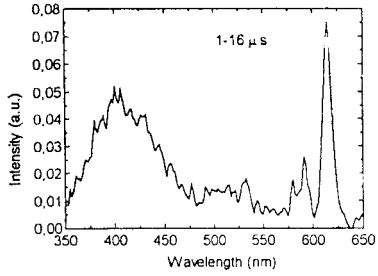

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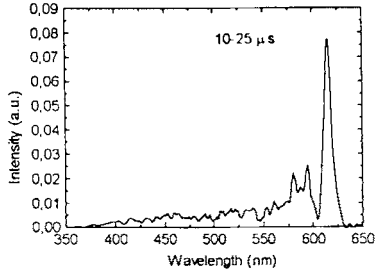

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Fig. 4. b. 1-7. Time-resolved emission spectra of Eu(III)/TTA/TX-100. Eu(III) $1x10^{-5}$ M, TTA $1x10^{-4}$ M.

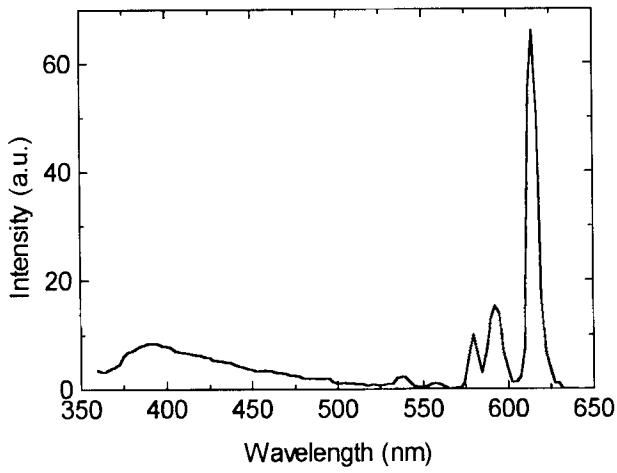


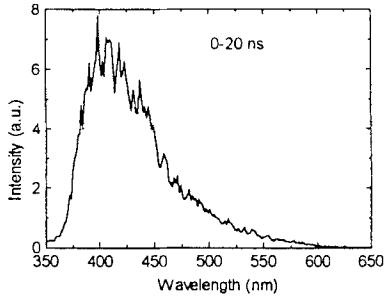
Fig. 5. Steady-state emission spectrum of Eu(III)/TTA/TX-100. Eu(III) $1x10^{-5}$ M, TTA $1x10^{-4}$ M.

TABLE 2.
Triplet-Triplet Transitions of Eu(III) Observed in Time-Resolved and Steady-State Emission Spectra.

$^5D_1 \rightarrow {}^7F_1$	$^5D_1 \rightarrow {}^7F_2$	$^5D_0 \rightarrow {}^7F_0$	$^5D_0 \rightarrow {}^7F_1$	$^5D_0 \rightarrow {}^7F_2$
		$^5D_1 \rightarrow {}^7F_3$		
543 nm	558 nm	580 nm	592 nm	615 nm

$^5D_1$ level of Eu(III), followed by phosphorescence from this level and relaxation to the $^5D_0$ level and phosphorescence from $^5D_0$ level.

The measurement of sub-μs lifetimes of Eu(III) is seriously disturbed by the TTA background which decays in similar timescale. Determination of the decay curve of Eu(III) emission at 540nm was carried out in the following way. The decay curves at 530nm (TTA emission only) and 540nm (TTA and Eu(III) emission) were both measured. The intensity ratio of TTA emission at 540nm and 530nm were known from the emission spectrum of TTA/TX-100 system. Now multiplying the decay curve data of 530nm emission by the ratio number mentioned before and subtracting the



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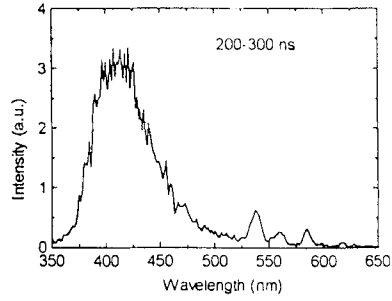

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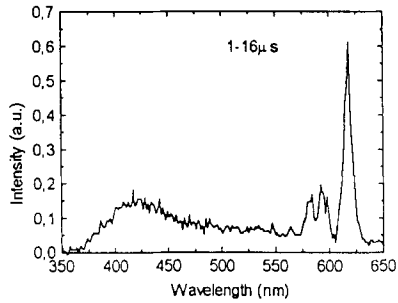

3.

Fig. 6. 1-3. Time-resolved emission spectra of Eu(III)/TTA/SDS. Eu(III) $1x10^{-5}$ M, TTA $1x10^{-4}$ M.

result from the decay curve data of 540nm emission the decay curve data of Eu(III) emission at 540nm can be got. Exponential function was fitted to the 200-1000ns region of this curve. There is a slight difference between this data and the true luminescence lifetime of $^5D_1$ level, because the energy transfer from TTA makes a virtual increase on this time region. The phosphorescence lifetimes of Eu(III) are : 144μs (at 615nm) and 0.75μs (at 543nm).

The most probable way of energy transfer is depicted by the diagram of Figure 7. The excitation light (337.1nm) is absorbed by the TTA

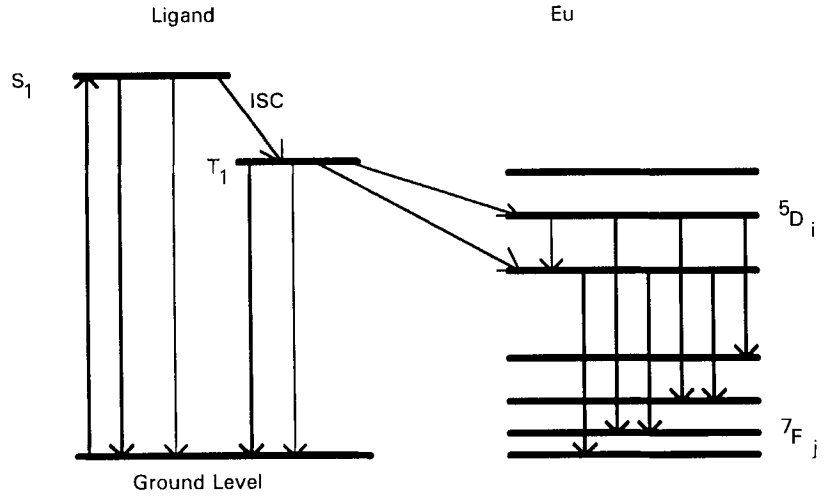

Fig. 7. Principal path of energy transfer processes in Eu(III)/TTA/detergent systems. ➔ , radiative transitions; → , radiationless transitions.

molecules. After this singlet-singlet absorption a singlet-triplet intersystem crossing follows. From the T_1 level of TTA the energy is transferred to the $^5D_1$ level of Eu(III). $^5D_1$ level emits with a sub-μs lifetime and relaxes to $^5D_0$ level. $^5D_0$ level is finally deactivated by radiative and radiationless transitions to the ground state.

Emission from the $^5D_0$ level can already be observed in the first few hundred ns too, because in the lifetime of $^5D_1$ level the $^5D_0$ level is continuously populated and thus begins to emit. The reason that the emission line of Eu(III) at 580nm can be detected well both at short and longer delays is that the $^5D_1 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_0$ transitions are within the spectral resolution of the measurements, thus emission can be detected in the lifetimes of both the $^5D_1$ and the $^5D_0$ levels.

Finally, let us mention some differences between emission features of Eu(III)/TTA/TX-100 and Eu(III)/TTA/SDS systems. From the decay curves of TTA emission in solution containing SDS it can be found that the phosphorescence intensity relative to the fluorescence intensity is much less

TABLE 3.
Relative Emission Intensities of $^5D_0 \rightarrow {}^7F_i$ (i = 0, 1, 2) Transitions of Eu(III).

	Eu(III)/TTA/TX-100	Eu(III)/TTA/SDS
580 nm	1.0	2.2
592 nm	1.5	4.0
615 nm	6.5	6.5

than that is in the solution containing TX-100, i.e. the probability of energy transfer is much less towards Eu(III). This effect can be found in the steady-state emission curves too, in the relatively weaker emission intensities of Eu(III) lines compared to the emission of TTA. The second reason of the relatively lower intensity of Eu(III) emission is the shorter lifetime of the excited states (e.g. for $^5D_0$: 144μs (TX-100), 62μs (SDS)). The shorter lifetime shows that the rate constant of radiationless deactivation of $^5D_0$ level is higher. It means that in SLS detergent the O-H vibrations of the solvent (H_2O) molecules deactivate more effectively the $^5D_0$ level of Eu(III) than in TX-100 detergent. Table 3. reports the relative intensities of Eu(III) emission from the $^5D_0$ level in both of the detergents used.

The significant difference can be explained by the difference between the structure of aggregates, i.e. the different probability of $^5D_i \rightarrow {}^7F_j$ transitions. This effect is a subject of further investigations.

CONCLUSIONS

Temporal developing of TTA and Eu(III) photoemission of TTA and Eu(III)/TTA in TX-100 and SDS detergents were studied. In the presence of Eu(III) the structure of aggregation in the micelles changes, this can be observed in the excitation and emission spectra. The excitation bands belonging to the TTA or Eu(III) emission can be separated well. In the energy transfer process determined by the micellar structure two excited triplet states of Eu(III) play role: $^5D_1$ and $^5D_0$. Both time-resolved and steady-state spectra show the presence and role of the $^5D_1$ level of Eu(III) in the energy transfer processes. It is known well that the emission intensity

of Eu(III) lines can be increased considerably by adding some further compounds, e.g. Tb(III), TOPO etc. This can be attributed partly to a shielding effect which decreases the probability of radiationless deactivation and to an other effect which increases the yield of energy transfer from TTA towards Eu(III). In the next reports we will investigate the more complicated systems mentioned before.

ACKNOWLEDGEMENT

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