Luminescence properties of acridine dyes in micellar sodium dodecyl sulfate solutions containing thallium ions

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The effect of external "heavy" Tl^I ion on the luminescence properties of Trypaflavine, Acridine Yellow, and Acridine Orange solubilized in sodium dodecyl sulfate micelles was studied. An increase in the concentration of thallium ions results in a decrease in the intensity of prompt fluorescence, an increase in the intensity of delayed fluorescence, the appearance of phosphorescence at ~20 °C, and a shortening of the triplet state lifetime of the dyes. The effective and micellar Stern—Volmer constants of fluorescence quenching of the dyes by thallium ions were determined. The effective and micellar quenching rate constants of triplet states of the dyes by Tl(I) ions and lifetimes of the triplet states of the dyes in the absence of thallium ions were calculated on the basis of kinetic measurements.

Key words: acridine dyes, micelles, surfactants, triplet state, sensitized room temperature phosphorescence, triplet-triplet energy transfer, effect of heavy atom.

Acridine dyes find use in medicine, biology, analytical chemistry, and as luminescent substances.[1—3] In the last case, they are used as donors of triplet energy for sensitized room temperature phosphorescence (SRTP) of polycyclic aromatic hydrocarbons (PAH) in sodium dodecyl sulfate (SDS) micelles.[4] SRTP finds use for both studying radiative and nonradiative transitions in luminophore molecules and enhancing the selectivity of the luminescence analysis method.[5,6] The selectivity enhances because sensitized phosphorescence transforms the PAH molecules into the excited singlet (S) and triplet (T) states not by the direct light action at their absorption band but due to the triplet-triplet (T—T) energy transfer from the excited level of the donor molecules.

This method of excitation using dyes as triplet energy donors has two advantages. First, dyes absorb in the visible spectral region and exclude nonselective simultaneous excitation of all PAH molecules in the UV region. The second advantage is that the triplet energy can be transferred from the donor molecule to the acceptor only to the PAH molecules in which the energy of the triplet level is lower than that in the dye.

The presence of heavy atoms affects substantially intersystem crossing and other photophysical processes accompanying SRTP.[7] The effects due to, for example, thallium(I) ions, were described for the PAH molecules and some heterocyclic compounds solubilized in SDS micelles.[8—10]

The purpose of this work is to study the effect of thallium(I) ions on the luminescence properties of acridine dyes solubilized in SDS micelles.

Experimental

Acridine Yellow, Acridine Orange, Trypaflavine (Reaktiv, Russia), pyrene, and benz[*a*]anthracene (Fluka) were used as received. The purity of acridine dyes was monitored by TLC. Starting solutions of the dyes and PAH were prepared by dissolving of the weighed sample in 0.1 *M* SDS in an ultrasound bath. The completeness of dissolution was monitored by the achievement of the absorbance maximum of solutions. The dyes are completely dissolved in SDS micelles within 1 day, and PAH are dissolved within two days.

Thallium(I) nitrate (analytical purity grade) was used as the source of heavy atoms to observe phosphorescence. Its starting solution (C = 0.3 mol L^{-1}) was prepared by the dissolution of the weighed sample in water. O_2 was removed from the studied solutions by four freezing—evacuation—defrosting cycles. Absorption spectra were recorded on an SF-46 spectrophotometer (LOMO, Russia). Luminescence spectra were recorded under steady-state excitation on an SDL-1 spectrofluorimeter (Russia). The kinetics of luminescence decay was studied on a pulse fluorimeter with the unique design, which also provides delayed fluorescence and phosphorescence spectra of compounds under study.

Results and Discussion

Influence of Tl^I ions on the singlet state of acridine dyes. We found that the fluorescence intensity of micel-

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lar solutions of the studied dyes decreases in the presence of Tl^I ions. This is due to an increase in the rate of intersystem crossing from the excited singlet state to triplet ($S_1 \rightarrow T_1$) resulted by the spin-orbital coupling with the Tl^I ion. The observed fluorescence quenching is described by the Stern—Volmer equation

$$I^0/I - 1 = k_{St}{}^{eff}[Q],$$

where I^0 and I are the fluorescence intensities in the absence and presence of thallium ions, respectively; $[Q]$ is the concentration of $TlNO_3$; and $k_{St}{}^{eff}$ is the effective Stern—Volmer constant.

It is established that molecules of the studied dyes are almost completely solubilized in SDS micelles. This is proved, in particular, by the absence of quenching of their fluorescence in a micellar solution by the I^- anions (potassium iodide), which are electrostatically repulsed from the negatively charged surface of SDS micelles. The Tl^I cations are also bound to the micelles ($K_b = 5 \cdot 10^5$).[11] This suggests that the effect of Tl^I ions resulting in the fluorescence quenching of the dye molecules takes place only in the bulk of the micellar pseudo-phase.

Therefore, in addition to the effective rate constant, we calculated the fluorescence quenching rate constant of the dyes in the micellar systems ($k_{St}{}^m$) taking into account microheterogeneity of the medium and the local concentration of the quenching agent[12]

$$k_{St}{}^m = k_{St}{}^{eff}VC, \quad (2)$$

where V is the molar volume of the surfactant, which is 0.32 L mol^{-1} for SDS;[13] and C is the surfactant concentration.

The calculated rate constants of fluorescence quenching are presented in Table 1. The quenching of prompt fluorescence of the dyes is dynamic because, according to the previous data,[14] the Stern—Volmer constants increase with temperature. This is also confirmed by the absence of changes in the absorption spectra of solutions of the dyes when Tl^I is added.

Influence of Tl^I ions on the triplet state of dyes. We found that a decrease in the intensity of prompt fluorescence in the presence of Tl^I is accompanied by the appearance of bands of delayed fluorescence of the E (DF) type and RTP of Trypaflavine, Acridine Yellow, and Acridine Orange. These radiative processes appear because intersystem crossing from the S_0 to T_1 state occurs under the heavy atom effect. As a result of loss of a vibrational energy excess, the molecule finds itself at the lowest vibrational level of the T state from which it can undergo either transformation into the ground S_0 state, *i.e.*, phosphorescence, or intersystem crossing to the initial excited S_1 state from which DF emission occurs.

Table 1. Spectral parameters and quenching rate constants of the S states of acridine dyes by Tl^I ions in aqueous micellar solutions of SDS (C = 0.05 mol L^{-1})

Dye	λ_{abs}	λ_{fl}	$k_{eff} \cdot 10^{-2}$	k_m
	nm		L mol^{-1}	
Trypaflavine	450	517	1.31	1.7
Acridine Yellow	460	510	1.05	1.4
Acridine Orange	488	535	0.55	0.7

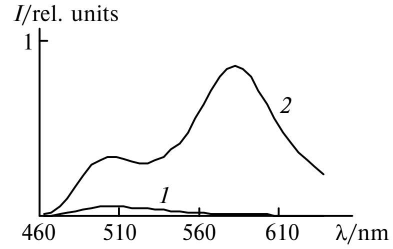

Fig. 1. Spectra of delayed fluorescence (λ_{max} = 517 nm) and phosphorescence (λ_{max} = 580 nm) of Trypaflavine ($C = 1.25 \cdot 10^{-5}$ mol L^{-1}) in a solution of SDS (C = 0.05 mol L^{-1}) in the absence (*1*) and presence (*2*) of Tl^I. $C_{Tl} = 2.25 \cdot 10^{-2}$ mol L^{-1}.

The luminescence spectra of Trypaflavine are presented in Fig. 1 as an example. The increase in the DF intensity and appearance of phosphorescence are related to an increase in the population of the T state of the dyes due to an increase in the rate of intersystem crossing $S_1 \rightarrow T$ under the effect of "heavy" Tl^I ions. Note that the phosphorescence intensity is higher than the DF intensity. It can be assumed that the heavy atom increases the rate of the radiative transition from the T state to the ground singlet state to a greater extent than the rate of the nonradiative transition from the T state to the excited state again. In aqueous solutions in the absence of SDS micelles, DF and TRP of the dyes do not occur under experimental conditions. Thus, the role of micelles is the protection of excited states of the molecules from the influence of foreign quenching agents and bringing together the dye and heavy atom molecules.[15]

The presence of Tl^I ions shortens the lifetime of the T state of the dyes along with increasing the phosphorescence intensity. As can be seen in Fig. 2, when the

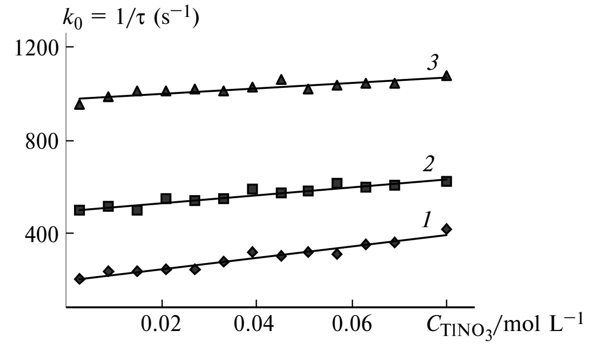

Fig. 2. Plots of the quenching rate constants (k_0) of delayed fluorescence of Trypaflavine (*1*), Acridine Yellow (*2*), and Acridine Orange (*3*) ($C = 1.25 \cdot 10^{-5}$ mol L^{-1}) in a solution of SDS (C = 0.05 mol L^{-1}) *vs.* concentration of thallium nitrate.

Table 2. Spectral parameters of quenching rate constants of the T states of acridine dyes by Tl^I ions in aqueous micellar solutions of SDS (C = 0.05 mol L^{-1}).

Dye	λ_{ph}/nm	$\tau_0{}^T$/s	$k_{Tl,eff}{}^T$	$k_{Tl,m}{}^T$
			L (mol s)$^{-1}$	
Trypaflavine	580	0.005	$2.4 \cdot 10^4$	$3.2 \cdot 10^2$
Acridine Yellow	550	0.002	$1.6 \cdot 10^4$	$2.2 \cdot 10^2$
Acridine Orange	600	0.001	$6.8 \cdot 10^2$	9.1

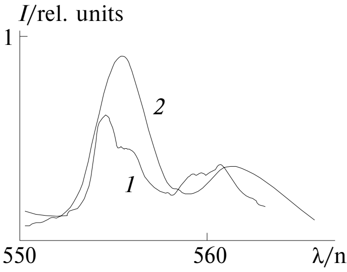

Fig. 3. Spectra of sensitized phosphorescence of pyrene (*1*) and benz[*a*]anthracene (*2*) ($C = 4 \cdot 10^{-6}$ mol L^{-1}) in a solution of SDS (C = 0.05 mol L^{-1}) in the presence of thallium nitrate ($C_{Tl} = 2.25 \cdot 10^{-2}$ mol L^{-1}), Trypaflavine ($C = 1.25 \cdot 10^{-5}$ mol L^{-1}) as the donor.

Tl^I concentration increases, the DF quenching rate constants of the studied dyes increase due to an increase in the rate of triplet state deactivation.

Figure 2 shows that the plot of the quenching rate constants *vs.* Tl^I concentration is linear. This enabled the determination of the effective and bimolecular rate constants of quenching by thallium ions of the T states of the dye molecules and the lifetimes of their T states in the absence of a quenching agent (see Table 2).

Triplet-triplet energy transfer. An increase in the population of the T state of molecules of acridine dyes in micellar solutions of SDS under the effect of $TlNO_3$ made it possible to use the dyes as triplet energy donors. We have previously shown[16] the possibility of the T—T energy transfer for the Trypaflavine—PAH system in which SRTP of some PAH molecules was observed.

Trypaflavine, Acridine Yellow, and Acridine Orange can be used as triplet energy donors due to their following properties: a high quantum yield to the T state in the presence of Tl^I ions, a higher energy of the triplet level toward molecules of the most PAH, and the combined solubilization of molecules of the acridine dyes, PAH, and Tl^I in SDS micelles.

According to the second condition, we observed the energy transfer from the Trypaflavine and Acridine Yellow to the pyrene, benz[*a*]anthracene, and anthracene molecules, and also from the Acridine Orange molecules to benz[*a*]anthracene and anthracene. The spectra of sensitized RTP of pyrene and benz[*a*]anthracene are presented in Fig. 3; trypaflavine was used as the triplet energy donor.

The quenching rate constant of the T states of Trypaflavine by the pyrene molecules was determined for the Trypaflavine (donor)—pyrene (acceptor) system. Its value, determined, according to Ref. 17, from the plot of the quenching rate constant of the T states of the donor molecule *vs.* acceptor concentration, is $4 \cdot 10^7$ L mol^{-1} s^{-1}.

The use of acridine dyes as triplet energy donors to observe sensitized phosphorescence of PAH made it possible to enhance the sensitivity of PAH determination, which was demonstrated by us for both model solutions and determination of several PAH in gasoline.[18]

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