Pyrene sensitized phosphorescence enhanced by the heavy atom effect in the water—heptane—sodium dodecyl sulfate—pentanol microemulsion

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The influence of the external Tl^+ "heavy" ion on the singlet and triplet excited states of the pyrene and Trypaflavine molecules solubilized in the water—heptane—sodium dodecyl sulfate—pentanol microemulsion was studied. The triplet-triplet (T—T) energy transfer in the system Trypaflavine (donor)—pyrene (acceptor) and the sensitized phosphorescence of pyrene were first observed in the microemulsion containing Tl^+ ions. The quenching rate constants of the excited states of the luminophores by Tl^+ ions were calculated.

Key words: pyrene, Trypaflavine, microemulsion, phosphorescence, energy transfer, heavy atom.

Sensitized phosphorescence of luminophores appears due to the transfer of the electron excitation energy from the triplet level of a donor molecule to the energetically lower triplet level of an acceptor molecule.[1] The phenomenon of sensitized phosphorescence has been observed for the first time for the aromatic aldehyde—naphthalene system in a solid solution at a low temperature.[2] Sensitized phosphorescence at room temperature (SPRT) is also observed in liquid solutions of aromatic compounds in organic solvents containing no dissolved O_2.

Then SPRT has been found in water-micellar media upon the solubilization of donors and acceptors of triplet energy in direct[4—7] and reverse[8,9] micelles of cationic[4,7] and anionic[5,6,8,9] surfactants. In almost all cases, diacetyl molecules served as an acceptor of the triplet energy, and the quantum phosphorescence yield for them was close to unity. This phenomenon was used for the indirect determination of polycyclic aromatic hydrocarbons (PAH).[5,6,9]

We have previously[10,11] shown that SPRT in water-micellar solutions of anionic surfactant sodium dodecyl sulfate (SDS) can also appear in the system Trypaflavine, dye of the acridine series (donor)—PAH (acceptor)—external "heavy" atom. The Tl^+ cation was used as the last atom, and its role was to increase the quantum yield of sensitized phosphorescence. The negatively charged surface of the SDS micelles binds cations of both the dye (triplet energy donor) and thallium. This provides for their approach to the PAH molecules localized in the near-surface layer of the micelle core and enables both efficient intersystem crossing and triplet energy transfer. Such an approach allowed the selectivity of the phosphorimetric method of PAH determination to be increased.[12,13]

Microemulsions differ from micelles by the complex composition and larger sizes of the particles, because they contain, along with the surfactant, a nonpolar solvent and alcohol with a short hydrocarbon chain, a so-called co-surfactant.[14] Due to this, they are characterized by a higher microheterogeneity of interfaces and a higher solubilizing capacity and they better model the functioning of systems that are the basis of living matter. The specific character of microemulsions is that the variation of the content of the nonpolar solvent in the hydrocarbon core can exert a substantial effect on the localization site of luminophore molecules and, hence, the distance between the donor and acceptor of triplet energy and triplet-triplet (T—T) transfer.

Phosphorescence at room temperature (PRT) in microemulsions has been observed only in a few works,[15,16] and SPRT has not been described at all. The purpose of this work is to study the occurrence of SPRT in the water—heptane—SDS—pentanol microemulsion.

Experimental

Pyrene and Trypaflavine (both high-purity grade, Fluka) were used. Background fluorescence was virtually absent from the solutions of sodium dodecyl sulfate (SDS) and *n*-heptane

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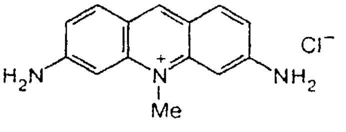
("chromatographically pure") that were used. The short-chain alcohol, *n*-pentanol (high-purity grade), was purified by distillation over a drying agent. Transparent microemulsions were prepared by the previously described procedure.[15] The starting concentrated microemulsion was primarily prepared by the dissolution of a weighed sample of pyrene in *n*-heptane (0.5 mL), addition of *n*-pentanol (0.5 mL), and dilution of the resulting mixture to 25 mL with an aqueous solution of SDS (0.5 mol L^{-1}). The following concentrations of the components in the starting microemulsion were used: [pyrene] = $4 \cdot 10^{-4}$ mol L^{-1}, [SDS] = 0.5 mol L^{-1}, [*n*-pentanol] = 2%, and [*n*-heptane] = 2%. Working solutions of microemulsions were prepared by the dilution of the starting solution with bidistilled water. The stock solution of Trypaflavine ($4 \cdot 10^{-4}$ mol L^{-1}) was prepared by the dissolution of a weighed sample in bidistilled water. Bidistilled water was used for the preparation of solutions of thallium(I) nitrate (analytical grade) and sodium sulfite (reagent grade).

Absorption spectra were recorded on an SF-46 spectrophotometer, and luminescence spectra were obtained on SDL-1 and FL spectrofluorimeters. The deactivation kinetics of triplet states of pyrene was studied on a pulse fluorimeter of unique design.

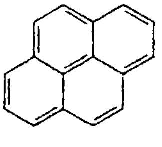
To remove O_2, along with the conventional approach, the fourfold alternation of freezing—evacuating—thawing out cycles, we used the chemical method based on the reduction of dioxygen dissolved in water by sodium sulfite.

Results and Discussion

We used the Trypaflavine (donor)—pyrene (acceptor) pair as the model system, and the Tl^+ cation served as the "heavy" atom.



Trypaflavine



Pyrene

This model system was chosen because the energy of the triplet level of the first compound ($17.8 \cdot 10^3$ cm^{-1}) is higher than that of the second compound ($16.6 \cdot 10^3$ cm^{-1}).[17,18] This is a condition for T—T transfer of the excitation energy.[1,2] Trypaflavine absorbs the light in the visible spectral region (λ = 450 nm) and transits to the triplet state in a sufficiently high quantum yield. The necessary condition that provides the appearance of sensitized phosphorescence in the system is a high quantum yield of pyrene phosphorescence in the presence of Tl^+ ions. The surface of the microemulsion used (oil/water type), as in the case of SDS micelles, is negatively charged and sorbs cations of both the donor (Trypaflavine) and quencher (thallium(I)).

Let us consider the effects observed when Tl^+ cations are added to the pyrene and Trypaflavine molecules solubilized in the microemulsion and to the pyrene—Trypaflavine mixture.

Pyrene—thallium(I) and Trypaflavine—thallium(I) systems

No change was observed in the absorption spectra of pyrene and Trypaflavine in the presence of thallium nitrate, which indicates the absence of the pyrene—thallium(I) and Trypaflavine—thallium(I) complexes in the ground state.

At the same time, the luminescence spectra of pyrene in the microemulsion (Fig. 1) show that an increase in the $TlNO_3$ concentration decreases the fluorescence intensity of pyrene (λ_{max} = 394 nm). This can be explained by the substitution on the negatively charged microemulsion surface of the Na^+ ions by Tl^+ cations, whose binding constant with the SDS micelles is $5 \cdot 10^5$ L mol^{-1}.[19] The localization and growth of the concentration of "heavy" ions on the surface of the microemulsion particles favors the approaching of these ions to the pyrene molecules solubilized in the near-surface layer of the particle. This increases the probability of intersystem crossing of the excited pyrene molecules from the singlet to triplet state.[4]

This assumption is favored by the appearance of a new band in the long-wave spectral region and an increase in its intensity (see Fig. 1). The sensitivity of the luminescence with λ_{max} = 596 nm to oxygen and the coincidence of the quenching constant (k = 112±6 s^{-1}) with the known value of the deactivation rate constant of the triplet state of pyrene (k = 115±12 s^{-1}) are inherent in its triplet state, and these make it possible to attribute the luminescence to PRT. These constants were calculated for the microemulsion at the thallium concentration of 0.01 mol L^{-1}. The appearance of PRT indicates

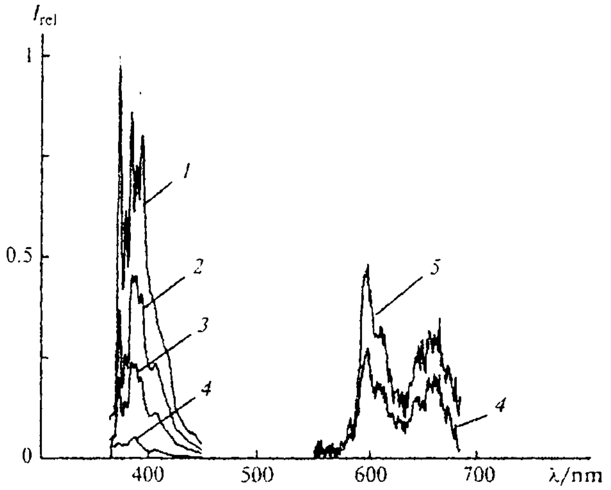


Fig. 1. Luminescence spectrum of pyrene ($4 \cdot 10^{-6}$ mol L^{-1}) in the water—heptane—SDS—pentanol microemulsion at different concentrations of thallium nitrate. [$TlNO_3$]/mol L^{-1}: *1*, 0; *2*, 0.00015; *3*, 0.0004; *4*, 0.003; and *5*, 0.006. The phosphorescence spectrum was obtained at 100-fold sensitivity; λ_{exc} = 340 nm (UFS-1 light filter). The intensity values (I_{rel}) were uncorrected.

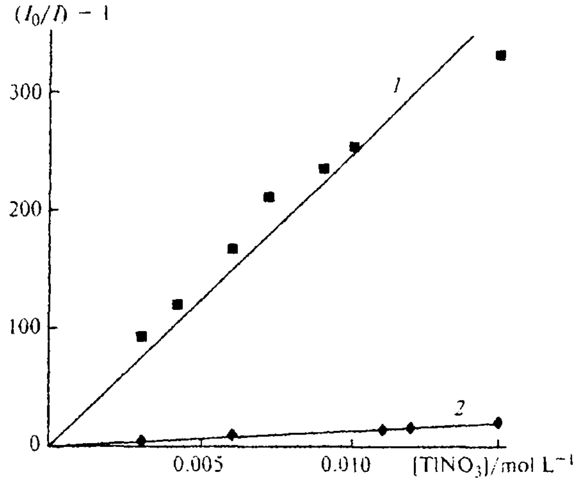


Fig. 2. The Stern—Volmer profiles of fluorescence quenching in the water—heptane—SDS—pentanol microemulsion: *1*, pyrene ($4 \cdot 10^{-6}$ mol L^{-1}); *2*, Trypaflavine ($1.2 \cdot 10^{-5}$ mol L^{-1}). I_0 and I are the fluorescence intensities of the luminophore in the absence and presence of the quencher, respectively.

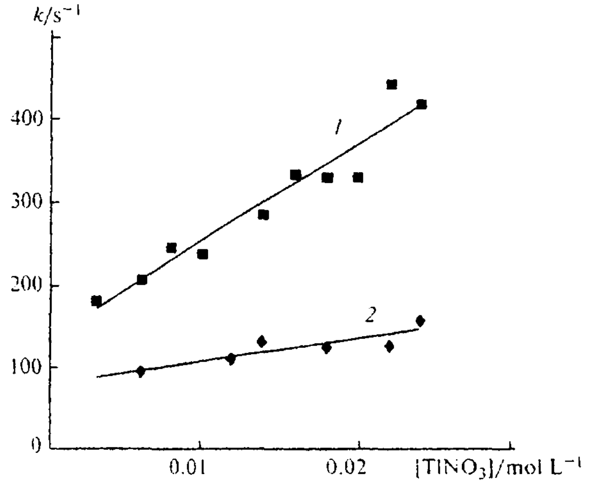


Fig. 3. Rate constant (k) of the deactivation of the triplet states of the pyrene molecules ($4 \cdot 10^{-6}$ mol L^{-1}) as a function of the concentration of thallium nitrate in the water—heptane—SDS—pentanol microemulsion: *1*, for excitation in the singlet absorption band; *2*, for the population of the triplet states of the pyrene molecules due to T—T energy transfer from the Trypaflavine molecules ($1.2 \cdot 10^{-5}$ mol L^{-1}).

that the pyrene molecules are rigidly localized in the microemulsion particle and their translation mobility is decreased. This results in a decrease in the probability of nonradiative losses of the triplet excitation energy and protection of the triplet states from external quenchers. Phosphorescence also indicates that the heavy atoms stimulate radiative transitions more strongly than nonradiative transitions.

Similar changes were observed when the Tl^+ ions were introduced into Trypaflavine solutions: the fluorescence intensity decreased and the radiation from the triplet state increased. It is of interest that the intensity of Trypaflavine phosphorescence in the presence of the Tl^+ ions increased more strongly than the intensity of delayed fluorescence. This also confirms a stronger influence of the Tl^+ ions on radiative processes from the triplet state than on nonradiative transitions.

The Stern—Volmer profiles for the concentration of the Tl^+ ion (Fig. 2) were plotted to estimate quantitatively the quenching of the singlet states of pyrene and Trypaflavine. The Stern—Volmer constants calculated for pyrene ($2.4 \cdot 10^4$ L mol^{-1} s^{-1}) and Trypaflavine ($3.0 \cdot 10^2$ L mol^{-1} s^{-1}) indicate that the Tl^+ ion more intensely quenches the singlet state of pyrene.

Trypaflavine—pyrene—thallium(I) system

We have shown for the first time that the SPRT of pyrene appeared due to the T—T transfer observed in the microemulsion in the absence of O_2. The shape and position of the band of sensitized phosphorescence do not differ from those for phosphorescence observed when pyrene is sensitized in the band of its singlet-singlet absorption. However, in the case of the sensitized phosphorescence of pyrene, excitation occurs in the absorption band of Trypaflavine (λ = 450 nm), where direct excitation of the pyrene molecules is absent.

It is of interest to compare the effect of an external heavy atom on the decay rate of pyrene SPRT in the Trypaflavine—pyrene system and PRT upon its direct excitation (Fig. 3). An increase in the thallium(I) concentration in the solution increases the decay rate of phosphorescence in both cases, but for SPRT the slope of the plot presented in Fig. 3 is greater. The linearity of the profile found indicates dynamic quenching. At the same time, Fig. 3 shows that the quenching rate constants of the triplet states of pyrene by Tl^+ ions for SPRT are higher ($k = 1.2 \cdot 10^4$ L mol^{-1} s^{-1}) than those for PRT upon its direct excitation ($k = 3.0 \cdot 10^3$ L mol^{-1} s^{-1}), *i.e.*, in the absence of T—T energy transfer. The stronger quenching of the triplet state of pyrene observed for SPRT is related, most likely, to the influence of thallium(I) on the triplet states of both the donor and acceptor of energy.

Thus, the sensitized phosphorescence of pyrene due to T—T transfer of the electron excitation energy from the energy donor, Trypaflavine, was observed in the water—heptane—SDS—pentanol microemulsion. The necessary condition of SPRT is the presence of thallium(I) ions that play the role of the external heavy atom. The SPRT observed indicates that pyrene, Trypaflavine, and Tl^+ ions are solubilized in one microemulsion particle.

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