PHOSPHORESCENCE OF MOLECULES OF POLYCYCLIC AROMATIC HYDROCARBONS IN AQUEOUS MICELLAR SOLUTIONS OF SODIUM DODECYLSULFATE AT ROOM TEMPERATURE

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Deactivation of the excited states of pyrene, benzoanthracene, and fluorene molecules in aqueous micellar solutions of sodium dodecylsulfate is studied using steady and pulsed fluorimetry. Quenching of the singlet states of polyatomic hydrocarbons by thallium ions is considered. Effective, micellar, and biomolecular constants for the quenching rate are obtained. Phosphorescence constants for the aforementioned compounds in micellar solutions at room temperature are ascertained.

Key words: solubilization, phosphorescence at room temperature, micelle, heavy atom, quenching, surfactants.

The features of microheterogeneous self-organizing systems (direct and inverse micelles, microemulsions, liposomes, and vesicles) formed in a solution by the diphyr molecules of surfactants manifest themselves in a reactant concentration, a local variation in the properties of a medium in the microenvironment of solubilized particles, a change in their physicochemical properties, reactivity, and also in the conditions for intra- and intermolecular deactivation of the energy for electronic excitation of luminescent probes [1-3]. The latter fact is of particular interest, since it makes it possible to expose ways of transforming the excitation energy in organized molecular systems. Naturally, this calls for systematic studies to evaluate the effects exerted by the nature of surfactant molecules and luminescent probes per se, the type of organized system, and the factors controlling the excitation energy transfer on deactivation of the excitation energy.

The current study aims at investigating the deactivation of the photoexcited states of luminescent probes in aqueous micellar solutions of sodium dodecylsulfate, which is an anionic surfactant. As a result of the partial dissociation of their constituent molecules, the surface of sodium dodecylsulfate micelles had a negative charge [1]. As probes use was made of such molecules of polycyclic aromatic hydrocarbons as pyrene, benzoanthracene, and fluorene. Their singlet excited states were quenched by adding thallium nitrate (I), which dissociated in an aqueous medium to form thallium cations (I), opposite in charge to the surfactant micelles, which were capable of stimulating spin-orbital interaction (the heavy-atom effect) [4].

Oxygen, which is an effective quencher of the electron-excited states of polycyclic aromatic hydrocarbons, was removed from the solution using a chemical method described in [5]. The sodium dodecylsulfate preparation of the Dia-M firm contained over 98% of the base material. Thallium nitrate and other employed salts were qualified as pure for analysis.

Luminescence spectra for a steady excitation were obtained on SDL-1 and Hitachi MRF-1 spectrofluorimeters. Deactivation of the energy of triplet states was studied with the aid of a pulse fluorimeter [6].

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In aqueous solutions of sodium dodecylsulfate with a concentration of surfactant molecules exceeding the critical concentration of micelle formation by no more than an order of magnitude ($\leq 10^{-1}$ M), spherical micelles form that are capable of solubilizing low-polarity molecules of polycyclic aromatic hydrocarbons. The efficiency of the conversion of polycyclic aromatic hydrocarbon molecules from an aqueous macrophase to a micellar micropseudophase is characterized by the magnitude of the distribution constant, which for example, for pyrene is $1.7 \cdot 10^6$ [7]. Such a large magnitude of the distribution constant indicates that over 99% of the molecules of this probe are bound to the micelle, and the observed processes of transfer and deactivation of the electronic excitation energy belong to a micellar pseudophase. It is well-known that the solubilized molecules of polycyclic aromatic hydrocarbons are localized in this case in the region of the surface layer of micelles, i.e., near the charged Stern layer [7].

Figure 1 presents the luminescence spectra for aqueous micellar solutions of pyrene and benzanthracene molecules. Clearly, in the absence of thallium ions (curves 1) there are intense fluorescence bands with $\lambda_{max} = 394$ nm for pyrene and 395 nm for benzanthracene. Adding TINO$_3$ even in small quantities (curves 2) decreases the fluorescence intensity for all polycyclic aromatic hydrocarbons considered. This phenomenon can be attributed to the fact the introduction of thallium nitrate into the micellar solution of sodium dodecylsulfate causes the replacement of Na$^+$ ions in the surface layer of micelles by Ti$^+$ ions. This leads to a localization of and an increase in the effective concentration of heavy Ti$^+$ ions in the Stern micellar layer, i.e., near the solubilized molecules of polycyclic aromatic hydrocarbons. The latter factor, according to [8], causes an enhancement of their intercombination conversion from the singlet to the triplet state. Naturally, in this case the process is accompanied by a decrease in the fluorescence intensity for the molecules of polycyclic aromatic hydrocarbons considered. We determined the effective, micellar, and biomolecular constants of fluorescence quenching for the polycyclic aromatic hydrocarbons considered [9, 10]. The Stern–Folmer effective quenching constant was obtained from the familiar equation