ESR study of photooxidation of phenothiazines in aqueous micellar solutions

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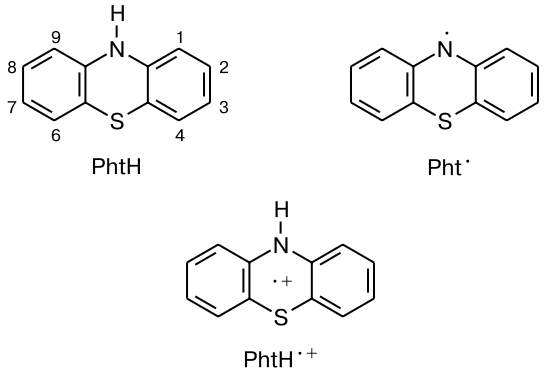
The mechanism of photooxidation of phenothiazine in liquid and frozen (77 K) aqueous micellar solutions of the surfactant (sodium dodecyl sulfate) was studied by ESR. The main reaction of electrons formed by the photochemical oxidation of phenothiazine in a liquid micellar solution of the anionic surfactant is the reduction of molecular oxygen dissolved in the aqueous bulk phase. 10-Methylphenothiazine was used as a stable radical cation probe in a liquid solution. The influence of electrolytes on the photoionization yield in both frozen and liquid solutions of the surfactant was studied.

Key words: ESR spectroscopy, phenothiazine, 10-methylphenothiazine, photochemical oxidation, sodium dodecyl sulfate, micellar solution, UV irradiation.

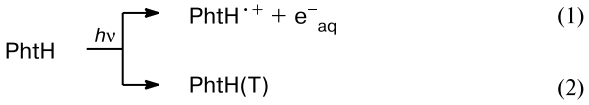
An interest in photoionization processes followed by electron transfer reactions is due to their importance in chemical and biological systems. Micelles and inverse micelles are used as models for light energy conversion into the chemical energy.[1] Such photosensitive compounds as ruthenium complexes,[2] chlorophylls,[3] porphyrins,[4] and phenothiazines[5] are used to achieve photoinduced charge separation in micellar systems. Surfactant micelles serve as both structural and functional models for complicated bioaggregates.[6] An important feature is the use of the visible light for such photoredox reactions as photosynthesis.[7]

In an aqueous micellar solution, phenothiazine (PhtH) is almost completely dissolved in the nonpolar internal part of micelles. This is indicated by the fact that hydrated electrons (e^-_{aq}) obtained by photolysis or pulse radiolysis decay with the same rate in solutions of sodium dodecyl sulfate (SDS) in both the presence and absence of PhtH. On the one hand, if a significant portion of PhtH is in the aqueous bulk phase, then the decay of e^-_{aq} is accelerated because PhtH is reduced by a solvated electron with the rate constant $\sim 3 \cdot 10^9$ L mol^{-1} s^{-1}.[8] On the other hand, PhtH localized in micelles of anionic surfactants is protected from the action of e^-_{aq} by the negative surface potential.



It is known[9] that the photolysis of PthH under the light with λ = 347.1 nm in a micellar solution of SDS results in the photoionization and formation of PhtH in the triplet (T) state (Scheme 1).

Scheme 1



In a micellar solution, the first process prevails over the second one. The results of laser photolysis studies showed[9] that the absorption from the phenothiazine radical cation ($PhtH^{\bullet +}$) disappears within several milliseconds and the phenothiazine free radical ($Pht^{\bullet}$) is formed. These species ($PhtH^{\bullet +}$ and $Pht^{\bullet}$) give the well-known ESR spectra.[10] In this work, the photooxidation of phenothiazines in aqueous micellar solutions and the influ-

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ence of electrolytes on photoionization were studied by the stationary ESR method.

Experimental

An aqueous micellar solution of the surfactant (0.1 mol L^{-1}) was prepared using triply distilled water. Phenothiazines, which were synthesized and purified according to a previously published procedure,[11] were dissolved in freshly prepared micellar solutions at a concentration of $5 \cdot 10^{-4}$ mol L^{-1} and were added under thorough stirring at 60 °C. The pH values of the aqueous solutions under study were changed by the addition of sulfuric acid.

All samples were studied in quartz tubes (inner diameter 2 and 3 mm for liquid and frozen solutions, respectively). The samples were frozen by the immersion of the tubes into liquid nitrogen for 2—3 s. Irradiation was carried out by the full light of a high-pressure DRSh-500-M lamp with a power of 250 W.

ESR spectra were recorded with a Bruker ER200D radiospectrometer. All HFS constants were determined by plotting theoretical spectra and comparing them with experimental spectra under assumption of the Lorentz shape of the ESR line.

Results and Discussion

Mechanism of phenothiazine photooxidation in a liquid aqueous micellar solution of the anionic surfactant. It has previously[8,9] been shown that hydrated electrons obtained by photoionization according to Eq. (1) (see Scheme 1) cannot be re-inserted into a micelle and recombine with the initial cations. In the opinion of the researchers,[9] the most probable mechanism of e^-_{aq} decay in a micellar solution is transformation into H_2 *via* the reaction

$$2\,H_2O + 2\,e^-_{eq} \longrightarrow 2\,OH^- + H_2. \qquad (3)$$

The authors of the work[10] studied the mechanism of photochemical oxidation of PhtH in EtOH and considered the reduction of molecular oxygen as the main pathway of the decay of e^-_{aq}

$$PhtH + O_2 \xrightarrow{h\nu} PhtH^{\bullet+} + O_2^{\bullet-}. \qquad (4)$$

In order to study the mechanism of PhtH photooxidation in an aqueous micellar solution of SDS, we used the samples both with and without evacuation of dissolved molecular oxygen. The UV irradiation time before recording ESR spectra and the pH of solutions were varied. The processes observed can be described by reactions (5)—(8).

$$O_2^{\bullet-} + H_2O \longrightarrow HO_2^{\bullet} + OH^- \qquad (5)$$

$$O_2^{\bullet-} + H_3O^+ \longrightarrow HO_2^{\bullet} + H_2O \qquad (6)$$

$$PhtH^{\bullet+} + O_2^{\bullet-} \longrightarrow Pht^{\bullet} + HO_2^{\bullet} \qquad (7)$$

$$PhtH^{\bullet+} + OH^- \longrightarrow Pht^{\bullet} + H_2O \qquad (8)$$

The occurrence of reaction (4) is confirmed by the results in Fig. 1. Figure 1 shows the ESR spectra after IR irradiation in the presence (see Fig. 1, *a*, *c*, *e*) and absence (see Fig. 1, *b*) of dissolved O_2 in micellar solutions of PhtH. These spectra, according to the published data,[11] belong to the $Pht^{\bullet}$ free radical with the hyperfine structure constants $a_N = 7.15$, $a_{H(3),H(7)} = 3.57$, $a_{H(2),H(8)} = 0.99$, $a_{H(1),H(9)} = 2.64$, and $a_{H(4),H(6)} = 0.70$ G. The assignment is confirmed by the construction of the theoretical spectrum with the above constants and individual ESR line width with the Lorentz shape and $\delta H = 0.14$ G (see Fig. 1, *d*).

When the nonevacuated liquid solution is permanently irradiated, the spectrum changes in time: the ESR line width of the $Pht^{\bullet}$ radical is gradually decreased (see Fig. 1, *a*, *c*, *e*), *i.e.*, paramagnetic molecular oxygen, which broadens signals, is consumed in reaction (4). After the triple pumping out of oxygen by the freezing—pumping—thawing method, the yield of $Pht^{\bullet}$ decreases substantially (see Fig. 1, *b*), indicating the efficient reduction of molecular oxygen upon the decay of electrons, which are released during photoionization.

Reactions (5), (7), and (8) occur in a neutral medium to yield $Pht^{\bullet}$ as the final product.

In an acidic medium (pH < 4), the process proceeds *via* Eq. (6) and reaction (8) is suppressed to enhance the stability of $PhtH^{\bullet+}$. This is confirmed by detection of the ESR spectrum of the $PhtH^{\bullet+}$ radical cation with the hyperfine structure constants $a_N = 6.2$, $a_{H(1)} = 7.30$, and $a_{H(3),H(7)} = 2.1$ G under photoirradiation of an acidified micellar solution of SDS of solubilized PhtH (Fig. 2). The found HFS constants correspond to the parameters of the $PhtH^{\bullet+}$ radical cation obtained by double electron nuclear resonance.[11] The reaction

$$PhtH^{\bullet+} + H_2O \longrightarrow Pht^{\bullet} + H_3O^+ \qquad (9)$$

seems improbable. In order to reveal the influence of water on the mechanism of photooxidation of PhtH to EtOH, we carried out the flash photolysis experiment[10] using ethanol thoroughly purified from water as a solvent. Since no changes are observed except an insignificant increase in the quantum yield, reactions of type (9) are excluded.

In a micellar solution of SDS, the signal of $PhtH^{\bullet+}$ during flash photolysis decays within several milliseconds[9] and the $Pht^{\bullet}$ free radical is formed. Since deprotonation in the aqueous bulk phase takes several microseconds,[9] the limiting step of $PhtH^{\bullet+}$ consumption in reactions (7) and (8) should be the escape from a micelle with a relatively low rate. The formation of $Pht^{\bullet}$ during $PhtH^{\bullet+}$ deprotonation is prevented by a decrease in the pH of the solution. At pH < 4 the stable signal of $PhtH^{\bullet+}$ is observed (see Fig. 2). The ESR spectrum of the $PhtH^{\bullet+}$

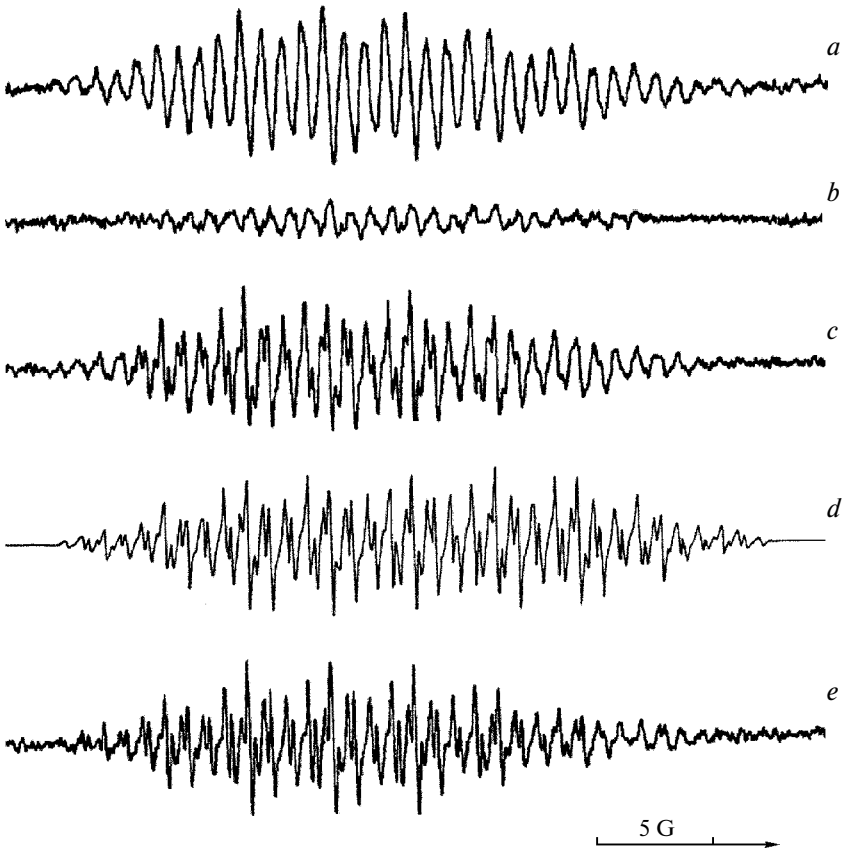


Fig. 1. Experimental (*a*—*c*, *e*) and model (*d*) ESR spectra of the Pht$^{\bullet}$ radical in an 0.1 *M* aqueous micellar solution of SDS at $T = 295$ K after UV irradiation for 6 (*a*, *b*), 20 (*c*) and 25 s (*e*) in the presence (*a*, *c*, *e*) and absence (*b*) of dissolved O_2.

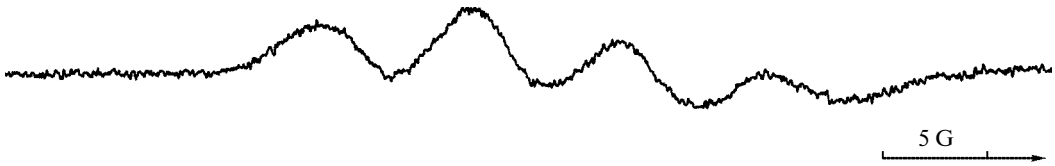


Fig. 2. ESR spectrum of the PhtH$^{\bullet+}$ radical cation in an 0.1 *M* aqueous micellar solution of SDS at $T = 295$ K after irradiation for 10 s with addition of H_2SO_4 to pH < 4.

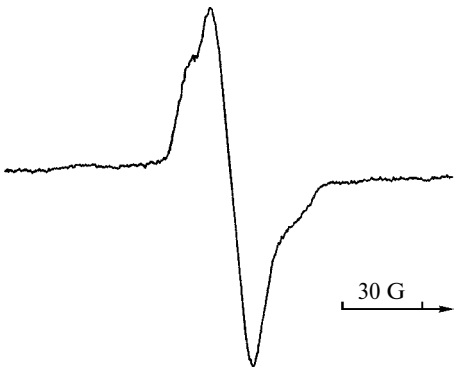
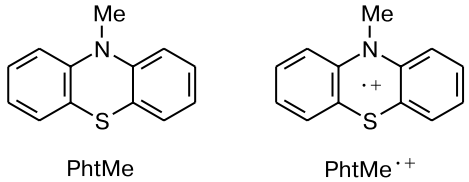


Fig. 3. ESR spectrum of the PhtH$^{\bullet+}$ radical cation in an 0.1 *M* aqueous micellar solution of SDS at $T = 77$ K after UV irradiation for 3 min.

radical cation measured 3 min after UV irradiation at 77 K is presented in Fig. 3.

10-Methylphenothiazine radical cation in micellar solutions of the anionic surfactant. Radical cations in a liquid solution can be stabilized using *N*-substituted phenothiazines.



After a micellar solution of 10-methylphenothiazine (PhtMe) was UV-irradiated for 1 min at ~20 °C, an in-

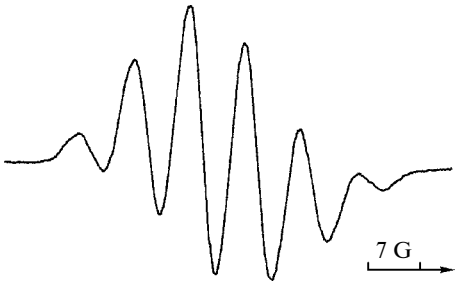


Fig. 4. ESR spectrum of the $PhtMe^{\bullet+}$ radical cation in an 0.1 *M* aqueous micellar solution of SDS at $T = 295$ K after UV irradiation for 1 min.

tense spectrum of six lines with $\delta H = 3.2$ G and an approximate intensity ratio of 1 : 4 : 7 : 7 : 4 : 1 appeared (Fig. 4). The spectral line width is mainly caused by the unresolved structure from the protons of the phenothiazine ring. The simulation of the theoretical ESR spectra provided the following HFS constants: $a_N = 7.3$ and $a_H(Me) = 6.8$ G. They correspond to the known[11] constants obtained for $PhtMe^{+\bullet}$ by double electron nuclear resonance in a toluene—nitromethane (1 : 4) mixture of solvents.

Influence of electrolytes on the photoionization yield. The intensity of the ESR spectra of the photogenerated stable tetramethylbenzidine radical cations ($TMB^{\bullet+}$) in frozen micellar solutions reflects the photoionization yields at 77 K.[12] Under these conditions, $PhtH^{\bullet+}$ is stable and the intensity of its spectrum also reflects the photoionization yield. The $PhtMe^{\bullet+}$ radical cation is stable in the anionic surfactant even at ~20 °C, which allows this paramagnetic species to be used as a probe for studying micellar systems in liquid solutions. Micellar systems of the anionic surfactant with solubilized PhtH and PhtMe were studied at different ionic strengths of the solution, which were changed by the addition of $LiClO_4$ or NaCl.

The intensity of the ESR signal of photogenerated $PhtH^{\bullet+}$ as a function of the $LiClO_4$ concentration in SDS micelles at 77 K is shown in Fig. 5. The amount of $PhtH^{\bullet+}$ first increases sharply up to a concentration of the electrolyte of ~0.03 mol L^{-1}. When lithium ions are added, the partial neutralization of the negative surface charge of micelles decreases the repulsion barrier for the escape of an electron from a micelle and the yield of $PhtH^{\bullet+}$ increases. However, a further increase in the electrolyte concentration decreases the amount of the radical cations formed. A similar plot can be explained by a change in the localization of the hydrophobic probe from the interphase region with an increased polarity to the nonpolar center of the micelle. A similar behavior of the TMB probes has previously[13] been confirmed experimentally by the electron spin echo data.

It seems interesting to elucidate the influence of electrolytes on the ESR signal intensity in liquid solutions. As

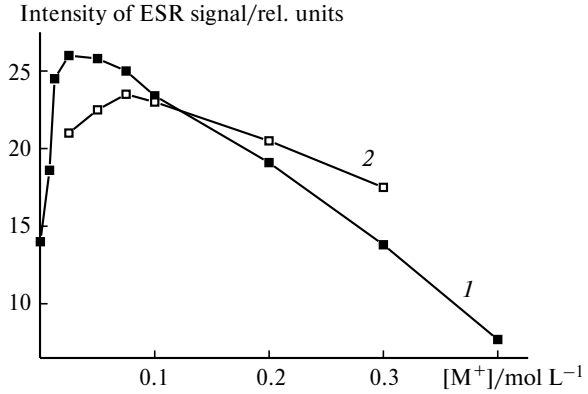


Fig. 5. Intensity of the ESR signal of the $PhtH^{\bullet+}$ radical cations photogenerated in SDS micelles at $T = 77$ K as a function of the $LiClO_4$ concentration (irradiation time for each point 2 min) (*1*) and of the $PhtMe^{\bullet+}$ radical cations at $T = 295$ K as a function of the NaCl concentration (irradiation time for each point 1 min) (*2*).

already mentioned, the PhtMe probe, which forms the stable $PhtMe^{\bullet+}$ radical cation, is appropriate for studying these systems. We explain the behavior of the ESR signal of the photogenerated $PhtMe^{\bullet+}$ radical cations at different concentrations of NaCl in SDS micelles at 295 K (see Fig. 5) by the same way as for the frozen $LiClO_4$—PhtH micellar solution at 77 K: an increase in the concentration of Na^+ ions partially neutralizes the negative surface charge, facilitates the escape of an electron from the micelle, and results in the increase in the $PhtMe^{\bullet+}$ concentration at the initial stage. A further increase in the electrolyte concentration changes the localization of hydrophobic PhtMe from the interphase region with the increased polarity to the nonpolar center of the micelle. The distance, which must be passed by an electron to escape from a micelle, increases and, hence, the photoionization yield decreases.

Thus, PhtH and PhtMe are convenient probes for studying micellar systems of the anionic surfactant. The negatively charged surface of micelles makes it possible to separate charges during the photoionization of solubilized probes. The main portion of electrons generated by PhtH photoionization in liquid micellar solutions of anion-active surfactants is consumed for the reduction of molecular oxygen dissolved in the aqueous bulk phase. It is also shown that the $PhtH^{\bullet+}$ radical cations do not react with water molecules. It is established that the addition of electrolytes to the system can affect charge separation in micellar solutions.

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