

Influence of sodium dodecyl sulfate on the reaction between Nile Blue A and hydrogen peroxide

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The influence of the anionic surfactant sodium dodecyl sulfate on the rate of the reaction between the cationic form of Nile Blue A and hydrogen peroxide was investigated in the pH range from 5 to 8.5. A retardation of the oxidation of Nile Blue A with hydrogen peroxide of three orders of magnitude was observed at pH 8.5 in the presence of anionic micelles compared to the kinetic data in water. The retardation effect was less pronounced at lower pH values. These effects were explained by the electrostatic interaction of the species involved in the reaction with the negatively charged micellar surface and their effective separation in the vicinity of the micellar surface.

Key words: Nile Blue A, hydrogen peroxide, sodium dodecyl sulfate, micelles.

It is well-established that, in many cases, the rates and pathways of all kinds of chemical reactions can be altered by performing the reactions in micellar media instead of pure bulk solvents.^{1,2} Micellar effects on the rate of chemical and biochemical processes can be quite varied, ranging from inhibition to activation.³ These kinetic effects are generally explained in terms of the partition of the substrate between the aqueous and the micellar phase. Surfactants affect reaction rates by incorporating one or both of the reactants into the micellar aggregates. Together with this concentration effect through hydrophobic and electrostatic interactions, micelles also exert a medium effect (microviscosity, polarity, *etc.*) that influence the reactivity.

Many results have been published in the literature showing the different catalytic or inhibitory effects of anionic, cationic and non-ionic surfactants.^{4–15} Because of the structural similarities between micelles and globular proteins, these studies are important from biochemical aspects, as model systems for electron-transfer and ligand-exchange reactions on the surfaces of biomembranes or at the interfaces of globular proteins.

In the present paper, the influence of the anionic surfactant sodium dodecyl sulfate (SDS) on the rate of oxidation of the protonated form of the phenoxazine dye Nile Blue A persulfate ($\text{NBA}^+\text{HSO}_4^-$) with hydrogen peroxide (both reactants being hydrophilic)

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was studied. This reaction, whose characteristics in water are well understood, has been used for the analytical determination of traces of selenium.¹⁶

EXPERIMENTAL

Nile Blue A persulfate (Fluka), sodium dodecyl sulfate (Sigma) and hydrogen peroxide (Merck) were of analytical grade and used without further purification. Water purified by a Millipore Milli-Q system was used for the preparation of solutions. The pH of the solutions were adjusted with phosphate or borate buffer (0.5 mM). The hydrogen peroxide solutions were prepared from 30% H₂O₂ by dilution, and their concentrations were determined from the concentration of H₂TiO₄ formed in the reaction of hydrogen peroxide with Ti(IV).¹⁷

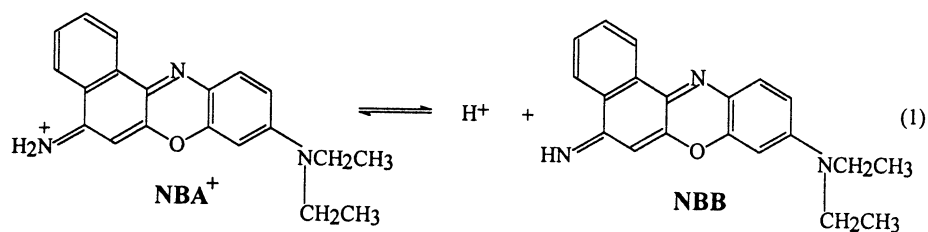
All spectrophotometric and kinetic measurements were performed on a Perkin Elmer Lambda 5 UV-vis spectrophotometer thermostated at 35 °C. When the reaction time (at least four half-lives) was less than 5 min, the universal rapid kinetic accessory HI-TECH model SFA12 was fitted to the spectrophotometer. The kinetic experiments were performed by mixing equal volumes of NBA⁺ and hydrogen peroxide solutions, SDS being added in equal concentrations to both solutions prior to mixing. The reaction rates were determined from the decrease of the absorbance at the NBA⁺ absorption maximum in the visible spectral range with time. Pseudo-first-order rate constants with respect to hydrogen peroxide (k_{obs}) were obtained from the slopes of $\ln A_t$ versus time. The quoted values of k_{obs} are the averages of at least ten runs under identical experimental conditions. All kinetic measurements were reproducible within the limits of error of $\pm 10\%$.

The critical micellization concentration (CMC) of SDS in the presence of hydrogen peroxide was determined by measuring the relative light scattering intensity using a Chromatix KMX-6 low-angle laser photometer operating at 633 nm.

RESULTS AND DISCUSSION

Absorption spectra and pK_a of NBA⁺ in the presence of anionic micelles

Aqueous solutions of NBA⁺ exhibit a characteristic absorption spectrum with absorption maxima at 279, 329 and 639 nm. The absorption maxima of its conjugated base, the neutral compound Nile Blue base (NBB), are shifted to lower wavelengths (265, 313 and 500 nm, respectively).



Scheme 1.

From the decrease of the absorbance at 639 nm on increasing the pH from 7 to 12, the protonation constant of NBA⁺ in aqueous solution was estimated to be $pK_a = 9.25 \pm 0.05$. From the spectrophotometric pH titration of a Nile Blue solution containing 10 mM SDS in the pH range from 8.5 to 12.5, using both the decrease of the absorbance at 645 nm and the increase of the absorbance at 500 nm, the

protonation constant of NBA^+ localized at the negatively charged micellar surface was estimated to be $\text{p}K_a = 11.4 \pm 0.1$. The apparent increase of the $\text{p}K_a$ of NBA^+ in micellar solutions of about two pH units can be explained by the higher concentration of hydrogen ions in the vicinity of the micellar surface compared to bulk solution.^{18,19} It must be pointed out that the pH of the solution, measured using a glass electrode, refers to the bulk concentration of H^+ ions.

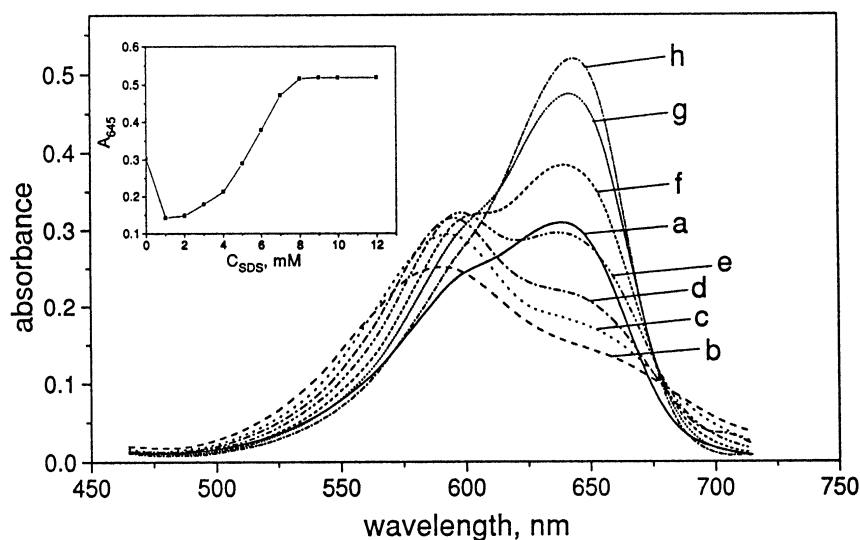


Fig. 1. The effect of the SDS concentration on the absorption spectrum of a $10 \mu\text{M}$ Nile Blue A per-sulfate solution at pH 8.5: a) without SDS; b) 2 mM SDS; c) 3 mM SDS; d) 4 mM SDS; e) 5 mM SDS; f) 6 mM SDS; g) 7 mM SDS; h) 8–12 mM SDS. Inset: Absorbance at 645 nm as a function of the concentration of SDS.

Significant changes of the intensity and slight changes in the position of the absorption maxima of NBA^+ were observed in the presence of SDS, the greatest effect being obtained in the visible spectral region (see Fig. 1). It is well known that changes in the optical properties of some molecules can be induced by the presence of surfactant molecules, providing an easy way for the estimation of the CMC of the surfactant.²⁰ The saturation of the absorbance of NBA^+ was observed at a SDS concentration of 8 mM (see inset in Fig. 1), which corresponds to the CMC value of SDS. The obtained CMC value in the presence of a low concentration of NBA^+ ($10 \mu\text{M}$) is in good agreement with the reported CMC value at zero ionic strength.²¹

The increase of the absorption coefficient of NBA^+ in the presence of anionic micelles of more than 50%, compared with an aqueous solution, indicates a diminution in the polarity in the immediate vicinity of the organic cation as a result of its localization at the negatively charged micellar surface. This was proved by recording the spectra of NBA^+ in media of variable dielectric constant (water/ethanol mixtures²²). The absorbance at 640 nm increases with increasing ethanol content, *i.e.*, with decreasing medium polarity.

The kinetics of the oxidation of NBA^+ with hydrogen peroxide in the presence of SDS

The oxidation of NBA^+ in the presence of hydrogen peroxide results in the formation of a colorless product and, consequently, a decrease of the absorbance at 639 nm. It has been shown that the oxidation of NBA^+ with hydrogen peroxide is base catalyzed and a rate equation for the reaction in aqueous solutions was postulated ($-\text{d}[\text{NBA}^+]/\text{d}t = k_0 [\text{NBA}^+] [\text{H}_2\text{O}_2] [\text{buffer}] [\text{H}_3\text{O}^+]^{-0.5}$).¹⁶ However, the significantly slower spontaneous decomposition of NBA^+ was not taken into account.

The kinetics of the oxidation of NBA^+ with hydrogen peroxide in the presence of the micelle forming surfactant SDS was followed in the pH range from 5 to 8.5. Under pseudo-first-order conditions ($[\text{H}_2\text{O}_2] \gg [\text{NBA}^+]$), defined pH and constant buffer concentration (0.5 mM), the experimentally determined rate constant (k_{obs}) followed the simple rate expression:

$$k_{\text{obs}} = k_s + k [\text{H}_2\text{O}_2] \quad (2)$$

where k_s corresponds to the spontaneous decomposition of NBA^+ in the absence of hydrogen peroxide, while k is the pH dependent second-order rate constant.

The values of $k [\text{H}_2\text{O}_2] = k_{\text{obs}} - k_s$ at constant acidity both in the presence and absence of SDS (k_{SDS} and k_w , respectively) are presented in Table I. Over the entire investigated range of acidity, the values of k_s were $<10^{-6} \text{ s}^{-1}$ and $(5.0 \pm 0.5) \times 10^{-5} \text{ s}^{-1}$ in the case of micellar and aqueous solutions, respectively. The significant increase of the pseudo-first-order rate constant with decreasing acidity, both in the presence and in the absence of micelles, confirmed that the oxidation of NBA^+ with hydrogen peroxide is base catalyzed.

TABLE I. Pseudo-first-order rate constants $k [\text{H}_2\text{O}_2] = k_{\text{obs}} - k_s$ for the reaction of oxidation of NBA^+ (6 μM) with H_2O_2 (1 M) as a function of pH in water (k_w) and in the presence of 10 mM SDS (k_{SDS}), as well as the retardation factor ($RF = k_w/k_{\text{SDS}}$)

pH	5.0	5.9	7.0	8.0	8.5
k_w/s^{-1} ^{a)}	$(4.2 \pm 0.4) \times 10^{-4}$	$(1.1 \pm 0.1) \times 10^{-3}$	$(8.5 \pm 0.6) \times 10^{-3}$	$(5.8 \pm 0.4) \times 10^{-2}$	$(4.3 \pm 0.2) \times 10^{-1}$
$k_{\text{SDS}}/\text{s}^{-1}$	$(2.4 \pm 0.2) \times 10^{-6}$	$(4.5 \pm 0.3) \times 10^{-6}$	$(2.3 \pm 0.1) \times 10^{-5}$	$(6.4 \pm 0.1) \times 10^{-5}$	$(2.2 \pm 0.1) \times 10^{-4}$
RF	175 \pm 35	244 \pm 45	370 \pm 45	900 \pm 80	1955 \pm 190

^{a)}Corrected for the spontaneous decay of NBA^+ , $k_s = (5.0 \pm 0.5) \times 10^{-5} \text{ s}^{-1}$

A significant retardation of the oxidation of NBA^+ with hydrogen peroxide was observed in the presence of micelles. At pH 8.5, the retardation factor (the ratio between the pseudo-first-order rate constants in the absence and in the presence of SDS) was around two thousand. Increasing the acidity led to a gradual decrease of the retardation factor up to a few hundreds. It should be pointed out that the effect of micelles on the oxidation of NBA^+ with hydrogen peroxide is more pronounced (three orders of magnitude) compared to the kinetic data obtained under similar experimental conditions for complex formation involving hydrophilic species (one order of magnitude).⁹⁻¹¹ Also, the observed micellar effect is comparable to the

kinetic data obtained for electron-transfer reactions involving reactants of opposite polarities.^{5,6}

Retardation of the oxidation of NBA^+ with hydrogen peroxide in the pH range from 5 to 8.5 can be explained in terms of the effective separation of the species involved in the reaction in the presence of anionic micelles. Anionic micelles provide a dispersed negatively charged surface in the solution. As a consequence, the positively charged NBA^+ ions partition out of the bulk aqueous phase into the surface region of the micelles. Apart from the electrostatic interaction, the hydrophobic interaction cannot be neglected since, due to its aromatic structure, NBA^+ is very probably located in the interfacial "water-rich" region of the micelle where the polarity is lower than in water (effective dielectric constant of the micellar surface was estimated as 36^3). The retardation of the oxidation of NBA^+ with hydrogen peroxide in the presence of SDS can be explained keeping in mind that the reaction is base catalyzed. Due to the electrostatic repulsion between the negatively charged micellar surface and the negatively charged hydroxyl ions, the OH^- ions are located solely in the bulk aqueous phase. Therefore, in the presence of anionic micelles, the species involved in the reaction are effectively separated and the oxidation process is slowed down.

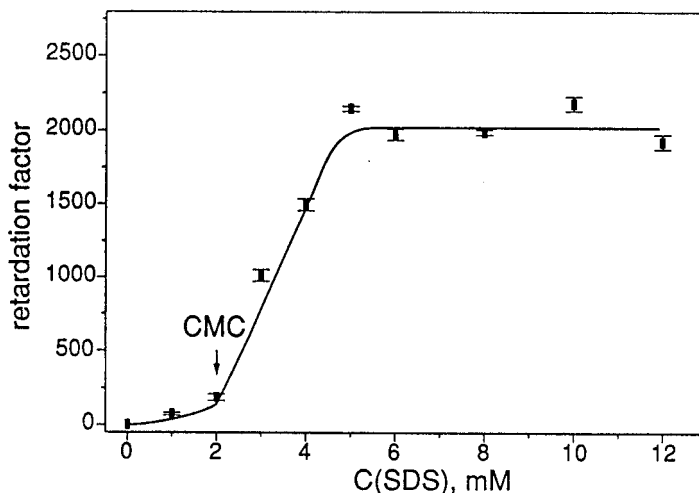


Fig. 2. The dependence of the retardation factor ($\text{RF} = k_w/k_{\text{SDS}}$) on the concentration of SDS for the reaction of NBA^+ (6 μM) with hydrogen peroxide at 35 $^{\circ}\text{C}$ and pH 8.5.

Since the influence of SDS on the rate of NBA^+ oxidation with hydrogen peroxide is very pronounced, the kinetic measurements can be used for the precise detection of the surfactant concentration at which micelle formation occurs, which is generally considered to be the CMC of the surfactant. A typical dependence of the retardation factor on the concentration of SDS at pH 8.5 is shown in Fig. 2. The estimated CMC value (2 mM) is smaller than the reported CMC value at zero ionic strength.²¹ The lower CMC value can be explained by the presence of the high

concentration (1 M) of hydrogen peroxide, which lowers the CMC of the surfactant. The CMC values, at different acidities in the presence of 1 M H₂O₂, were also determined by measuring the relative light scattering intensity as a function of the surfactant concentration. Agreement between the CMC values determined from light scattering and kinetic measurements was found.

ИЗВОД

УТИЦАЈ НАТРИЈУМ-ДОДЕЦИЛСУЛФАТА НА РЕАКЦИЈУ
Nile Blue А И ВОДОНИК-ПЕРОКСИДАИВАНА А. ЈАНКОВИЋ,^{1*} МИРА М. ЧАКАР² И ЈОВАН М. НЕДЕЉКОВИЋ¹¹Институт за нуклеарне науке Винча, б.бр. 522, 11001 Београд и²Фармацеутски факултет, Универзитет у Београду, Београд

Испитиван је утицај анијонског сурфактанта натријум-додецилсулфата на брзину реакције катјонског облика *Nile Blue* А и водоник-пероксида у рН опсегу од 5 до 8,5. У поређењу са кинетичким резултатима добијеним у воденим растворима, у присуству анијонских мицела на рН 8,5 примећено је успорење оксидације *Nile Blue* А водоник пероксидом за три реда величине. У киселим растворима ефекат успорења је мање изражен. Ови ефекти су објашњени електростатичком интеракцијом између негативно наелектрисане површине мицела и реагујућих врста, што води њиховом ефикасном раздвајању у близини површине мицеле.

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