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# Micellar rate effects in the alkaline fading of crystal violet in the presence of various surfactants

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## ABSTRACT

The influence of surfactants of various types (nonionic, cationic, anionic, and zwitterionic) on the rate of reaction of the crystal violet, cationic triphenylmethane dye, with the hydroxide ion in unbuffered aqueous solutions was studied using the spectrophotometric method. It was found that the values of the rate constants increase in the presence of the cationic, nonionic and zwitterionic surfactants, and decrease on the addition of the anionic surfactant at concentrations both below and above the CMC. The variation of the rate constants along with the change in the concentration of the surfactants may be explained on the basis of conception about distribution of the reagents between aqueous and micellar phases and the changing of their properties depending on local microenvironment. The character of the salt effects upon the rate constants was explained. It was revealed, that the Piszkiwicz's model of micellar catalysis is inapplicable even semi-quantitatively to the most of the examined systems.

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## 1. Introduction

The present paper is devoted to the analysis of the effect of surfactants on the rate of the alkaline fading of the cationic dye crystal violet.

Numerous attempts have been made to investigate the change of the rate constants of different reactions by micelles of surfactants. Colloidal surfactants are amphiphilic compounds, which form micelles in solutions. Micelles effect on the rate of reactions owing to: (i) concentration of reagents within their volume; (ii) stabilization or destabilization of substrates, intermediates, and products; (iii) specific orientation of reagents that changes their physico-chemical properties [1]. Micelles provide microreaction medium that is similar to that for many biochemical processes. Kinetic rules of reaction proceeding in micelles have general analogy to enzymatic catalysis [2,3]. Micellar kinetic effects depend on the nature of the surfactants hydrophobic and hydrophilic groups, and on the counter-ion [4,5].

Among the most widely investigated reactions in micelles is the alkaline fading of triphenylmethane dyes: crystal violet (CV) [6–13], malachite green [6,14–19], and brilliant green [6,20–22]. This is due to their high solubility both in aqueous and micellar phases. The important property of these reactions is that its rate is very convenient for simple kinetic measurements. The effect of the micellar systems on the kinetics

of these reactions is analyzed in terms of the micellar pseudophase model, which assumes that reactants are partitioned between the aqueous and micellar pseudophases [10]. An alternative model of micellar catalysis has been proposed by Bruice [23] and developed by Piszkiwicz [24–26].

The effect of the micelles on the rate of alkaline fading of CV is similar to that of amphiphilic macrocycles like calixarenes and cyclodextrins. In such systems, the change in observed rate constants is caused by interaction between CV and macrocycle, which proceeds as host–guest complex formation reaction [10,27,28].

Recently, several papers concerning the fading of some triphenylmethane dyes in micellar media have been published [15,16,18–20,29,30]. The Piszkiwicz's model was successfully used for describing the variation of the rate constants along with the surfactant concentration [16,19,20,29,30]. Similar model has been used in other papers [15,18]. However, in our previous work [22], we have studied the fading reactions of these dyes in micellar media and a weak correlation of experimental data with the Piszkiwicz's model was found.

This model is often used for the processing of such kind of experimental data. Therefore, we decided to examine the applicability of the Piszkiwicz's model for the proceeding of the reaction in the presence of the cationic surfactants cetyltrimethylammonium bromide (CTAB) and dimeric bis-quaternary ammonium bromide surfactant (16–4–16, gemini surfactant), the anionic surfactant sodium dodecyl sulfate (SDS), the zwitterionic surfactant 3-(dimetyldodecylammonio)-propanesulfonate (DMDAPS), and nonionic surfactants Triton-X-100 (TX-100) and Brij-35 in both pre-

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micellar and micellar concentration range in non-buffered systems with the fixed NaOH concentration.

## 2. Experimental

### 2.1. Materials

The samples of CTAB, SDS, TX-100 and Brij-35 were purchased from Merck (99% of the main substance). 3-(dimetyldodecylammonio)propanesulfonate was from Fluka. Gemini surfactant was synthesized and purified by S. V. Shekhovtsov (Department of Physical Chemistry, Kharkov V. N. Karazin National University) [31]. All other chemicals were of analytical reagent grade. All reagents were used without further purification. Aqueous solution of NaOH was prepared from saturated stock solution using CO<sub>2</sub>-free water and kept protected from the atmosphere.

Critical micelle concentrations (CMCs) of surfactants in pure water at 25 °C are as follows. Gemini 16-4-16:  $1 \times 10^{-4}$  M<sup>1</sup> [31], CTAB:  $9.8 \times 10^{-4}$  M [32], SDS:  $8.2 \times 10^{-3}$  M [32], TX-100:  $2.4 \times 10^{-4}$  M [33], Brij-35:  $6.8 \times 10^{-5}$  M [34], and DMDAPS:  $2.7 \times 10^{-3}$  M [35].

### 2.2. Kinetic measurements

In water solution, crystal violet exists in the intensively colored cationic form (CV<sup>+</sup>). The reaction of CV<sup>+</sup> with the hydroxide ion results in the fading of the color due to formation of the colorless carbinol. The reaction is given in Scheme 1.

The  $k_1$  and  $k_2$  on Scheme 1 are rate constants for direct and reverse reactions of the OH<sup>-</sup> ion addition to the dye cation. At the pH value of solution used in our experiments, the reaction proceeds to the complete fading of the dye and the formation of colorless solution at the end of the reaction. This means that under these conditions,  $k_1 \gg k_2$ .

The kinetic measurements were made spectrophotometrically, with cuvettes having an internal thickness of 1.00 cm, at 25 °C employing the SF-46 and Hitachi U-2000 UV-visible spectrophotometers equipped with a cuvette holders through which a thermostated water was continuously circulated. The reaction of CV<sup>+</sup> alkaline fading was followed by observing the decrease in absorbance at 590 nm as a function of time. In all kinetic runs, the initial CV<sup>+</sup> concentration of  $1.00 \times 10^{-5}$  M was used, whereas that of sodium hydroxide concentration was  $4.6 \times 10^{-3}$  M. The last-named corresponds the initial pH value of solution in the concentration scale  $\approx 11.7$ . Under the above conditions,  $[CV^+] \ll [OH^-]$  and the reaction proceeds as the pseudo-first-order one. The observed pseudo-first-order rate constants,  $k'$ , were obtained from the slopes of the dependence of  $\ln A$  versus time using the equation:

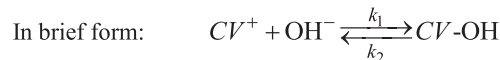
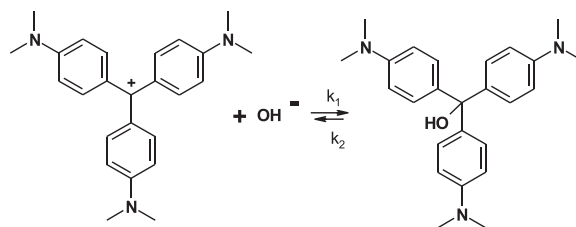
$$\ln A = \ln A_0 - k't, \quad (1)$$

where  $A$  and  $A_0$  are the absorbance of the solution at time  $t$  and the initial absorbance, respectively. Eq. (1) describes the experimental dependences of  $\ln A$  on  $t$  as a straight line; the good linearity was observed for all experimental data with correlation coefficient more than 0.96 and the standard error for  $k'$  always less than 5%. The second-order rate constants of the reaction were calculated as  $k = k'/[OH^-]$ .

## 3. Results and discussion

### 3.1. Rate constant of the reaction in water

The rate constant of interaction between crystal violet and hydroxide ion determined in the present work at 25 °C in aqueous solution



Scheme 1.

Q2

without surfactant equals  $0.157 \text{ M}^{-1} \text{ s}^{-1}$ . This value is in good agreement with a number of previously reported values given in Table 1.

### 3.2. Influence of the media on the rate constants of the reaction

The effect of surfactants on the rate constant of the reaction is shown in Figs. 1–3. The analysis of kinetic data obtained can be made on the basis of the following considerations.

- The successive addition of the surfactant to the solution may lead to the formation of the pre-micellar and then the micellar aggregates. The presence of the aggregates causes the distribution of the dye between aqueous phase and the aggregates. The most probable location of the dye in the micellar pseudophase is the Stern layer of the micelles of ionic surfactants and the interfacial layer for the aggregates of nonionic ones. The change of the reaction rate at the addition of the surfactant indicates that the dye interacts with the surfactant molecules or ions and aggregates. There are two parallel reactions of the crystal violet cation with the OH<sup>-</sup> ions in the presence of surfactant, namely: in the aqueous phase and in the dye–surfactant aggregates [1]. Under these conditions, the experimentally determined rate constant is an effective, or observed, value that is dependent on the rate constants of the processes in each phase and on the local concentrations of the reacting ions. The increase in the total surfactant concentration in solution causes the increase of the degree of dye binding by the aggregates [36].
- As the crystal violet fading is a reaction between ions, the effect of the solvent on its rate constant is partly described by Scatchard equation [37]. The CV<sup>+</sup> and OH<sup>-</sup> ions are oppositely charged. As it follows from Scatchard equation, in this case the decrease in the relative permittivity of the local surrounding of the dye cation leads to the increase in the rate constant. This corresponds to the increase in the reaction rate when the dye cation moves from aqueous phase to the location site in the Stern layer of the micelle, because the effective relative permittivity of the interfacial micellar layer, where the dye is localized, is lower than that of the bulk water [1].
- The hydroxide ions are distributed between bulk phase and the micellar pseudophase where the dye cations are localized on the surface. In general, at equilibrium the distribution of the charged particles between two phases is described by the equation following equation [36].

$$\frac{[i]_m}{[i]_w} = \frac{f_{i,w}}{f_{i,m}} \cdot \gamma_i \cdot \exp\left(-\frac{z_i F \Psi}{RT}\right) \quad (2)$$

where  $[i]_m$  and  $[i]_w$  are concentrations of the component  $i$  in micellar pseudophase and water, respectively;  $\gamma_i$  is the transfer activity coefficient of the species from water to micellar phase;  $f_{i,m}$  and  $f_{i,w}$  are the concentration activity coefficients in the micellar and the aqueous phases, respectively;  $z_i$  is the charge of the ion;  $\Psi$  is the difference between the electrical potentials of the phases;  $T$  is the absolute temperature;  $F$  is the Faraday constant; and  $R$  is the gas constant.

<sup>1</sup> Hereafter, 1 M = 1 mol dm<sup>-3</sup>.

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