Short communication

Kinetics and Mechanism of the Alkaline Fading of Brilliant Green in Aqueous Solutions of a Double-tailed and Some Single-tailed Cationic Surfactants

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Abstract

The alkaline fading of Brilliant green (a triphenylmethane dye) was studied in aqueous solutions of dodecyltrimethylammonium bromide (DTAB), didodecyldimethylammonium bromide (DDAB) and cetyltrimethylammonium bromide (CTAB) at 25 °C. The pseudo-first order rate constant variation with surfactant concentration shows a sigmoid shaped curve, which is analogous to the positive cooperativity in enzymatic reactions.

The catalytic factors k_ψ / k_w (the ratio of the rate constant in presence of surfactant additives to that in the pure water) of 1.8, 11.9 and 30.4 were obtained for DDAB, DTAB and CTAB respectively. The kinetic analysis shows that the bifurcated surfactant does not affect the observed rate appreciably as compared with the single-tailed surfactants. This is consistent with the length of the carbon chain being the dominant influence on the rate enhancement.

The data obtained fit the Pieszkiewicz model with the value of the cooperativity index n greater than unity in all cases, but less than the number of surfactant molecules found in micelle, which indicates the presence of pre-micelle aggregates.

Keywords: Alkaline fading; brilliant green; cationic surfactants.

1. Introduction

The rates of chemical reactions are known to be altered or modified by self- organized assemblies such as micelles. This phenomenon has received considerable attention from many workers in recent past.[1–16] Results from such investigations provided evidence that surfactant aggregates can be utilized in controlling the rate of chemical reactions and as probes for studying reaction mechanisms.[17–20] Effects of micelles on these reactions can be attributed to electrostatic and hydrophobic interactions. It had been reported that the rate of some of these reactions in aqueous surfactant media showed a marked dependence on the length of the carbon chain for a homologous series of surfactants.[4,21–22] As an example, the rate of the alkaline fading of crystal violet increases with increase in the chain length of the *n*-alkyltrimethylammonium bromide surfactants.[4]

The triphenylmethane dyes, such as crystal violet, brilliant green and malachite green represent a class of synthetic dyes of commercial and analytical importance.[23] Numerous applications capitalize on the intensity, range, and lightfastness of color exhibited by these dyes. For example, triphenylmethane dyes are used as colorants in the textile, food, cosmetic, and ink industries, as saturable absorbers in laser mode locking, reagents in protein assays, histological stains, and as indicators in spectrophotometric determinations of surfactants, metal ions and pesticides.[23]

Though highly appealing as reaction media because of their structure, little attention had been given to the study of the effects of double tail surfactants on the rate of reactions. Hence in the present work, we have studied the alkaline fading of Brilliant green (BG) in the presence of didodecyldimethylammonium bromide (DDAB) and compared with the same reaction in conventional single tailed surfactants: dodecyltrimethylammonium bromide (DTAB) and cetyltrimethylammonium bromide (CTAB).

2. Experimental

2.1. Materials

Brilliant green was obtained from Sigma-Aldrich. It was characterized by carrying out an UV spectrum of its solution between 200 to 800 nm. The spectrum shows a maximum peak (λ_{max}) at 626 nm which is consistent with the literature data.[24,25] Didodecyldimethylammonium bromide and dodecyl and hexadecyltrimethylammonium bromide were obtained from Fluka. Sodium hydroxide was purchased from Merck. All solutions were prepared in glass distilled water.

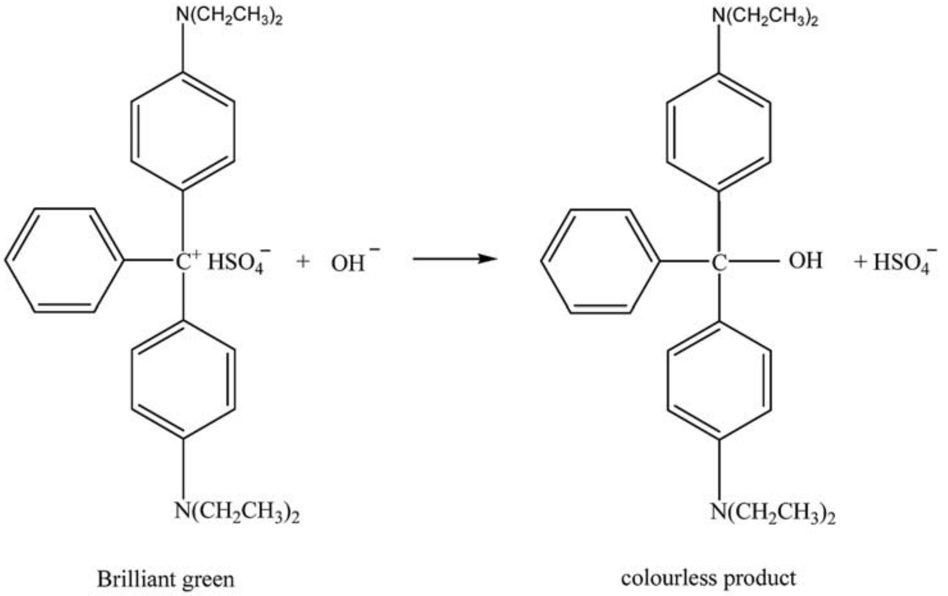
2.2. Kinetics

The entire rate constants were measured spectrophotometricaly using a α-Heλios Pye-unicam spectrophotometer through which water from a thermostatted water bath (Grant) was continuously circulated. The fading of the Brilliant green was followed at 626 nm with an initial dye concentration of 2×10^{-5} moldm^{-3}. Sodium hydroxide concentration was 0.003 moldm^{-3}. Pseudo-first order kinetics was observed to more than three half-lives throughout. The observed rate constants k_ψ and k_W were obtained from the slope of $\ln(A_t - A_\infty)$ versus time where A_t and A_∞ are the absorbance at a given time t and at infinity time respectively. The reaction proceeded to completion as judged from the complete fading of the dye at the end of the reaction. All reactions were carried out at 25 ± 0.1 °C

3. Results and Discussion

3.1. Alkaline Fading of Brilliant Green in DTAB and CTAB

The equation for the alkaline fading of Brilliant green (BG) is;



The concentration of BG used throughout the course of this investigation was 2×10^{-5} mol dm^{-3}. This concentration was chosen because of the higher absorbance of the dye (about 0.350 for this concentration) and to prevent dye induced micellisation of the surfactant, the possibility already reported by various authors.[23,26] At this dye concentration the critical micelle concentrations (cmc) of the surfactants were not significantly affected. The cmc of surfactants in the presence of the dye are 1.45×10^{-2}, 8.90×10^{-4} and 1.45×10^{-4} mol dm^{-3} for DTAB, CTAB and DDAB respectively, which are not significantly different from their cmc's of 1.5×10^{-2}, 9.2×10^{-4} and 1.6×10^{-4} mol dm^{-3} in pure water.

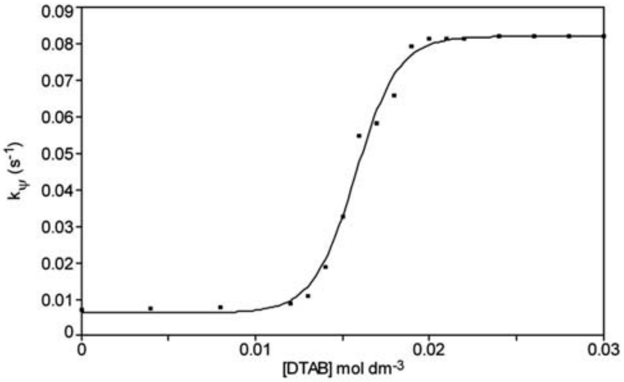


Figure 1: The variation of pseudo-first order rate constant with [DTAB]

Figure 1 shows a plot of k_ψ versus [DTAB] at 0.003 mol dm^{-3} OH$^-$ and 2×10^{-5} mol dm^{-3} BG at 25 °C, the [DTAB] covering before and after the cmc of the surfactant (cmc = 0.015 M). At low [DTAB] there is little or no change in k_ψ up to 0.01 M, beyond which there is a rapid increase in k_ψ, approaching saturation at concentration greater than the cmc. This observation shows strong premicellar activity which is due to the dye-surfactant monomer interactions with the formation of dye-surfac-

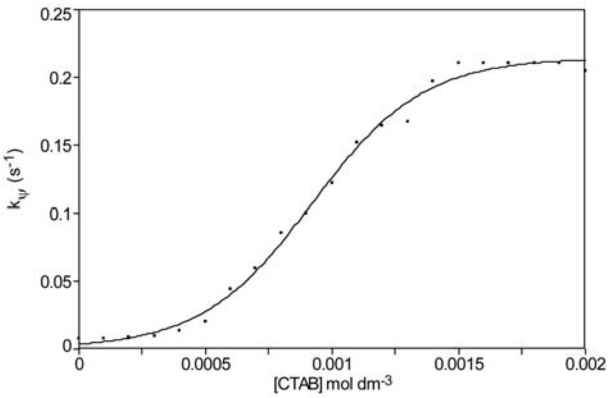


Figure 2: The variation of pseudo-first order rate constant with [CTAB]

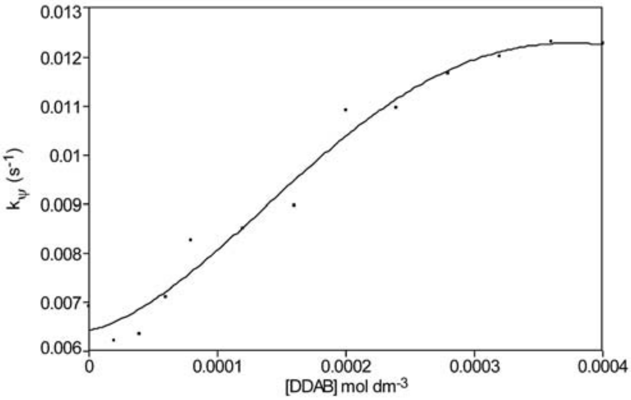


Figure 3: The variation of pseudo-first order rate constant with [DDAB]

tant aggregates of varying sizes made up of a few monomers (dimers, trimers, etc), a phenomenon that has been observed in many systems.[27,28] The structure of k_ψ vs. [DTAB] (Figure 1) is associated with dye-surfactant aggregates in different stages of micellar evolution.

Figure 2 shows a similar plot of the effect of CTAB on the alkaline fading of BG under similar conditions as in DTAB, with [CTAB] before and after the cmc (cmc = 0.00092 M). A similar profile as in DTAB could be seen with a higher maximum catalytic factor of 30.4 compared with 11.9 for DTAB. A comparative analysis (Figures 1 and 2) show that the rate of hydrolysis of BG by hydroxide ion increases with increase in chain length of the cationic surfactants, i.e., the rate is higher with CTAB than with DTAB. This is an indication that the substrate is more reactive when the micelles are formed from more hydrophobic surfactants which is in agreement with the observation of earlier workers.[4,21–22]

3.2. Alkaline Fading of Brilliant Green in DDAB:

The effects of DDAB on the alkaline fading of the dye was examined at constant NaOH concentration of 3×10^{-3} mol dm^{-3}, dye concentration of 2×10^{-5} mol dm^{-3} and DDAB concentration ranging from zero to 4.0×10^{-4} mol dm^{-3}. As can be seen in Figure 3, the observed rate constant increases only slightly but highly reproducible from 0.0069 s^{-1} at zero DDAB concentration to 0.0123 s^{-1} at highest DDAB concentration used, corresponding to a maximum catalytic factor of 1.8.

The rate of alkaline hydrolysis of triphenylmethane carbonium ion is generally known to be accelerated with increasing hydrophobicity of the cationic surfactants.[4] This is not the case with DDAB as compared to the observed acceleration with DTAB and CTAB, and can be explained on the basis of the structure of DDAB under the experimental condition. It is obvious that whereas DTAB and CTAB formed normal micelles, DDAB forms vesicle or a bilayer as reported for previously studied double-tailed surfactants.[1] If a bilayer structure is assumed, then the observed rate can be explained in terms of local increase in concentration of the BG in DDAB bilayer in which the hydrophobic reactant is partially encapsulated within the bilayer making it less accessible to attack by the hydroxide ion.

3. 3. Mechanism of the Reaction:

Our data do not fit into the pseudo-phase model of Menger and Portnoy[8] because the plot $1/k_\psi - k_W$ versus 1/[D] was non-linear. However, the data fits the model developed by Piszkiewicz[29] which is analogous to the Hill model for enzyme-catalyzed reactions.[30] This model assumes that the substrate S which is BG in this study, associates with *n* number of surfactant molecules D to form critical micelle D_nS, which may react according to the following scheme:

$$\mathrm{nD + S} \xrightleftharpoons{K_D} \mathrm{D_nS}$$

$$\mathrm{D_nS} \xrightarrow{k_m} \text{Products}$$

$$\mathrm{S} \xrightarrow{k_w} \text{Products}$$

The observed rate constant k_ψ is expressed as a function of surfactant concentration by the following equation:

$$k_\psi = \frac{k_m[D]^n + k_w K_D}{K_D + [D]^n} \qquad (1)$$

which can be linearized as

$$\log\left\{\frac{k_\psi - k_w}{k_m - k_\psi}\right\} = \mathrm{n}\log[\mathrm{D}] - \log \mathrm{K_D} \qquad (2)$$

The k_m was taken as the maximum rate constant in the presence of surfactants. The plot $\log\left\{\frac{k_\psi - k_w}{k_m - k_\psi}\right\}$ against log[D] were fairly linear (r > 0.9) for the reaction in the three surfactants investigated.

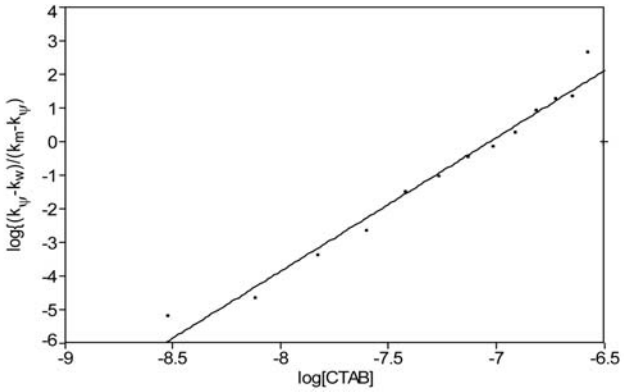


Figure 4: The Piszkiewicz plot for the alkaline fading of BG in CTAB (r = 0.9877)

The slope of the plot gives *n* known as the cooperativity index by analogy to cooperativity in enzymatic reactions. It formally describes the stoichiometry of the reaction given in the scheme, but practically serves as a measure of the association of additional surfactant molecules to an aggregate as a result of the interaction of the first surfactant molecules. The observed values for *n* are 3.34, 7.16 and 3.98 for DDAB, DTAB and CTAB respectively, which are all greater than one, indicating positive cooperativity. These is in agreement with earlier observations,[29] but are far less than the number of surfactant molecules found in the micelle and has been previously interpreted as evidence for the presence of premicellar aggregates.[9,26–27]

The surfactants attained one-half of their maximum catalytic effect at $\log\left\{\frac{k_\psi - k_w}{k_m - k_\psi}\right\} = 0$. At that point $n\log[D] = K_D$. For convenience, the value of log[D] is designated $\log[D]_{50}$, and it is equal to $\log K_D/n$. The values of *n*, $[D]_{50}$, and K_D are summarized in Table 1.

Table 1: Piszkiewicz Cooperativity Constants for the Alkaline Fading of Brilliant Green.

Surfactants	***n***	**$[D]_{50}$**	**log $[D]_{50}$**	**$K_D \times 10^{13}$**
DDAB	3.34	0.000145	–8.84	1.470
DTAB	7.16	0.014500	–4.23	0.695
CTAB	3.98	0.000890	–7.02	7.240

The values of the decomposition constants K_D are very small indicating that the dissociation of the bounded substrate and surfactant to its free component is negligible.

The values of $[D]_{50}$ for the three surfactants studied are very close to their respective cmc's, which implies that the half of the maximum reaction velocity were attained at surfactant concentration very close to their critical micelle concentration.

4. Conclusions

We have chosen a structurally related family of single-chain cationic surfactants, dodecyldimethylammonium bromide, added a second identical tail as in didodecyldimethylammonium bromide and elongating the carbon-carbon chain length as in cetyltrimethylammonium bromide as reaction media for the alkaline hydrolysis of Brilliant Green, a triphenylmethane dye. One expects increased hydrophobicity of DDAB to enhance the hydrolysis, but the bifurcated surfactant presents no obvious advantage in the rate enhancement. The rate enhancement is small for the double-tailed surfactant as compared with the single-tailed surfactants. The observation is consistent with the observation that the length of the carbon chain have the dominant influence on rate enhancement.[4,6]

This work also shows that micelle-catalyzed reaction can be a good model for the enzymatic reactions, although the plot in Figure 4 is not perfectly linear but within the limits of the experimental error.

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Povzetek

V prispevku je proučevano alkalno razbarvanje trifenilmetanskega barvila Brillant zeleno v vodnih raztopinah dodeciltrimetilamonijevaga bromida (DTAB), didodecildimetilaminijevega bromida (DDAB) in cetiltrimetilamonijevega bromida pri 25 °C. Odvisnost konstante reakcijske hitrosti psevdo-prvega reda od koncentracije tenzida je opisala krivulja sigmoidne oblike, ki ustreza pozitivni kooperativnosti v encimatskih reakcijah. Za DDAB, DTAB in CTAB so bili dobljeni katalitični faktorji k_Ψ/k_ω (razmerje konstant reakcijskih hitrosti v prisotnosti tenzida v vodi) enaki 1.8, 11.9 in 30.4. Kinetična analiza je pokazala, da razvejanost hidrofobne verige tenzida ne vpliva znatno na preučevano hitrosti v primerjavi z linearnima tenzidoma. To je v skladu z ugotovitvijo, da na povečanje hitrosti prvenstveno vpliva dolžina ogljikovodikove verige. Dobljene vrednosti se dobro ujemajo z Pieszkiewiczovim modelom; z vrednostjo kooperativnega indeksa n, ki je v vseh primerih večji od ena, manj pa s številom molekul tenzida v micelu, kar kaže na prisotnost predmicelarnih agregatov.