

EFFECT OF CARBONATE ION ON THE HYDROLYSIS OF BRILLIANT GREEN IN AQUEOUS SOLUTION AND IN MICELLAR MEDIA

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ABSTRACT

In an aqueous solution of dodecyltrimethylammonium bromide (DTAB), tetradecyltrimethylammonium bromide (TTAB), cetyltrimethylammonium bromide (CTAB), hexadecylpyridinium bromide (C₁₆PyBr), and hexadecyltriphenylphosphonium bromide (C₁₆TPPBr) at 25 °C, the effect of carbonate ion on the hydrolysis of brilliant green was studied. The change in pseudo-first order rate constant (k_{obs}) with surfactant concentration displays a sigmoid shaped curve which is similar to positive co-operativity in enzymatic reaction. The catalytic factors of the surfactants (k_{obs}/k_w) on the reaction are 7.51, 10.14 and 18.50 in aqueous solutions of DTAB, TTAB and CTAB respectively which is consistent with the hydrophobic effect due to change in the alkyl chain length of the surfactants. In C₁₆PyBr, CTAB and C₁₆TPPBr the catalytic factors are 23.40, 18.50 and 4.02 respectively. This can be explained to be due to modification in the head groups of the surfactants and the competition between electrostatic and hydrophobic effects of the carbonate ion and brilliant green for the cationic surfactant. The data obtained fit the pseudophase model of micellar catalyzed reaction.

Keywords: Brilliant green, Catalytic factor, Hydrophobic effect, Pseudophase model.

INTRODUCTION

People have always been drawn to elements or things that stimulate their senses and emotions. Color is one such aspect of nature that adds beauty and excitement to contemporary human living. Hence, man has predominantly sourced these colorants, also known as dye or pigments, from plants and animals. As societal demands for colour and industry demand for dye grows, the primary sources of these colorants become insufficient to supply the demand, necessitating the use of synthetic dyes.

Synthetic dyes are a kind of organic compounds with a complex aromatic molecular structure that can brighten and firm colour to other substances. In this investigation, brilliant green dye was used, which is a triphenylmethane cationic dye. Due to brilliant green's ability to cause cancer, mutation, and allergies, its use has been banned in many nations (Au *et al.*, 1979; Thomas and MacPhee, 1984). However, its continuous use could be attributed to its availability and affordability. It is used as dye to colour in textile industries, to stain in biological laboratories, and as an additive to poultry feed to slow down the growth of mold, parasites and fungus in intestine. However, these synthetic dyes and pigments are released as textile effluents on daily bases. The continuous discharge

of these dangerous dyes destabilizes the microbial activities in wastewater habitats. Several methods such as adsorption, reverse osmosis, biological treatment, chlorination, ozonation, electrochemical treatment, photolysis, ion pair extraction, and redox reactions are most of the time used to remove these contaminants (Banat *et al.*, 1996; Chandravanshi and Upadhyay, 2012; Rashid *et al.*, 2020). The elimination of such coloured compounds from aqueous effluents is therefore crucial from a commercial, technological, and environmental standpoint. The hydrolysis of stable dye is a reaction which has been studied extensively. (Funasaki, 1977; Simoncic and Span, 2000; Owoyomi *et al.*, 2007; Blair and Boyd, 2008; Samiiry and Toosi, 2009; Samiey and Dargahi, 2010; London, 2016; Laguta *et al.*, 2018; Saeed *et al.*, 2020). However, employing alternative nucleophiles besides hydroxide ion (OH⁻) to fade the dye according to Ritchie N⁺ nucleophilicity scale, such as nitrate ion (NO₃⁻), carbonate ion (CO₃²⁻), and sulphite ions (SO₃²⁻), is a task that has not been thoroughly documented by researchers (Mayr *et al.*, 2008). This present study is intended to investigate the decolourization of brilliant green with carbonate ion (CO₃²⁻) in aqueous and micellar media of cationic surfactants. The interest has arisen because the

reaction will be studied in different organized media such as cation surfactant solution. In this organized media, there will be different types of interactions with the reacting species by electrostatic and hydrophobic interactions, substrate partitioning, charge transfer and solubilization effects. (Fendler and Fendler, 1975; Soriyan *et al.*, 2009). All these interactions can play a crucial role in changing the rate and the mechanism of the reaction. Also in this work, the effect of surfactant chain length and head-group modification on the rate of the reaction will be investigated

MATERIALS AND METHODS

Brilliant green (BG⁺) with 99 percent purity was purchased from the Sigma-Aldrich Chemical Company and utilized directly. It was identified by its UV-Visible spectrum, which produced a molar extinction coefficient at 624 nm that agrees with the value found in the literature (Fita *et al.*, 2009; Drozd and Tishakova, 2011; Medhekar *et al.*, 2012). The cationic surfactants used in this study are hexadecylpyridinium bromide (C₁₆PBr) and hexadecyltriphenylphosphonium bromide (C₁₆TPPBr), both of which were purchased from Lancaster Synthesis in England. Other cationic surfactants used in this study are cetyltrimethylammonium bromide (CTAB), dodecyl trimethylammonium bromide (DTAB) were obtained from Sigma Aldrich Chemical Company. They were used exactly as received and were of the highest purity possible (98%). The critical micelle concentration in aqueous solution at 25 °C was used to ascertain their purity, and the results were in good agreement with the values from the literature. (Fendler and Fendler, 1975). Without additional purification, analytical grade sodium carbonate (Na₂CO₃), purchased from the Sigma-Aldrich chemical Company was used. Every solution was made with glass distilled water.

Kinetics

Using a thermostable UV-Visible 1800 Shimadzu Spectrophotometer made in Kyoto, Japan, kinetic data for the oxidation of brilliant green (BG⁺) were obtained by observing the decline in dye absorbance as a function of time at the highest absorption wavelength (λ_{\max} of 624 nm). The reaction components were mixed in 1 cm (3 cm³)

quartz cell. The dye was added last to prevent minimum pre-mixing reaction. All reactions data were obtained at 25.0 ± 0.1 °C. The concentration of the brilliant green dye in the reaction mixture was kept constant at 2.0 × 10⁻⁶ mol.dm⁻³ (0.2 absorbance) in order to avoid the problem that may rise from the dependence of the oxidation on the concentration of the dye. The carbonate ion concentration was maintained at 1.0 × 10⁻³ mol dm⁻³. Pseudo first order kinetics were used for all of the reaction runs. The slope of ln ($\lambda_t - \lambda_\infty$) with time, where λ_t and λ_∞ are the absorbance at a specific time (t) and at infinity time, respectively, was used to obtain the observed rate constants. The dye completely fading away at the end of the reaction indicates that the reaction advanced to completion.

RESULTS AND DISCUSSION

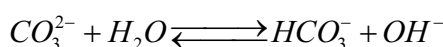
Dependence of the observed rate constant on the surfactant concentration

The change of the observed rate constant, k_{obs} with surfactant concentrations of dodecyl trimethyl ammonium bromide (DTAB), dodecyl trimethyl ammonium bromide (DTAB), tetradecyltrimethyl ammonium bromide (TTAB) and cetyltrimethyl ammonium bromide (CTAB) as shown in Figure 1. For each run, the carbonate ion concentration in all the surfactants utilized was maintained at 1.0 × 10⁻³ mol.dm⁻³. The k_{obs}^{-1} [Surfactant] profiles are structured. The observed rate constant changes just slightly or not at all at low [Surfactant]. The observed rate constant, rapidly changes as the concentration rises until it approaches saturation as the concentration becomes greater than the critical micelle concentration (cmc). This observed profile is a result of the interaction between the dye and the surfactant monomers, which leads to the creation of dye-surfactant aggregates with a range of sizes due few monomers (dimer, trimer, etc.). This phenomenon has been observed in many systems (Fendler and Fendler, 1975; Ige and Soriyan, 1986; Soriyan *et al.*, 2009). As a result, dye-surfactant aggregates at various phases of micellar development are connected to the structure of [Surfactant] (Figure 1).

The maximum catalytic factor which is ratio of rate constants in micelle and in aqueous

media(k_m/k_w) is 7.5, 10.1 and 18.5 for DTAB, TTAB and CTAB respectively (Table 1). Because the brilliant green (BG) and the nucleophile (carbonate ion) are drawn to the micellar surface with various partition factors based on electrostatic and hydrophobic consideration, catalysis is seen in all the surfactants used in this study.

From Ritchie N^+ nucleophilicity scale, (Mayr *et al.*, 2008) it is not possible for carbonate to oxidize the brilliant green. However, carbonate ion can hydrolysis very fast in water by the following reaction:



It is OH^- ion produced from the hydrolysis that is actually responsible for the hydrolysis of the brilliant green observed in this work (Funasaki

1977; Soriyan *et al.*, 2009; Samiey and Dargahi, 2010; Laguta *et al.*, 2018).

A comparison of the three surfactants used in this study reveals that the rate of brilliant green (BG) hydrolysis rises as the cationic surfactants' chain lengths increase. (Figure 1).

For example: Rate (DTAB) < Rate (TTAB) < Rate (CTAB). According to earlier researchers, this demonstrates that substrates are more reactive when micelles are produced from highly hydrophobic surfactants (Funasaki, 1977; Ige *et al.*, 1986; Laguta *et al.*, 2018).

The two surfactants have similar chain length of C_{16} but different head group. The k_{obs} -[Surfactant] profiles of the two surfactants show similar structure.

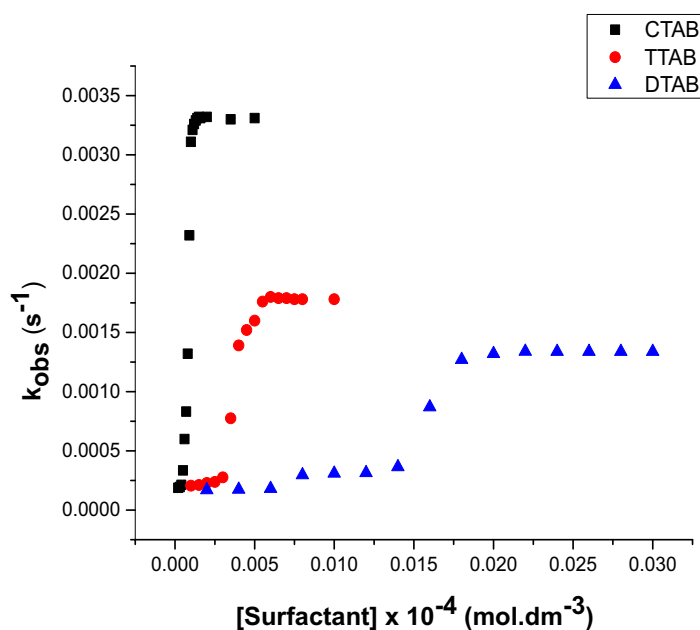


Figure 1: The plot of k_{obs} – [Surfactant] for the three surfactants: CTAB, TTAB and DTAB.

The results of observed k_{obs} -[Surfactant] profiles for hexadecylpyridinium bromide (C_{16} PyBr) and hexadecyltrimethylammonium (CTAB) at fixed

CO_3^{2-} ion concentration of 1.0×10^{-3} mol dm⁻³ as in other surfactants are shown in Figure 2.

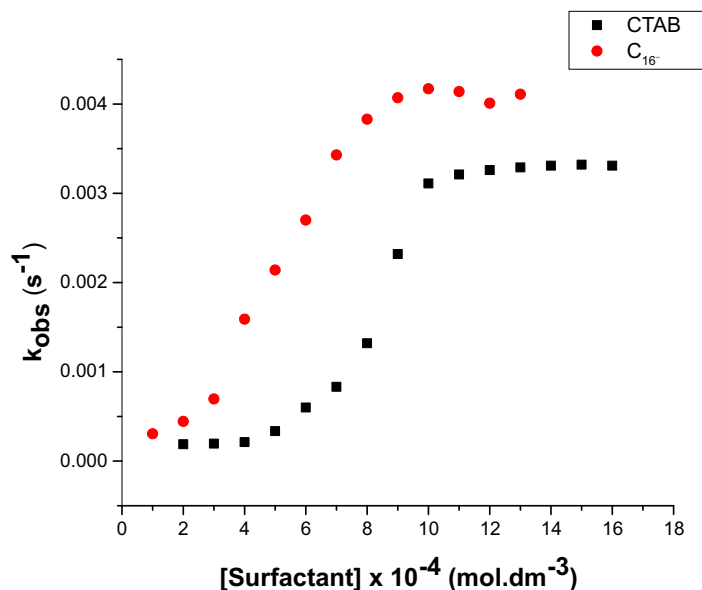


Figure 2: The plot of $k_{obs} - [\text{Surfactant}]$ for the two surfactants: CTAB and $C_{16}\text{PyBr}$

The profiles show overall catalysis at all surfactant concentration. The catalytic factor (k_{obs}/k_w) is 18.59 and 23.30 in CTAB and $C_{16}\text{PyBr}$ respectively which shows that the rate of hydrolysis of Brilliant green increases with change in the head group. The enhancement in the rate constants at all concentration in $C_{16}\text{PyBr}$ compared to CTAB may be due to two major factors operating in the two surfactants.

- The donating effect of the electrons due to the three methyl groups attached to the positive nitrogen atom of CTAB. This reduces the effective attraction for carbonate ion to the surface of the micelle formed which in turns decreases the rate

of hydrolysis of brilliant green (BG^+) with OH^- which takes place on the micellar surface when compared with $C_{16}\text{PyBr}$ head group.

- The rate enhancement in $C_{16}\text{PyBr}$ is due to the stable positive charge on nitrogen atom due to the resonance effect on pyridinium group on the head of the micelle (Figure 3) This stable positive charge attracts more carbonate ions to the surface of the micelle which increases the reaction rate in $C_{16}\text{PyBr}$ than in CTAB

These two factors are responsible for the high catalytic factor in $C_{16}\text{PyBr}$ (23.30) than CTAB (18.5).

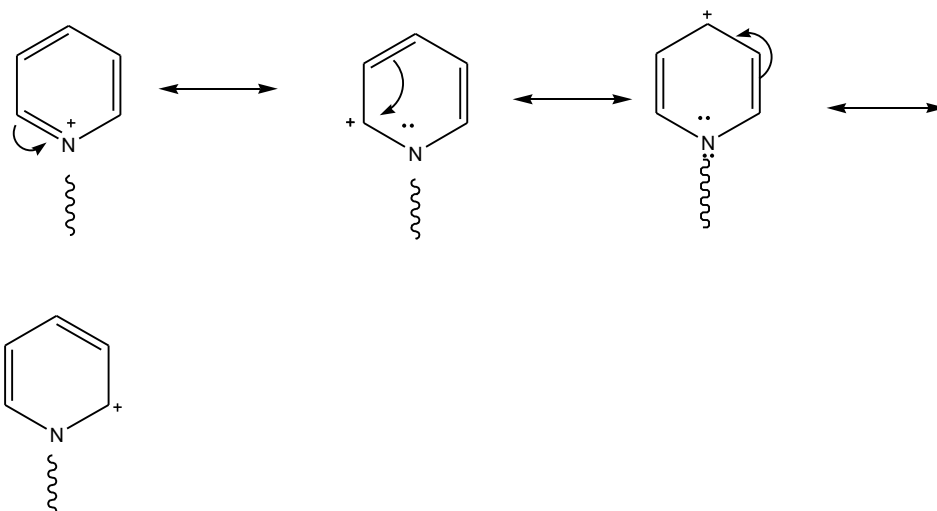


Figure 3: Resonance stabilization of pyridine nitrogen positive charge on the surfactant

The k_{obs} -[Surfactant] profile structure of hexadecyltriphenylphosphonium bromide (C_{16} TPPBr) (Figure 4) is similar to other

surfactants discussed above with maximum catalytic factor of 4.02.

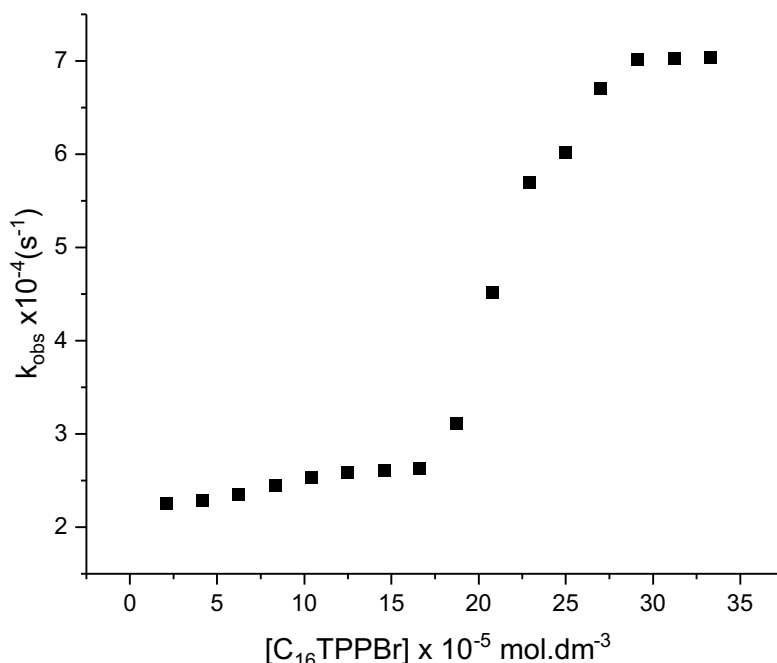


Figure 4: The plot of k_{obs} – $[C_{16}TPPBr]$

On comparing with k_{obs} -[Surfactant] profile for hexadecyltriphenylphosphonium bromide (C_{16} TPPBr), the rate constant is strongly reduced in C_{16} TPPBr. This reduction in quaternary phosphonium cation is due the fact that the phosphorous center bears a positive charge which is reduced drastically due to the steric effect due to the phenyl groups that are attached to the phosphorous atom couple with the donating effect of electrons on the positive atom. The drastic reduction also reduces the carbonate ion

attraction to the micellar surface and hence great reduction in catalytic factor. The variation of the observed rate constants k_{obs} with the surfactants concentrations shows that the oxidation of brilliant green (BG) increases in the order $k_{C_{16}PyBr} > k_{CTAB} > k_{C_{16}TPPBr}$.

The maximum catalytic factors which is ratio of rate constants in micelle and in aqueous media (k_m/k_w) for CTAB, C_{16} PyBr and C_{16} TPPBr are shown in Table 1.

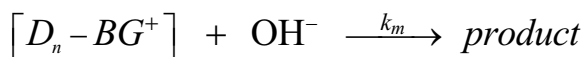
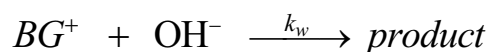
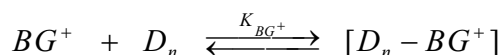
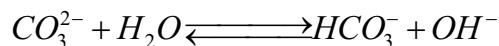
Table 1: The maximum catalytic factors (k_m/k_w) of the surfactants used.

Surfactant	DTAB	TTAB	CTAB	C_{16} PyBr	C_{16} TPPBr
Catalytic Factor	7.51	10.14	18.50	23.30	4.02

Mechanism of the Reaction

The pseudo-phase separation kinetic model developed by Menger and Portnoy (Menger and Portnoy, 1967) and modified by other workers (Bunton et al., 1991; Xiancheng and Yong, 2000) was taken into consideration in this work while

evaluating the kinetic data. The model assumes that the substrate, BG^+ associates with n number of surfactant molecules D to form critical micelle $D_n - BG^+$ which reacts with carbonate ion according to the following scheme:



The k_w and k_m are the second order rate constants in aqueous and micellar pseudo phase respectively while K_{BG^+} is the substrate-micelle binding constant.

$$[D_n] = \{[\text{Surfactant}] - \text{cmc}\} \quad (1)$$

cmc is the critical micelle concentration.

The electrostatic contact between the negative hydroxyl ion and the positive cationic micelle of CTAB results in the OH⁻ ions being located on the surface of the micelle, which is how the aforementioned reaction mechanism is diagrammatically represented in Figure 5.

The dye carbonations are partially embedded in the micelle due to hydrophobic interaction.

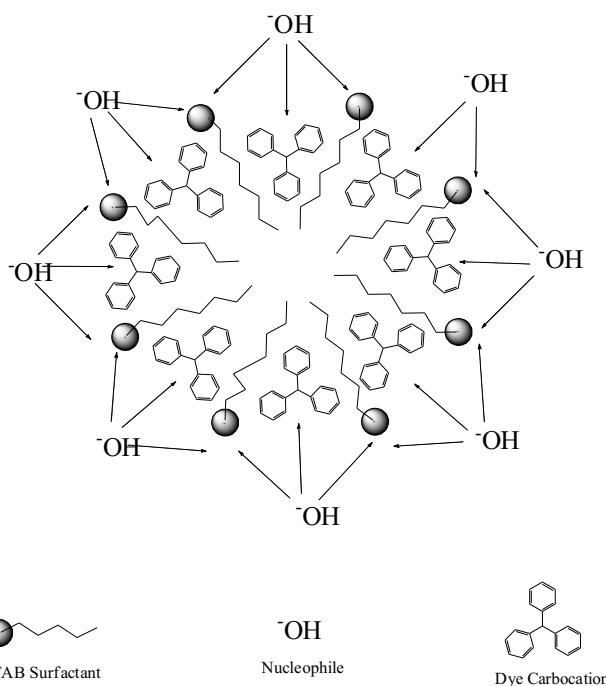


Figure 5: A diagrammatic illustration of the carbonate ion fading of brilliant green in presence of cationic surfactant medium (CTAB).

The observed rate constant k_{obs} is expressed as a function of surfactant concentration by the following equation:

$$k_{obs} = \frac{\{k_w + k_m K_{BG^+} [D_n]\} [\text{OH}^-]_w}{1 + K_{BG^+} [D_n]} \quad (2)$$

The above equation predicts saturation and

variance of k_{obs} at higher surfactant concentrations as we have observed in the plots of k_{obs} against $[D_n]$ for all the surfactants used in this work. The data was curve fitted using a software called 2D Table Curve 5.01 and from which we were able to obtain the kinetic parameters. A typical example of these plots is shown in Figure 6.

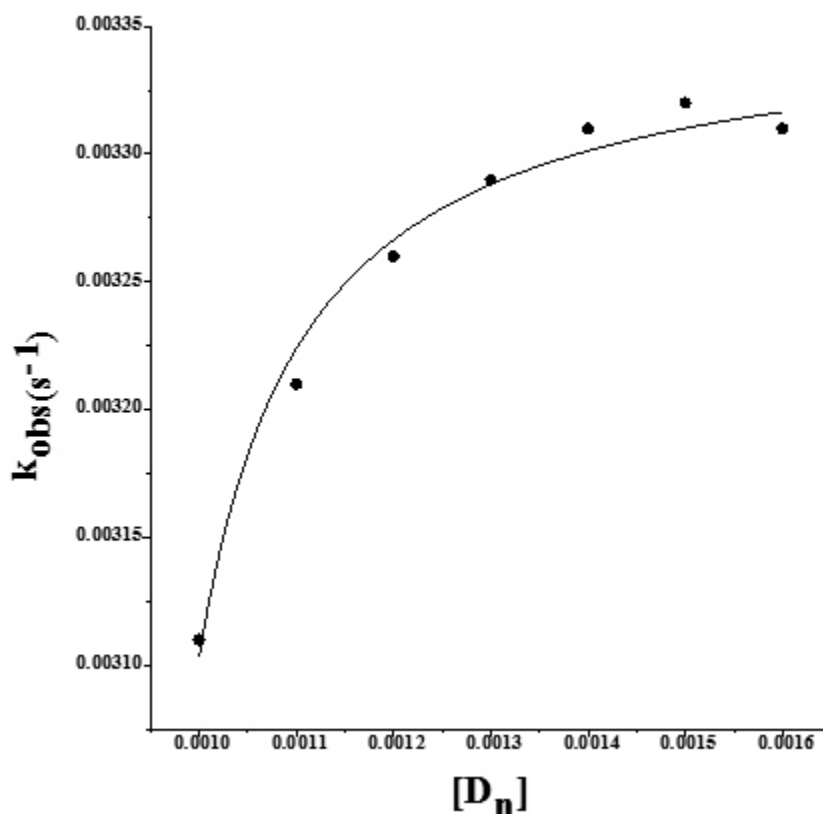


Figure 6: A Typical plot of k_{obs} against $[D_n]$ for all the surfactants used.

The values of the kinetic parameters k_m and K_{BG^+} obtained for the various surfactants are shown in Table 2. From the data in Table 2, it can be seen that the binding constant of brilliant green to the surfactant (K_{BG^+}) increases with increase in change length of the surfactant (i.e. from DTAB, TTAB to CTAB) while the rate constant in micellar phase, k_m also increases with the change length. This is an indication of strong hydrophobic interaction between brilliant green and the surfactant as the chain length increases. The trend in k_m also shows the reaction is faster in micellar phase than in the bulk water phase as the overall rate increases with increase in chain length.

In comparing CTAB, C_{16} PyBr and C_{16} TPPBr, with all having sixteen carbon chain length, the change in k_m and K_{BG^+} can only be due to the polar head group and steric hindrance due bulky group attached to the charged surface. For CTAB and C_{16} PyBr, the change is due to steric effect of the pyridium group the charged surface of the micelle. However drastic change in the substrate binding constant of brilliant green, K_{BG^+} in C_{16} TPPBr is due to strong steric hindrance by the three-phenyl group attached to the atom in hexadecyltriphenyl phosphonium bromide (C_{16} TPPBr) couple with reduction in the charge on the head group.

Table 2: Kinetic parameters obtained from the model for the oxidation of brilliant green by carbonate ion.

SURFACTANT	k_m ($dm^3 mol^{-1}s^{-1}$)	K_m ($dm^3 mol^{-1}$)
DTAB	$(1.51 \pm 0.07) \times 10^{-3}$	727.57 ± 212.37
TTAB	$(2.12 \pm 0.09) \times 10^{-3}$	1361.12 ± 267.83
CTAB	$(3.40 \pm 0.01) \times 10^{-3}$	50992.32 ± 300.25
C_{16} PyBr	$(4.31 \pm 0.07) \times 10^{-3}$	39291.31 ± 707.55
C_{16} TPPBr	$(2.79 \pm 0.85) \times 10^{-4}$	12413.75 ± 317.79

CONCLUSION

The oxidation of brilliant green by carbonate ion in the presence of some cationic surfactant has been studied. The observed catalysis in each of the surfactant is due to the dye-surfactant monomer interaction and the formation of dye-surfactant aggregates of variable sizes made up of few monomers. The k_{obs} -[Surfactant] profiles are structured and are associated with dye-surfactant aggregates in different micellar evolution. In each of the surfactant, there is overall catalysis with the catalytic factor (k_{obs}/k_w) ranging from 1 to 25.43. The rate of hydrolysis of brilliant green by carbonate ion increases with increase in the length of carbon chain length of the cationic surfactant which is a suggestion that the substrates are more reactive when micelles are formed from more hydrophobic surfactants. The rate constants increase in the following order: $k_{DTAB} < k_{TTAB} < k_{CTAB}$ while the maximum catalytic factor is of the order: 8.16, 10.97 and 20.24, respectively.

In the k_{obs} -[Surfactant] profiles for CTAB, C_{16} PyBr and C_{16} TPPBr show also overall catalysis at all surfactant concentrations. The maximum factor is catalytic is 20.24, 25.43 and 4.28 respectively. These profiles are explained by change on the charge on head groups of the surfactants, the steric effect due to the donating effect of the electrons of the methyl and phenyl groups attached to the positive nitrogen atom in CTAB, C_{16} TPPBr and stable positive charge on the nitrogen atom because of the resonance effect on pyridinium group of the head of the micelle in C_{16} PyBr.

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