Alkaline hydrolysis of brilliant green in mixed cationic surfactant systems

Owoyomi Olanrewaju¹ * , Jide Ige¹ and Soriyan O. Omopariola¹

¹Department of Chemistry, Faculty of Science Obafemi Awolowo University, Ile Ife 220005, Nigeria

Received 13 March 2010; Accepted 25 September 2010

Abstract: Kinetic measurements were performed for the alkaline hydrolysis of brilliant green — a triphenylmethane dye used as a model compound for probing micellar rate effects. This reaction was studied both in the presence of tetradecyltrimethylammonium bromide (TTAB) and tetradecyltriphenylphosphonium bromide (TTPPBr) and also in binary mixtures of these surfactants at different mole fractions of each. All rate surfactant profiles were analyzed using the pseudo-phase model in order to obtain the regression parameters, including binding constants and rate constants in the micellar pseudo-phase. The reaction was catalyzed by both surfactants. The catalytic factor increases from about 10 for pure TTPPBr to about 38 for pure TTAB. Binding of BG to micellar surface is greater in pure TTAB than in pure TTPPBr but significantly reduced in the surfactant mixtures than in pure components. Reduction of the binding constant becomes more significant as the mole fraction of TTAB is increased in the mixture. The kinetic data have been analyzed in terms of models of Piszkiewicz and Raghavan-Srinivasan which are in good agreement.

Keywords: Hydrolysis • Kinetics • Brilliant green • Pseudo-phase • Piszkiewicz’s model

© Versita Sp. z o.o.

1. Introduction

In many applications, mixed surfactant systems often give rise to enhanced performance over single component systems [1]. Consequently surfactant blends are employed in a wide variety of practical applications such as enhanced oil recovery [2,3], food [4,5] and cosmetic production [6], detergency [7,8], textiles [9] and paint production [10].

Most of the works in literature have been on the thermodynamics and structural aspects of mixed micelle formation [11-14]. The body of knowledge of the effects of mixed surfactant systems on reaction rates is rather scanty and mostly on cationic/non-ionic, anionic/non-ionic and cationic/anionic mixed systems [15-19]. Very few studies on the effects of mixed cationic/cationic surfactant systems on reaction rates are reported in literature.

Most of the investigations involving cationic surfactant systems have focused on the alkyltrimethylammonium and alkylpyridinium bromides [20,21]; it was not until recently that investigation on micellar behavior and catalytic properties of the alkyltriphenylphosphonium bromide surfactants were reported.

Palepu et al. [22] studied the effects of the alkyltriphenylphosphonium bromides (ATPPB’s) and their binary mixtures on the reaction of methyl-4-nitrobenzenesulfonate with bromide ion and rationalized their results on the basis of the pseudo-phase ion exchange model. Their results showed that the reaction rate is enhanced between three to eight fold for the ATPPB’s series over those found for the other cationic surfactants investigated and attributed this to catalysis at the micellar surface and effects caused by the phosphorous centre. These surfactants offer significantly bulkier head groups than those of the commonly investigated ammonium and pyridinium based cationic surfactants. They also possess aromatic moieties at the micellar surface.

Triphenylmethane dyes, such as BG, represent a class of synthetic dyes of commercial and analytical importance [23]. Numerous applications are promoted by the intensity, range and light-fastness of colour exhibited by these dyes. The hydrolysis of this dye and its derivatives has been extensively studied in aqueous medium [24-26]. Such works investigated the substituent effect on the rate of reaction. The present work, while not dealing with this aspect of substituent effect, concerns itself with the more fundamental study

* E-mail: owooyomi@oauife.edu.ng
of medium effects as reflected in the rate-surfactant concentrations profiles.

The alkaline hydrolysis of this dye in pure TTAB and other n-alkyltrimethylammonium bromide was recently reported by our group [27]. An increase in observed rate constant with increase in surfactant chain length was observed. This is consistent with similar investigations reported before [28].

In the present work, the effects of tetradecyltriphenylphosphonium bromides (TTPPBr), tetradecyltrimethylammonium bromide (TTAB) and their binary mixtures on the alkaline hydrolysis of Brilliant green (BG) — a triphenylmethane dye (a cationic substrate) — have been investigated with the aim of examining the effects of surfactant head group modifications on the kinetic parameters of this reaction (Eq. 1).

2. Experimental Procedure

2.1. Materials

The tetradecyltriphenylphosphonium bromide used in this work was of the highest purity commercially available from Lancaster Synthesis of England, and the tetradecyltrimethylammonium bromide was obtained from Fluka and has a purity ≥98%. Sodium hydroxide was analytical reagent grade from Sigma-Aldrich and Brilliant green was from Avondale Laboratory, the wavelength scan gave a wavelength of maximum absorption at 626 nm. The water used was doubly distilled with specific conductivity between 2-5 µS cm⁻¹.

2.2. Determination of the critical micelle concentration

The critical micelle concentration (cmc) of the surfactants and their binary combinations in the absence and presence of the 3.76×10⁻⁶ mol dm⁻³ of the dye and 0.0020 mol dm⁻³ of NaOH were determined by measuring the specific conductivities of various concentrations of the surfactant solutions at different mole fractions α_{TTAB} of TTAB. The breakpoint in the conductivity-concentration profile was taken as the cmc. The concentrations of BG and the hydroxide ion did not show any noticeable effect on the cmc of the pure surfactants or their binary mixtures. The cmc obtained are: 0.495 mM, 0.526 mM, 0.725 mM, 1.00 mM and 3.57 mM for mole fractions of TTAB of 0.00, 0.25, 0.50, 0.75 and 1.00, respectively. Respective values for the degree of counter-ion binding of 0.44, 0.42, 0.36, 0.34 and 0.71 were obtained. The conductivity meter used was CMD 210 from Walden Precision Apparatus (UK) with a dipped type electrode and a cell constant of 1.00. The meter was calibrated with standard solutions of potassium chloride.

2.3. Kinetic measurements

Kinetic studies designed for the investigation of the alkaline hydrolysis rate profiles of the dye were carried out at a fixed temperature of 25.0±0.1°C by monitoring the decrease in absorbance of the dye as a function of time at the wavelength of maximum absorption (λ_{max}) 626 nm in pure water and pure TTPPBr as there was no change in the λ_{max} of the dye in the presence of TTPPBr. The alkaline fading of the dye in the presence of TTAB and its binary mixtures with TTPPBr were carried out at 634 nm because there was a shift in the λ_{max} of the dye from 626 nm to 634 nm in the presence of TTAB and its binary mixture with TTPPBr. Constant temperature was maintained by using a combination of Grant thermostating unit immersed in a water bath equipped with a pump, which circulated water from the thermostatted water bath at 25°C around the cell compartment of the Unicam UV1 spectrophotometer.

The kinetics were investigated under pseudo-first order conditions with the hydroxide concentration (0.0020 mol dm⁻³) in excess of the BG concentration (3.76×10⁻⁶ mol dm⁻³) by more than a factor of 500. The first order rate constants, k_{obs} (s⁻¹), were obtained from the slopes of ln (A_t-A_∞) against time plots, where A_t and A_∞ are the absorbance at time t and at the end of the reaction, respectively. The pseudo-first order kinetic profiles were always linear for more than 85% of the reaction. Each kinetic run was repeated at least twice and the rate constants were reproducible within ±5% precision.

3. Results and Discussion

Fig. 2 shows the influence of TTPPBr and TTAB on the alkaline hydrolysis of BG. The observed rate constant, k_{obs} is plotted against various mole fractions of TTAB at 0.0020 mol dm⁻³ of hydroxide ion. The mole fraction of TTAB is defined as:

$$\alpha_{TTAB} = \frac{\text{mole of TTAB}}{\text{mole of TTAB} + \text{mole of TTPPBr}}$$

Catalysis is observed in both surfactants because both the substrateBG and the nucleophile (the hydroxide ion) are attracted to the micellar surface

![4,4'-bisdiethylaminophenylmethyl sulfate (BG)](image-url)
with different partition constants based on electrostatic and hydrophobic considerations. The interesting feature of the rate-surfactants profile is the enhanced catalysis by TTAB compared with TTPPBr. The faster rate of reaction in pure TTAB than in pure TTPPBr is paralleled by an increase in rate as the mole fraction of TTAB is increased in the mixtures. This is in sharp contrast to the $S_N2$ reaction of methyl-4-nitrobenzene sulphonate (MNBS) with bromide ion in similar systems [22], where three to eight fold rate enhancements in alkyltriphenylphosphonium bromides is observed compared with other cationic surfactants investigated.

Molecular modeling calculations [22] have shown that the positive charge of the quaternary ammonium head groups is distributed over the substituent groups; consequently, the nitrogen atom in TTAB adopts a negative charge. In contrast, for the quaternary phosphonium cations, the phosphorous centre bears a large positive charge. Because of this, the positively charged substrate binds more to the quaternary ammonium head group of TTAB than the phosphonium head group of TTPPBr, hence the rate accelerated more in TTAB than in TTPPBr.

The experimental results obtained for the alkaline fading of BG in the presence of the surfactants and their mixtures can be easily explained in terms of the Piszkiewicz model [29], which is analogous to the Hill model of enzyme-catalyzed reactions [30]. This model assumes that the substrate BG$^+$ associates with surfactant aggregates to form an aggregated complex D$_n$BG$^+$ which may react according to the following scheme:

$$nD + BG^+ \xrightarrow{K_D} D_nBG^+$$  \hspace{2cm} (2)

$$D_nBG^+ \xrightarrow{k_m} \text{Products}$$  \hspace{2cm} (3)

$$BG^+ \xrightarrow{k_w} \text{Products}$$  \hspace{2cm} (4)

**Figure 1.** Structures of TTAB and TTPPBr used in this work.

**Figure 2.** Dependence of the observed rate constant, $k_{ob}$ for the alkaline hydrolysis of BG on total surfactant concentration, [Surfactant], at 298 K. Solid lines are the theoretical fit according to Eq. 5.
In the scheme $k_w$ and $k_m$ are the rate constants in bulk aqueous and micellar phases, respectively. $K_D$ is the dissociation constant between the BG+ and the micelle. According to Eqs. 2, 3 and 4 the observed rate constant $k_{obs}$ may be given as:

$$k_{obs} = \frac{k_m [D] + k_w K_D}{K_D + [D]}$$

with $K_D$ defined as:

$$K_D = \frac{[D] [BG^+]}{[D_a] [BG_a^+]$$

The regression parameters obtained for both pure surfactants and their binary mixtures using Eq. 5 are presented in Table 1. The table shows that the ratio $k_m/k_w$, the catalytic factor, increases with increase in the mole fraction of TTAB in the mixture. The dependence of the catalytic factor on the mole fraction of TTAB in the mixture is depicted in Fig. 3. The sigmoidal pattern of the curve in Fig. 2 for pure TTAB shows that there was no significant rate enhancement up to about 0.0030 mol dm$^{-3}$ of TTAB. Above this concentration, which is the concentration range for the onset of micellization (CMC = 0.00357 mol dm$^{-3}$), there was a drastic increase in reaction rate attaining saturation around 0.008 mol dm$^{-3}$. This observation shows that pre-micellar activity is not significant in the observed rate enhancement.

Also, as can be seen in the Table 2, the surfactant-substrate binding constant $1/K_D$ is greater in pure TTAB than in pure TTPPBr. This is consistent with the molecular modeling calculation which showed that the nitrogen in the ammonium head group is negatively charged, while the phosphorous centre in the phosphonium head group is positively charged — the positively charged substrate therefore binds more strongly in the TTAB aggregates than in the TTPPBr aggregates. The binding constants in the mixed systems are apparently smaller than in the pure systems, and this observation is in line with the trend observed in the degree of counter-ion binding. This may be due to evolution of different micellar sizes or geometry in the mixtures compared with the pure systems because the presence of any amount of TTPPBr in the mixture has a remarkable effect on the micellar size on account of the bulky and more hydrophobic head group in TTPPBr. The calculated values of $n$ are all greater than one, between 1.19 and 4.69, in agreement with earlier observations [29] and are viewed as an index of positive cooperativity. They are far less than the number of surfactant molecules found in the micelle and have been interpreted as evidence for the presence of pre-micellar aggregates [31,32].

For bimolecular micelle-catalyzed reactions, the model of Raghvan and Srinavasan [33] which also predicts constancy in the values of $k_{obs}$ at higher surfactants concentrations can be used for evaluating the binding constants of the reactants. The distribution of both the brilliant green and the hydroxide ion in aqueous

| Table 1. Kinetic Parameters obtained from the regression fit of Eq. 5 for the alkaline hydrolysis of BG in TTAB+TTPPBr mixtures at 298 K, [NaOH] = 0.0020 M |
|---|---|---|---|---|
| $\alpha_{TTAB}$ | $k_{m} \times 10^2$ s$^{-1}$ | $K_D$/M | $n$ | $k_m/k_w$ |
| 0.00 | 1.35±0.02 | (6.65±0.57) ×10$^4$ | 1.86±0.17 | 10.38 |
| 0.25 | 2.21±0.06 | (1.17±0.09) ×10$^5$ | 1.19±0.11 | 17.00 |
| 0.50 | 2.67±0.05 | (3.43±0.18) ×10$^4$ | 1.48±0.09 | 20.54 |
| 0.75 | 3.40±0.07 | (1.69±0.09) ×10$^5$ | 2.07±0.13 | 26.15 |
| 1.00 | 4.92±0.13 | (1.95±0.21) ×10$^11$ | 4.69±0.55 | 37.85 |

| Table 2. Binding Parameters obtained from the regression fit of Eq. 11 for the alkaline hydrolysis of BG in pure TTAB+TTPPBr mixtures at 298 K, [NaOH] = 0.0020 M |
|---|---|---|---|---|
| $\alpha_{TTAB}$ | $K_{BG}$ | $K_{OH}$ | $1/K_D$ |
| 0.00 | (1.54±0.13) ×10$^9$ | 0.999±0.014 | 1.50×10$^9$ |
| 0.25 | (8.79±0.64) ×10$^8$ | 0.997±0.026 | 8.54×10$^8$ |
| 0.50 | (2.98±0.16) ×10$^8$ | 0.998±0.020 | 2.92×10$^8$ |
| 0.75 | (5.86±0.32) ×10$^8$ | 1.001±0.020 | 9.29×10$^8$ |
| 1.00 | (5.05±0.55) ×10$^8$ | 1.001±0.027 | 5.13×10$^8$ |

Figure 3. Variation of the catalytic factor ($k_m/k_w$) with the mole fraction $\alpha_{TTAB}$ for the alkaline hydrolysis of BG at 25°C.

The regression parameters obtained for both pure surfactants and their binary mixtures using Eq. 5 are presented in Table 1. The table shows that the ratio $k_m/k_w$, the catalytic factor, increases with increase in the mole fraction of TTAB in the mixture. The dependence of the catalytic factor on the mole fraction of TTAB in the mixture is depicted in Fig. 3. The sigmoidal pattern of the curve in Fig. 2 for pure TTAB shows that there was no significant rate enhancement up to about 0.0030 mol dm$^{-3}$ of TTAB. Above this concentration, which is the concentration range for the onset of micellization (CMC = 0.00357 mol dm$^{-3}$), there was a drastic increase in reaction rate attaining saturation around 0.008 mol dm$^{-3}$. This observation shows that pre-micellar activity is not significant in the observed rate enhancement.

Also, as can be seen in the Table 2, the surfactant-substrate binding constant $1/K_D$ is greater in pure TTAB than in pure TTPPBr. This is consistent with the molecular modeling calculation which showed that the nitrogen in the ammonium head group is negatively charged, while the phosphorous centre in the phosphonium head group is positively charged — the positively charged substrate therefore binds more strongly in the TTAB aggregates than in the TTPPBr aggregates. The binding constants in the mixed systems are apparently smaller than in the pure systems, and this observation is in line with the trend observed in the degree of counter-ion binding. This may be due to evolution of different micellar sizes or geometry in the mixtures compared with the pure systems because the presence of any amount of TTPPBr in the mixture has a remarkable effect on the micellar size on account of the bulky and more hydrophobic head group in TTPPBr. The calculated values of $n$ are all greater than one, between 1.19 and 4.69, in agreement with earlier observations [29] and are viewed as an index of positive cooperativity. They are far less than the number of surfactant molecules found in the micelle and have been interpreted as evidence for the presence of pre-micellar aggregates [31,32].

For bimolecular micelle-catalyzed reactions, the model of Raghvan and Srinavasan [33] which also predicts constancy in the values of $k_{obs}$ at higher surfactants concentrations can be used for evaluating the binding constants of the reactants. The distribution of both the brilliant green and the hydroxide ion in aqueous
and micellar pseudo-phases is considered in this model. This model assumes that the substrate BG associates with surfactant aggregates to form an aggregated complex $D_nBG^+$ to which the hydroxide binds to give a ternary complex $D_nBG^+OH^-$ which may react according to the following scheme:

$$\begin{align*}
    nD + BG^+ & \rightarrow K_{BG}^+ D_nBG^+ \\
    D_nBG^+ + OH^- & \rightarrow K_{OH}^- D_nBG^+OH^- \\
    D_nBG^+OH^- & \rightarrow k_m \text{Products} \\
    BG^+ + OH^- & \rightarrow k_w \text{Products}
\end{align*}$$

According to this model the observed rate constant in the presence of surfactant is given by the equation

$$k_{obs} = \frac{k_m + k_w K_{BG}^+ K_{OH}^- [D]^n}{1 + K_{BG}^+ [D]^n + K_{OH}^- [S]}$$  \hspace{1cm} (11)

In Eq. 11, $K_{BG}^+$ and $K_{OH}^-$ are the binding constants of the substrate, BG, and the nucleophile, OH$^-$ ion, respectively. Using the experimentally obtained $k_w$ and the values of $k_m$ and $n$ from the Pizkiewicz model above (Eq. 5), the values of $K_{BG}^+$ and $K_{OH}^-$ are obtained using Eq. 11 and are tabulated in Table 2.

The kinetic results have been rationalized in terms of both the Pizkiewicz model and its modification for bimolecular reaction as proposed by Raghavan and Srinivasan. Both models gave good interpretation for the observed rate acceleration in the two cationic surfactants and their binary mixtures.

### Acknowledgment

The authors gratefully acknowledge the management of the Central Science Laboratory of the Obafemi Awolowo University for provision of technical supports for this work.

### References

[1] K.Ogino, M. Abe (Eds.), Mixed Surfactant Systems (Dekker, New York, 1993)
[2] M. El-Batanoney, T. Abdel-Moghny, M. Ramzi, J. Surf. Det. 2, 201 (1999)
[3] M.J. Rosen, H. Wang, P. Shen, Y. Zhu, Langmuir 2, 3749 (2005)
[4] A.E. Kharlov, G.P. Yampol'skaya, Moscow Univ. Chem. Bull. 62, 22 (2007)
[5] F.T. Tadros, Applied Surfactants (Wiley-VCH Verlag GmbH and Co. KGaA, Weinheim, 2005)
[6] T.J. Hall-Manning, G.H. Holland, G. Rennie, P. Revell, J. Hines, M.D. Barret, D.A. Basketter, Food Chem. Toxic. 36, 233 (1998)
[7] Y. Yu, Z. Jin, A.E. Bayly, Chin. J. Chem. Eng. 16, 517 (2008)
[8] T. Satsuki, Y. Nagoh, H. Yoshimura, J. Jap. Oil Chemist Soc. 48, 109 (1999)
[9] J.L. Parra, J.J. Garcia-Dominuguez, A. de la Maza, J.S. Leal, J. Soc. Dyer's Colourists 102, 227 (2008)
[10] R.J. Goetz, M. El-Aasser, Langmuir 17, 993 (1990)
[11] H. Hoffmann, G. Poessnecker, Langmuir 10, 381 (1994)
[12] E. Marques, K. Khan, M. de-Miguel, B. Lindman, J. Phys. Chem. 97, 4729 (1993)
[13] T. P. Goloub, R.J. Pugh, B.V. Zhmud, J. Colloid Interface Sci. 229, 72 (2000)
[14] M. Bergstrom, Langmuir 17, 993 (2001)
[15] M. Munoz, M. Rodriguez, M. D. Graciani, M.L. Moya, Int. J. Chem. Kinet. 34, 445 (2002)
[16] M.N. Khan, E. Ismail, M.R. Yussof, J. Phys. Org. Chem. 14, 669 (2001)
[17] G. Fernandez, A. Rodriguez, M. D. Graciani, M. Munoz, M.L. Moya, Int. J. Chem. Kinet. 35, 45 (2003)
[18] H.M. Joshi, T.N. Nagar, Asian J. Chem. 14, 1763 (2002)
[19] K.K. Ghosh, A. Pandey, J. Indian Chem. Soc. 76, 191 (1999)
[20] R. Bacaloglu, A. Blasko, C.A. Bunton, G. Cerichelli, F. Ortega, J. Phys. Chem. 94, 5062 (1990)
[21] R. Bacaloglu, C.A. Bunton, G. Cerichelli, F. Ortega, J. Phys. Chem. 94, 5068 (1990)
[22] M.M. Mohareb, K.K. Ghosh, G. Orlova, R.M. Palepu, J. Phys. Org. Chem. 19, 281 (2006)
[23] D.F. Duxbury, Chem. Rev. 93, 381 (1993)
[24] B.M. Fox, G. Hallas, J.D. Hepworth, D. Mason, J. Chem. Tech. Biotech. 30, 317 (1980)
[25] B.M. Fox, J.D. Hepworth, D. Mason, G. Hallas, J. Chem. Soc. (Perkin Trans. 2), 8, 987 (1982)
[26] J.D. Hepworth, D.J. Lythgoe, D. Mason, G. Hallas, Dyes Pigments 15, 31 (1991)
[27] O. Owoyomi, J. Ige, O. Soriyan, G. Ogunlusi, S.E. Olaseni, O. Olanrewaju, Acta Chim. Slov. 54, 370 (2007)
[28] D.J. Jobe, V.C. Reinsborough, Aust. J. Chem. 37, 1593 (1984)
[29] D. Piszkiewicz, J. Amer. Chem. Soc. 99, 1550 (1977)
[30] A.V. Hill, J. Physiol. (London) 40, 4 (1910)
[31] E. Pandey, S.K. Uphaday, Colloids Surf. A: Physicochem. Eng. Aspects 269, 7 (2005)
[32] C.E. Drennan, R.J. Hughes, V.C. Reinsborough, O.O. Soriyan, Can. J. Chem. 76, 152 (1998)
[33] P.S. Raghavan, V.S. Srinavasan, Proc. Indian Acad. Sci. (Chem. Sci.) 98, 199 (1987)
[34] L.S. Romsted, In K.L. Mittal (Ed.), Micellization, Solubilization and Microemulsions (Plenum Press, New York, 1977) 2, 509
[35] R.L. Reeves, J. Amer. Chem. Soc. 97, 6019 (1975)