Kinetics of brilliant green fading in the presence of TX-100, DTAB and SDS

Babak Samiey · Mohammad Rafi Dargahi

Abstract The rate constant of alkaline fading of brilliant green (BG^+) was measured in the presence of non ionic (TX-100), cationic (DTAB) and anionic (SDS) surfactants. This reaction was studied under pseudo first-order conditions at 283–303 K. The rate of reaction showed remarkable dependence on the electrical charge of the used surfactants. It was observed that the reaction rate constant increases in the presence of TX-100 and DTAB (catalytic effect) and decreases in the presence of SDS (inhibitory effect). Binding constants and the related thermodynamic parameters were obtained by the classical model. The results show that binding of BG^+ to TX-100 is exothermic and binding of BG^+ to DTAB and SDS is endothermic in the used concentration range of surfactants.

Keywords Classical model · Brilliant green · Kinetics · Fading · Surfactant

Introduction

The rates of chemical reactions are known to be changed by self-organized assemblies such as micelles [1–9]. Effects of micelles on these reactions can be attributed to electrostatic and hydrophobic interactions. Brilliant green (BG^+) is a triphenylmethane dye. These dyes are aromatic compounds, and are used extensively in the textile industry to dye silk and cotton, and in paper and leather industries [10, 11]. Some of these dyes are used as biological stains and in

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veterinary medicine [12]. BG^+ has been used as an antiseptic. It is used in the laboratory practice for biological staining and as a disinfectant for instruments [13]. Also, BG^+ has antifungal properties similar to those of malachite green (MG^+) [14]. In continuation of our earlier works [15, 16], we studied the BG^+ alkaline fading in the presence of different concentrations of TX-100, DTAB and SDS at 283-303 K. BG^+ fading is a one-step reaction and kinetics of these kinds of reactions in the presence of surfactants can be studied using cooperativity and classical models [15, 16]. Also, in this work, substituent effects of ethyl groups of BG^+ and methyl groups of MG^+ on the fading reaction rates of these two dyes were compared to each other.

Experimental

Materials

Brilliant green (hydrogen sulfate), polyoxyethylene (number of segments 9.5) glycol *tert*-octylphenyl ether (Triton X-100 or TX-100), dodecyltrimethylammonium bromide (DTAB), sodium dodecyl sulfate (SDS) and NaOH were purchased from Merck.

Methods

The fading of BG^+ was followed at its maximum wavelength (λ_{max}) values in a thermostated cell compartment of a Shimadzu UV–1650PC spectrophotometer. The reaction of BG^+ with hydroxide ion brings about fading the color of the BG^+ and results in the formation of colorless carbinol base, Fig. 1. The experiments were conducted at 283, 293 and 303 K within $\pm$ 0.1 K. All the kinetic runs were carried out at least in triplicate. To perform each kinetic run, a 100 μl aliquot of 9.39×10^{-4} M BG^+ solution was added by a microsyringe into 2.8 ml of a solution containing 1.42×10^{-3} M sodium hydroxide and a certain concentration of surfactant. To study all interactions occurring between the surfactant and substrate molecules, we carried out the experiments in the surfactant concentration ranges in which the reaction rate finally reaches its maximum value (in the case of the catalytic effect) or becomes very slow (in the case of the inhibitory effect). The reaction between BG^+ and hydroxide ion has been found to be bimolecular but pseudo first-order conditions (excess alkali) were used in all cases. We used the second-order reaction rate constants in our calculations.

Results and discussion

Analysis of kinetic data by the classical model

In the classical (or stoichiometric) model [15], it is assumed that in each range of surfactant concentration, the surfactant and substrate can bind together and there is
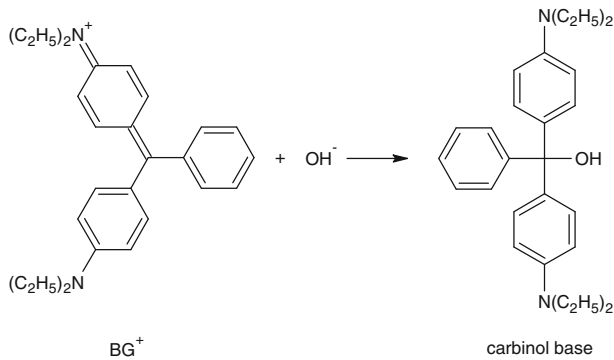
Fig. 1 Schematic representation of the BG$^+$ fading reaction

an equilibrium relation between them. A concentration of surfactant is called "*substrate-surfactant complex formation point*" (or abbreviated as sc point) in which the equilibrium relation between added surfactant and the species already present in the solution ends and a new equilibrium relation between added surfactant and compound resulting from the previous equilibrium relation starts. The critical micelle concentration (cmc) value of a surfactant is also a sc point and there may be some sc points before and after cmc as well. The range of surfactant concentration which covers an equilibrium relation is named "*region*". Surfactant molecules can bind to the substrate either monomeric or micellar (by one or more number of their molecules). Thus, we can obtain the stoichiometric ratios and binding constants of interactions of surfactants with substrate molecules in various ranges of surfactant concentrations. For each assumed equilibrium relation, the following equation holds for:

$$\ln k' = c - \frac{E_S}{RT}[S]_t \tag{1}$$

where $E_S = -RTd\ln k' \frac{d\ln k'}{d[S]_t}$ and k', c, $[S]_t$, R and T are the rate constant in the presence of surfactant, $\ln k$ (in the first region) or $\ln k_{sc}$ (for other regions), total surfactant concentration, universal gas constant, absolute temperature, respectively. k_{sc} is the k_{obs} in the starting of every region except region one. Eq. 1 can determine the concentration range of each region [15]. If the reaction rate is decreased upon increasing the surfactant concentration, the sign of E_S is positive and is called "*inhibition energy*" and if the reaction rate is increased with increasing the surfactant concentration, the sign of E_S is negative and is named "*catalytic energy*" at constant temperature and various surfactant concentrations. The unit of E_s is kJ (mol molar(surfactant))$^{-1}$.

In this model, it is assumed that one substrate molecule, BG$^+$ in this work, binds to n molecules of surfactant in each region and we have:

$$BG^+ + nS \overset{K}{\leftrightarrow} S_n BG^+ \tag{2}$$

where K is the binding constant of the substrate–surfactant interaction in each region. According to the classical model [15], these interactions are of type I or II, in

which the surfactant has an inhibitory or catalytic effect on the fading reaction of BG^+ and k_{obs} is related to the surfactant concentration as follows [15]:

$$k_{obs} = \frac{k + k_S K[S]_t^n}{1 + K[S]_t^n} \quad \text{(region one)} \tag{3}$$

and

$$k_{obs} = \frac{k_{sc} + k_S K([S]_t - [sc])^n}{1 + K([S]_t - [sc])^n} \quad \text{(all the other regions)} \tag{4}$$

where k and k_{sc} are the reaction rate in the absence of surfactant and at every sc point. k_S is the reaction rate in the substrate–surfactant complex and $k_S = 0$ for inhibition. The total binding constant (K_{tot}^i) and total stoichiometric ratio (n_{tot}^i) values for each substrate, in the ith region, can be obtained from below equations:

$$K_{tot}^i = K_1 \ldots K_{i-1} K_i = \prod_{j=1}^{i} K_j \tag{5}$$

$$n_{tot}^i = n_1 \ldots n_{i-1} n_i = \sum_{j=1}^{i} n_j \tag{6}$$

Going from one region to the next one, if the $K^{1/n}$ value (the average binding constant of the interaction between one substrate molecule with one surfactant molecule in each region) increases, the cooperativity of interaction is positive and if the $K^{1/n}$ value decreases, the cooperativity is negative.

Comparison of substituent effects on the BG^+ and MG^+ fading rate

As seen in Table 1, fading rate constants of BG^+ in water are 7.97, 20.93 and 52.05 M^{-1} min^{-1} at 283, 293 and 303 K, whereas the fading rate constants of MG^+ in water are 18.89, 46.98 and 118.60 M^{-1} min^{-1} at 283, 293 and 303 K, respectively [16]. As we know, the electron-releasing inductive effect of the ethyl groups of BG^+ is greater than that of the methyl groups of MG^+. This makes the $(C_2H_5)_2N^+=$ group of BG^+ more stable than the $(CH_3)_2N^+=$ group of MG^+ and results in a decrease in the fading rate constant values of BG^+ in water compared to those of MG^+.

Effect of TX-100 on the BG^+ fading

As shown in Figs. 2 and 3, with an increase in TX-100 concentration, the λ_{max} value of BG^+ shifts to red and the reaction rate of BG^+ fading increases.

As seen in Table 1, the kinetics of BG^+ fading in the presence of TX-100 has three regions. The cmc value of TX-100 in pure water is 0.29 mM [17] and the first region is below its cmc point. As given in Table 2, in acidic solution, the interaction of TX-100 with BGH^{2+} results in the blue shift in λ_{max} value of BGH^{2+}, Fig. 4.

This indicates that a preliminary electrostatic interaction occurs in this region between the $(C_2H_5)_2N^+=$ group of BG^+ and the oxygen atom of the ethoxy chains

Table 1 Parameters obtained from the classical model for the interaction of BG^+ with TX-100 at 283–303 K

T (K)	Region	sc (mM)	k_{sc} (M^{-1} min^{-1})	Equation[b]	E_s^a	$\log K^b$	n	k_s (M^{-1} min^{-1})	Cooperativity
283	1st	0.00	7.97	$\ln k' = 1842.02[TX]_l +2.06$	−4334.4	7.37	2.21	29.49	−
	2nd	0.65	26.10	Reaction rate is approximately constant	−	−	−	−	+
	3rd	14.00	42.78	$\ln k' = 61.47[TX]_l +3.00$	−144.6	2.62	1.53	252.33	→
293	1st	0.00	20.93	$\ln k' = 1452.33[TX]_l +3.05$	−3537.9	6.88	2.01	54.21	−
	2nd	0.60	50.43	Reaction rate is approximately constant	−	−	−	−	+
	3rd	14.00	79.39	$\ln k' = 53.03[TX]_l +3.68$	−129.2	1.95	1.36	567.82	→
303	1st	0.00	52.05	$\ln k' = 1184.37[TX]_l +3.97$	−2983.6	6.23	1.78	110.28	−
	2nd	0.56	103.03	Reaction rate is approximately constant	−	−	−	−	+
	3rd	14.00	147.48	$\ln k' = 43.09[TX]_l +4.44$	−108.5	0.80	1.09	2655.98	→

TX is an abbreviation for TX-100 and the unit of its concentration in Eq. 1 is M. k_{sc} and sc values obtained from intersection of Eq. 1 of adjacent regions are shown in italic. [a] Unit of E_s is kJ (mol molar (surfactant))$^{-1}$. [b] Unit of K is M^{-n}

Fig. 2 Values of λ_{max} of BG$^+$ vs. concentrations of SDS (*open triangle*), TX-100 (*open square*) and (*open diamond*) DTAB under alkaline conditions
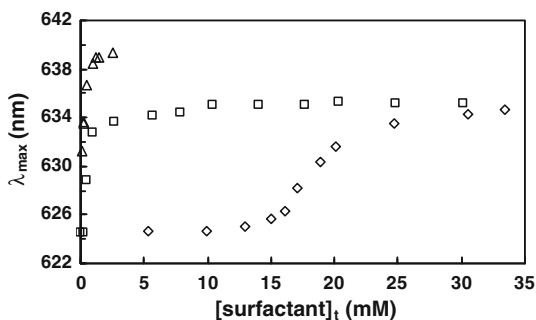

Fig. 3 Values of k_{obs} of the BG$^+$ fading reaction vs. concentrations of TX-100 at 283 (*open diamond*), 293 (*open square*) and 303 K (*open triangle*) under alkaline conditions
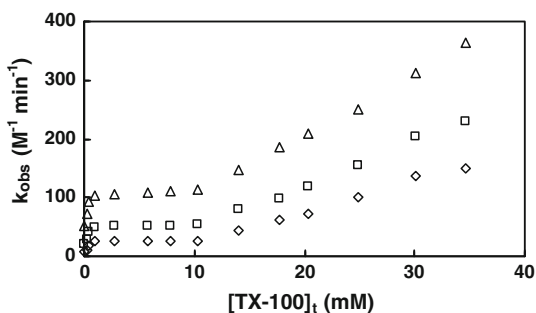

Table 2 Typical λ_{max} values of BG$^+$ in the presence of TX-100, DTAB and SDS in acidic and alkaline solution

In 1 M HCl	λ_{max} (nm)	In 1.37×10^{-3}M NaOH	λ_{max} (nm)
–	448	–	624.5
0.3 mM TX-100	446	0.3 mM TX-100	626.3
15 mM DTAB	448	15 mM DTAB	625.7
1 mM SDS	448, 632.5	0.93 mM SDS	638.5

It is necessary to say that BGH^{2+} fades in 1 M HCl

of TX-100 molecules which is similar to the interaction of silanol groups of silica gel with TX-100 [17, 18]. This interaction along with further hydrophobic interaction of BG$^+$ with TX-100 molecules results in a sharp red shift in λ_{max} value of BG$^+$. The red shift has been previously reported for other compounds upon going from polar to apolar solvents, as a result of hydrophobic interaction [15, 19–21]. It seems that TX-100 molecules decrease the dielectric constant of the BG$^+$ micro-environment. According to Hughs–Ingold rules for nucleophilic substitution reactions [22, 23], the formation of the neutral carbinol base from two oppositely charged reactants is favorable in lower dielectric constant media and thus with increase in TX-100 concentration, the rate of BG$^+$ fading increases in the first region. In this region, as seen from log K values in Table 1, the interaction of BG$^+$ with TX-100 is exothermic.
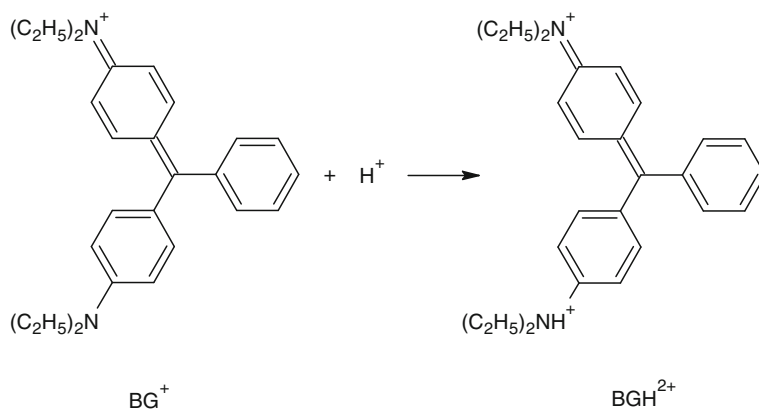
Fig. 4 Scheme of the BG^+ reaction with H^+

Table 3 Thermodynamic parameters obtained from the classical model for the interaction of BG^+ with TX-100 at 283–303 K

T (K)	$\log K_{tot}^a$	ΔG (kJ mol^{-1})	ΔH	ΔS (J mol^{-1} K^{-1})
283	9.99	−54.1		
293	8.83	−49.5	−241.7	−660.7
303	7.035	−40.8		

[a] Unit of K_{tot} is $M^{-n_{tot}}$

In the second region, above the cmc value of TX-100, the reaction rate and λ_{max} value of BG^+ fading keep approximately constant (Figs. 2 and 3). In the third region, the reaction rate increases with an increase in TX-100 concentration, but there is no shift in the λ_{max} value of BG^+. This indicates that BG/TX-100 forms through hydrophobic association between bound TX-100 molecules. In this region, the interaction is exothermic (Table 1).

As seen in Table 3, the interaction of BG^+ with TX-100 molecules throughout the concentration range of TX-100 is exothermic and its ΔS value is negative.

The electron-releasing inductive effect of the ethyl groups of BG^+ is greater than that of the methyl groups of MG^+. This makes the $(C_2H_5)_2N^+=$ group of BG^+ more stable than the $(CH_3)_2N^+=$ group of MG^+ and results in an increase in K_{tot} and thus fading rate constant values of BG/TX-100 at 283–303 K, Tables 1 and 3, compared to those of MG/TX-100 [16].

Effect of DTAB on the BG^+ fading

As seen in Figs. 2 and 5 and Table 4, the kinetics of BG^+ fading in the presence of DTAB has three regions.

The cmc value of DTAB in pure water is 13.77 mM [24] and the first region is below the cmc value of DTAB. In this region, with an increase in DTAB

Fig. 5 Values of k_{obs} of the BG$^+$ fading reaction vs. concentrations of DTAB at 283 (*open diamond*), 293 (*open square*) and 303 K (*open triangle*) under alkaline conditions
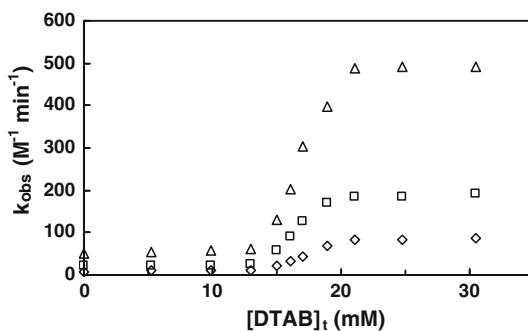
concentration, the rate constant of BG$^+$ fading and the λ_{max} value of BG$^+$ keep approximately constant and it seems that there is no interaction between BG$^+$ and DTAB molecules. Obviously, at the beginning of the second region (≈ 13 mM $\approx$ cmc value of DTAB), a weak electrostatic interaction occurs between the $(C_2H_5)_2N-$ group of BG$^+$ and the positive head group of DTAB molecules and along with hydrophobic interaction of BG$^+$ with nonpolar moiety of DTAB molecules results in the red shift in the λ_{max} value of BG$^+$. Confirming this result, it is seen from Table 2 that 15 mM DTAB acidic solution has no effect on the λ_{max} value of BGH^{2+}. According to Hughs–Ingold rules for nucleophilic substitution reactions, under these conditions, the rate constant of BG$^+$ fading increases with increase in DTAB concentration. Similar results were obtained by Olanrewaju et al. [25]. The positive ΔS value of this interaction (996.6 J mol^{-1} K^{-1}) shows the increased randomness which suggests that the hydrocarbon chain of DTAB molecules replace some water molecules of solvating BG$^+$, Table 5. These displaced molecules gain more translational entropy than is lost by DTAB molecules, thus allowing the prevalence of randomness in the system.

In the third region, the rate constant of BG$^+$ fading and λ_{max} value of BG$^+$ keep approximately constant and it seems that there is no interaction between BG$^+$ and DTAB molecules (Table 4 and Fig. 2). As given in Table 5, the interaction of BG$^+$ with DTAB molecules throughout concentration range of DTAB is endothermic and its ΔS value is positive.

The electron-releasing inductive effect of the ethyl groups of BG$^+$ is greater than that of the methyl groups of MG$^+$. This makes the $(C_2H_5)_2N^+=$ group of BG$^+$ more stable than the $(CH_3)_2N^+=$ group of MG$^+$ and results in a decrease in K_{tot} and thus the fading rate constant values of BG/DTAB compound at 283–303 K (Tables 4, 5) compared to those of MG/DTAB compound [16].

Effect of SDS on the BG$^+$ fading

As seen in Figs. 2 and 6 and Table 6, the kinetics of BG$^+$ fading in the presence of SDS has five regions.

The cmc value of SDS in 0.001 N NaOH is 3.5 mM [26] and the used concentration range of SDS is below its cmc value. It seems that a preliminary

Table 4 Parameters obtained from the classical model for the interaction of BG$^+$ with DTAB at 283–303 K

T (K)	Region	sc (mM)	k_{sc} (M^{-1}min^{-1})	Equation 1[a]	E_s^b	logK^c	n	k_s (M^{-1}min^{-1})	Cooperativity
283	1st	0.00	7.97	Reaction rate is approximately constant		–	–	–	+
	2nd	*12.94*	*11.12*	ln k' = 313.70[DTAB]$_t$ –1.64	–7381	3.51	1.87	330.76	–
	3rd	19.27	81.86	Reaction rate is approximately constant		–	–	–	
293	1st	0.00	20.93	Reaction rate is approximately constant		–	–	–	+
	2nd	*12.94*	*25.55*	ln k' = 323.89[DTAB]$_t$ –0.83	–789.0	5.59	2.37	238.85	–
	3rd	*18.63*	*182.01*	Reaction rate is approximately constant		–	–	–	
303	1st	0.00	52.05	Reaction rate is approximately constant		–	–	–	+
	2nd	*12.94*	*60.10*	ln k' = 327.26[DTAB]$_t$ –0.05	–824.4	6.69	2.80	511.59	–
	3rd	*19.06*	*486.66*	Reaction rate is approximately constant		–	–	–	

k_{sc} and sc values obtained from intersection of Eq. 1 of adjacent regions are shown in italic. [a] The unit of DTAB concentration in Eq. 1 is M. [b] Unit of E_s is kJ (mol molar(surfactant))$^{-1}$. [c] Unit of K is M^{-n}

Table 5 Thermodynamic parameters of the interaction of BG^+ with DTAB obtained from classical model at 283–303 K

T (K)	$\log K_{tot}$	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
283	3.51	−19.0		
293	5.59	−31.4	262.3	996.6
303	6.69	−38.82		

Unit of K_{tot} is $M^{-n_{tot}}$

Fig. 6 k_{obs} values of BG^+ fading reaction vs. concentrations of SDS at 283 (*open diamond*), 293 (*open square*) and 303 K (*open triangle*) under alkaline conditions
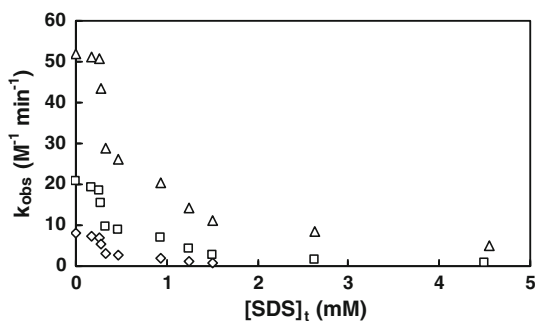
electrostatic interaction occurs between the $(C_2H_5)_2N^+=$ group of BG^+ and the negative charge on the sulfate head group of SDS. As shown in Table 2, in acidic solution, appearance of a peak at 632.5 nm shows that BG/SDS has been formed. This electrostatic interaction along with further hydrophobic interaction of BG^+ with the nonpolar moiety of SDS results in the red shift in the λ_{max} value of BG^+ and thus a decrease in reaction rate of BG^+ fading with an increase in SDS concentration.

The BG/SDS complex has no positive electric charge or may be negatively charged and SDS nonpolar moiety decreases the dielectric constant of BG^+ micro-environment. According to Hughs–Ingold rules, under these conditions, formation of the neutral carbinol base is not favorable. Similar results were reported for interaction of MG^+ with SDS [16].

It is clear from Fig. 2 that the λ_{max} value of BG^+ keeps constant at the end of region 3 (0.93 mM) where the rate constant of fading decreases. This indicates that in regions 2 and 3, BG/SDS complex forms via electrostatic and hydrophobic interactions between BG^+ and SDS molecules and in regions 4 and 5, BG/SDS forms through hydrophobic association between free SDS with bound SDS molecules. It is found that the electrostatic interaction between the sodium salt of carboxymethylcellulose (NaCMC) and CTAB increases hydrophobicity of the polymer-surfactant complex [27]. The interaction of BG^+ with SDS in regions 2, 3, 4 and 5 is endothermic. As seen in Table 7, throughout the concentration range of SDS, the interaction of BG^+ with SDS is endothermic and its ΔS value is positive.

The electron-releasing inductive effect of the ethyl groups of BG^+ is greater than that of the methyl groups of MG^+. This makes the $(C_2H_5)_2N^+=$ group of BG^+ more stable than the $(CH_3)_2N^+=$ group of MG^+ and results in an increase in K_{tot} values of BG/SDS at 283–303 K, Table 7, compared to those of MG/SDS [16] and thus the fading rate constants of BG/SDS, Table 6, are less than those of MG/SDS [16].

Table 6 Parameters obtained from the classical model for the interaction of BG^+ with SDS at 283–303 K

T (K)	Region	sc (mM)	k_{sc} ($M^{-1}min^{-1}$)	Equation 1[a]	E_s[b]	$\log K$[c]	n	Cooperativity
283	1st	0.00	7.97	$\ln k' = -626.26[SDS]_t + 2.08$	1473.5	3.41	1.16	+
	2nd	0.26	6.75	$\ln k' = -10296.37[SDS]_t + 4.62$	24225.9	4.58	1.09	−
	3rd	0.34	3.20	$\ln k' = -745.34[SDS]_t + 1.41$	1753.7	3.01	1.01	+
	4th	0.93	2.05	$\ln k' = -1781.55[SDS]_t + 2.36$	4191.7	4.39	1.28	−
	5th	–	–	Reaction rate is very slow	–	–	–	
293	1st	0.00	20.93	$\ln k' = -449.03[SDS]_t + 3.04$	1093.8	2.64	0.99	+
	2nd	0.26	18.59	$\ln k' = -9254.46[SDS]_t + 5.37$	22543.9	4.68	1.14	−
	3rd	0.34	9.56	$\ln k' = -519.44[SDS]_t + 2.43$	1265.4	2.95	1.05	+
	4th	0.93	7.03	$\ln k' = -1559.53[SDS]_t + 3.37$	3799.0	3.77	1.11	−
	5th	1.51	2.84	$\ln k' = -445.37[SDS]_t + 1.09$	1084.9	3.88	1.36	
303	1st	0.00	52.05	$\ln k' = -101.80[SDS]_t + 3.95$	256.5	1.88	0.96	+
	2nd	0.26	50.67	$\ln k' = -7955.62[SDS]_t + 6.03$	20041.3	4.65	1.15	−
	3rd	0.34	28.68	$\ln k' = -564.52[SDS]_t + 3.54$	1422.1	2.87	1.01	+
	4th	0.93	20.50	$\ln k' = -1025.09[SDS]_t + 3.95$	2582.4	2.88	0.92	−
	5th	1.51	11.31	$\ln k' = -271.84[SDS]_t + 2.85$	684.8	6.68	2.78	

[a] Unit of SDS concentration in Eq. 1 is M. [b] Unit of E_s is kJ $(mol\ molar(surfactant))^{-1}$. [c] Unit of K is M^{-n}

Table 7 Thermodynamic parameters of the interaction of BG^+ with SDS obtained from the classical model at 283–303 K

T (K)	$\log K_{tot}$[a]	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
283	15.39	−83.4		
293	17.94	−100.6	295.0	1341.2
303	18.97	−110.0		

[a] Unit of K_{tot} is $M^{-n_{tot}}$

Effect of DTAB and TX-100 mixtures on the BG^+ fading rate

This test was carried out to verify the existence of regions and is called Pardis test [15]. Pardis is an abbreviation for the statement "*p*roof of *a*djacent *r*egions by *d*estructive *i*nteraction with *s*urfactant". In this test, the concentrations of DTAB

Table 8 Parameters obtained from the Pardis test for the interaction of BGTX$_n$ with DTAB at 293 K

[DTAB] (mM)	[TX-100] (mM)	k_{obs} (M^{-1} min^{-1})	k_{BGTX} (M^{-1} min^{-1})	λ_{max} (nm)	Parameters
2nd region of TX-100					
1.26	1.58	126.66 ± 3.55	50.50	631.1	$m = 0.546$
1.98	3.50	158.32 ± 3.06	50.60	633.1	$K = 60.8$[a]
3.11	5.26	185.32 ± 6.30	50.71	633.3	
3.78	6.98	194.92 ± 5.90	50.81	633.6	
3rd region of TX-100					
1.02	15.15	209.10 ± 11.09	88.54	634.7	$m = 0.845$
2.04	17.80	323.73 ± 10.60	101.89	634.8	$K = 481.9$[a]
3.01	20.59	614.04 ± 28.90	118.14	635.5	
3.86	23.01	692.68 ± 11.00	134.32	635.7	

The used DTAB concentrations are in its first region, Table 4. k_{BGTX} values were obtained from Eq. 1 of the second and third regions of BG$^+$ in the presence of TX-100, Table 1

[a] Unit of K is M^{-m}

used were in the range of 1–4 mM (its first region) in which there is no effect on the rate of BG$^+$ fading (Table 4, Fig. 5) and the concentrations of TX-100 were in the range of 1–7 mM (its second region) and 15–23 mM (its third region). In the second region, there is no effect and, in the third region, there is a large effect on the rate of BG$^+$ fading (Table 1, Fig. 3). As seen in Table 8, an increase in DTAB concentration increases the reaction rate of BG$^+$ fading.

In the used concentrations of DTAB and TX-100, mixed micelles of them form [28, 29], which results in a decrease in the apparent dielectric constant values for the different mixed systems compared to that of TX-100 or DTAB solution [30]. It seems that BG/TX100 (or abbreviated as BGTX$_n$) complexes formed in the second and third region of TX-100, interact with DTAB molecules via hydrophobic interaction between bound TX-100 molecules and DTAB molecules. Confirming this result, the λ_{max} values of BG$^+$ in the mixtures of DTAB and TX-100 depend only on the TX-100 concentration (Fig. 2, Table 8). This interaction is as follows:

$$BGTX_n + mDTAB \leftrightarrow BGTX_nDTAB_m \quad K = \frac{[BGTX_nDTAB_m]_f}{[BGTX_n]_f[DTAB]_f^m} \qquad (7)$$

and its reaction rate equation is as follows

$$v = k_{BGTX}[BGTX_n]_t = k_{BGTX}\left([BGTX_n]_f + [BGTX_nDTAB_m]_f\right) \qquad (8)$$

where k_{BGTX} is the fading rate constant of BGTX$_n$ and subscripts t and f represent the total and free concentrations of complexes, respectively. By substituting Eq. 7 into Eq. 8 we have

$$v = k_{\text{BGTX}}\left(1 + K[\text{DTAB}]_f^m\right)[\text{BGTX}_n]_f = k_{\text{obs}}[\text{BGTX}_n]_f \qquad (9)$$
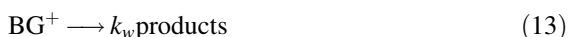
where

$$k_{\text{obs}} = k_{\text{BGTX}}\left(1 + K[\text{DTAB}]_f^m\right) \qquad (10)$$

The data fitted in Eq. 10 along with m and K values are given in Table 8. The results show that in the third region of TX-100, above the cmc point of TX-100, with an increase in the number of TX-100 molecules bound to the BGTX_n, the m and K values of interaction of DTAB with BGTX_n increase. The interaction of BGTX_n with DTAB molecules increases the positive charge of this compound and decreases the dielectric constant of its micro-environment and thus highly increases the BG^+ fading reaction rate.

Analysis of kinetic data by the cooperativity model

The Piszkiewicz model [31–33; http://en.wikipedia.org/wiki/Hill_equation], analogous to the Hill model applied to the enzyme-catalyzed reactions may be considered here with some modifications. According to this model, it is assumed that substrate molecule, BG^+ in this work, associates with n number molecules of surfactant to form micelle $S_n\text{BG}^+$, which may react as follows:

$$nS + \text{BG}^+ \overset{K_D}{\leftrightarrow} S_n\text{BG}^+ \qquad (11)$$

$$S_n\text{BG}^+ \longrightarrow k_m \text{products} \qquad (12)$$

$$\text{BG}^+ \longrightarrow k_w \text{products} \qquad (13)$$

The model gives the following rate equation:

$$\log[(k_{\text{obs}} - k_w)/(k_m - k_{\text{obs}})] = n\log[S]_t - \log K_D \qquad (14)$$

where K_D is the dissociation constant of micellized surfactant–substrate complex back to its components and $[S]_t$ gives the total surfactant concentration. Here, k_w is the reaction rate without any surfactant, and k_m is the reaction rate with the maximum amount of surfactant concentration within the given range and if reaction is inhibited by adding surfactant, $k_m \approx 0$. n is known as the cooperativity index and is a measure of the association of additional surfactant molecules to an aggregate in the whole surfactant concentration range. If the value of n is greater than one, the

Table 9 n and K_D values obtained from the cooperativity model for the interaction of BG^+ with TX-100, DTAB and SDS at 283–303 K

T (K)	TX-100		DTAB		SDS	
	n	$\log K_D^{a}$	n	$\log K_D$ [a]	n	$\log K_D^{a}$
283	0.78	−1.25	4.94	−8.77	1.91	6.41
293	0.69	−1.10	6.32	−11.23	1.68	5.48
303	0.61	−0.98	6.30	−11.23	1.78	5.45

[a] Unit of K_D is M^{-n}

cooperativity of interaction is positive and if its value is less than one, the cooperativity of interaction is negative and if its value is equal to 1, the interaction is noncooperative. It is clear that Eq. 14, a two-parameter equation, cannot fit properly the data of different types of surfactant-substrate interactions.

As shown in Figs. 3, 5 and 6, there are positive catalytic effects by TX-100 and DTAB and negative catalytic effect by SDS in the whole range of the reaction. As seen from Table 9, values of n show positive cooperativity in the used concentration range of SDS and DTAB and negative cooperativity for TX-100. Also, the calculated values of K_D show that binding of BG^+ to TX-100 is exothermic and binding of BG^+ to SDS and DTAB is endothermic.

As an important remark, due to various assumptions used in classical and cooperativity models, occurrence of similar results is definitely random.

Conclusions

The rate constant of alkaline fading of brilliant green (BG^+) was measured in various concentrations of TX-100, DTAB and SDS. It was observed that the reaction rate constant increases in the presence of TX-100 and DTAB and decreases in the presence of SDS. The rate of fading reaction showed noticeable dependence on the electrical charge of the used surfactants. According to Hughs–Ingold rules for nucleophilic substitution reactions, the electric charge of BG/surfactant complex along with decrease in dielectric constant of micro-environment of BG^+ in this compound varies the rate of fading reaction. Binding constants of surfactant molecules to BG^+ were obtained using cooperativity and classical models and the related thermodynamic parameters were calculated by classical model. The results show that the binding of BG^+ to TX-100 is exothermic and the binding of BG^+ to DTAB and SDS is endothermic in the used concentration range of surfactants.

References

1. Fendler JH, Fendler EJ, Chang SA (1973) J Am Chem Soc 95:3273
2. Munoz M, Rodriguez A, Del Mar Graciani M, Moya ML (2002) Int J Chem Kinet 34:445
3. De TK, Maitra A (1995) Adv Colloid Interface Sci 59:95
4. Tang SS, Chang GG (1995) J Org Chem 60:6183
5. Liou JY, Huang TM, Chang GG (1999) J Chem Soc Perkin Trans 2:2171
6. Kambo N, Upadhyay SK (2009) Int J Chem Kinet 41:123
7. Ghosh KK, Verma SK (2009) Int J Chem Kinet 41:377
8. Saha B, Sarkar S, Chowdhury KM (2008) Int J Chem Kinet 40:282
9. Bravo-Diaz C, Pastoriza-Gallego MJ, Lasada-Barreiro S, Sanchez-Paz V, Fernandez-Alonso A (2008) Int J Chem Kinet 40:301
10. Gregory P (1993) Dye and dye intermediates. In: Kroschwitz JI (ed) Encyclopedia of chemical technology, vol 8. Wiley, Indiana, USA, p 544
11. Duxbury DF (1993) Chem Rev 93:381
12. Kingsland GV, Anderson J (1976) Poult Sci 55:852
13. Balabanova MB, Popova L, Tchipeva R (2003) Clin Dermatol 21:2
14. Alderman DJ (1982) J Fish Dis 5:113

15. Samiey B, Alizadeh K, Moghaddasi MA, Mousavi MF, Alizadeh N (2004) Bull Korean Chem Soc 25:726
16. Samiey B, Raoof Toosi A (2009) Bull Korean Chem Soc 30:2051
17. Huang Z, Gu T (1987) Colloids Surf 28:159
18. Parida SK, Mishra BK (1998) Colloids Surf A 134:249
19. Caetano W, Tabak M (2000) J Colloid Interface Sci 225:69
20. Welti R, Mulikin LJ, Yoshimura T, Helmkamp JM (1984) Biochemistry 23:6086
21. Samiey B, Alizadeh K, Mousavi MF, Alizadeh N (2005) Bull Korean Chem Soc 26:384
22. Hughes ED (1941) Trans Faraday Soc 37:603
23. Ingold CK (1993) Structure and mechanism in organic chemistry. Bell, London
24. Chotipong A, Scamehorn JF, Rirksomboon T, Chavadej S, Supaphol P (2007) Colloids Surf A 297:163
25. Olanrewaju O, Ige J, Soriyan O, Grace O, Segun Esan O, Olanrewaju O (2007) Acta Chim Slov 54:370
26. Rabiller-Baudry M, Paugam L, Bégion L, Delaunay D, Fernandez-Cruz M, Phina-Ziebin C, Laviades-Garcia de Guadiana C, Chaufer B (2006) Desalination 191:334
27. Chakraborty T, Chakraborty I, Ghosh S (2006) Langmuir 22:9905
28. Mandeep MS, Shweta S, Singh K, Shaheen A (2005) J Colloid Interface Sci 286:369
29. Soboleva OA, Badun GA, Summ BD (2006) Colloid J 68:255
30. Carnero Ruiz C, Aguiar J (2000) Langmuir 16:7946
31. Piszkiewicz DJ (1976) J Am Chem Soc 98:3053
32. Piszkiewicz DJ (1976) J Am Chem Soc 99:7695
33. Piszkiewicz DJ (1976) J Am Chem Soc 99:1550