

## Kinetics Study of Malachite Green Fading in the Presence of TX-100, DTAB and SDS

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The rate constants of alkaline fading of malachite green ( $\text{MG}^+$ ) was measured in the presence of nonionic (TX-100), cationic (DTAB) and anionic (SDS) surfactants. This reaction was studied under pseudo-first-order conditions at 283 ~ 303 K. The rate of fading reaction showed noticeable dependence on the electrical charge of the used surfactants. It was observed that the reaction rate constants were increased in the presence of TX-100 and DTAB and decreased in the presence of SDS. According to Hughs-Ingold rules for nucleophilic substitution reactions, the electric charge of  $\text{MG}^+$ /surfactant compound along with decrease in dielectric constant of  $\text{MG}^+$  micro-environment in this compound varies the rate of fading reaction. Binding constants of surfactant molecules to  $\text{MG}^+$  were calculated using cooperativity, pseudo-phase ion exchange and classical models and the related thermodynamic parameters were obtained by classical model. The results show that the binding of  $\text{MG}^+$  to TX-100 is exothermic and binding of  $\text{MG}^+$  to DTAB and SDS in some concentration ranges of the used surfactants is endothermic and in the other ones is exothermic.

**Key Words:** Classical model, Malachite green, Kinetics, Fading, Surfactant

### Introduction

The rates of chemical reactions are known to be changed by self-organized assemblies such as micelles.<sup>1-9</sup> Effects of micelles on these reactions can be attributed to electrostatic and hydrophobic interactions. Malachite green ( $\text{MG}^+$ ) is a triphenylmethane dye. These dyes represent a class of dyes of commercial and analytical importance.<sup>10,11</sup> Malachite green is used to dye materials like silk, leather, cotton and paper and can be used as a saturable absorber in dye lasers, as a pH indicator or as a bacteriological stain.<sup>12</sup> It is also used as a topical antiseptic or treat parasites and bacterial infections in fish and fish eggs.<sup>13</sup> Due to the vast applications of  $\text{MG}^+$ , its interactions with other compounds, such as surfactants, are of great importance. As found,<sup>14</sup> the rate of alkaline hydrolysis of  $\text{MG}^+$  increased in aqueous solutions of CTAB. Also, the rate of alkaline fading of other cationic triphenylmethane dyes, brilliant green<sup>15</sup> and crystal violet,<sup>16</sup> increases in the presence of *n*-alkyltrimethylammonium bromide surfactants. In continuation of our earlier work,<sup>17</sup> we studied the  $\text{MG}^+$  fading reaction in the presence of TX-100, DTAB and SDS at 283 - 303 K. The  $\text{MG}^+$  fading is a one-step reaction<sup>18,19</sup> and kinetics of these kinds of reactions in the presence of surfactants can be studied using pseudo-phase ion exchange, cooperativity and classical models.<sup>14,15,17</sup>

### Experimental Section

**Reagent.** Malachite green oxalate, 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.

**Procedure.** The fading of  $\text{MG}^+$  was followed at its maximum wavelength ( $\lambda_{\text{max}}$ ) values in a thermostated cell compartment of a Shimadzu UV-1650PC spectrophotometer. The experiments

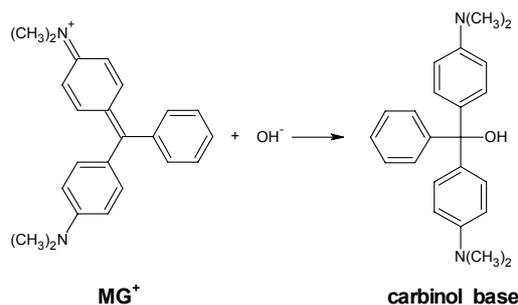
were conducted at 283, 293 and 303 K within  $\pm 0.1$  K. All the kinetic runs were carried out at least in triplicate. To perform each kinetic run, a 100  $\mu\text{L}$  aliquot of  $1.38 \times 10^{-4}$  M  $\text{MG}^+$  solution was added by a microsyringe into 2.9 mL of a solution containing  $5.44 \times 10^{-4}$  M sodium hydroxide and a certain concentration of surfactant. To study all interactions occurred between surfactant and substrate molecules, we carried out the experiments in the surfactants concentration ranges which reaction rate finally reaches to its maximum value (in the case of catalytic effect) or becomes very slow (in the case of inhibitory effect). The reaction between  $\text{MG}^+$  and hydroxide ion has been found to be bimolecular but pseudo-first-order conditions (excess alkali) were used in all cases, Scheme 1. To obtain the pseudo-first-order rate constants, the following equation was used:

$$A = A_0 \exp(-k_p t) \quad (1)$$

where  $A$  is the absorption of  $\text{MG}^+$  at any time,  $A_0$  is its initial absorption and  $k_p$  and  $t$  are the pseudo-first-order rate constant and time, respectively. We used the second-order reaction rate constants,  $k_{\text{obs}}$ , in our calculations.  $k_{\text{obs}}$  is obtained from the relation  $k_{\text{obs}} = \frac{k_p}{[\text{OH}^-]}$ , where  $[\text{OH}^-]$  is the used concentration of sodium hydroxide.

### Results and Discussion

**Analysis of kinetic data by classical model.** In classical model,<sup>17</sup> it is assumed that in each range of surfactant concentration, the surfactant and substrate can bind together and there is an equilibrium relation between them. A concentration of surfactant is called "substrate-surfactant compound formation point" (or abbreviated as *sc* point) in which the equilibrium relation between added surfactant and species already presented in



Scheme 1

solution ends and a new equilibrium relation between added surfactant and compound resulted from the previous equilibrium relation starts. Critical micelle concentration (*cmc*) 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, following equation holds for:

$$\ln k' = c - \frac{E_s}{RT} [S]_t \quad (2)$$

where  $k'$ ,  $c$ ,  $[S]_t$ ,  $R$ ,  $T$  and  $E_s$  are the rate constant in the presence of surfactant,  $\ln k$  (at first region) or  $\ln k_{sc}$  (for other regions), total surfactant concentration, universal gas constant, absolute temperature and activation energy of reaction in constant temperature and various surfactant concentrations, respectively.  $k_{sc}$  is the  $k_{obs}$  in the starting of every region except region one. Equation (2) is named Samiey equation and can determine the concentration range of each region.<sup>17</sup> 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.

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



where  $K$  is the binding constant of the substrate-surfactant interaction in each region. According to classical model, this reaction is of type I. In this type of reaction, solvent molecules do not act as a reactant and  $k_{obs}$  is related to the surfactant concentration as follows:<sup>17</sup>

$$k_{obs} = \frac{k + k_s K [S]_t^n}{1 + K [S]_t^n} \quad (\text{region one}) \quad (4)$$

and

$$k_{obs} = \frac{k_{sc} + k_s K ([S]_t - [sc])^n}{1 + K ([S]_t - [sc])^n} \quad (\text{all the other regions}) \quad (5)$$

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

$$K_{tot}^i = K_1 \dots K_{i-1} K_i = \prod_{j=1}^i K_j \quad (6)$$

$$n_{tot}^i = n_1 \dots n_{i-1} n_i = \sum_{j=1}^i n_j \quad (7)$$

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

**Effect of TX-100 on the  $MG^+$  fading.** As seen in Figures 1 and 2 and Table 1, with increase in TX-100 concentration, the  $\lambda_{max}$  value of  $MG^+$  shifts to red and the reaction rate of  $MG^+$  fading increases. As given in Table 1, kinetics of  $MG^+$  fading in the presence of TX-100 is three-region. The *cmc* value of TX-100 in pure water is 0.29 mM<sup>20</sup> and the first region is below its *cmc* value. As seen in Table 2 and Scheme 2, in acidic solution, interaction of TX-100 with  $MGH^{2+}$  results in the red shift in  $\lambda_{max}$  value of  $MGH^{2+}$ . This indicates that in this region, a preliminary

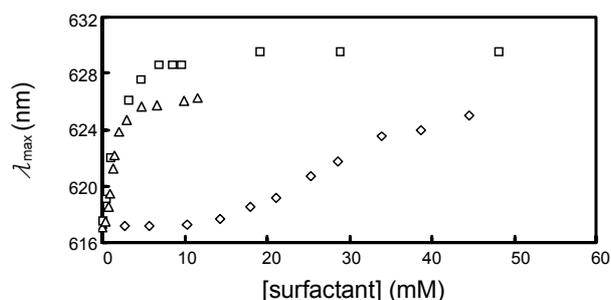


Figure 1.  $\lambda_{max}$  values of  $MG^+$  vs. concentrations of  $\Delta$  SDS,  $\square$  TX-100 and  $\diamond$  DTAB under alkaline conditions.

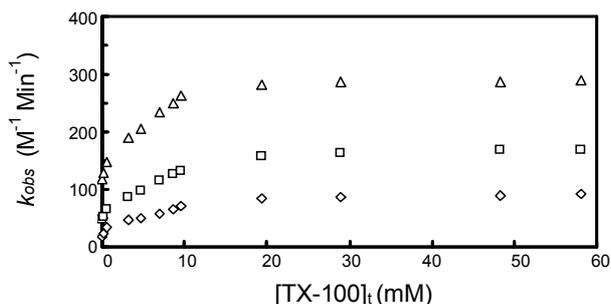


Figure 2.  $k_{obs}$  values of  $MG^+$  fading reaction vs. concentrations of TX-100 at  $\diamond$  283,  $\square$  293 and  $\Delta$  303 K under alkaline conditions.

**Table 1.** Parameters Obtained from Classical Model for Interaction of  $\text{MG}^+$  with TX-100 at 283 - 303 K

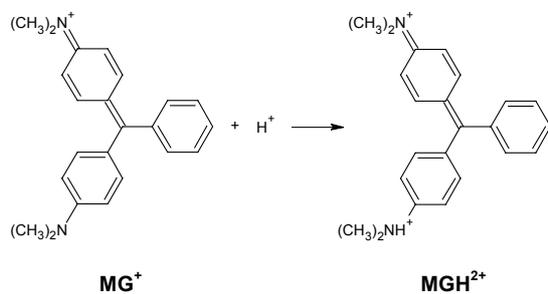
T (K)	Region	sc (mM)	$k_{sc}$ ( $\text{M}^{-1}\text{min}^{-1}$ )	Samiey equation	$E_s^a$	log K	n	$k_s$ ( $\text{M}^{-1}\text{min}^{-1}$ )	Cooperativity
283	1st	0.00	18.89	$\ln k' = 937.54[\text{TX}]_t + 2.98$	-2205.9	2.822	0.95	59.14	↓ -
	2nd	0.75	39.70	$\ln k' = 63.31[\text{TX}]_t + 3.64$	-149.0	2.375	1.41	186.79	↓ ↓ -
	3rd	12.27	82.34	Reaction rate is approximately constant	-	-	-	-	↓ ↓
293	1st	0.00	46.98	$\ln k' = 616.89[\text{TX}]_t + 3.86$	-1502.7	2.519	1.01	182.13	↓ -
	2nd	0.72	73.93	$\ln k' = 67.48[\text{TX}]_t + 4.25$	-164.4	2.361	1.20	216.97	↓ ↓ -
	3rd	11.92	157.01	Reaction rate is approximately constant	-	-	-	-	↓ ↓
303	1st	0.00	118.60	$\ln k' = 371.67[\text{TX}]_t + 4.80$	-936.6	1.956	0.74	230.16	↓ -
	2nd	3.14	189.88	$\ln k' = 51.405[\text{TX}]_t + 5.085$	-129.5	1.393	1.03	807.54	↓ ↓ -
	3rd	10.81	281.66	Reaction rate is approximately constant	-	-	-	-	↓ ↓

<sup>a</sup>Dimension of  $E_s$  is in  $\text{kJ}(\text{mol molar}(\text{surfactant}))^{-1}$ . TX is an abbreviation for TX-100 and dimension of its concentration in Samiey equation is in M.  $k_{sc}$  and  $sc$  values obtained from intersection of adjacent regions are given in the box.

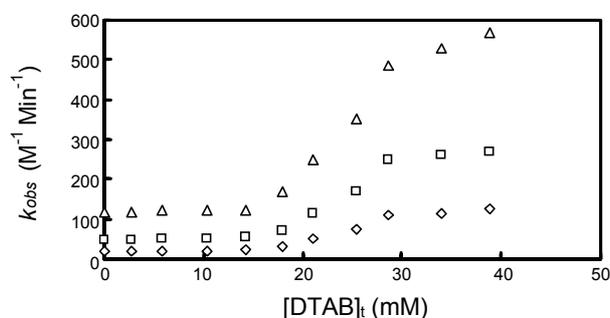
**Table 2.** Typical  $\lambda_{\text{max}}$  Values of  $\text{MG}^+$  in the Presence of TX-100, DTAB and SDS in Acidic and Alkaline Solutions

In 1 M HCl	$\lambda_{\text{max}}$ (nm)	In $5.3 \times 10^{-4}$ M NaOH	$\lambda_{\text{max}}$ (nm)
-	446.0	-	617.0
0.3 mM TX-100	450.0	0.3 mM TX-100	618.2
15 mM DTAB	447.0	15 mM DTAB	618.0
1 mM SDS	446, 627	1 mM SDS	619.5

It is necessary to say that  $\text{MGH}^{2+}$  fades in 1 M HCl.



electrostatic interaction occurs between  $(\text{CH}_3)_2\text{NH}^+$ -group of  $\text{MG}^+$  and the oxygen atom of ethoxy chain of TX-100 molecules which is similar to interaction of silanol groups of silica gel with TX-100.<sup>20,21</sup> This interaction along with further hydrophobic interaction of  $\text{MG}^+$  with TX-100 molecules results in a sharp red shift in  $\lambda_{\text{max}}$  value of  $\text{MG}^+$ . The red shift has been previously reported for other compounds upon going from polar to apolar solvents, as a result of hydrophobic interaction.<sup>22-24</sup> It seems that TX-100 molecules decrease dielectric constant of the  $\text{MG}^+$  micro-environment. According to Hughs-Ingold rules for nucleophilic substitution reactions,<sup>25,26</sup> formation of the neutral carbinol base from two oppositely charged reactants is more favorable in lower dielectric constant media and thus with increase in TX-100 concentration, the rate of  $\text{MG}^+$  fading increases in the first region. In this region, as seen from log  $K$  values in Table 1, interaction of  $\text{MG}^+$  with TX-100 is exothermic, Table 5.

**Figure 3.**  $k_{\text{obs}}$  values of  $\text{MG}^+$  fading reaction vs. concentrations of DTAB at  $\diamond$  283,  $\square$  293 and  $\triangle$  303 K under alkaline conditions.

In the second region,  $\lambda_{\text{max}}$  value of  $\text{MG}^+$  and fading reaction rate increase with increase in TX-100 concentration, Table 1. It seems that likewise first region, electrostatic and hydrophobic interactions occur between  $\text{MG}^+/\text{TX-100}$  and free TX-100 molecules in the second region. In this region, interaction is exothermic, Table 1.

In the third region, the rate of  $\text{MG}^+$  fading and  $\lambda_{\text{max}}$  value of  $\text{MG}^+$  keep approximately constant.

As seen in Table 5, interaction of  $\text{MG}^+$  with TX-100 molecules throughout concentration range of TX-100 is exothermic and its  $\Delta S$  value is negative.

**Effect of DTAB on the  $\text{MG}^+$  fading.** As seen in Figures 1 and 3 and Table 3, kinetics of  $\text{MG}^+$  fading in the presence of DTAB is three-region. The  $cmc$  value of DTAB in pure water is 13.77  $\text{mM}$ <sup>27</sup> and the first region is below its  $cmc$  value. In this region, with increase in DTAB concentration, the rate constant of  $\text{MG}^+$  fading and  $\lambda_{\text{max}}$  value of  $\text{MG}^+$  increase slightly and it seems that there is a weak endothermic interaction between  $\text{MG}^+$  and DTAB molecules, Table 3. Obviously, in the beginning of the second region ( $\approx 14.74 \text{ mM} > cmc$  value of DTAB), a weak electrostatic interaction occurs between  $(\text{CH}_3)_2\text{N}^+$ -group of  $\text{MG}^+$  and positive head group of DTAB molecules and along with hydrophobic interaction of  $\text{MG}^+$  with nonpolar moiety of DTAB molecules results in the red shift in  $\lambda_{\text{max}}$  value of  $\text{MG}^+$ . Confirming this result, it is seen from Table 2 that 15 mM DTAB acidic solution has no effect on the  $\lambda_{\text{max}}$  value of  $\text{MGH}^{2+}$ .

**Table 3.** Parameters Obtained from Classical Model for Interaction of  $MG^+$  with DTAB at 283 - 303 K

T (K)	Region	sc (mM)	$k_{sc}$ ( $M^{-1}min^{-1}$ )	Samiey equation	$E_s^a$	log K	n	$k_s$ ( $M^{-1}min^{-1}$ )	Cooperativity
283	1st	0.00	18.89	Reaction rate is approximately constant	-	-	-	-	↓ +
	2nd	14.74	21.84	$\ln k' = 113.29[DTAB]_t + 1.475$	-266.6	5.111	2.44	97.28	↓ ↓ -
	3rd	28.44	109.74	$\ln k' = 12.30[DTAB]_t + 4.35$	-28.9	1.938	1.52	304.72	↓ ↓
293	1st	0.00	46.98	$\ln k' = 9.36[DTAB]_t + 3.85$	-22.8	1.565	1.23	86.83	↓ +
	2nd	14.74	53.60	$\ln k' = 106.74[DTAB]_t + 2.43$	-260.0	4.720	2.37	264.81	↓ ↓ -
	3rd	28.92	248.12	$\ln k' = 8.83[DTAB]_t + 5.26$	-21.5	2.789	1.38	290.74	↓ ↓
303	1st	0.00	118.60	$\ln k' = 2.72[DTAB]_t + 4.775$	-6.85	2.226	1.34	131.31	↓ +
	2nd	14.74	123.20	$\ln k' = 95.63[DTAB]_t + 3.45$	-240.9	3.865	1.97	570.89	↓ ↓ -
	3rd	28.62	486.45	$\ln k' = 15.38[DTAB]_t + 5.75$	-38.7	3.161	1.58	650.69	↓ ↓

<sup>a</sup>Dimension of  $E_s$  is in kJ (mol molar(surfactant))<sup>-1</sup>.  $k_{sc}$  and  $sc$  values obtained from intersection of adjacent regions are given in the box. Dimension of DTAB concentration in Samiey equation is in M.

**Table 4.** Parameters Obtained from Classical Model for Interaction of  $MG^+$  with SDS at 283 - 303 K

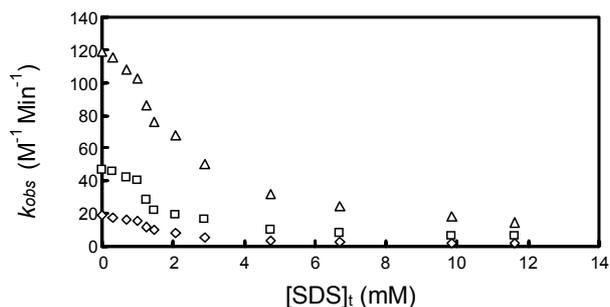
T (K)	Region	sc (mM)	$k_{sc}$ ( $M^{-1}min^{-1}$ )	Samiey equation	$E_s^a$	log K	n	Cooperativity
283	1st	0.00	18.89	$\ln k' = -202.44[SDS]_t + 2.94$	476.3	2.555	1.07	↓ +
	2nd	1.02	15.45	$\ln k' = -935.97[SDS]_t + 3.67$	2202.2	4.473	1.42	↓ ↓ +
	3rd	1.54	9.62	$\ln k' = -323.33[SDS]_t + 2.74$	760.7	3.622	1.34	↓ ↓ -
	4th	4.92	3.41	$\ln k' = -69.37[SDS]_t + 1.52$	163.2	1.445	0.76	↓ ↓
293	1st	0.00	46.98	$\ln k' = -166.17[SDS]_t + 3.86$	404.8	3.076	1.27	↓ +
	2nd	1.02	39.94	$\ln k' = -1218.90[SDS]_t + 4.89$	2969.2	3.884	1.20	↓ ↓ -
	3rd	1.54	21.63	$\ln k' = -229.99[SDS]_t + 3.43$	560.3	3.417	1.36	↓ ↓ -
	4th	4.92	10.32	$\ln k' = -75.71[SDS]_t + 2.66$	184.4	1.528	0.78	↓ ↓
303	1st	0.00	118.60	$\ln k' = -145.46[SDS]_t + 4.78$	366.4	3.069	1.29	↓ -
	2nd	1.02	102.89	$\ln k' = -602.87[SDS]_t + 5.23$	1518.7	2.963	1.04	↓ ↓ +
	3rd	1.54	75.99	$\ln k' = -268.67[SDS]_t + 4.735$	676.8	3.381	1.30	↓ ↓ -
	4th	4.92	32.09	$\ln k' = -107.78[SDS]_t + 3.97$	271.5	2.386	1.09	↓ ↓

<sup>a</sup>Dimension of  $E_s$  is in kJ (mol molar(surfactant))<sup>-1</sup>.  $k_{sc}$  and  $sc$  values obtained from intersection of adjacent regions are given in the box. Dimension of SDS concentration in Samiey equation is in M.

Under these conditions, according to Hughs-Ingold rules for nucleophilic substitution reactions rate constant of  $MG^+$  fading increases with increase in DTAB concentration. This interaction is exothermic, Table 6. In the third region, the rate of  $MG^+$  fading and  $\lambda_{max}$  value of  $MG^+$  increase with increase in DTAB concentration and it seems that  $MG^+$ /TX-100 interacts with TX-100 molecules *via* hydrophobic and electrostatic interactions. As seen in Table 3, this interaction is endothermic and its positive  $\Delta S$  value ( $394.3 J mol^{-1} K^{-1}$ ) shows the increased randomness which suggests that the hydrocarbon chain of DTAB molecules replace some water molecules of solvating  $MG^+$ . These displaced molecules gain more translational entropy than is lost by DTAB molecules, thus allowing the prevalence of randomness in the system. As seen in Table 6, interaction of  $MG^+$  with DTAB molecules throughout concentration range of DTAB is endothermic and its  $\Delta S$  value is positive.

**Effect of SDS on the  $MG^+$  fading.** As seen in Figures 1 and 4 and Table 4, kinetics of  $MG^+$  fading in the presence of SDS is four-region. The *cmc* value of SDS in 0.001 N NaOH is 3.5 mM.<sup>28</sup>

It seems that a preliminary electrostatic interaction occurs between  $(CH_3)_2N^+$  group of  $MG^+$  and the negative charge on the sulfate head group of SDS. This electrostatic interaction along with further hydrophobic interaction of  $MG^+$  with nonpolar moiety of SDS results in the red shift in  $\lambda_{max}$  value of  $MG^+$  and a decrease in the rate of  $MG^+$  fading with increase in SDS concentration. Confirming this result, in acidic solution, appearance of a peak at 627 nm shows that  $MG^+$ /SDS compound has been formed, Table 2. The  $MG^+$ /SDS compound has no positive electric charge or its electric charge may be negative and SDS nonpolar moiety decreases the dielectric constant of  $MG^+$  micro-environment. According to Hughs-Ingold rules, under these conditions, formation of the neutral carbinol base is not favorable. As reported,<sup>29</sup> At  $pH \leq 2$ , SDS molecules bound to protonated amines on the outer rims of a amine terminated PAMAM dendrimer driven by electrostatic interaction, which induced the formation of PAMAM/SDS supramolecular complex *via* hydrophobic association between bound SDS molecules. At  $pH$  of 7.4, the formation of PAMAM/SDS com-



**Figure 4.**  $k_{obs}$  values of  $MG^+$  fading reaction vs. concentrations of SDS at  $\diamond$  283,  $\square$  293 and  $\Delta$  303 K under alkaline conditions.

**Table 5.** Thermodynamic Parameters Obtained from Classical Model for Interaction of  $MG^+$  with TX-100 at 283 - 303 K

T (K)	$\log K_{tot}$	$\Delta G$ (kJ mol <sup>-1</sup> )	$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )
283	5.198	-28.2		
293	4.880	-27.4	-150.5	-428.5
303	3.349	-19.4		

**Table 6.** Thermodynamic Parameters of Interaction of  $MG^+$  with DTAB Obtained from Classical Model at 283 - 303 K

T (K)	$\log K$	$\Delta G$ (kJ mol <sup>-1</sup> )	$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )
Region 2				
283	5.111	-27.7		
293	4.720	-26.5	-101.8	-260.3
303	3.864	-22.4		
Regions 1 and 3				
283	1.938	-10.5		
293	4.354	-24.4	284.3	1045.3
303	5.387	-31.2		
Regions 1, 2 and 3				
283	7.049	-38.2		
293	9.074	-50.9	182.5	785.1
303	9.252	-53.6		

The total  $\Delta H$  and  $\Delta S$  values were obtained by adding the related values of all regions.

plex was observed at higher SDS concentration and it resolubilized with further increase of SDS concentration due to weaker electrostatic interaction at higher pH.

In the first region, interaction of  $MG^+$  with SDS is endothermic, Table 4. In regions 2 and 3 which are below the *cmc* value of SDS, an increase in SDS concentration results in a decrease in fading reaction rate and a red shift in  $\lambda_{max}$  value of  $MG^+$  and interaction is exothermic, Figure 1 and Table 4. This indicates that in regions 2 and 3,  $MG^+$ /SDS compound forms *via* electrostatic and hydrophobic interactions between  $MG^+$  and SDS molecules. In region 4 which starts at 4.92 mM, (above the *cmc* value of SDS), with increase in SDS concentration, the reaction rate decreases and  $\lambda_{max}$  value of  $MG^+$  keeps approximately constant, Figure 1 and Table 4. This indicates that in this region, hydrophobic interaction occurs between  $MG^+$  com-

**Table 7.** Thermodynamic Parameters of Interaction of  $MG^+$  with SDS Obtained from Classical Model at 283 - 303 K

T (K)	$\log K$	$\Delta G$ (kJ mol <sup>-1</sup> )	$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )
Regions 1 and 4				
283	4.000	-21.7		
293	4.604	-25.8	200.4	780.6
303	6.457	-37.5		
Regions 2 and 3				
283	8.095	-43.9		
293	7.301	-40.9	-143.5	-351.4
303	6.344	-36.8		
Regions 1, 2, 3 and 4				
283	12.095	-65.6		
293	11.904	-66.7	56.9	429.2
303	12.801	-74.3		

The total  $\Delta H$  and  $\Delta S$  values were obtained by adding the related values of all regions.

pound with free SDS molecules. As reported,<sup>30</sup> electrostatic interaction between sodium salt of carboxymethylcellulose (NaCMC) and CTAB increases hydrophobicity of polymer-surfactant complex.

In region 4, interaction of  $MG^+$  with SDS is endothermic, Table 4. Interaction of  $MG^+$  with SDS throughout concentration range of the SDS is endothermic and its  $\Delta S$  value is positive, Table 7.

**Analysis of kinetic data by cooperativity model.** The Piszkie-wicz model,<sup>15,31-33</sup> analogous to the Hill model applied to the enzyme-catalyzed reactions<sup>34</sup> may be considered here with some modifications. According to this model, it is assumed that substrate molecule,  $MG^+$ , associates with  $n$  number molecules of surfactant to form critical micelle  $S_nMG^+$ , which may react as follows:



The model gives the following rate equation:

$$\log[(k_{obs} - k_w)/(k_m - k_{obs})] = n \log[S]_t - \log K_D \quad (11)$$

where  $K_D$  is the dissociation constant of micellized surfactant-substrate compound 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,  $k_m = 0$ .  $n$  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  $n$  value is greater than one,

**Table 8.**  $n$  and  $\log K_D$  Values Obtained from Cooperativity Model for Interaction of  $\text{MG}^+$  with TX-100, DTAB and SDS at 283 - 303 K

T (K)	TX-100		DTAB		SDS	
	$n$	$\log K_D$	$n$	$\log K_D$	$n$	$\log K_D$
283	1.034	-2.611	2.934	-4.697	1.423	-3.827
293	1.145	-2.826	3.255	-5.313	1.448	-3.823
303	1.285	-3.445	3.539	-5.569	1.497	-3.829

**Table 9.**  $k_m$  and  $K_s$  Values Obtained from PPIE Model for Interaction of  $\text{MG}^+$  with TX-100, DTAB and SDS at 283 - 303 K

T (K)	TX-100		DTAB		SDS	
	$k_m$	$K_s$	$k_m$	$K_s$	$k_m$	$K_s$
283	97.92	185.7	502.52	12.2	1.96	8169.2
293	185.90	157.0	1056.11	12.6	5.58	5937.0
303	305.20	265.0	2860.85	8.4	13.64	3503.5

cooperativity of interaction is positive, if its value is less than one, cooperativity of interaction is negative and if its value is equal to 1, interaction is noncooperative. It is clear that eq. (11), a two-parameter equation, can not fit properly the data of different types of surfactant-substrate interactions.

As shown in Figures 1-3, there are positive catalytic effects by TX-100 and DTAB and negative catalytic effect by SDS in the whole range of the reaction. It is seen from Table 8 that  $n$  values show positive cooperativity in the used concentration range of SDS, DTAB and TX-100. Also, the calculated  $K_D$  values show that binding of  $\text{MG}^+$  to TX-100 and DTAB is endothermic and its binding to SDS is athermic.

**Analysis of kinetic data by pseudo-phase ion exchange (PPIE) model.** In the PPIE model, the binding constants of the interaction of surfactant molecules to  $\text{MG}^+$  were calculated using the following equation:<sup>35</sup>

$$k_{obs} = \frac{k_w + k_m K_s ([S]_t - cmc)}{1 + K_s ([S]_t - cmc)} \quad (12)$$

where  $[S]_t$ ,  $K_s$ ,  $k_{obs}$ ,  $k_m$  and  $k_w$  are the total surfactant concentration, binding constant, observed reaction rate and reaction rates in micellar media and in the bulk phase, respectively. This model can not study the surfactant-substrate interactions below the  $cmc$  value of surfactants. It is seen in Table 9 that binding of  $\text{MG}^+$  to SDS is exothermic. On the other hand, due to oscillation in the values of binding constants of  $\text{MG}^+$  to TX-100 and DTAB,  $\Delta H$  and  $\Delta S$  values of these interactions can not be calculated.

### Conclusion

The rate constant of alkaline fading of malachite green ( $\text{MG}^+$ ) was measured in the presence of TX-100, DTAB and SDS. The rate of fading reaction showed noticeable dependence on the electrical charge of the used surfactants. It was observed that the reaction rate constants were increased in the presence of TX-100 and DTAB and decreased in the presence of SDS. Binding constants of surfactant molecules to  $\text{MG}^+$  were cal-

culated using cooperativity, pseudo-phase and classical models and the related thermodynamic parameters were obtained by classical model. The results show that the binding of  $\text{MG}^+$  to TX-100 is exothermic and binding of  $\text{MG}^+$  to DTAB and SDS in some regions is endothermic and in the other ones is exothermic.

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