

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 (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 MG^+ /surfactant compound along with decrease in dielectric constant of MG^+ micro-environment in this compound varies the rate of fading reaction. Binding constants of surfactant molecules to 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 MG^+ to TX-100 is exothermic and binding of 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.¹⁻⁹ Effects of micelles on these reactions can be attributed to electrostatic and hydrophobic interactions. Malachite green (MG^+) is a triphenylmethane dye. These dyes represent a class of dyes of commercial and analytical importance.^{10,11} 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.¹² It is also used as a topical antiseptic or treat parasites and bacterial infections in fish and fish eggs.¹³ Due to the vast applications of MG^+ , its interactions with other compounds, such as surfactants, are of great importance. As found,¹⁴ the rate of alkaline hydrolysis of MG^+ increased in aqueous solutions of CTAB. Also, the rate of alkaline fading of other cationic triphenylmethane dyes, brilliant green¹⁵ and crystal violet,¹⁶ increases in the presence of *n*-alkyltrimethylammonium bromide surfactants. In continuation of our earlier work,¹⁷ we studied the MG^+ fading reaction in the presence of TX-100, DTAB and SDS at 283 - 303 K. The MG^+ fading is a one-step reaction^{18,19} and kinetics of these kinds of reactions in the presence of surfactants can be studied using pseudo-phase ion exchange, cooperativity and classical models.^{14,15,17}

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 MG^+ was followed at its maximum wavelength (λ_{max}) values in a thermostated cell compartment of a Shimadzu UV-1650PC spectrophotometer. The experiments

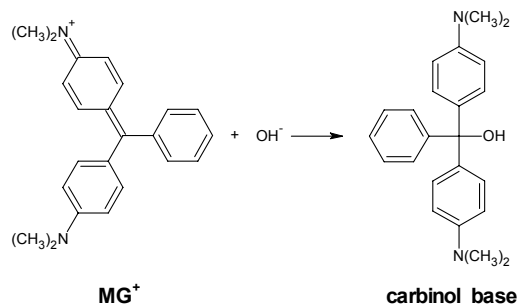
were conducted at 283, 293 and 303 K within ± 0.1 K. All the kinetic runs were carried out at least in triplicate. To perform each kinetic run, a 100 μL aliquot of 1.38×10^{-4} M MG^+ solution was added by a microsyringe into 2.9 mL of a solution containing 5.44×10^{-4} M sodium hydroxide and a certain 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 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 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_{obs} , in our calculations. k_{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,¹⁷ 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.¹⁷ 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:¹⁷

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

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 λ_{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 mM²⁰ 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 λ_{max} value of MGH^{2+} . This indicates that in this region, a preliminary

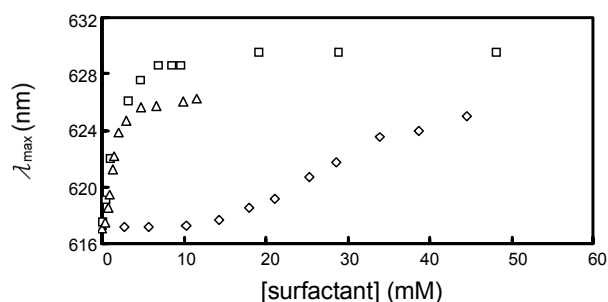


Figure 1. λ_{max} values of MG^+ vs. concentrations of Δ SDS, \square TX-100 and \diamond DTAB under alkaline conditions.

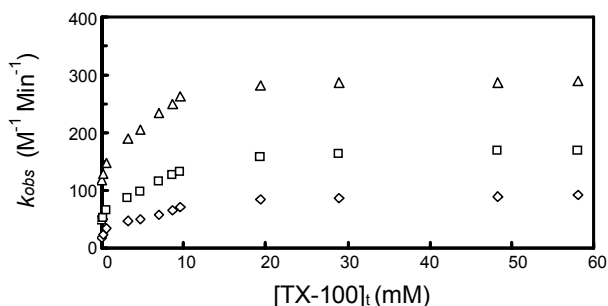


Figure 2. k_{obs} values of MG^+ fading reaction vs. concentrations of TX-100 at \diamond 283, \square 293 and Δ 303 K under alkaline conditions.

Table 1. Parameters Obtained from Classical Model for Interaction of MG^+ with TX-100 at 283 - 303 K

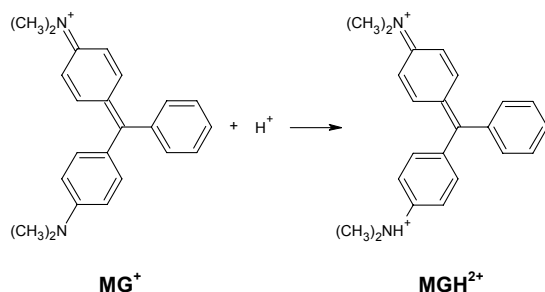
T (K)	Region	sc (mM)	k_{sc} ($\text{M}^{-1}\text{min}^{-1}$)	Samiey equation	E_s^a	log K	n	k_s ($\text{M}^{-1}\text{min}^{-1}$)	Cooperativity
283	1st	0.00	18.89	$\ln k' = 937.54[\text{TX}]_t + 2.98$	-2205.9	2.822	0.95	59.14	↓ -
	2nd	0.75	39.70	$\ln k' = 63.31[\text{TX}]_t + 3.64$	-149.0	2.375	1.41	186.79	↓ ↓ -
	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	-	-	-	-	↓ ↓

^aDimension of E_s is in kJ (mol molar(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.

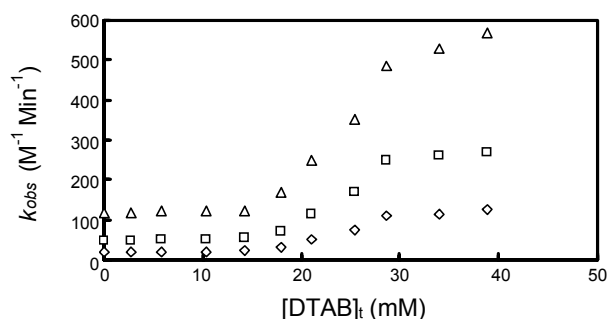
Table 2. Typical λ_{max} Values of MG^+ in the Presence of TX-100, DTAB and SDS in Acidic and Alkaline Solutions

In 1 M HCl	λ_{max} (nm)	In 5.3×10^{-4} M NaOH	λ_{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 MGH^{2+} fades in 1 M HCl.

**Scheme 2**

electrostatic interaction occurs between $(\text{CH}_3)_2\text{NH}^+$ -group of 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.^{20,21} This interaction along with further hydrophobic interaction of MG^+ with TX-100 molecules results in a sharp red shift in λ_{max} value of MG^+ . The red shift has been previously reported for other compounds upon going from polar to apolar solvents, as a result of hydrophobic interaction.²²⁻²⁴ It seems that TX-100 molecules decrease dielectric constant of the MG^+ micro-environment. According to Hughs-Ingold rules for nucleophilic substitution reactions,^{25,26} 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 MG^+ fading increases in the first region. In this region, as seen from log K values in Table 1, interaction of MG^+ with TX-100 is exothermic, Table 5.

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

In the second region, λ_{max} value of 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 MG^+ fading and λ_{max} value of MG^+ keep approximately constant.

As seen in Table 5, interaction of MG^+ with TX-100 molecules throughout concentration range of TX-100 is exothermic and its ΔS value is negative.

Effect of DTAB on the MG^+ fading. As seen in Figures 1 and 3 and Table 3, kinetics of MG^+ fading in the presence of DTAB is three-region. The cmc value of DTAB in pure water is 13.77 mM²⁷ and the first region is below its cmc value. In this region, with increase in DTAB concentration, the rate constant of MG^+ fading and λ_{max} value of MG^+ increase slightly and it seems that there is a weak endothermic interaction between MG^+ and DTAB molecules, Table 3. Obviously, in the beginning of the second region ($\approx 14.74 \text{ mM} > \text{cmc}$ value of DTAB), a weak electrostatic interaction occurs between $(\text{CH}_3)_2\text{N}^+$ - group of MG^+ and positive head group of DTAB molecules and along with hydrophobic interaction of MG^+ with nonpolar moiety of DTAB molecules results in the red shift in λ_{max} value of MG^+ . Confirming this result, it is seen from Table 2 that 15 mM DTAB acidic solution has no effect on the λ_{max} value of 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} ($\text{M}^{-1}\text{min}^{-1}$)	Samiey equation	E_s^a	log K	n	k_s ($\text{M}^{-1}\text{min}^{-1}$)	Cooperativity
283	1st	0.00	18.89	Reaction rate is approximately constant	-	-	-	-	↓ +
	2nd	14.74	21.84	$\ln k' = 113.29[\text{DTAB}]_t + 1.475$	-266.6	5.111	2.44	97.28	↓ -
	3rd	28.44	109.74	$\ln k' = 12.30[\text{DTAB}]_t + 4.35$	-28.9	1.938	1.52	304.72	↓
293	1st	0.00	46.98	$\ln k' = 9.36[\text{DTAB}]_t + 3.85$	-22.8	1.565	1.23	86.83	↓ +
	2nd	14.74	53.60	$\ln k' = 106.74[\text{DTAB}]_t + 2.43$	-260.0	4.720	2.37	264.81	↓ -
	3rd	28.92	248.12	$\ln k' = 8.83[\text{DTAB}]_t + 5.26$	-21.5	2.789	1.38	290.74	↓
303	1st	0.00	118.60	$\ln k' = 2.72[\text{DTAB}]_t + 4.775$	-6.85	2.226	1.34	131.31	↓ +
	2nd	14.74	123.20	$\ln k' = 95.63[\text{DTAB}]_t + 3.45$	-240.9	3.865	1.97	570.89	↓ -
	3rd	28.62	486.45	$\ln k' = 15.38[\text{DTAB}]_t + 5.75$	-38.7	3.161	1.58	650.69	↓

^aDimension of E_s is in kJ (mol molar(surfactant))⁻¹. 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} ($\text{M}^{-1}\text{min}^{-1}$)	Samiey equation	E_s^a	log K	n	Cooperativity
283	1st	0.00	18.89	$\ln k' = -202.44[\text{SDS}]_t + 2.94$	476.3	2.555	1.07	↓ +
	2nd	1.02	15.45	$\ln k' = -935.97[\text{SDS}]_t + 3.67$	2202.2	4.473	1.42	↓ +
	3rd	1.54	9.62	$\ln k' = -323.33[\text{SDS}]_t + 2.74$	760.7	3.622	1.34	↓ -
	4th	4.92	3.41	$\ln k' = -69.37[\text{SDS}]_t + 1.52$	163.2	1.445	0.76	↓
293	1st	0.00	46.98	$\ln k' = -166.17[\text{SDS}]_t + 3.86$	404.8	3.076	1.27	↓ +
	2nd	1.02	39.94	$\ln k' = -1218.90[\text{SDS}]_t + 4.89$	2969.2	3.884	1.20	↓ -
	3rd	1.54	21.63	$\ln k' = -229.99[\text{SDS}]_t + 3.43$	560.3	3.417	1.36	↓ -
	4th	4.92	10.32	$\ln k' = -75.71[\text{SDS}]_t + 2.66$	184.4	1.528	0.78	↓
303	1st	0.00	118.60	$\ln k' = -145.46[\text{SDS}]_t + 4.78$	366.4	3.069	1.29	↓ -
	2nd	1.02	102.89	$\ln k' = -602.87[\text{SDS}]_t + 5.23$	1518.7	2.963	1.04	↓ +
	3rd	1.54	75.99	$\ln k' = -268.67[\text{SDS}]_t + 4.735$	676.8	3.381	1.30	↓ -
	4th	4.92	32.09	$\ln k' = -107.78[\text{SDS}]_t + 3.97$	271.5	2.386	1.09	↓

^aDimension of E_s is in kJ (mol molar(surfactant))⁻¹. 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 λ_{max} value of MG^+ increase with increase in DTAB concentration and it seems that $\text{MG}/\text{TX-100}$ interacts with TX-100 molecules *via* hydrophobic and electrostatic interactions. As seen in Table 3, this interaction is endothermic and its positive ΔS value ($394.3 \text{ J mol}^{-1} \text{ K}^{-1}$) 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 ΔS 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.²⁸

It seems that a preliminary electrostatic interaction occurs between $(\text{CH}_3)_2\text{N}^+$ 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 λ_{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,²⁹ At $\text{pH} \leq 2$, 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-

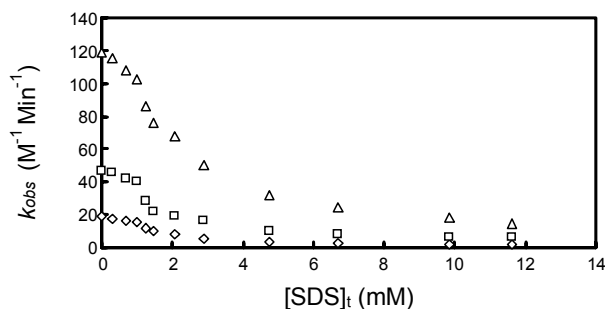


Figure 4. k_{obs} values of MG^+ fading reaction vs. concentrations of SDS at \diamond 283, \square 293 and Δ 303 K under alkaline conditions.

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

T (K)	$\log K_{tot}$	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)
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)	$\log K$	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)
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 ΔH and ΔS 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 λ_{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 λ_{max} value of MG^+ keeps approximately constant, Figure 1 and Table 4. This indicates that in this region, hydrophobic interaction occurs between MG^+ /SDS com-

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

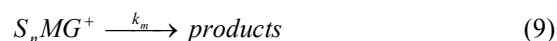
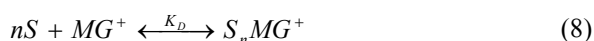
T (K)	$\log K$	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)
Regions 1 and 4				
283	4.000	-21.7		
293	4.604	-25.8	200.4	780.6
303	6.457	-37.5		
Regions 2 and 3				
283	8.095	-43.9		
293	7.301	-40.9	-143.5	-351.4
303	6.344	-36.8		
Regions 1, 2, 3 and 4				
283	12.095	-65.6		
293	11.904	-66.7	56.9	429.2
303	12.801	-74.3		

The total ΔH and ΔS values were obtained by adding the related values of all regions.

pound with free SDS molecules. As reported,³⁰ 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 ΔS value is positive, Table 7.

Analysis of kinetic data by cooperativity model. The Piszkie-wicz model,^{15,31-33} analogous to the Hill model applied to the enzyme-catalyzed reactions³⁴ 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 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 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 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 MG^+ were calculated using the following equation:³⁵

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

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 MG^+ to SDS is exothermic. On the other hand, due to oscillation in the values of binding constants of MG^+ to TX-100 and DTAB, ΔH and ΔS values of these interactions can not be calculated.

Conclusion

The rate constant of alkaline fading of malachite green (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 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 MG^+ to TX-100 is exothermic and binding of MG^+ to DTAB and SDS in some regions is endothermic and in the other ones is exothermic.

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