

Kinetics of Methyl Green Fading in the Presence of TX-100, DTAB and SDS

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The rate constant of alkaline fading of methyl green (ME^{2+}) was measured in the presence of non ionic (TX-100), cationic (DTAB) and anionic (SDS) surfactants. ME^{2+} hydrolyses and fades in neutral water and in this work we search the effects of surfactants on its fading rate. The rate of reaction showed remarkable dependence on the electrical charge of the used surfactants. It was observed that the reaction rate constant decreased in the presence of DTAB and SDS and increased in the presence of TX-100. Binding constants of ME^{2+} to TX-100, DTAB and SDS and the related thermodynamic parameters were obtained by classical (or stoichiometric) model. The results show that binding of ME^{2+} to TX-100 and DTAB are two-region and that of SDS is three-region. Also, the binding constants of ME^{2+} to surfactant molecules in DTAB/TX-100 and SDS/TX-100 mixed solutions and their stoichiometric ratios were obtained.

Key Words : Methyl green, Stoichiometric model, Fading, Surfactant

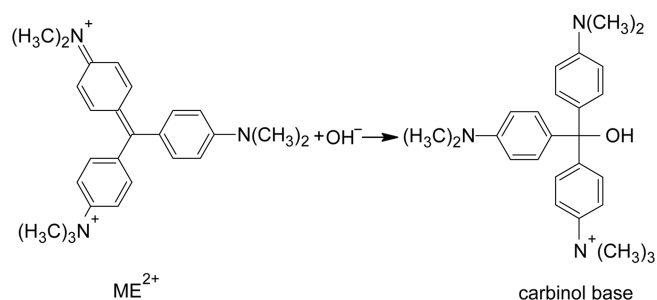
Introduction

The chemical reaction rates are changed by change in ionic strength, pH, temperature, surfactants,¹⁻⁶ etc. Effects of surfactants molecules and their micelles on the reaction rates are due to their interactions with reactants. Methyl green (ME^{2+}) is a cationic triphenylmethane dye.⁷ This dye is suitable for the selective staining of nucleic acids,⁸ as sensitizer⁹ and as a pH indicator. The kinetics of the alkaline fading of triphenylmethane dyes is well studied.¹⁰ In continuation of our earlier works,¹¹⁻¹³ we studied the ME^{2+} alkaline fading in the presence of different concentrations of TX-100, DTAB and SDS at 283-303 K. Kinetics of these kinds of reactions in the presence of surfactants can be studied using pseudo-phase ion exchange, cooperativity and classical (or stoichiometric) models.¹¹⁻¹³ Also, in this work, the binding constants of ME^{2+} to surfactant molecules in mixed solutions of TX-100 with DTAB or SDS were obtained and it showed that their interaction with ME^{2+} is competitive.

Experimental

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

The fading of ME^{2+} was followed at its maximum wavelength (λ_{max}) values in a thermostated cell compartment of a Shimadzu UV-1650PC spectrophotometer. The reaction of ME^{2+} with hydroxide ion brings about fading the color of the ME^{2+} and results in the formation of colorless carbinol base, Scheme 1. The experiments were conducted at 283-303 K within ± 0.1 K. All the kinetic runs were carried out at least



Scheme 1

in triplicate. To perform each kinetic run, a 100 μL aliquot of 4.45×10^{-4} M ME^{2+} solution was added by a microsyringe into 2.9 mL of a solution containing 4.82×10^{-4} M sodium hydroxide and a certain concentration of surfactant. Here, surfactants have an inhibitory effect on the reaction and to study all interactions occurred between surfactant and substrate molecules, we carried out the experiments in the surfactant concentration range which reaction rate finally becomes very slow. The reaction between ME^{2+} and hydroxide 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 Classical Model. In classical (or stoichiometric) model¹¹ 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 complex formation point" (or abbreviated as *sc* point) in which the equilibrium relation between added

surfactant and species already presented in solution ends and a new equilibrium relation between added surfactant and compound resulted from the previous equilibrium relation starts. 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, following equation holds for:

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

where k' , c , $[S]_t$, R and T 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, respectively. E_S is the catalytic or inhibition energy of reaction in constant temperature and various surfactant concentrations. k_{sc} is the k_{obs} in the starting of every region except region one. Eq. (1) is introduced as "Samiey equation"¹¹ and can determine the concentration range of each region.¹¹ 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. Dimension of E_S is in kJ (mol molar (surfactant))⁻¹.

In this model, it is assumed that in each region one substrate molecule, ME^{2+} in this work, 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 model¹¹ these interactions are of type I which surfactant has an inhibitory effect on the fading reaction of ME^{2+} , respectively and k_{obs} is related to the surfactant concentration as follows:¹¹

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

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

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 complex 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:

$$K_{tot}^i = K_1 \dots K_{i-1} K_i = \prod_{j=1}^i K_j \quad (5)$$

$$n_{tot}^i = n_1 \dots n_{i-1} n_i = \sum_{j=1}^i n_j \quad (6)$$

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.

Comparison of Substituent Effects on the ME^{2+} and Malachite Green (MG^+) Fading Rate. As seen in Table 1, alkaline fading rate constants of ME^{2+} in water are 110.75, 246 and 516.88 $M^{-1} \text{min}^{-1}$ at 283, 293 and 303 K, respectively, whereas those for MG^+ in water are 18.89, 46.98 and 118.60 $M^{-1} \text{min}^{-1}$ at 298, 303 and 308 K, respectively.¹¹ ME^{2+} has two $-N(CH_3)_2$ and one $(CH_3)_3N^+$ substituent groups whereas MG^+ has two $-N(CH_3)_2$ substituent groups. Due to the presence of $(CH_3)_3N^+$ substituent group in ME^{2+} , this dye hydrolyses in neutral water and reacts very slowly with H_2O molecules. The first-order fading rate constants of ME^{2+} in neutral water (at $\lambda_{max} = 633 \text{ nm}$) are 0.0023, 0.0064 and 0.013 M^{-1} at 283, 293 and 303 K, respectively and second-order fading rate constants of this reaction are 4.28×10^{-5} , 1.19×10^{-4} and $2.33 \times 10^{-4} M^{-1} \text{min}^{-1}$, respectively. In this work, we use different kinds of surfactants for stabilizing ME^{2+} color in water.

Effect of TX-100 on the ME^{2+} Fading. As seen in Figure 1 and Table 1, kinetics of ME^{2+} fading in the presence of TX-100 is two-region at 283, 293 and 303 K. The *cmc* value of TX-100 in pure water is 0.29 mM.¹⁴ The first region is above its *cmc* point, Table 1. In this region, increase in TX-100 concentration increases the ME^{2+} fading rate constant

Table 1. Parameters obtained from stoichiometric (classical) model for interaction of ME^{2+} with TX-100 at 283-303 K

T (K)	Region	<i>sc</i> (mM)	k_{sc} ($M^{-1} \text{min}^{-1}$)	Samiey equation	E_S	$\log K$	n	k_S ($M^{-1} \text{min}^{-1}$)	Cooperativity
283	1st	0.0	110.75	$\ln k' = 71.53[\text{TX}]_t + 4.72$	-168.3	2.43	1.28	320.76	↓ -
	2nd	6.8	178.42	$\ln k' = 41.15[\text{TX}]_t + 4.91$	-96.8	1.54	1.20	965.52	
293	1st	0.0	246.00	$\ln k' = 57.45[\text{TX}]_t + 5.52$	-139.9	3.25	1.45	488.90	↓ -
	2nd	6.8	359.29	$\ln k' = 20.59[\text{TX}]_t + 5.76$	-50.2	0.94	0.92	1175.09	
303	1st	0.0	516.88	$\ln k' = 36.49[\text{TX}]_t + 6.26$	-91.9	4.25	1.71	696.79	↓ -
	2nd	6.8	653.80	$\ln k' = 7.78[\text{TX}]_t + 6.43$	-19.6	0.69	1.07	2216.36	

Dimension of E_S is in kJ (mol molar (surfactant))⁻¹. TX is an abbreviation for TX-100 and dimension of TX concentration in Samiey equation is in M. Dimension of K is in M^{-n}

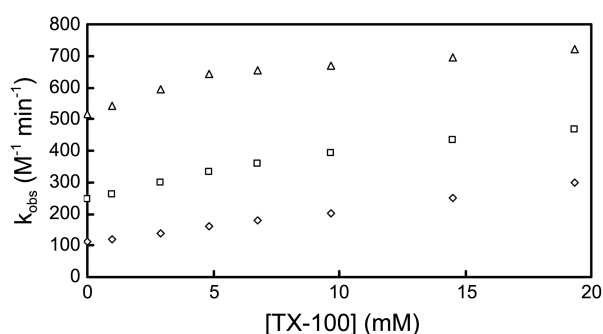


Figure 1. k_{obs} values of ME^{2+} fading reaction vs. concentrations of TX-100 at \diamond 283, \square 293 and \triangle 303 K under alkaline conditions.

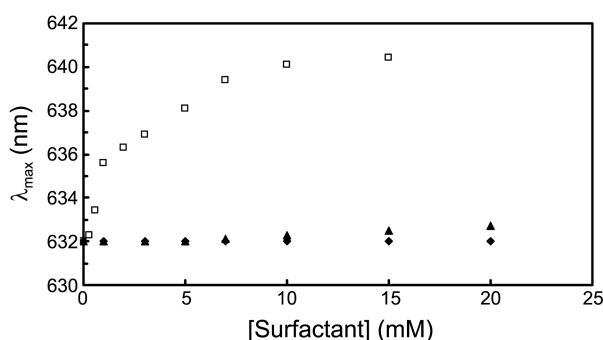


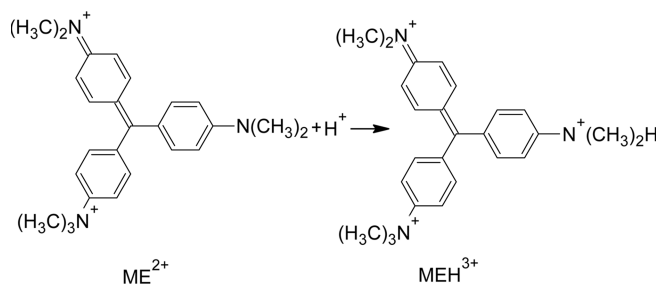
Figure 2. λ_{max} values of ME^{2+} vs. concentrations of \blacklozenge DTAB, \square SDS and \blacktriangle TX-100 under alkaline conditions.

but λ_{max} value of ME^{2+} keeps approximately constant, Figures 1 and 2.

This indicates that in this region, a preliminary weak electrostatic interaction occurs between $(CH_3)_3N^+$ substituent group of ME^{2+} and oxygen atom of ethoxy chains of TX-100 molecules which is similar to interaction of silanol groups of silica gel with TX-100.^{14,15} This interaction along with further hydrophobic interaction of ME^{2+} with TX-100 molecules decreases dielectric constant of the ME^{2+} micro-environment. ME^{2+} is dicationic and according to Hughs-Ingold rules^{16,17} formation of a positively charged carbinol base from interaction of ME^{2+} and OH^- , is favorable in lower dielectric constant media.

To confirm this result, in acidic solution, interaction of TX-100 with $(CH_3)_3N^+$ group of quinone-like part of MEH^{3+} results in the blue shift in its λ_{max} value, Table 2 and Scheme 2.

In the second region at 283, 293 and 303 K, with increase in TX-100 concentration, λ_{max} value of ME^{2+} and its fading



Scheme 2

Table 2. Typical λ_{max} values of ME^{2+} in the presence of DTAB, SDS and TX-100 in acidic and alkaline solutions

In 1 M HCl	λ_{max} (nm)	In 4.3×10^{-4} M NaOH	λ_{max} (nm)
–	432.5	–	632.0
14.5 mM DTAB	427.5	14.5 mM DTAB	632.0
0.97 mM SDS	428.5	0.97 mM SDS	635.6
0.29 mM TX-100	428.5	0.29 mM TX-100	632.0

Table 3. Thermodynamic parameters obtained from stoichiometric (classical) model for interaction of ME^{2+} with TX-100 at 283–303 K

T (K)	logK	ΔG		ΔH	ΔS
		(kJ mol ⁻¹)			
Region 1					
283	2.43	–13.2		149.0	572.2
293	3.25	–18.2			
303	4.25	–24.6			
Region 2					
283	1.54	–8.3		–30.4	–95.1
293	0.94	–5.3			
303	0.69	–4.0			
Regions 1 and 2					
283	3.97	–21.5		118.6	477.1
293	4.19	–23.5			
303	4.94	–28.6			

The total ΔH , ΔS , and logK values were obtained from addition of the related values of the first and second regions. Dimension of K is in M^{-n}

rate constant change similar to those of the first region, Figure 1 and Table 1. As given in Table 1, binding constant values and stoichiometric ratios of ME^{2+} formed in the first region (TX is an abbreviation for TX-100) with TX-100 molecules in the second region are smaller than those of the first region.

As seen in Table 3, interactions of ME^{2+} with TX-100 molecules in the first and second regions are endothermic and exothermic, respectively. E_s values of each region increase with increase in temperature and also E_s values in each temperature increase from the first region to the second one which the latter is due to the binding more numbers of TX-100 molecules to ME^{2+} .

Effect of DTAB on the ME^{2+} Fading. As seen in Figure 3

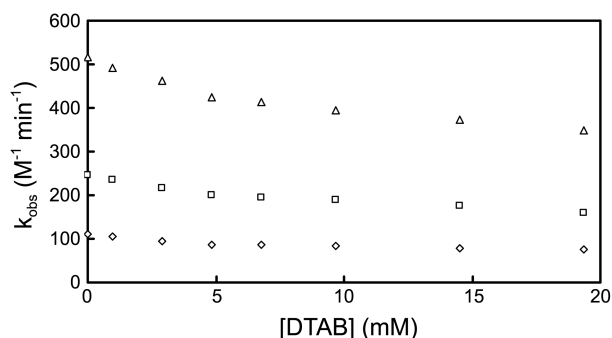


Figure 3. k_{obs} values of ME^{2+} fading reaction vs. concentrations of DTAB at \diamond 283, \square 293 and \triangle 303 K under alkaline conditions.

Table 4. Parameters obtained from stoichiometric (classical) model for interaction of ME^{2+} with DTAB at 283-303 K

T (K)	Region	sc	k_{sc}	Samiey equation	E_s	$\log K$	n	Cooperativity
		(mM)	($M^{-1}min^{-1}$)					
283	1st	0.0	110.75	$\ln k' = -47.18[DTAB]_t + 4.70$	111.0	1.61	0.95	↓ -
	2nd	4.8	87.75	Reaction rate is constant	-	-	-	
293	1st	0.0	246.00	$\ln k' = -42.14[DTAB]_t + 5.50$	102.7	1.66	1.00	↓ -
	2nd	4.8	200.84	$\ln k' = -14.92[DTAB]_t + 5.37$	36.3	1.54	1.18	
303	1st	0.0	516.88	$\ln k' = -39.73[DTAB]_t + 6.25$	100.1	1.72	1.03	↓ -
	2nd	4.8	424.53	$\ln k' = -13.37[DTAB]_t + 6.11$	33.7	1.17	1.00	

Dimension of E_s is in kJ (mol molar(surfactant))⁻¹. Dimension of DTAB concentration in Samiey equation is in M. Dimension of K is in M^{-n}

and Table 4, kinetics of ME^{2+} fading in the presence of DTAB is three-region.

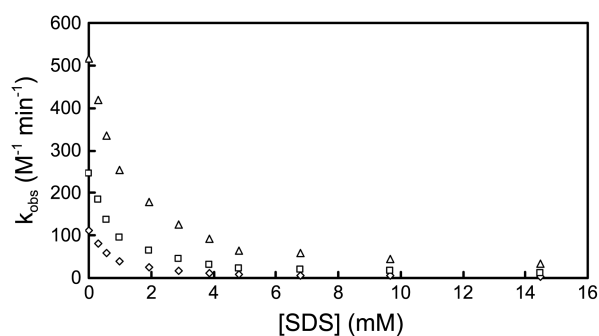
The *cmc* value of DTAB in pure water is 13.77 mM¹⁸ and the first region and a part of the second region are below the *cmc* value of DTAB. In the first region, with increase in DTAB concentration, the rate constant of ME^{2+} fading decreases. Electrostatic and then hydrophobic interaction of ME^{2+} with DTAB and formation of $MEDTAB_n^{2+n}$ complex increases positive charge of the formed transition state and makes its formation less favorite comparing to that of ME^{2+} . As seen in Figure 2, in the presence of DTAB, λ_{max} value of ME^{2+} molecules keep approximately constant. This is due to electron-withdrawing effect of $(CH_3)_3N^+$ – substituent group of ME^{2+} on weak electrostatic interaction between its $-N(CH_3)_2$ substituent groups with positive head group of DTAB molecules. This interaction is endothermic and their binding constants (K) and stichiometric ratios of DTAB to ME^{2+} (n) values increase with increase in temperature, Tables 4 and 5. To confirm this interaction, as seen in Table 2, in acidic solution interaction of DTAB with $(CH_3)_3N^+$ = group of quinone-like part of MEH^{3+} , Scheme 2, results in blue shift of its λ_{max} value, Table 2.

In the second region, the rate constant of ME^{2+} fading increases with increase in DTAB concentration, Figure 3. There is an interaction between $MEDTAB_n^{2+n}$ formed in the second region and DTAB molecules and their K and n values are greater than those of the first region, Table 4. As given in Table 5, interaction of ME^{2+} with DTAB molecules in this

Table 5. Thermodynamic parameters obtained from stoichiometric (classical) model for interaction of ME^{2+} with DTAB at 283-303 K

T (K)	$\log K$	ΔG	ΔH	ΔS
		(kJ mol ⁻¹)		(J mol ⁻¹ K ⁻¹)
Region 1				
283	1.61	-8.7		
293	1.66	-9.3	9.0	62.5
303	1.72	-10.0		
Region 2				
283	-	-		
293	1.54	-8.6	Exothermic	-
303	1.17	-6.8		

Dimension of K is in M^{-n}

**Figure 4.** k_{obs} values of ME^{2+} fading reaction vs. concentrations of SDS at \diamond 283, \square 293 and \triangle 303 K under alkaline conditions.

region is exothermic. E_s values of each region decrease with increase in temperature and also E_s values in each temperature decrease from the first region to the second one which the latter is due to the binding more numbers of DTAB molecules to ME^{2+} .

Effect of SDS on the ME^{2+} Fading. As seen in Figure 4 and Table 6, kinetics of ME^{2+} fading in the presence of SDS is third-region and its fading rate constant decreases with increase in SDS concentration.

The *cmc* value of SDS in 0.001 N NaOH is 3.5 mM.¹⁹ The first region is in the range of 0-0.97 mM of SDS concentration. In this region, a strong electrostatic interaction occurs between $(CH_3)_3N^+$ = and $(CH_3)_3N^+$ – substituent groups of ME^{2+} and sulfate head group of SDS that follows with a hydrophobic interaction between ME^{2+} and nonpolar moiety of SDS molecules and results in the red shift in ME^{2+} λ_{max} value. These interactions decrease dielectric constant values of ME^{2+} microenvironment and according to Hughs-Ingold rules result in a great decrease in the rate constant of ME^{2+} fading with increase in SDS concentration. To confirm this kind of interaction, interaction of SDS with $(CH_3)_3N^+$ = group of quinone-like part of MEH^{3+} , Scheme 2, results in a blue shift of its λ_{max} value.

Second and third regions are in the 0.97-4.8 mM and greater than 4.8 mM of SDS concentration range respectively, Figure 4 and Table 6. In these regions, $MESDS_n^{2-n}$ formed in the previous region interacts with SDS, as monomer in the second and as micelle in the third region. Binding constants (K) values of SDS to ME^{2+} (and its complexes with SDS) decrease from the first region to the

Table 6. Parameters obtained from stoichiometric (classical) model for interaction of ME²⁺ with SDS at 283-303 K

T (K)	Region	<i>sc</i> (mM)	<i>k_{sc}</i> (M ⁻¹ min ⁻¹)	Samiey equation	<i>E_s</i>	log <i>K</i>	<i>n</i>	Cooperativity
283	1st	0.0	110.75	ln <i>k'</i> = -1084.72[SDS] _t + 4.70	2552.2	4.28	1.33	↓ -
	2nd	0.97	39.00	ln <i>k'</i> = -438.05[SDS] _t + 4.06	1030.7	4.22	1.49	↓ -
	3rd	4.80	7.51	ln <i>k'</i> = -87.73[SDS] _t + 2.41	206.4	2.38	1.11	↓ -
293	1st	0.0	246.00	ln <i>k'</i> = -981.53[SDS] _t + 5.50	2391.0	4.07	1.29	↓ -
	2nd	0.97	95.29	ln <i>k'</i> = -379.99[SDS] _t + 4.92	925.7	3.88	1.41	↓ -
	3rd	4.80	21.63	ln <i>k'</i> = -68.87[SDS] _t + 3.41	167.8	2.46	1.24	↓ -
303	1st	0.0	516.88	ln <i>k'</i> = -739.72[SDS] _t + 6.25	1863.5	3.75	1.24	↓ -
	2nd	0.97	253.66	ln <i>k'</i> = -350.77[SDS] _t + 5.87	883.6	3.75	1.38	↓ -
	3rd	4.80	65.05	ln <i>k'</i> = -70.46[SDS] _t + 4.52	177.5	2.54	1.28	↓ -

Dimension of *E_s* is in kJ (mol molar(surfactant))⁻¹. Dimension of SDS concentration in Samiey equation is in M. Dimension of *K* is in M^{-*n*}

Table 7. Thermodynamic parameters of interaction of ME²⁺ with SDS obtained from stoichiometric (classical) model at 283-303 K

T (K)	log <i>K</i>	ΔG (kJ mol ⁻¹)	ΔH	ΔS (J mol ⁻¹ K ⁻¹)
Regions 1 and 2				
283	8.50	-46.0		
293	7.94	-44.5	-82.0	-127.5
303	7.50	-43.5		
Region 3				
283	2.38	-12.9		
293	2.46	-13.8	13.7	93.7
303	2.54	-14.7		
Regions 1, 2 and 3				
283	10.88	-58.9		
293	10.40	-58.3	-68.3	-33.8
303	10.04	-58.2		

The total ΔH , ΔS and log*K* values were obtained from addition of the related values of the first, second and regions. Dimension of *K* is in M^{-*n*}

third one and thus the rate of decrease in ME²⁺ fading rate constant decreases. This results in a decrease in the velocity of the red shift of λ_{\max} values of ME²⁺ with increase in SDS concentration, Figure 2.

As given in Table 7, interaction of ME²⁺ with SDS in the first and second regions and in throughout used SDS concentration is exothermic, Table 7. *E_s* values of each region decrease with increase in temperature and also *E_s* values in each temperature decrease from the first region to the third one which the latter is due to the binding more numbers of SDS molecules to ME²⁺ which in turn decreases acceleration in the ME²⁺ fading rate constant.

Effect of DTAB and TX-100 Mixtures on the ME²⁺ Fading Rate. The used concentrations of DTAB were in its first region and those of TX-100 were in the range of its first and second regions at 293 K, Table 8. As given in Tables 1 and 4, increase in TX-100 and DTAB concentration (separately) increases and decreases ME²⁺ fading reaction rate, respectively. As seen in Table 8, an increase in DTAB and TX-100 concentration in their mixed solutions decreases the rate constant of ME²⁺ fading reaction.

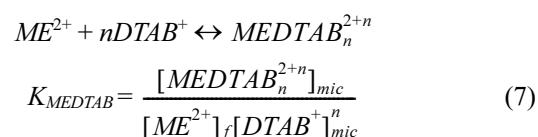
It is previously found that in the used concentration ranges

Table 8. Parameters obtained from interaction of ME²⁺ with DTAB/TX-100 mixed solutions in different regions of TX-100 and DTAB at 293 K

[DTAB] (mM)	[TX-100]	<i>k_{obs}</i> (M ⁻¹ min ⁻¹)	λ_{\max} (nm)	Parameters
First region of TX-100				$K_{MEDTAB_n} = 0.83$ $n = 0.33$
0.00	0.00	246.00	632.0	
2.90	0.96	220.42	631.7	
0.96	1.93	237.35	631.7	
1.93	2.90	205.77	631.7	
4.35	2.90	213.24	631.7	
3.86	5.80	228.56	631.7	$K_{METX_m} = 82.94$ $m = 1.02$ $K_{MEDTAB_n} = 3.08 \times 10^6$ $n = 2.74$
Second region of TX-100				
0.00	0.00	246.00	632.0	
0.96	8.70	400.18	631.9	
2.90	10.63	342.58	631.7	
3.86	12.56	252.25	631.6	
1.93	14.50	464.74	632.0	
4.35	17.40	292.90	631.8	
1.93	19.33	545.49	631.9	

The used DTAB concentrations are in its first region, Table 4. Dimensions of K_{MEDTAB_n} and K_{METX_m} are in M^{-*n*} and M^{-*m*}, respectively

of DTAB and TX-100, mixed micelles of them form^{20,21} which results in a decrease in the apparent dielectric constant values for different mixed systems compared to those of TX-100 or DTAB solution.²² As given in Table 8, calculations show that in the first region of TX-100 and DTAB, ME²⁺ molecules interact with DTAB molecules of DTAB/TX-100 mixed micelles. This interaction is as follows:



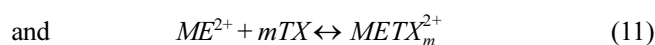
and its reaction rate equation is as follows

$$v = \frac{k[ME^{2+}]_f}{1 + K_{MEDTAB}[DTAB]_{mic}^n} = k_{obs}[ME^{2+}]_f \quad (8)$$

where

$$k_{\text{obs}} = \frac{k}{1 + K_{\text{MEDTAB}}[\text{DTAB}]_{\text{mic}}^n} \quad (9)$$

k is The fading rate constant of ME^{2+} in water ($246 \text{ M}^{-1}\text{min}^{-1}$ at 293 K) and subscript f represents free concentrations of ME^{2+} , respectively. Subscript mic represents the concentration of surfactant in the mixed micelles and MEDTAB is an abbreviation for MEDTAB_n^{2+n} . The data were fitted in Eq. (9) and n and K_{MEDTAB} values were given in Table 8. When TX-100 concentration is in its second region and DTAB concentration is in its first region, calculation of data shows that ME^{2+} interacts with DTAB and TX-100 according to following relations:



and the related reaction rate equation is as follows

$$v = \frac{k(1 + K_{\text{METX}}[\text{TX}]_{\text{mic}}^m)[\text{ME}^{2+}]_f}{1 + K_{\text{MEDTAB}}[\text{DTAB}]_{\text{mic}}^n} = k_{\text{obs}}[\text{ME}^{2+}]_f \quad (12)$$

where TX and METX are abbreviations for TX-100 and METX_m^{2+} , respectively and

$$k_{\text{obs}} = \frac{k(1 + K_{\text{METX}}[\text{TX}]_{\text{mic}}^m)}{1 + K_{\text{MEDTAB}}[\text{DTAB}]_{\text{mic}}^n} \quad (13)$$

The data were fitted in Eq. (13) and m , n , K_{METX} and K_{MEDTAB} values were given in Table 8. The results show under these conditions interaction of TX-100 and DTAB with ME^{2+} is competitive and interaction of ME^{2+} with TX-100 is very stronger than its interaction with DTAB molecules.

Effect of SDS and TX-100 Mixtures on the ME^{2+} Fading Rate

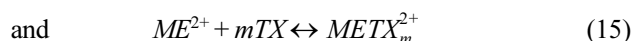
Table 9. Parameters obtained from interaction of ME^{2+} with SDS/TX-100 mixed solutions in different regions of TX-100 and SDS at 293 K

[SDS] (mM)	[TX-100] (mM)	k_{obs} ($\text{M}^{-1}\text{min}^{-1}$)	λ_{max} (nm)	Parameters
First region of SDS				
0.00	0.00	246.00	632.0	$K_{\text{METX}_m} = 3.13 \times 10^4$ $m = 2.01$ $K_{\text{MESDS}_n} = 3.50 \times 10^4$ $n = 1.33$
0.19	0.96	179.64	636.8	
0.29	2.90	199.55	637.2	
0.96	2.90	78.45	638.5	
0.39	3.86	163.26	637.3	
0.58	4.83	148.01	637.5	
0.48	5.80	220.17	637.0	
Second region of SDS				
	0.00	246.00	632.0	$K_{\text{METX}_m} = 233.9$ $m = 0.94$ $K_{\text{MESDS}_n} = 5.38$ $n = 0.36$
1.45	0.96	45.55	638.3	
2.90	2.90	53.31	638.5	
3.86	4.83	62.42	630.7	
4.35	6.76	73.86	631.0	
1.93	5.80	87.00	631.5	

The used TX-100 concentrations are in its first region, Table 1. Dimensions of K_{METX_m} and K_{MESDS_n} are in M^{-m} and M^{-n} , respectively

ing Rate. The used concentrations of TX-100 were in the first region and those of SDS are in the first and second regions of ME^{2+} fading at 293 K, Table 9. As seen in Tables 1 and 6, an increase in SDS and TX-100 concentrations (separately) decreases and increases the reaction rate of ME^{2+} fading, respectively. It is found that in the used concentrations of SDS and TX-100, they form mixed micelles.²³

The results show that in the used concentration range of surfactants, TX-100/DTAB mixed micelles interact with ME^{2+} molecules through their TX-100 and SDS molecules and decrease the ME^{2+} fading reaction rate. These interactions are as follows:



and the related reaction rate equation is as follows

$$v = \frac{k(1 + K_{\text{METX}}[\text{TX}]_{\text{mic}}^m)[\text{ME}^{2+}]_f}{1 + K_{\text{MESDS}}[\text{SDS}]_{\text{mic}}^n} = k_{\text{obs}}[\text{ME}^{2+}]_f \quad (16)$$

where k is The fading rate constant of ME^{2+} in water ($246 \text{ M}^{-1}\text{min}^{-1}$ at 293 K), TX, METX and MESDS are abbreviations for TX-100, METX_m^{2+} and MESDS_n^{2-n} , respectively and

$$k_{\text{obs}} = \frac{k(1 + K_{\text{METX}}[\text{TX}]_{\text{mic}}^m)}{1 + K_{\text{MESDS}}[\text{SDS}]_{\text{mic}}^n} \quad (17)$$

The data were fitted in Eq. (17) and m , n , K_{METX} , and K_{MEDTAB} values were given in Table 9. The results show that under the used conditions, there is a competitive interaction between ME^{2+} with TX-100 and SDS molecules. As seen in Table 9, in the first region of SDS, m , n , K_{METX} , and K_{MESDS} values are greater than those of its second region. As given in Table 9, λ_{max} values of the first region of SDS (in its mixed solutions) shift to red that shows SDS molecules in SDS/TX-100 mixed micelles similar to SDS molecules in pure SDS micelles (Table 6, in SDS second and third regions) interact with $(\text{CH}_3)_2\text{N}^+$ = substituent group of ME^{2+} too. But, λ_{max} values of ME^{2+} in the second region of SDS are approximately constant that shows in this region SDS interacts preferably with $(\text{CH}_3)_2\text{N}^+$ – substituent group of ME^{2+} and competes to TX-100 for interaction with this substituent group.

Analysis of Kinetic Data by Cooperativity Model. The Piskiewicz model²⁴⁻²⁶ 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, ME^{2+} in this work, associates with n number molecules of surfactant to form micelle S_n ME^{2+} which may react as follows:



The model gives the following rate equation:

Table 10. n and K_D values obtained from cooperativity model for interaction of ME^{2+} with DTAB, SDS and TX-100 at 283-303 K

T (K)	DTAB		SDS		TX-100	
	n	$\log K_D$	n	$\log K_D$	n	$\log K_D$
283	0.68	-0.89	1.18	-3.78	1.47	-3.00
293	0.79	-1.11	1.07	-3.38	1.54	-3.42
303	0.77	-1.04	1.07	-3.22	1.44	-3.44

Dimension of K_D is in M^{-n}

$$\log[(k_{obs} - k_w)/(k_m - k_{obs})] = n \log[S]_t - \log K_D \quad (21)$$

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 constant without any surfactant, and k_m is the reaction rate constant 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 n value is greater than one, cooperativity of interaction is positive and 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. (21), a two-parameter equation, can not fit properly the data of different types of surfactant-substrate interactions.

As shown in Figures 1, 3 and 4, there is positive catalytic effect by TX-100 and negative catalytic effect by DTAB and SDS in the whole range of the reaction. As shown in Table 10, values of n show positive cooperativity in the used concentration range of SDS and TX-100 and negative cooperativity in the case of DTAB. Also, the calculated values of K_D show that binding of ME^{2+} to TX-100 is exothermic and binding of ME^{2+} to SDS is endothermic.

Analysis of Kinetic Data by Pseudo-phase Ion Exchange (PPIE) Model. In the PPIE model, the binding constants of the interaction of surfactant molecules with BG^+ were calculated using the following equation²⁷

$$k_{obs} = \frac{k_w + k_m K_s ([S]_t - cmc)}{1 + K_s ([S]_t - cmc)} \quad (22)$$

where $[S]_t$, K_s , k_{obs} , k_m and k_w are the total surfactant concentration, binding constant, observed reaction rate constant and reaction rate constants in micellar media and in the bulk phase, respectively. This model can not study the surfactant-substrate interactions below the cmc value of surfactants. As

Table 11. k_m and K_S values obtained from PPIE model for interaction of AF^{2-} with DTAB, SDS and TX-100 at 283-303 K

T (K)	DTAB		SDS		TX-100	
	k_m	K_S	k_m	K_S	k_m	K_S
283	85.22	1.43×10^8	—	—	3295.61	3.26
293	187.25	1.37×10^8	—	—	683.40	53.72
303	399.37	1.33×10^8	—	—	774.19	172.90

Dimensions of k_m and K_S are in $M^{-1} \text{min}^{-1}$ and M^{-1} , respectively

seen in Table 11, data of ME^{2+} fading in the presence of DTAB and TX-100 were fitted in Eq. (22) and according to this model ME^{2+} fading reaction in the presence of DTAB and TX-100 were exothermic and endothermic, respectively.

Conclusion

The rate constant of alkaline fading of ME^{2+} was measured in various concentrations of TX-100, DTAB and SDS. It was observed that the reaction rate constant was increased in the presence of TX-100 and decreased in the presence of DTAB and SDS. Interaction of surfactant molecules to ME^{2+} was studied using cooperativity, pseudo-phase ion exchange and classical (or stoichiometric) models. Binding constants of surfactant molecules to ME^{2+} and the related thermodynamic parameters were calculated by classical (or stoichiometric) model. The results show that binding of ME^{2+} to TX-100 and DTAB are two-region and that of SDS is three-region. Binding ME^{2+} to TX-100, DTAB and SDS is exothermic in one or more regions and endothermic in other region of the used concentration range of these surfactants. Cooperativity of these interactions is negative from one region to another one. Binding constants and stoichiometric ratios of ME^{2+} to surfactant molecules in DTAB/TX-100 and SDS/TX-100 were obtained using stoichiometric model and interaction of surfactant molecules in these mixed solutions with ME^{2+} is competitive. ME^{2+} hydrolyses in neutral water and adding SDS to ME^{2+} neutral and alkaline solutions decreases its hydrolysis rate.

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