Study of Kinetics of Bromophenol Blue Fading in the Presence of SDS, DTAB and Triton X-100 by Classical Model

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In this paper, kinetics of reaction between Bromophenol blue (BPB) and OH^-, called fading, has been studied through a spectrophotometric method in the presence of nonionic Triton X-100 (TX-100), anionic sodium dodecyl sulfate (SDS) and cationic dodecyl trimethylammonium bromide (DTAB) surfactants. The influence of changes in the surfactant concentration on the observed rate constant was investigated. The results are treated quantitatively by pseudophase ion-exchange (PPIE) model and a new simple model called "classical model". The binding constants of BPB molecules to the micelles and free molecules of surfactants, their stoichiometric ratios and thermodynamic parameters of binding have been evaluated. It was found that SDS has nearly no effect on the fading rate up to 10 mM, whereas TX-100 and DTAB interact with BPB which reduce the reaction rate. By the use of fading reaction of BPB, the binding constants of SDS molecules to TX-100 micelles and their Langmuir and Freundlich adsorption isotherms were obtained and when mixtures of DTAB and TX-100 were used, no interaction was observed between these two surfactants.

Key Words : Classical model, Kinetics, Surfactant, Bromophenol blue

Introduction

Bromophenol blue (BPB) is a member of triphenylmethane dyes family.[1-3] In alkaline solution, it forms dibasic salt which gradually fades.[4] This reaction is first order respect to both dye and hydroxide.[5]

The fading of BPB in alkaline solution was observed and studied by Kilpatrick and colleagues.[6-8] Amis and his co-workers studied the effect of dielectric constant in water and water-alcohol mixtures on this reaction.[9] Chen and Laidler[10] studied the effect of temperature and pressure on the alkaline fading of BPB. Duynstee and Grunwald[11] investigated the fading of BPB in the presence of surfactants. They reported that the rate of fading of BPB is virtually unchanged when sodium dodecyl sulfate is added, but BPB is protected from fading in the presence of cetyl trimethylammonioum bromide (CTAB). In this paper, we have studied the effects of SDS, DTAB and TX-100 on the alkaline fading of BPB over a range of surfactant concentrations and temperatures. The changes in the rate of fading reaction are quantitatively treated by the PPIE and classical models.

Experimental Section

Reagent. Sodium hydroxide, sodium dodecyl sulfate, dodecyl trimethylanmonium bromide, Triton X-100, dimethyl sulfoxide (DMSO) and bromophenol blue were purchased from Merck Co. Materials were used without further purification.

Procedure. For preparation of dye solution, 0.015 gr dye was dissolved in 0.5 cm^3 ethanol (99.8%) which, after dilution with double distilled water, was transformed into a 100 cm^3 volumetric flask and was filled to the mark and its concentration was 2.31×10^{-4} M. The rate of fading was studied by photometric method. A small volume (0.2 cm^3) of dye solution was added to 2.5 cm^3 of a solution of NaOH (0.2 M), prepared in the surfactant solution, which was previously placed in the thermostatted cell compartment of a UV-VIS 2100 Shimadzu spectrophotometer (controlled to ± 0.1°C).The changes of absorption of dye were recorded at its maximum wavelength (λ_{max}).

Theory

In the recent years many papers concerned with the catalysis or inhibition of reaction rates by surfactant micelles have been published. Kinetics of reactions in the presence of surfactants, above the critical micelle concentration (cmc) of surfactants, can be investigated using cooperativity[12,13] and pseudophase ion-exchange (PPIE)[14-16] models. These models have some limitations.

Here, a new simple model is introduced by one of the authors, Babak Samiey, which is called "*classical model*" and bears none of the above models limitations. In this model, it is assumed that in each range of surfactant concentration, the surfactant and substrate molecules can bind together and there is one 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 solution ends and another equilibrium relation between added surfactant and compound resulted from the previous equilibrium relation starts. The range of surfactant concentration which covers an equilibrium

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relation is named "*region*". The cmc point is also a sc point and there may be some sc points before and after the cmc point as well. Surfactant molecules either monomeric or micellar can bind to the substrate molecules. Micelles can bind to the substrate by one or more number of their surfactant molecules. Thus we can obtain the stoichiometric ratios and binding constants of interactions of surfactants with substrate molecules in various ranges of surfactant concentrations.

In this paper it is supported that for each assumed equilibrium relation, following equation holds for:

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

where, k', c, $[S]_t$, R, T and E_S are the rate constant in the presence of surfactant, lnk (at the first region) or $\ln k_{sc}$, total surfactant concentration, universal gas constant, absolute temperature and activation energy of reaction in constant temperature and various surfactant concentrations, respectively. Also, k_{sc} and k are the rate constant at the sc point and in the absence of surfactant, respectively.

Equation (1) is initiated and derived by one of the authors, Babak Samiey, and is presented after his family name "*Samiey equation*". Samiey equation is a pathfinder equation which can determine the concentration range of each region.

Proof of Samiey equation. Samiey equation was derived from Arrhenius equation. By taking the partial derivative of logarithmic form of Arrhenius equation with respect to the total surfactant concentration in constant temperature, pressure and in constant concentrations of reactants (or substrates) and other components we obtain:

$$\left(\frac{\partial \ln k'}{\partial [S]_t}\right)_{T,P,\ldots} = \left(\frac{\partial \ln A}{\partial [S]_t}\right)_{T,P,\ldots} - \frac{1}{RT}\left(\frac{\partial E_a}{\partial [S]_t}\right)_{T,P,\ldots} \tag{2}$$

or

$$\left(\frac{\partial \ln k'}{\partial [S]_t}\right)_{T,P,\ldots} = -\frac{E_S}{RT} \tag{3}$$

where $E_S = -RT\left(\frac{\partial \ln A}{\partial [S]_t}\right)_{T,P,\ldots} - \left(\frac{\partial E_a}{\partial [S]_t}\right)_{T,P,\ldots}$. E_S is a combination of two effects. The first term, *frequency factor term*, shows the effect of collision change on the reaction rate with the surfactant concentration raise.

The second term, *activation energy term*, shows the effect of change in activation energy on the reaction rate with the surfactant concentration raise. These terms may be positive or negative. If the E_S value is assumed independent of surfactant concentration, we can integrate equation (3). So, we have:

$$\ln k' = c - \frac{E_S}{RT}[S]_t \tag{4}$$

where c is the natural logarithm of the reaction rate constant at the start point of each region. If the reaction rate is decreased upon increasing the surfactant concentration, the sign of E_S is positive and E_S is termed "*inhibition energy*" and if the reaction rate is increased with increasing the surfactant concentration, the sign of E_S is negative and is termed "*catalytic energy*" at constant temperature and various concentrations of surfactant.

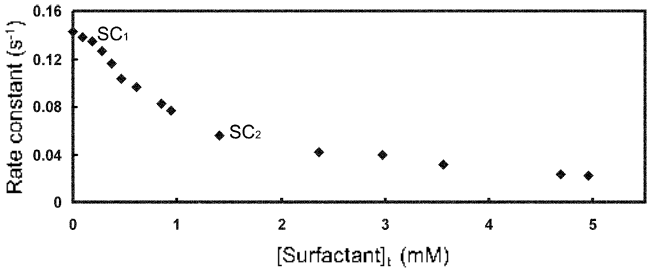


Figure 1. Reaction rate constant as a function of total surfactant concentration for a typical reaction. The sc points, obtained from crossing of Samiey equations for adjacent regions, are shown in figure.

E_S dimension is in kJ (mol.molar (surfactant))$^{-1}$ or abbreviated as kJ mol^{-1} molar^{-1}. Samiey equations of adjacent regions cross each other at the sc points, Figure 1.

Derivation of classical model. Here two general cases are defined:

Case I: In this case, with increasing the surfactant concentration in each region, the rate of reaction decreases.

First, it is assumed that in each region one substrate molecule (R) binds to n molecules of surfactant (S) as follows:

$$R + nS \Leftrightarrow RS_n \quad K = \frac{[RS_n]}{[R]_f [S]_f^n} \tag{5}$$

where K is the binding constant of the substrate-surfactant interaction in each region.

For simplicity, it is assumed that the resulted compound (RS_n) doesn't react and surfactant molecules mask the substrate molecules.

In each concentration of surfactant, the rate equation is as follows:

$$V = k[R]_f^m \ldots \tag{6}$$

where k, $[R]_f$ and m are the rate constant in the absence of surfactant, free substrate concentration and order of reaction in R, respectively. If we consider:

$$[R]_t = [R]_f + [RS_n] \tag{7}$$

substituting (5) for (7):

$$[R]_t = [R]_f (1 - K[S]_f^n) = [R]_f \alpha \tag{8}$$

where

$$\alpha = 1 + K[S]_f^n \tag{9}$$

replacing (8) in (6) we have:

$$V = \frac{k[R]_t^m}{\alpha^m} = k'[R]_t^m \ldots \tag{10}$$

where $k' = k/\alpha^m$. k' and $[R]_t$ are the rate constant in the presence of surfactant and total substrate concentration, respectively.

Equating (6) and (10) we have:

$$[R]_f = \left(\frac{k'}{k}\right)^{\frac{1}{m}}[R]_t \tag{11}$$

also $$[S]_f = [S]_t - n[RS_n] \tag{12}$$

if $[S]_t >> [RS_n]$ then, we have:

$$[S]_f \cong [S]_t \tag{13}$$

and also $$[RS_n] = [R]_t - [R]_f = [R]_t\left(1 - \left(\frac{k'}{k}\right)^{\frac{1}{m}}\right) \tag{14}$$

where $[S]_t$ and $[S]_f$ are the total and free surfactant concentrations, respectively. Substituting equations (11), (13) and (14) for (5), we have:

$$k' = \frac{k}{(1 + K[S]_t^n)^m} \tag{15}$$

In a case that surfactant, in each region, has an inhibition interaction with more than one kind of substrate molecule, we have:

$$k' = \frac{k}{\prod_j (1 + K_j[S]_t^{n_j})^{m_j}} \tag{16}$$

where K_j, n_j and m_j are the binding constant, stoichiometric ratio and order of reaction in jth substrate. These relations hold for the first region. In other regions, for each equilibrium relation after each sc point, $[S]_t$-$[sc]$ must be substituted for $[S]_t$ (because the added surfactant after each sc point interacts with the species already presented in solution) and k_{sc} for k, where $[sc]$ and k_{sc} values are the total surfactant concentration and reaction rate constant at sc point, respectively. Thus equations(15) and (16) are given as:

$$k' = \frac{k_{sc}}{(1 + K([S]_t - [sc])^n)^m} \tag{17}$$

$$k' = \frac{k_{sc}}{\prod_j (1 + K_j([S]_t - [sc])^{n_j})^{m_j}} \tag{18}$$

Equations (15), (16), (17) and (18) are called the *Rate constant equations*. The binding constant and stoichiometric ratio values for each region are calculated by these equations.

Case II: In this case, with increasing the surfactant concentration in each region, the rate of reaction increases.

First, it is assumed that in each region one substrate molecule (R) binds to n surfactant molecules (S), as in equation (5). Also, it is supposed that the resulted compound (RS_n) reacts more rapid than the free substrate.

In each concentration of surfactant, the rate equation can be represented by following equation:

$$V = (k[R]_f^m + k_s[RS_n]^m)\ldots \tag{19}$$

where k_s is the rate constant in substrate-surfactant compound. Replacing equation (5) in (19) we have:

$$V = (k[R]_f^m + k_sK^m[R]_f^m[S]_f^{n-m})\ldots \tag{20}$$

Since in experimental work, changes in total substrate concentration would be measured, then:

$$V = k'[R]_t^m\ldots \tag{21}$$

Equating (20) and (21) and using (5), (7) and (13), we can write

$$k' = \frac{k + k_SK^m[S]_t^{n+m}}{(1 + K[S]_t^n)^m} \tag{22}$$

In a case that one type of surfactant, in each region, has a catalytic interaction with two kinds of substrate molecules, R_1 and R_2, we have:

$$k' = \frac{k + k_{S3}K_1^{m1}K_2^{m2}[S]_t^{n1-m1+n2+m2} + \sum_{j=1}^{2} k_{S_j}K_j^{m_j}[S]_t^{n_j+m_j}}{\prod_{j=1}^{2}(1 + K_j[S]_t^{n_j})^{m_j}} \tag{23}$$

where m_1 and m_2 are the reaction orders of R_1 and R_2, respectively. K_1 and K_2 are the binding constants of R_1 and R_2 with surfactant molecules and n_1 and n_2 are the stoichiometric ratios of interactions of R_1 and R_2 with surfactant molecules, respectively. k_{s1}, k_{s2} and k_{s3} are the rate constants of the reactions of R_1S_{n1} with R_2, R_2S_{n2} with R_1 and R_1S_{n1} with R_2S_{n2}, respectively. These relations hold for the first region. In other regions, for each equilibrium relation after each sc point, we must substitute $[S]_t$-$[sc]$ for $[S]_t$ and k_{sc} for k.Thus equations (22) and (23) are written as

$$k' = \frac{k_{sc} + k_SK^m([S]_t - [sc])^{n+m}}{(1 + K([S]_t - [sc])^n)^m} \tag{24}$$

$$k' = \frac{k_{sc} + k_{S3}K_1^{m1}K_2^{m2}([S]_t - [sc])^{n1+m1+n2-m2} + \sum_{j=1}^{2} k_{S_j}K_j^{m_j}([S]_t - [sc])^{n_j+m_j}}{\prod_{j=1}^{2}(1 + K_j([S]_t - [sc])^{n_j})^{m_j}} \tag{25}$$

Equations (22), (23), (24) and (25) are called the *Rate constant equations*. The binding constant and stoichiometric ratio values for each region are calculated by these equations.

Following the same process for cases I and II, we can calculate the rate constant equations of interaction of several types of surfactants with several types of substrates.

In cases I, II and also for the case in which the reaction rate increases in one range of surfactant concentration and decreases in another range (which is a combination of cases I and II), 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:

$$K_{tot}^i = K_1K_2\ldots K_{i-1}K_i = \prod_{j=1}^{i} K_j \tag{26}$$

Table 1. Kinetic Parameters of Reaction between OH^- and Coumarin in the Presence of CTAB and the Binding Constants and Stoichiometric Ratios Obtained from the Classical Model at 30 °C (Ref. 17)

$[CTAB]_t$ 10^3(M)	k' (min^{-1})	Samiey equation	E_S (*)	log$K$	n	k_S (min^{-1})
0	0.5	$\ln k' = -0.67 + 59.5\,[CTAB]_f$	-150	0.747	0.887	4.84
4.33	0.687					
6.47	0.76					
8.67	0.833 < sc					
14	0.807					
18.3	0.793	$\ln k' = -0.115 - 7\,[CTAB]_f$	17.6	1.15	1.18	–
24.3	0.747					
36.7	0.687					

*E_S dimension is in kJ (mol.molar (surfactant))$^{-1}$. In this reaction, the reaction order in substrate (Coumarin) is equal to 1 and equations (17) and (22) were used for calculation of K and n values.

Table 2. Binding Constant, Stoichiometric Ratio,E_S values and Cooperativities of Some Reactions in the Presence of Surfactants (with one substrate-surfactant Interaction in each region), Obtained from the Classical Model

Reaction (surfactant)	k_w	[sc] (mM)	Region	E_S (*)	log$K$	n	k_S	Cooperativity	Ref.
(a) **Coumarin** – OH^-(CTAB)	–	–	1st	-150	0.747	0.887	4.84	+	17
	0.833	8.67	2nd	17.6	1.15	1.18	–		
(b) **Coumarin** + OH^-(SDS)	–	–	1st	108	3.8	2.16	–	-	17
	0.22	19.3	2nd	37.8	1.46	1.05	–		
(c) **Indoaniline Dye** – OH^-	–	–	1st	k' is approximately constant				+	18
(Triton X-100)	1.9×10^{-3}	0.142	2nd	11107	4.653	1.22	–		
(d) Hydrolysis of	–	–	1st	k' is approximately constant				+	19
Mono-p-nitrophenyl	7.78×10^{-3}	6.34	2nd	168.5	3.529	1.82	–	-	
Dodecanedionate (Laurate)	1.84×10^{-3}	30.6	3rd	51.3	1.34	0.92	–		
(e) [Cd(II)-histidine]$^-$	–	–	1st	54.5	2.025	1.1	–	-	20
+ **Ninhydrin** (CTAB)	0.895×10^{-4}	11.9	2nd	38.7	1.326	1.08	–		
(f) Hydrolysis of **Phenyl**	–	–	1st	456	2.8	1.17	–		23
Chlorophormate ($Brij_{35}$)	1.16×10^{-2}	1.06	2nd	142	2.01	1.05	–		
	5.74×10^{-3}	13.3	3rd	51	1.76	1.2	–	-	
	4.08×10^{-3}	30	4th	16	1.02	1.1	–		
(g) Oxidation of 4-*tert*-	–	–	1st	-19545	1.09	1.64	7.51		24
Butylcatechol by **Polyphenol**	1.1×10^{-4}	0.216	2nd	-836	0.3	0.4	0.0008	+	
Oxidase (SDS)	1.71×10^{-4}	0.867	3rd	207	1.3	0.75	–		
(h) Oxidation of	–	–	1st	-15158	2	1.47	0.164	+	25
4-*tert*-Butylcatechol by	1.03×10^{-4}	0.267	2nd	16409	6.35	1.61	–		
Polyphenol Oxidase (Dodecanesulfonic acid)									

*E_S dimension is in kJ (mol.molar (surfactant))$^{-1}$. Reactants shown in bold are substrates which interact with the surfactant molecules. Enzymatic reactions (g) and (h) occurr under cmc of surfactants and instead of rate constants, velocities (in M min^{-1}) are used and the dimensions of I'_{ss} and I'_f in these reactions are in M min^{-1}. Dimensions of k_w and k_s in reactions (a) and (b) are in min^{-1} and in reactions (c), (d), (e) and (f) are in s^{-1}. In all above reactions, the reaction order in substrate is equal to 1. $Brij_{35}$ is an abbreviation for dodecyl tricosaoxyethylene glycol ether.

$$n'_{tot} = n_1 + n_2 - \ldots - n_{i-1} + n_i = \sum_{j}^{i} n_j \qquad (27)$$

where indices represent the region numbers.

Cooperativity. Going from one region to another region, 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.

The results obtained from classical model could be shown in a tabular form, such as Table 1. An abstracted form of the experimental results of a number of papers, analyzed by classical model, is given in Tables 2 and 3.

Comparison of PPIE and Classical Models.

(A) In the PPIE model, the colloidal particles of surfactant (after cmc) are considered such as an ion-exchanger and the binding of substrate to them is considered like the partition of a substance between the two phases.

In the PPIE model, the stoichiometric ratio of surfactant (as micelle) to the substrate is 1 : 1 and there is one average binding constant for substrate-surfactant compound in the whole surfactant concentration range, while in the classical model the stoichiometric ratio of surfactant (either micellar

Table 3. Binding Constant, Stoichiometric Ratio and E_s values of Some Reactions in the Presence of Surfactants, Obtained from the Classical Model

Reaction (surfactant)	k_{sc}	[sc] (mM)	Region	E_s (*)	Rate constant equation	Ref.
(i) **[Ni(II)-histidine]$^+$ + Ninhydrin** (CTAB)	–	–	1st	-296.6	Data are not sufficient	22
	3.31×10^{-5}	6.59	2nd	-50.2	$k' = \frac{3.31\times10^{-5}+k_sK_{Ni}([CTAB]_t-0.659\times10^{-2})^p}{(1+K_{ni}([CTAB]_t-0.659\times10^{-2})^r)(1+K_{Ni}([CTAB]_t-0.659\times10^{-2})^p)}$	
					r = 2.42 p= 1.5 K_{Ni}= 25.6 K_{ni}= 875 k_s= 3.67x10^{-4} s^{-1}	
	5.8×10^{-5}	40	3rd	–	k' is approximately constant	
(j) Hydrolysis of **Phenyl Chlorophormate** (SDS/$Brij_{35}$ (0.67/0.33))	–	–	1st	343	Data are not sufficient	23
	0.0109	1.86	2nd	102	$k' = \frac{0.0109}{1+6451([SDS]_t-1.228\times10^{-3})^{0.36}([Brij]_t-6.32\times10^{-4})^{1.38}}$	
	0.0053	20	3rd	46	$k' = \frac{0.0053}{1+65([SDS]_t-0.0132)^{0.7}([Brij]_t-0.0068)^{0.36}}$	

*E_s dimension is in kJ (mol.molar (surfactant))$^{-1}$. Reactants shown in bold are substrates which interact with the surfactant molecules. Dimensions of k_{sc} and k_s in reactions (i) and (j) are in s^{-1}. In reaction (i), interaction of ninhydrin with CTAB molecules slows the reaction rate and binding of CTAB molecules to the [Ni(II)-histidine]$^-$ complex increases the reaction rate. In the rate constant equation, K_{Ni} and K_{ni} are the binding constants of CTAB to the [Ni (II)-histidine]$^-$ and ninhydrin and p and r are the stoichiometric ratios of binding of CTAB to [Ni(II)-histidine]$^+$ and ninhydrin, respectively and are calculated from $k' = \frac{k_{sc} + k_sK_{Ni}([CTAB]_t+[CTAB]_{sc})^p}{(1 + K_{ni}([CTAB]_t-[CTAB]_{sc})^r)(1 + K_{Ni}([CTAB]_t-[CTAB]_{sc})^p)}$. In reaction (*j*), the binding constant (K) and stoichiometric ratios (n and m) of the (phenyl Chlorophormate) $(SDS)_n(Brij_{35})_m$ compound are calculated from $k' = \frac{k_{sc}}{1 + K([SDS]_t-[SDS]_{sc})^n([Brij_{35}]_t-[Brij_{35}]_{sc})^m}$. Where $[SDS]_{sc}$ and $[Brij_{35}]_{sc}$ are the concentrations of SDS and $Brij_{35}$ at sc point, respectively. In mixed surfactant solutions, Samiey equations are calculated using the total concentration of all surfactants in solution.

Table 4. Comparison of $\overline{K}$ and K_S Values

Reaction (surfactant)	$\overline{K}$ (M^{-1})	K_S(M^{-1})	Ref.
Coumarin + OH^- (CTAB)	8.3	27	17
Coumarin + OH^- (SDS)	43.5	83	17
Indoaniline Dye + OH^- (Triton X-100)	6.5×10^3	2×10^4	18
Hydrolysis of **Mono-p-nitrophenyl Dodecanedionate** (Laurate)	60	136.4	19
[Cd(II)-histidine]$^+$ + **Ninhydrin** (CTAB)	34.5	100	20
Hydrolysis of **Phenyl Chlorophormate** ($Brij_{35}$)	48	209	23

*Reactants shown in bold are substrates which interact with surfactant molecules.

or monomeric) to the substrate is n : 1 and in each region there is a new equilibrium relation and therefore a new binding constant. a new stoichiometric ratio and negative or positive cooperativity.

Thus. for the case of interaction of one kind of substrate with one kind of surfactant in each region, data from some papers were analyzed by classical model and $\overline{K} = (K_{tot})^{1/n_{tot}}$ values in the classical model were compared with their related K_s values (as given in the literature. K_s values are the binding constants obtained from the PPIE model) and the results are shown in Table 4.

(B) Using equations (15) and (22) for the full concentration range of the used surfactant. the mean values for total binding constant (K_t) and total stoichiometric ratio (n_t) of surfactant-substrate interaction would be obtained. For the case of interaction of one kind of substrate with one kind of surfactant in each region, data from some papers were

Table 5. Comparison of $(K_t)^{1/n_t}$ and K_S Values

Reaction (surfactant)	n_t	K_t	$(K_t)^{1/n_t}$ (M^{-1})	K_S(M^{-1})	Ref.
Coumarin + OH^- (SDS)	1.3	162	50.1	83	17
Indoaniline Dye + OH^- (SDS)	1.51	3.4×10^4	2.1×10^4	4600	18
Hydrolysis of **Mono-p-nitrophenyl Dodecanedionate** (Laurate)	2.42	1.65×10^4	55.3	136.4	19
[Cd(II)-histidine]$^+$+**Ninhydrin** (CTAB)	0.82	26.5	54.4	100	20
Methyl 4-Nitrobenzene-sulfonate + Cl^- (CTAC)	1.18	48	26.5	75	21
Methyl 4-Nitrobenzene-sulfonate + Cl^- ((CTAC/Triton X-100 (0.9/0.1))	1.2	58	29.5	106	21
Methyl 4-Nitrobenzene-sulfonate + Cl^- ((CTAC/Triton X-100 (0.8/0.2))	0.96	22	25	127	21
Hydrolysis of **Phenyl Chlorophormate** (SDS)	1.22	90	40	61	23
Hydrolysis of **Phenyl Chlorophormate** ($Brij_{35}$)	0.37	7.5	228	209	23

*Reactants shown in bold are substrates which interact with surfactant molecules. In the presence of mixed micelles of CTAC/Triton X-100. only CTAC interacts with Methyl-4-Nitrobenzene-sulfonate. CTAC is an abbreviation for hexadecyltrimethylammonium chloride.

analyzed by classical model and $(K_f)^{1/n_f}$ values in the classical model were compared with their related K_s values and the results were shown in Table 5.

(C) The PPIE model is not applicable in the region before the cmc point of surfactant, but in the classical model the binding of substrate to the monomeric surfactant is considered.

(D) In the PPIE model, for the cases in which the reaction rate increases in one range of surfactant concentration and decreases in another range, it is assumed that in average there is one type of interaction between surfactant and substrate molecules. Therefore, there is one binding constant for whole range of the surfactant concentrations.

But in these cases, in the classical model it is assumed that the substrate molecules have different interactions with surfactant molecules and the reaction is catalyzed in one or more regions and inhibited in another region(s). Therefore, the binding constants are not identical in different regions.

(E) In the PPIE model, it is assumed that the rate constant in micelle (k_m) is not usually equal to zero. But in the classical model, it is assumed that the rate constant in micelle for catalysis of reaction is more than the rate constant of free substrate and in the state of inhibition of reaction, it is equal to zero.

(F) In the PPIE model, only one sc point is assumed which corresponds to the cmc of surfactant. But in the classical model, there are various sc points which cmc is counted to be one of them.

(G) In the PPIE model, the binding constant and stoichiometric ratio of interaction of only one type of substrate molecule with one type of surfactant molecule is measured. But in the classical model, we can evaluate, by using a suitable curve fitting software, the stoichiometric ratios and binding constants of interactions of several kinds of substrate molecules with several types of surfactant molecules in each region

It must be mentioned that in the classical model for each region, there is a good agreement between Samiey equation and related rate constant equation. This would be possible only when the E_s value is independent of the surfactant concentration in each region.

Results and Discussion

Effect of SDS on the BPB fading. As seen in Figures 2 and 3, while the SDS concentration increases up to 10 mM, the λ_{max} values of BPB and its reaction rate constants are nearly constant.

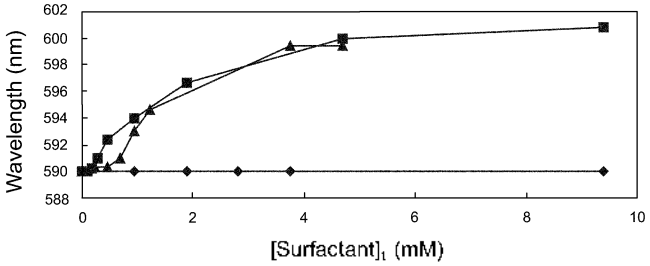


Figure 2. Variation of λ_{max} values of BPB with concentration of ◆ SDS, ▲ DTAB and ■ Triton X-100.

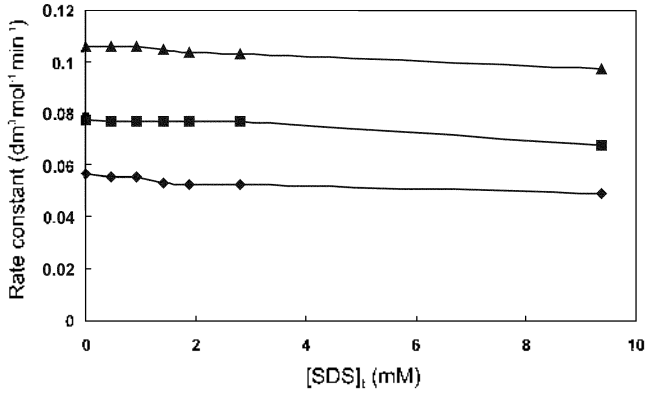
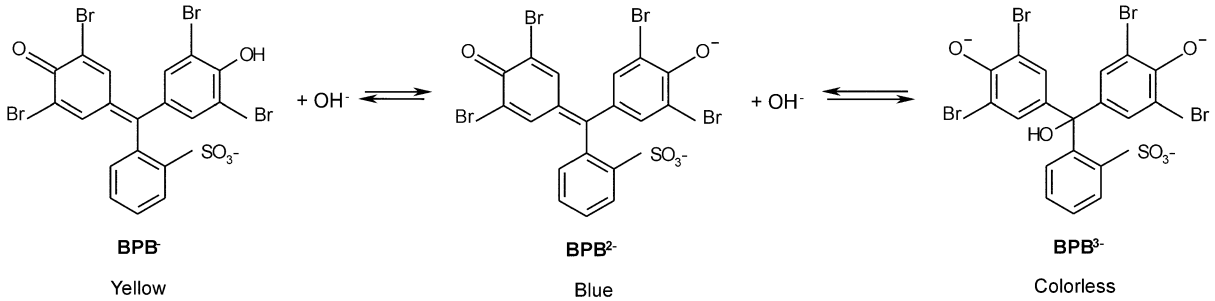


Figure 3. Variation of rate constant of BPB fading with concentration of SDS at ◆ 298 K, ■ 303 K and ▲ 308 K.

Under experimental conditions, there is no interaction between SDS and BPB molecules, because both of them are negatively charged. The cmc of SDS in the ionic strength used in this work and in the absence of BPB is 0.94 mM.[26] It was reported that upon increasing the SDS concentration, the dielectric constant of the solution decreases[27] and as seen in Figure 3, according to Amis equation,[28] it causes a slight decrease in the reaction rate of BPB fading.

Effect of DTAB on the BPB fading. We can see in Table 6 and Figures 2 and 4 that with the increase in DTAB concentration, the reaction rate constants decrease and the λ_{max} values shift to red. These effects result from the positive charge of DTAB molecules.

We observed that the λ_{max} values of acidic solutions of



BPB$^-$ BPB^{2-} BPB^{3-}

Yellow Blue Colorless

Scheme

Table 6. Binding Constants, Stoichiometric Ratios, E_s values and Cooperativities of BPB Fading in the Presence of DTAB, Obtained from the Classical Model at 298-308 K

T(K)	Region	$\lvert sc \rvert$ 10^3 (M)	$10^2 k_{sc}$ ($dm^3 mol^{-1} min^{-1}$)	Samiey equation	E_s (*)	log$K$	n	Cooperativity
298	1st	–	–	$\ln k' = -2.864 - 269.28\,[DTAB]_f$	667	1.59	0.753	
	2nd	0.381	5.15	$\ln k' = -2.045 - 2416.7\,[DTAB]_f$	5987.6	5.96	1.676	
	3rd	1.22	0.71	$\ln k' = -3.88 - 863.3\,[DTAB]_f$	2139	3.77	1.215	
303	1st	–	–	$\ln k' -2.55 - 173.5\,[DTAB]_f$	437	1.282	0.73	
	2nd	0.234	7.48	k' is approximately constant	–	–	–	
	3rd	0.469	7.52	$\ln k' -1.63 - 2326\,[DTAB]_f$	5859	3.93	1.05	
	4th	1.3	0.95	$\ln k' -3.34 - 1012.7\,[DTAB]_f$	2551	3.61	1.15	
308	1st	–	–	k' is approximately constant	–	–	–	
	2nd	0.469	10.5	$\ln k' = -1.336 - 2173.66\,[DTAB]_f$	5566	4.074	1.11	
	3rd	1.22	1.98	$\ln k' = -2.15 - 1465\,[DTAB]_f$	3752	3.91	1.165	

*E_s dimension is in kJ (mol.molar (surfactant))$^{-1}$. Those sc points which are obtained from the intersection of Samiey equations for adjacent regions, are shown in a box. Here, the substrate is BPB.

Table 7. Thermodynamic Parameters of Interaction of BPB with DTAB in the Classical Model

T (K)	log K_{int}	ΔG	ΔH	ΔS
		(kJ $mole^{-1}$)		(J mol^{-1} K^{-1})
298	11.28	-64.4		
303	8.822	-51.2	-602	-1806
308	7.984	-47.1		

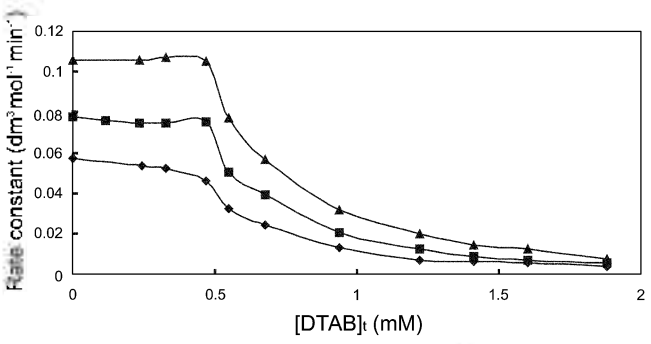


Figure 4. Variation of rate constant of BPB fading with concentration of DTAB at ◆ 298 K, ■ 303 K and ▲ 308 K.

BPB had no shift in the presence of DTAB. Therefore, it seems that a preliminary electrostatic interaction occurs between BPB and DTAB molecules.

It was observed that by adding DMSO to aqueous solution of BPB, the λ_{max} value of its alkaline form, as a result of hydrophobic interaction, shifts to red. Thus, those interactions of DTAB with BPB which result to red shift, can be attributed to the hydrophobic interactions between them. The red shift has been previously reported for other compounds upon going from polar to apolar solvents[29] and upon going from the aqueous solution to the more hydrophobic micellar environment.[30]

Thermodynamic parameters of this interaction are given in Table 7. The reaction is exothermic in the whole concentration range of surfactant. The cmc of DTAB in the ionic

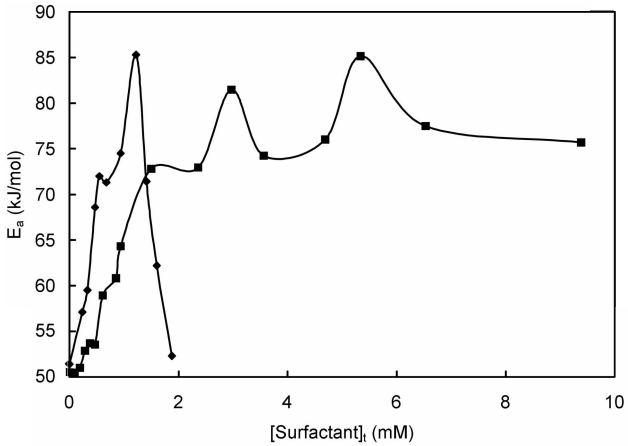


Figure 5. Variation of activation energy of BPB fading with concentration of ◆ DTAB and ■ Triton X-100.

strength used in this work and in the absence of BPB is more than 2.54 mM[31] and as it is seen from Figure 4, the fading reaction occurs in the concentration range of DTAB which is below its cmc point.

In Figure 5, changes in activation energy of BPB fading reaction in the presence of different DTAB concentrations are seen. At the beginning, activation energy would increase in sc_1 and sc_2 points which suggests a great structural change in activated complex and reactants in these points.

Effect of Triton X-100 on the BPB fading. As we can see in Figures 2 and 6 and Table 8, with increasing the TX-100 concentration the rate constants decrease and the λ_{max} values shift to red. Here, it seems that a preliminary interaction of hydrogen bonding type occurs between the BPB and hydroxyl end of TX-100 molecules. Then, the hydrophobic interactions take place and cause to the red shift of λ_{max} values of BPB.

Thermodynamic parameters of this interaction are given in Table 9. The reaction is exothermic in the whole concentration range of TX-100. For the fact that binding constants

Table 8. Binding Constants, Stoichiometric Ratios, E_s values and Cooperativities of BPB Fading in the Presence of Triton X-100, Obtained from the Classical Model at 303-313 K

T (K)	Region	[sc] 10^3 (M)	$10^2 k_{sc}$ ($dm^3 mol^{-1} min^{-1}$)	Samiey equation	E_s (*)	log$K$	n	Cooperativity
303	1st	–	–	$\ln k' = -2.55-373.13\,[TX]_f$	940	2.11	0.883	+
	2nd	0.1876	7.31	$\ln k' = -2.451-945.67\,[TX]_f$	2382	3.587	1.143	
	3rd	1.41	2.27	$\ln k' = -3.396-275\,[TX]_f$	693	3.24	1.248	-
	4th	5.34	0.747	$\ln k' = -4.41-88.76\,[TX]_f$	234	3.045	1.42	
308	1st	–	–	$\ln k'$ $-2.245-351.8\,[TX]_f$	901	1.68	0.767	+
	2nd	0.1876	9.94	$\ln k'$ $-2.172-821.08\,[TX]_f$	2102	3.467	1.127	
	3rd	1.5	3.3	$\ln k'$ $-3.03-249.2\,[TX]_f$	638	3.137	1.23	-
	4th	4.79	1.47	$\ln k'$ $-3.65-119.64\,[TX]_f$	306	2.694	1.2	
313	1st	–	–	$\ln k' = -1.948-293.18\,[TX]_f$	763	1.42	0.71	+
	2nd	0.1876	13.5	$\ln k' = -1.924-682.9\,[TX]_f$	1777	3.397	1.12	
	3rd	1.41	5.57	$\ln k' = -2.51-267.7\,[TX]_f$	697	3.07	1.186	-
	4th	4.95	2.16	$\ln k' = -3.27-114.3\,[TX]_f$	297	2.574	1.164	

*E_s dimension is in kJ (mol.molar (surfactant))$^{-1}$. Those sc points which are obtained from the intersection of Samiey equations for adjacent regions, are shown in a box. Here, the substrate is BPB.

Table 9. Thermodynamic Parameters of Interaction of BPB with Triton X-100 in the Classical Model

T (K)	log K_{tot}	ΔG	ΔH	ΔS
		(kJ mole^{-1})		(J mol^{-1} K^{-1})
303	11.982	-69.4		
308	10.978	-64.6	-290.8	-732
313	10.461	-62.6		

Table 10. Binding constants of Triton X-100 and BPB obtained from the Classical and PPIE Models in Various Temperatures

T (K)	$(K_{tot})^{1/n_m}$ (M^{-1})	K_s (M^{-1})	10^3 k_m ($dm^3 mol^{-1} min^{-1}$)
303	357	1843	1.32
308	346	1657	3.57
313	318	1435	6.02

used in this calculations are K_{tot} (for binding of n_m molecules of TX-100 to one BPB molecule), the calculated thermodynamic parameters values are higher than the calculated by PPIE model (for the binding of one molecule of TX-100 to one BPB molecule).

In Figure 5, changes in activation energy of the BPB fading, in the presence of different TX-100 concentrations are seen. At first, the activation energy is constant and in sc_1, sc_2 and sc_3 points it suddenly goes higher which suggests a great structural change in activated complex and reactants in these points.

In the PPIE model, the binding constants of the interaction of TX-100 with BPB were calculated using the following equation[32]:

$$k' = \frac{k_w + k_m K_S([S]_t - cmc)}{1 + K_S([S]_t - cmc)} \quad (28)$$

where $[S]_t$, K_S, k', k_m and k_w are the total surfactant concentration, binding constant, reaction rates in micellar media, in micellar phase and in the bulk phase, respectively. K_S and $(K_{tot})^{1/n_m}$ values in different temperatures are shown and compared in Table 10.

The cmc of TX-100 in the ionic strength used in this work and in the absence of BPB is 0.24 mM.[33]

Proof of Adjacent Regions by Destructive Interaction with Surfactant (PARDIS) Test. To prove the existence of adjacent regions in the classical model, the BPB fading was studied in the presence of different concentrations of TX-100 (in its second and third regions) along with the low concentrations of SDS at 308 K. It is good to mention that pardis is an ancient persian word and it means paradise.

From Figure 3, it is clear that low concentrations of SDS have no effect on the rate of BPB fading. Therefore, any change in the reaction rate between TX-100 and BPB results from the SDS interaction with TX-100.

If adjacent regions are not available, there should be only one kind of interaction between TX-100 and BPB, as well between TX-100 and SDS. Otherwise, the existence of different interactions between TX-100 and SDS shows that adjacent regions are available. So, the micellar structures of TX-100 and consequently the interactions of TX-100 micelles with BPB are not the same in these regions.

For interaction of SDS with TX-100 (here abbreviated as TX)we can write:

$$nSDS + TX \Leftrightarrow TX(SDS)_n \quad K_{TS} = \frac{[TX(SDS)_n]}{[SDS]_f^n [TX]_f} \quad (29)$$

$$[TX]_t = [TX]_f + [TX(SDS)_n] = [TX]_f(1 - K_{TS}[SDS]_f^n) \quad (30)$$

$$[SDS]_f = [SDS]_t - n[TX(SDS)_n] \quad (31)$$

substituting equation (31) for (30) we have:

$$[TX]_t - [TX]_f(1 + K_{TS}([SDS]_t - n[TX(SDS)_n])^n) \quad (32)$$

Table 11. Pardis Test of BPB Fading in the Presence of the Mixtures of Triton X-100 (in its second and third regions) and SDS at 308 K

Second region			Third region		
10^5 [SDS]$_t$ (M)	$10^2 k'$ (dm^3 mol^{-1} min^{-1})		10^5 [SDS]$_t$ (M)	$10^2 k'$ (dm^3 mol^{-1} min^{-1})	
3	6.61 ± 0.02		10.16	2.7 ± 0.05	n = 0.079
5.63	7.36 ± 0.03	n = 0.156	12.5	2.95 ± 0.04	K_{TS} = 1.855
9.38	7.79 ± 0.01	K_{TS} = 4.436	19.5	3.1 ± 0.05	
13.5	8.11 ± 0.02		31.25	3.79 ± 0.03	
20	8.16 ± 0.03				

*In second region. $[TX]_t = 8.55 \times 10^{-4}$ M and for calculation of $[TX]_f$ we used ln $k' = -2.172 - 821.08[TX]_f$. In third region. $[TX]_t = 2.97 \times 10^{-3}$ M and for calculation of $[TX]_f$ for the first three points we used ln $k' = -3.03 - 249.2\ [TX]_f$ and for fourth point we used ln $k' = -2.172 - 821.08[TX]_f$.

Then by defining $\alpha' \equiv \frac{[TX]_t}{[TX]_f}$, we can write:

$$\alpha' = 1 + K_{TS}([SDS]_t - n[TX(SDS)_n])^n \quad (33)$$

also $$[TX(SDS)_n] = [TX]_t - [TX]_f \quad (34)$$

Replacing experimental values of α', $[SDS]_t$ and $[TX(SDS)_n]$ in equation (33) and using the sigmaplot curve fitting software, n and K values were calculated. The results of these experiments are given in Table 11.

It is clear from this Table that with increasing the concentration of SDS, the reaction rate increases and also the binding constants of TX-100 with SDS (in the second and third regions of TX-100) are not the same. As seen from Table 11, the rate constant goes higher than the rate constant at sc_2, the experimental data does not fit in equation (33).

The $1/n$ values obtained from Table 11 are respectively 6.45 and 12.5 and the products of these interactions are $TX_{6.45}$ SDS and $TX_{12.5}$ SDS, respectively.

This observation is in agreement with the fact that, under experimental conditions, the TX-100 molecules are in micellar form and the SDS molecules are monomeric. Therefore, we can consider the TX-100 micelle as an adsorbent, on the surface of which SDS molecules are adsorbed. In fact, the SDS molecules are adsorbed in those adsorption sites with average number of $1/n$ molecules of TX-100. With this hypothesis we can use the Langmuir isotherm for interpretation of aforesaid observations. We can write:

$$\frac{1}{m_{ad}} = \frac{1}{m_{mon}} + \frac{1}{K_{ad} m_{mon} c_{eq}} \quad (35)$$

Where K_{ad} is the adsorption binding constant, c_{eq} is the equilibrium concentration of adsorbate, m_{mon} is the required mass of adsorbate (in mole) to form a complete monolayer on the total mass of adsorbent (in mole) and m_{ad} is the mass of adsorbate (in mole) which is adsorbed on the total mass of adsorbent (in mole) under each c_{eq} value. Here, we can write:

$$m_{ad} = n[TX(SDS)_n] \times 1 \text{ lit} \quad (36)$$

and $$c_{eq} = [SDS]_t - [SDS]_{ad} \quad (37)$$

where $[SDS]_{ad} = n[TX(SDS)_n]$. As seen from their Langmuir adsorption isotherms in Table 12, the K_{ad} and m_{mon} values in the second and third regions of TX-100 are not the same. It is clear that although the concentration of TX-100 from second to third region has been raised 3.5 times, the values of m_{mon} and m_{mon}' (which are proportional to the surface area of the TX-100 micelles) are raised 2 times. These show that the TX-100 micelles structures are not the same in these two regions.

m_{mon}' (or the required mass of adsorbate, in mole, to form a complete monolayer on the surface of 1 mole of adsorbent) values in Table 12 are 0.081 and 0.037 mole, respectively. It seems that the SDS molecules and TX-100 micelles can interact by means of hydrogen bonding between sulfate headgroups of SDS molecules and OH and ethylene oxide

Table 12. Langmuir Adsorption Isotherms for the Adsorption of SDS Molecules on the Triton X-100 Micelles at 308 K (from Table 11)

Concentration region of TX-100	$\frac{1}{m_{ad}} = \frac{1}{m_{mon}} + \frac{1}{K_{ad} m_{mon} c_{eq}}$		
	K_{ad} (M^{-1})	m_{mon} (mole)	correlation coefficient (r^2)
2nd	3.997×10^5	6.95×10^{-5}	0.95
3rd	1.407×10^6	10.94×10^{-5}	0.98

*The total mass of adsorbent in 1 liter of solution, in Triton X-100 second and third regions is 8.55×10^{-4} and 2.97×10^{-3} mole, respectively.

Table 13. Freundlich Parameters for the Adsorption of SDS Molecules on the TX-100 Micelles at 308 K (from Table 11)

Concentration region of TX-100	$m_{ad}' = K c_{eq}^n$		
	K (dm^{3}mol^{-1})^n	n	correlation coefficient (r^2)
2nd	0.2374	0.1165	0.97
3rd	0.056	0.045	0.97

*m_{ad}' is the adsorbed mass of adsorbate,in mole, on the surface of 1 mole of adsorbent

Table 14. The k' and λ_{max} Values of BPB Fading in the Mixtures of Triton X-100 and DTAB at 308 K

$[TX]_t$ 10^4 (M)	[DTAB]$_t$ 10^4 (M)	$10^2 k'$ (dm^{3}mol^{-1}min^{-1})	λ_{max} (nm)
(a) 3.28	1.875	8.08 ± 0.08	590
(b) 3.28	4.69	3.36 ± 0.02	593
(c) 3.28	5.16	2.8 ± 0.03	595
(d) 4.15	4.76	2.32 ± 0.03	596.5

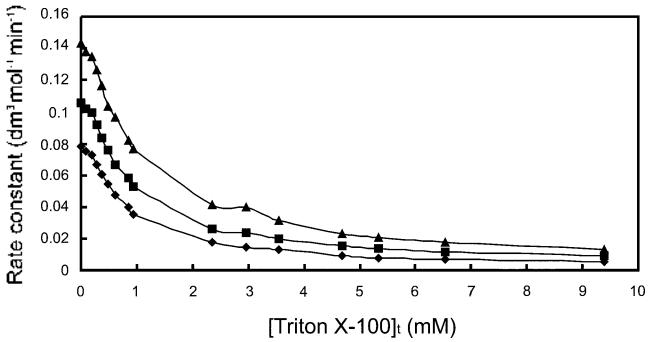


Figure 6. Variation of rate constant of BPB fading with concentration of Triton X-100 at ◆ 303 K, ■ 308 K and ▲ 313 K.

groups over TX-100 micelles surface.

Freundlich isotherm is used to model experimental data as well, the results of which are presented in Table 13. In the case of Freundlich isotherm, the affinity of the adsorbent for an adsorbate[34] can be measured by the parameter K. The K value obtained for the second region of TX-100 is slightly higher than its third region. The reason is that in these two regions, TX-100 micelles structures and the binding of BPB molecules to TX-100 micelles are different.

Mckay considers the parameter n in the Freundlich isotherm as a measure of the heterogenity of the adsorbent binding sites.[35] Values of n range from 0 to 1 for decreasing of heterogenity. Following that statement, the heterogenity of the adsorption sites of TX-100 micelles is higher for the third region of TX-100 than its second region. Recently, it has been found that in mixtures of TX-100 and SDS, the methylene groups nearest the polar head of SDS are located between the phenoxy rings of TX-100 in the mixed micelles and the hydrocarbon chains of SDS are not extended inside the hydrophobic micellar core.[36]

In another test, we tried the effect of a mixture of TX-100 and DTAB on the BPB fading at 308 K. The results are shown in Table 14. In all experiments, TX-100 concentrations were located in its second region in micellar form.

In experiment (a), DTAB concentration was in its first region where DTAB can not interact with BPB. Using Samiey equation of the second region of TX-100, from Table 8, we obtained $k' = 8.07 \times 10^{-2}$ dm^{3}mol^{-1} min^{-1}. Thus from Table 14, it seems that in experiment (a), only TX-100 interacts with BPB and DTAB has no interaction with them. In experiments (b), (c) and (d), DTAB concentrations were in its second region. We considered that the below equilibrium relation satisfies between DTAB, TX-100 and BPB:

$$\mathrm{BPB} + p\mathrm{TX} + n\mathrm{DTAB} \Leftrightarrow \mathrm{BPB\,TX_p\,DTAB_n} \quad (38)$$

$$K_{BTD} = \frac{[BPBTX_pDTAB_n]}{[BPB]_f[TX]_f^p[DTAB]_f^n} \quad (39)$$

where p and n are the stoichiometric ratios of TX-100 and DTAB, respectively and K_{BTD} is the binding constant of $\mathrm{BPBTX_p\,DTAB_n}$ compound.

Using an equation similar to (10), we have :

$$k' = \frac{k}{\alpha} = \frac{0.106}{1 + K_{BTD}[TX]_f^p[DTAB]_f^n} \quad (40)$$

assuming that the interaction between DTAB and TX-100 molecules is negligible, we assumed that $[TX]_f \cong [TX]_t$ and $[DTAB]_f \cong [DTAB]_t$. The results of experiments (b), (c) and (d) fitted properly in equation (40) and p, n and K_{BTD} values were found to be 1.976, 2.691 and 1.5×10^{16}, respectively.

From Tables 6 and 8, it is obvious that the total stoichiometric ratios of separate interactions of TX-100 and DTAB (in their second region) with BPB, individually are 1.9 and 1.1, respectively. These stoichiometric ratios are respectively equal with and smaller than p and n derived from the mixtures of TX-100 and DTAB in the aforesaid tests. It seems that the hydrogen binding among superficial OH groups of TX-100 micelles and BPB phenoxide and sulfonate groups would localize the negative charge density of these groups more and BPB would interact with a higher numbers of DTAB molecules.

At the end, it must be mentioned that TX-100, due to its benzene ring, has a λ_{max} value approximately at 274 nm and in the concentration range of 3.97×10^{-5}-2×10^{-3} M, the related Beer's law is A = 802.2c–0.0146 (r = 0.999). Where A and c are the observed absorbance and concentration of TX-100, respectively.

It was observed that dissolution of SDS or DTAB powders in TX-100 solutions had no effect on the λ_{max} value of TX-100. Thus, it seems that, under experimental conditions, SDS and DTAB have no interaction with hydrophobic portion of TX-100.

Measurement of Surfactant Concentration Using Its Effect on the Reaction Kinetics (MOSCUERK) Test. For measuring the concentration of a given surfactant, we should find a suitable chemical reaction and obtain its *reaction rate-surfactant concentration* (abbreviated as *r-s*) curve in a certain concentration range for that surfactant and use it as a calibration curve.

Using Samiey equation for adjacent regions, we can determine the concentrations of unknown surfactant samples. For example, we can use all three *r-s* curves in Figure 4 for determining the concentrations of DTAB solutions which are more concentrated than 0.47 mM.

It must be mentioned that, in each moscuerk test, similarity of type and concentration of other components of solutions, diluting the concentrated surfactant solutions and other analytical points should be considered depending on the experiment.

Conclusion

In the interaction of BPB with SDS, DTAB and TX-100 surfactants in test conditions, a primary electrostatic interaction would be necessary. It was found that there is no interaction between BPB and SDS while BPB has an

interaction with DTAB and TX-100.

Using the BPB fading reaction and analysis of data by classical model, the Langmuir adsorption isotherms of SDS molecules on the surface of TX-100 micelles were obtained, by which it is determined that the structures of TX-100 micelles and their interactions with SDS are not the same in different concentration regions of TX-100.

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