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Review

The study of Sunset Yellow anionic dye interaction with gemini and conventional cationic surfactants in aqueous solution

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ABSTRACT

In the present study, the interaction of an anionic azo dye, Sunset Yellow, with two cationic gemini surfactants with different spacer lengths ($s = 3$, 6 methylene groups) and their monomeric counterpart, dodecyl trimethyl ammonium bromide (DTAB), was investigated by surface tension, UV–Vis spectroscopy, and zeta potential measurements. The critical micelle concentration (CMC) was determined from plots of the surface tension (γ) as a function of the logarithm of total surfactant concentration. Moreover, the values of binding constants (K_b) of dye-surfactant complexes were calculated by UV–Vis spectroscopy. The UV–Vis spectra showed that the dye–surfactant interaction occurred in the solution at concentrations far below the CMC of each surfactant. The gemini surfactant with a shorter spacer showed stronger interaction with dye in comparison to DTAB and the gemini with longer spacer. The effect of surfactant chemical structure on solubilization of dye-surfactant aggregates at surfactant concentration above CMC was investigated by zeta potential.

1. Introduction

Dye–surfactant interactions in diluted aqueous solutions have been widely studied in recent years due to their practical importance and applications. The study on nature and strength of these interactions particularly for the system in which both dye and surfactant present has found a notable practical importance in textile dyeing and finishing, photography, printing, ink, hair coloring, and etc. [1–3]. Surfactants with different chemical structures are widely used as wetting agents, leveling agent, dye solubilizers, and etc. in textile dyeing processes [4–6]. Among novel surfactants, gemini surfactants have attracted more attention for their superior properties than that of the conventional single-chain surfactants. Gemini surfactants consist of two amphiphilic moieties in which their head groups are chemically connected to each other by a linkage or spacer [7]. In comparison to their conventional analogs, gemini surfactants show much lower CMCs, higher surface activity, better dispersing, wetting, and solubilizing properties [8,9]. Cationic gemini surfactants have found some applications for solubilization of oils [10], the emulsification of monomers in polymerization [11] and gene transfection [9]. The parameters affecting the dye–surfactant interaction can be summarized as: the charge density of both dye and surfactant, nature and length of spacer in gemini surfactants, the type and position of the substituent in the aromatic ring of the dye molecules [2–8,12]. Tehrani et al. have investigated interaction between DTAB and a series of gemini cationic surfactants with two anionic azo dyes, methyl orange (MO) and Congo Red (CR) using UV–Vis spectroscopy. They observed that the dye and surfactant structures affect the interactions. They have concluded that higher charge density of gemini surfactants caused a stronger electrostatic interaction with anionic dye than that of monomeric counterpart [13]. Different experimental methods were used for qualitative and quantitative determination of dye–surfactant interactions such as potentiometry, conductometry, tensiometry, voltammetry, spectroscopy and zeta potential measurements. Among these methods, the spectrophotometric method was used more extensively [2–14]. The zeta potential measurement is also a very good method for investigating the surface phenomena such as the magnitude of the interaction between colloidal particles, particle size, agglomeration and deposition of colloids. This method can be used to estimate the stability of colloidal systems [15].

In studies of oppositely charged dye–surfactant interaction, the formation of dye-surfactant aggregates in the system has been attributed mainly to formation of dye-surfactant salts, ion-pairs, the existence of ion-association complexes between ionic

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surfactants and dyes and self aggregations of dye [5,16]. These aggregations were organized by the of attachment dye molecules to surfactants via noncovalent interactions, such as electrostatic, hydrophobic, hydrogen-bond, and π–π stacking interactions [17]. Aggregations were indicated by changes of the main absorption band of the dye. Interestingly, the largest spectral changes were observed at low surfactant concentration in aqueous solution. Besides, one of the most essential factors in the spectral changes of dye-surfactant mixture is dye aggregations such as J-aggregate and H-aggregate. Therefore, the control of these aggregations is very vital in various industrial processes.

Investigating the interaction of novel surfactants (e.g. gemini surfactant) with dye in an aqueous solution can provide very useful information to control and optimize the process conditions [17]. Gemini surfactants have much lower CMC than their monomeric counterparts and therefore, the concentration at which they start to solubilize the dye-surfactant aggregates would be much lower and this would be very important from environmental point of view as less surfactant is needed to provide a certain application [18].

Azo dyes are in an important and fascinating class of synthetic organic colorants and their main characteristic is the presence of the azo group (–N=N–) which connect two aromatic rings [19]. The azo dyes have found many applications in different industry such as textile, papers, additives, foodstuffs, cosmetic, leathers, agrochemical and pharmaceutical industries [20,21].

Sunset Yellow (sodium (E)-6-hydroxy-5-((4-sulfonatophenyl) diazenyl naphthalene-2-sulfonate) is a dianionic monoazo dye compound, often known to form lyotropic liquid crystal phases as a function of temperature and composition [22]. Sunset Yellow is mainly used in food coloring, and it used to provide red color to pharmaceutical and cosmetic [19]. It is a well soluble in aqueous solution due to the presence of two sulfonate groups in either end of the molecule. The azo-hydrazone tautomerism in Sunset Yellow has been widely reported in aqueous solutions. This compound has more affinity to form dye aggregates (H-aggregates rather than J-aggregates) by π–π stacking interactions between the aromatic rings in aqueous solution [23,24].

The main aim of the present work is to examine the nature and strength of interactions between anionic azo dye (Sunset Yellow) and a series of cationic surfactants (monomeric and gemini type). Sunset Yellow is mainly used in the food industry, and it used to provide red color to pharmaceutical and cosmetic, so the study of Sunset Yellow–surfactant interaction is very useful in these industries. Also Sunset Yellow is demonstrated to be a successful dye for the investigation of electrostatic interaction between dye and Gemini & conventional surfactants because it has got suitable configuration (the presence of two $-SO_3^-$ groups) to interact with head groups of surfactant and ion-pairing formation. The SO_3^- groups present in the structure help in the water solubility, since, the role of hydrophobic interactions between dye and surfactant is negligible and contribution of electrostatic interactions is major. Since, the study of electrostatic interactions and ion-pairing formation are important for us, hence, Sunset Yellow is convenient dye for our research.

In addition, the interfacial and micellar properties of these systems have been determined by spectrophotometric, surface tension and zeta potential methods. The location of dye in surfactant micelles as well as the stability of dye-surfactant colloidal systems has been discussed accordingly.

2. Experimental

2.1. Materials

Dodecyl trimethyl ammonium bromide (DTAB) was purchased from, Merck and Sunset Yellow dye (sodium (E)-6-hydroxy-5-((4-sulfonatophenyl) diazenyl naphthalene-2-sulfonate) was obtained from Sandal Pakistan Ltd. Doubly distilled and deionized water was used for samples preparation and dilution.

Cationic gemini surfactants with the general formula $[C_{12}H_{25}-(CH_3)_2N^+-(CH_2)_s-N^+\ (CH_3)_2\text{-}C_{12}H_{25}]$, $2Br^-$ (where, $s = 3$, 6 methylene groups) were synthesized according to known procedure by reacting dodecyl trimethyl amine with the corresponding alkyl bromide in ethanol and purified by repeated recrystallization ethanol/diethylether [13,25].

2.2. Methods

2.2.1. Surface tension measurements

Surface tension measurements were carried out at 298 K by the ring method using a Sigma 700 tensiometer under atmospheric pressure [26,27]. The platinum ring was thoroughly cleaned and flame-dried before each measurement. To measure the surface tension, the vertically hung ring was dipped into the liquid and then removed; the maximum force required to pull the ring through the interface is then the surface tension, γ/mN m^{-1}. Measurements of the surface tension of pure water at 298 K were used to calibrate the tensiometer and to check the cleanliness of the glassware. In all cases, more than three successive measurements were carried out, and the standard deviation did not exceed ±0.1 mN m^{-1}. The temperature was controlled to within ±0.1 °C by circulating thermostated water through the jacketed glass cell. Each sample solution was stirred with a magnetic stirrer, and then the stirring of the sample was discontinued for 3 min and the surface tension was measured.

2.2.2. UV–Vis spectroscopy

Visible absorption spectra were recorded with a Shimadzu mini 1240 UV–visible spectrophotometer (Shimadzu, Japan) using a matched pair of glass cuvettes of 1 cm optical length placed in a thermostated cell compartment. The visible spectrum of dye in the surfactants systems was recorded for wavelengths in the range of 300–700 nm. Dye solution was prepared in double distilled water by addition of different amounts of surfactants below and above the CMC point. The concentration of Sunset Yellow was kept constant during the study and was equal to 4×10^{-5} mol dm^{-3}. Experiments were performed at 298 K.

Dye/surfactant binding constant and Gibbs free energy were determined from the absorbance of a series of solutions containing a fixed concentration of dye and increasing concentration of surfactants.

2.2.3. Zeta potential measurements

Nano-ZS (MALVERN) using laser Doppler velocimetry and phase analysis light scattering was used for zeta potential measurement. The temperature of the scattering cell was controlled at 298 K. A light scattering angle 17° was combined with the reference beam, and the data were analyzed with the software supplied for the instrument. All the experiments are carried out at 298 K.

2.3. Calculations

2.3.1. Determination of binding constant

The values of binding constants K_b of dye-surfactant complexes are predictable for the submicellar surfactant concentrations. According to the fact that 1:1 molecular complexes are formed as a result of interaction between the anionic dye and either cationic surfactant binding of surfactant to dye is equilibrium, consequently Eqs. (1) and (2) can be represented as [14,28]:

$$S^+ + D^- \leftrightarrow S^+D^- \tag{1}$$

$$K_b = \frac{[S^+D^-]}{[S^+] \times [D^-]} \tag{2}$$

where, K_b, S^+ and D^-, represent the binding constant, the surfactant and the dye, respectively, assuming [complex S^+D^-] = C_c and C_{dye} and $C_{surfactant}$ are the analytical concentrations of dye and surfactant in solution, respectively:

$$K_b = \frac{C_c}{\left(C_{dye} - C_c\right)\left(C_{surfactant} - C_c\right)} \tag{3}$$

From the assumption that absorbance occurs in agreement to the Beer–Lambert Law, the relations were obtained:

$$C_{dye} = \frac{A_0}{\varepsilon_{dye} \times l} \tag{4}$$

$$C_c = \frac{A_0 - A}{\varepsilon_c \times l} \tag{5}$$

where, A_0 and A show the absorbance of dye at λ_{max} in the absence and the presence of surfactant, respectively. ε_{dye} and ε_c are the molar extinction coefficients of a dye and dye-surfactant complex. l is the light path of the cuvette (1 cm).

By applying C_{dye} and C_c in Eq. (3) by Eqs. (4) and (5), Eq. (6) can be written as:

$$\frac{A_0}{A - A_0} = \frac{\varepsilon_{dye}}{\varepsilon_c} + \frac{\varepsilon_{dye}}{\varepsilon_c K_b}\left(\frac{1}{C_{surfactant}}\right) \tag{6}$$

So, plot of $1/(A - A_0)$ versus $1/C_{surfactant}$ is linear, and K_b can be calculated from the intercept to the slope ratio.

2.3.2. Gibbs free energy

The standard free energy of dye-surfactant complex formation, ΔG°, can be estimated from values of K_b and written as:

$$\Delta G^\circ = -RT\ln K_b \tag{7}$$

where, R and T are gas constant and absolute temperature (298 K) and K_b is binding constant.

3. Results and discussion

3.1. Ion-pairing between surfactants and dye

The interaction of aqueous Sunset Yellow solution azo dye and cationic surfactant (DTAB) can be revealed by UV–Vis spectroscopy. The variation in the UV–Vis spectra of dye upon successive addition of DTAB surfactant from premicellar to micellar region can be seen in Fig. 1.

As can be seen in the figure, Sunset Yellow exhibits a maximum absorption at 480 nm. By increasing the small concentration of DTAB, the intensity of absorption band reduces at 480 nm. The decrease in absorbance with the consecutive increase in surfactant concentration in the submicellar regions is significantly to be caused by the dye-surfactant complex [29,30]. The aggregation forms between Sunset Yellow dye and DTAB surfactant are possibly displayed as ion-pairs formation [3].

$$D^+ + S^{2-} \rightarrow DS^- \tag{8}$$

$$D^+ + DS^- \rightarrow \left(D^+DS^-\right)\text{ion pair} \tag{9}$$

Decreasing the intensity of absorbance of dye at λ_{max} and hypsochromic shift occurs spontaneously. Formation of dye-surfactant complex is a result of long-range electrostatic and short-range hydrophobic forces [13]. The Sunset Yellow molecule has two sodium sulphonate groups, which leads to a higher solubility in water, hence, the majority of interaction occurred by electrostatic interaction between the positive charge on head group of DTAB and negative charge on sulphonate groups of dye that leads to form stable structures of dye-surfactant complexes. Some of these complexes include ion-pairs and premicellar aggregates in the solution. The formation of ion-pairs is also expected to increase with increasing the surfactant concentration [10]. These aggregations partly can justify the loss of absorbance in dye solution in premicellar region. Besides, it has been shown that surfactants were able to encourage the dye aggregation (namely, J- and H-aggregates) in aqueous solution at low surfactant concentration, accompanied with change in the absorption spectra [28,31]. Actually, the real systems tend to form both H- and J-aggregates [32]. J- and H-aggregates are characterized by a red and blue shift of the absorbance band compared with the monomer, respectively [17]. Fig. 1 shows a hypsochromic shift at low DTAB concentrations, suggesting that the molecular Sunset Yellow forms H-aggregate rather than J-aggregate on DTAB solution. In fact, the DTAB

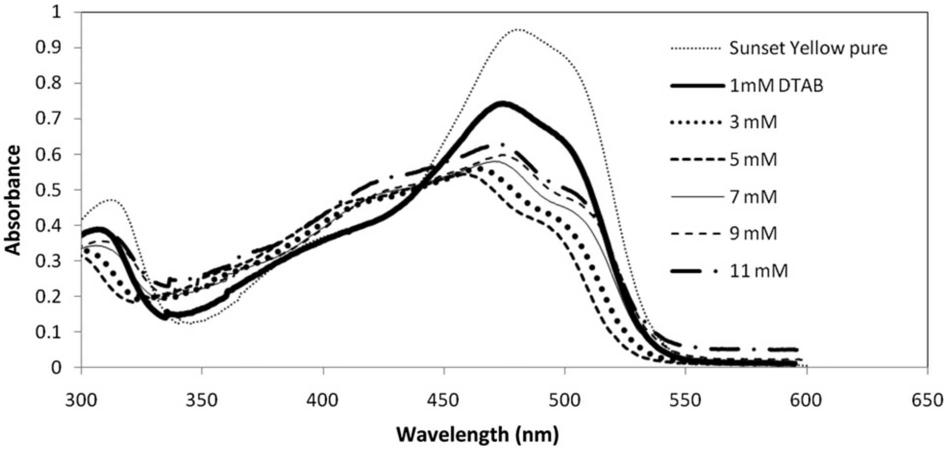

Fig. 1. Effect of different concentration of DTAB on the absorption spectrum of [Sunset Yellow] = 4×10^{-5} mol dm^{-3} in aqueous solution at 298 K.

surfactant (at very low concentrations of surfactant) decreases the electrostatic repulsion between dye monomers and help the aggregation of H-type in Sunset Yellow [32]. These aggregations are often controlled by $\pi-\pi$ stacking interactions between the aromatic rings. At concentration close to CMC, an inconsiderable bathochromic shift along with increasing the intensity of absorption band in the visible spectra of dye is observed. It is concluded that the dye molecules' penetration into micelles is responsible for this phenomenon. Indeed, solubilization of the dye-surfactant ion-pairs in the micellar phase and/or the incorporation of the dye into the micelles is taking place [30]. At concentration above CMC, a large amount of Sunset Yellow solubilized into the micelles.

Fig. 2 shows the UV–Vis spectra of gemini surfactants with dye at different concentrations for 12-3-12 and 12-6-12 gemini surfactants. Different results are obtained for spectral behavior of gemini surfactants in comparison to DTAB, where at low concentrations of such gemini surfactants for constant concentration (4×10^{-5} mol dm^{-3}) of aqueous Sunset Yellow solution, the aggregation formed between dye and gemini surfactants and interaction between the aromatic rings of Sunset Yellow structure are reflected by a little bathochromic shifts along with a decrease in the intensity of absorbance band. In premicellar region of gemini surfactant/Sunset Yellow aqueous solution, the ion-pair formation is chiefly a justification of reducing the intensity of absorption band of Sunset Yellow. These aggregates show identical spectral behavior like free dyes. Because, simple ion-pairing between a negative group such as $-SO_3^-$ of the dye and a quaternary ammonium ion of surfactant does not perturb chromophore [30]. Thus, the characteristics of absorption spectra of dye-surfactant aqueous solution are similar to free dyes in the premicellar region [33]. These ion-pairs are 1:1 stoichiometry of Sunset Yellow dye and either one gemini surfactant. An unexpected and novel description involves the formation of dye aggregates in side-by-side arrangement (J-aggregation) and face-to-face arrangement (H-aggregation) in gemini surfactant/dye solutions. It seems that the spacer length of the gemini surfactants has an excellent control on the kind of aggregations of dye (at low concentration of gemini surfactant). It is interesting that the gemini surfactants with shorter spacer have more stacking and relatively non-uniform charge distribution of the head groups, which prefers the H-aggregations, while the longer one favors the formation of the J-aggregation [17]. Therefore, 12-3-12 surfactant with short spacer prefers the formation of H-aggregate rather than J-aggregate. Since 12-6-12 gemini surfactant has relative uniform charge distribution on head groups, either orientation of dye on the head groups of 12-6-12 is possible. But the spectroscopic results indicate that the majority of aggregation between Sunset Yellow and 12-6-12 is J-aggregate. As a result of the above discussion, mixture of aggregation of Sunset Yellow, as J- and

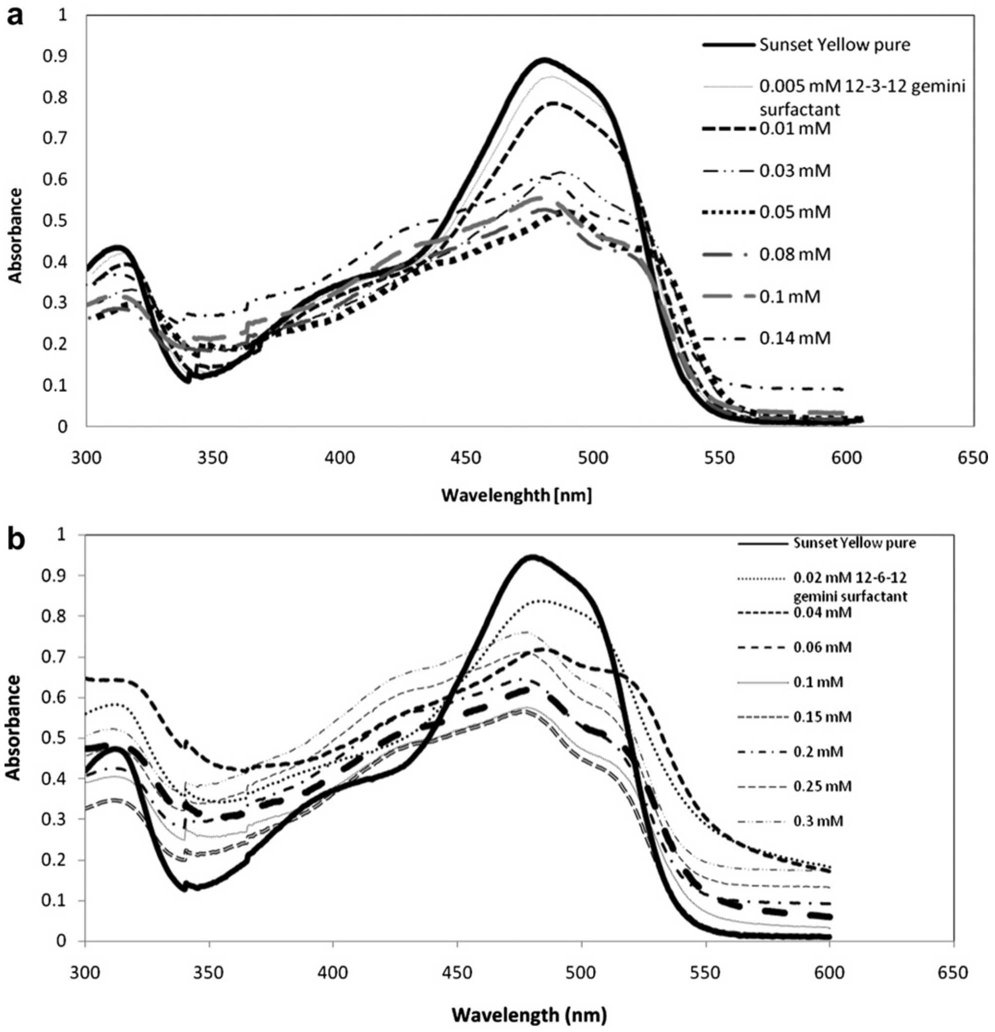

Fig. 2. Effect of different concentration of 12-3-12 (a) and 12-6-12 (b) gemini surfactants on the absorption spectrum of [Sunset Yellow] = 4×10^{-5} mol.dm^{-3} in aqueous solution at 298 K.

H-aggregation (J- rather than H-aggregation), affect the spectral behavior of gemini surfactants/dye solutions and could be the result of inconsiderable bathochromic shift at low concentration of gemini surfactants (particularly for 12-6-12). This seems to be a property peculiar to gemini surfactants. The interaction of cationic gemini surfactants with Sunset Yellow is due to a strong guest–host interaction between the two mentioned species. This often leads to the formation of close-packed ion-pairs between anionic dye and cationic gemini surfactants. These interactions continue until the dye molecules are completely saturated with bound cationic gemini surfactants [6,32]. After this region, the spectra of Sunset Yellow display an increase in absorbance that may be due to disaggregation and solubilization of the complexes into gemini surfactant micelles [34].

3.2. Analysis of cationic surfactant–dye interactions

The values of binding constants and Gibbs free energies attributed to complexes of Sunset Yellow dye with 3 surfactants are illustrated in Table 1.

The formation of the dye-surfactant complexes is as a result of mutual electrostatic and hydrophobic interactions. Although these factors are important and useful in dye-surfactant complex formation, other reasons such as conformation, dispersivity of surfactant and intermolecular interactions due to hydrogen bonding in dye molecules may also play important roles for dye-surfactant aggregations. DTAB and Gemini surfactants have the same chain length and their discrepancy are charge density on head groups. Gemini surfactants have two cationic head groups in close proximity to each other and the charge density on their polar head is much higher than that of DTAB. Therefore, the short-range electrostatic interactions play a very important role in dye–surfactant interactions. In addition, Sunset Yellow dye possesses two strong polar groups that dissociate from ions in aqueous solution so strong electrostatic attraction between sulfonate groups of dye and cationic head groups of surfactants can be expected. Therefore, the close-packed ion-pairs of gemini surfactants–Sunset Yellow, whose original charges are located on the ions, can be formed.

As seen in Table 1, binding constants of dye-surfactant complexes are in the order 12-3-12 > 12-6-12 > DTAB. This suggests that increase in the strength of the interaction is in the same order too. Accordingly, ΔG° showed the order 12-3-12 < 12-6-12 < DTAB. The values of the constants in gemini surfactants were higher than those of the DTAB surfactant; meaning that double positive charges on gemini surfactant head groups may introduce stronger interactions with double negative charges on sulfonate groups in Sunset Yellow and the strength of the interactions is due to more charge density and hydrophobic forces of both gemini surfactants in comparison to that of DTAB. Moreover, the influence of spacer length of gemini surfactants on their interactions with Sunset Yellow is noticeable and the interaction is more significant for 12-3-12 than that of 12-6-12. Since the charge density is non-uniform, interacting by dye leads to the contribution of charge on head groups of 12-3-12 as well as the reduction of electrostatic repulsion between the positive charges. We concluded that, the lower value of Gibbs free energies of dye-surfactant complex formation indicates the stability of the complex, suggesting that the tendency of gemini surfactants (particularly those with shorter spacer length) for interaction with Sunset Yellow and close-packed ion-pair formation is stronger and easier than that of conventional surfactants.

Table 1
Values of the dye-surfactant complex formation constant (K_b), standard Gibbs free energy, (ΔG°) at fixed dye concentration.

	DTAB	12-3-12	12-6-12
K_b	254	9983	6690.6
ΔG° (kJ mol^{-1})	−21.82	−40.63	−23.13

3.3. The ion-pair formation effect on the properties of monolayer phase in Sunset Yellow dye–cationic surfactants systems

Fig. 3 shows the plots of surface tension (γ) in the aqueous solutions of surfactants as a function of the 12-3-12 concentrations in the presence and absence of Sunset Yellow (4×10^{-5} mol dm^3). In dye/surfactant mixture, the plots of surface tension show noticeable deviation of linear state in submicellar region. These deviations explain a consequence of dye aggregation and also close-packed ion pair formation between the dye and surfactant in solution. Initial decrease of γ in aqueous solutions at a much lower concentration of surfactants suggested the formation of dye aggregation via π–π stacking, dispersion force, H-band, etc., which are usually hydrophobic in the nature. These hydrophobic dye-surfactant aggregates adsorbed at air/solution interface and reduced the surface tension. Therefore, the existence of any process such as the dye aggregation, dye-surfactant complexes, ion-pairs formation, etc. in aqueous solutions is the main reason of unusual changes in the structure of monolayer at air/solution interface and consequently the surface tension curves [16,35]. This suggestion is confirmed by the plots shown in Fig. 3.

The surface excess concentration, $\Gamma_{\max}$, at the air/solution interface and minimum area per surfactant molecules, $A_{\min}$/nm^2, (When, $\Gamma_{\max}$ is expressed in units of molar per centimeter squared) were calculated by using the Gibbs adsorption equations [36]:

$$\Gamma_{\max} = \left(\frac{-1}{nRT}\right)\left(\frac{d\gamma}{d\ln C}\right)_{T,P} \tag{10}$$

$$A_{\min} = \frac{10^{14}}{N_A \Gamma_{\max}} \tag{11}$$

where $d\gamma/d\ln C$ is the maximum slope in each case and R, T, C, and N are the gas constant, absolute temperature, concentration of surfactants at the interface, and Avogadro's constant, respectively. n is a constant which depends on the number of species constituting the surfactant and are adsorbed at the interface for conventional and gemini surfactants $n = 2$, 3, respectively.

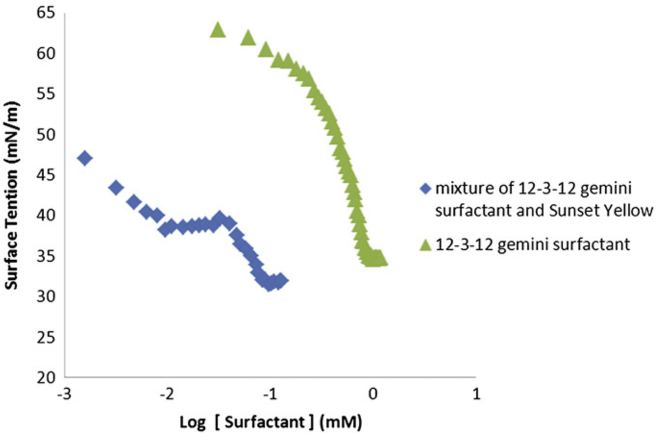

Fig. 3. Surface tension as a function of concentration for pure 12-3-12 and 12-3-12/Sunset Yellow mixtures at 298 K.

Table 2
The values of $\Gamma_{\max}$ and $A_{\min}$ for surfactants and their mixture with Sunset Yellow.

	$\Gamma_{\max}$ ($\times 10^6$ mol m^{-2})		$A_{\min}$ (nm^2)	
[Dye] mol dm^{-3}	0	4×10^{-5}	0	4×10^{-5}
DTAB	2.03	1.82	0.81	0.91
12-3-12	1.87	0.903	0.88	1.83
12-6-12	1.22	0.75	1.36	2.21

Table 2 shows the adsorption parameters, $\Gamma_{\max}$ and $A_{\min}$, of surfactant solutions in the presence and absence of Sunset Yellow dye. The obtained values of $\Gamma_{\max}$ and $A_{\min}$ in pure water are in good accordance with literature data [8,37].

Table 2 reveals that the surface excess concentration and the occupied area per molecule in the monolayer of surfactant solutions in the presence of Sunset Yellow dye are smaller and larger than those of pure surfactant solutions, respectively.

This demonstrates that the ion-pairs are the same as nonionic surfactant, which has a larger head group, higher effectiveness and affinity to the air/water interface than a sole surfactant [16], therefore, a larger surface area per surfactant in the monolayer at air/solution is required for these ion-pairs. In comparison, the surface excess concentrations of gemini surfactants are almost lower than those of single-chain amphiphile. Hence, $\Gamma_{\max}$ is in this order: DTAB > 12-3-12 > 12-6-12. There should be noted that two head groups of gemini surfactants occupied the surface instead of one head group in conventional surfactant. Therefore, the monolayer will be earlier saturated by gemini surfactants. Besides, the results show that $\Gamma_{\max}$ decreases and $A_{\min}$ increases when the spacer length of gemini surfactant increases from $s = 3$ to $s = 6$. Because, by increasing the spacer length, the average distance between two head group's centers increases and a larger space of monolayer at air/solution interface will be occupied.

3.4. *Evaluation of properties of micellar phases in Sunset Yellow dye–cationic surfactants systems*

3.4.1. *CMC*

Surface tension measurements help us to estimate the CMCs of pure surfactant solution (CMC*) and mixture of dye-surfactant (CMC′). The breaks in the curves are the CMC values. In the pure surfactant solutions, upon increasing of surfactant concentration, the surface tension decreases linearly then remains constant for concentrations above a CMC value. As shown in Fig. 3, the CMC of dye-surfactant mixture aqueous solutions is significantly lower than the CMC′ pure surfactant solutions. Because in the presence of low dye concentrations, the repulsion among head groups (particularly gemini surfactant with two head groups) decreases, so CMC reduces. CMC values of pure surfactant solutions as well as mixed dye-surfactant systems are presented in Table 3.

3.4.2. *Interaction parameter in micellar phase*

All the above results indicate that after disaggregation of aggregate to dye molecules and solubilize them into surfactant micelles, mixed micelles of dye-surfactant can be formed. So, knowing the strength and nature of dye–surfactant interaction in mixed micelles is essential and interesting.

Table 3
CMC values of pure surfactants and dye-surfactant mixtures at 298 K.

[Dye][a]	DTAB	12-3-12	12-6-12
0	14.85	0.96	1.2
4×10^{-5}	8.46	0.12	0.2

[a] CMCs are in mol dm^{-3}.

According to Rubbing's regular theory to the thermodynamic of the mixed systems such as mixed dye-surfactant micelles, the mixed CMC, (C_{12}^M), is given by [38]:

$$\frac{1}{C_{12}^M} = \frac{\alpha}{f_1 C_1^M} + \frac{(1-\alpha)}{f_2 C_2^M} \tag{12}$$

where, α is the mole fraction of surfactant in the mixture, f_1, f_2, C_1^M, C_2^M are active coefficients of surfactant and dye and the CMC values for surfactant and dye, respectively.

In the case of ideal behavior, $f_1 = f_2 = 1$ and Eq. (12) is reduced to:

$$\frac{1}{C_{12}^M} = \frac{\alpha}{C_1^M} + \frac{(1-\alpha)}{C_2^M} \tag{13}$$

The composition of mixed micelles of dye-surfactant and β^M parameter can be calculated by Eqs. (14) and (15), respectively.

$$\frac{\left(X_1^M\right)^2 \ln\left(\alpha C_{12}^M / X_1^M C_1^M\right)}{\left(1 - X_1^M\right)^2 \ln\left[(1-\alpha) C_{12}^M / \left(1 - X_1^M\right) C_2^M\right]} = 1 \tag{14}$$

$$\beta^M = \frac{\ln\left(\alpha C_{12}^M / X_1^M C_1^M\right)}{\left(1 - X_1^M\right)^2} \tag{15}$$

where C_1^M, C_2^M, C_{12}^M are the CMCs of individual surfactant 1 and dye and their mixtures, respectively. α is the mole fraction of surfactant 1 in solution; X_1^M is the mole fraction of surfactant in the total mixture in mixed micelle. β^M is the interaction parameter between dye and surfactant in mixed micelle. Since, the value of the β^M equivalent to the free energy of mixing of the micelles, a negative value β^M means that the attractive interaction between the dye and surfactant is stronger than the attractive interaction between two individual species. Besides, this parameter shows the deviation from ideality. The mixture of dye with the surfactants indicates strong deviation from ideally behavior. So, these mixtures are a sign of usually large values of interaction parameters [39]. As well, this parameter is negative due to the more attraction between anionic dye and cationic surfactants.

The measured values of the micellar composition and parameter β^M are presented in Table 4.

From these results, it seems that for all mixed dye-surfactant systems this parameter has a negative value. The calculated interaction parameter values for gemini surfactants and dye mixtures are significantly higher than this reported parameter in DTAB/Sunset Yellow. Also, the interaction of dye-gemini surfactant with shorter spacer length is the strongest one in this case. The orientation of the anionic dye molecules between cationic surfactant monomers leads to charge screening and lessening of the repulsion between cationic head groups which is noted by constant binding values.

3.4.3. *Size and zeta potential measurements*

Zeta potential is a very useful method to determine the mixed aggregate size in micellar region. Fig. 4 shows the variations of

Table 4
The mole fraction of surfactant in the total mixture in mixed micelle (X_1^M) and interaction parameter of surfactant and dye in mixed micelle (β^M).

	DTAB	12-3-12	12-6-12
β^M	−7.49	−16.38	−13.92
X_1^M	0.80	0.63	0.64

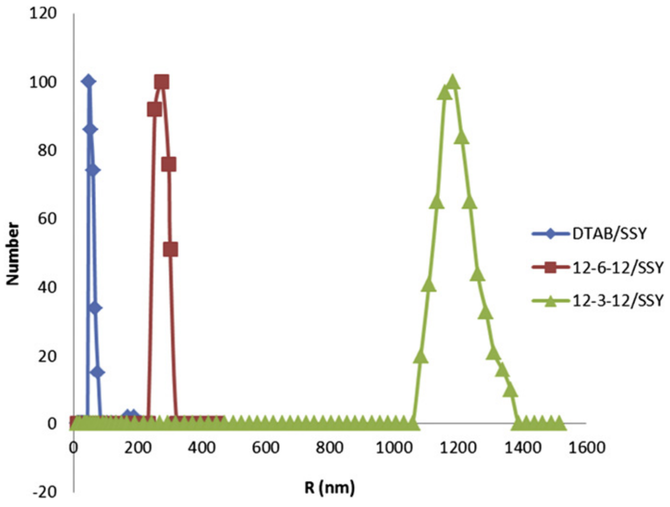

Fig. 4. The variations of number size distribution vs size of particles in solution for dye-surfactant systems in micellar region.

number size distribution vs size of particles in dye-surfactant systems by Z-potential. The effectiveness of solubilization of dye in surfactant aggregates at micellar region can also be expressed in terms of aggregate size. It is interesting to note that the Sunset Yellow molecule is mainly hydrophilic and polar in nature. The general agreement is that Sunset Yellow do not penetrate at the interior of the micelle or vesicle since, it is concluded that the Sunset Yellow molecules becomes incorporated into the micellar (or vesicle) surface rather than its interior. It has also been shown that aromatic compounds with sulphonate groups are incorporated into the stern layer of cationic micelles [29].

The results of Z-potential suggest that the predominant aggregates are vesicles (100–1000 nm) and enlargement vesicles (>1000 nm) in Sunset Yellow/gemini surfactants solutions, while mixed micelles (10–100 nm) are major aggregates in Sunset Yellow/DTAB surfactant solution. However, the size of the Sunset Yellow/12-3-12 vesicles is greater than that of the corresponding vesicles for Sunset Yellow/12-6-12. It was expected that the amounts of Sunset Yellow solubilized in the surfactant aggregates in the order of 12-3-12 > 12-6-12 > DTAB. It can be assumed that the electrostatic interaction between dye and surfactant is one of the factors which govern the size and shape of the mixed dye-surfactant aggregates. In the case of gemini surfactants, the electrostatic interaction with Sunset Yellow is larger than that of the conventional one. Therefore, many dye molecules are present in a gemini surfactant aggregate. Hence, vesicles are major aggregates in the Sunset Yellow/gemini surfactant solution. However, strong synergetic effects of positively charged polar groups of 12-3-12 particle interact with SO_3^- in Sunset Yellow particles could suggest solubilization of higher number of Sunset Yellow and this behavior is an indication of the formation of enlargement vesicles for Sunset Yellow/12-3-12 system. Fig. 4 shows that size distribution in Sunset Yellow/12-3-12 system take place from 1000 to 1400 nm, which agreed well with the enlargement vesicles size.

By determining the zeta potential, a measure for the net positive charge of the dye/surfactant system in micellar region can be obtained [40]. It is generally accepted that incorporation of Sunset Yellow into surfactant micelles or vesicles tends to change zeta potential values. Table 5 shows the values of the zeta potential of dye/surfactant systems, which reflects the stability of the colloidal systems. The value of zeta potential is maximum in Sunset Yellow/12-3-12 system where number of solubilized Sunset Yellow in surfactant vesicles seems to have a high value. The magnitude of the zeta potential gives an indication of the potential stability of the colloidal system. If all the particles in suspension have a large absolute value of the zeta potential, then they have an adequately high repulsion and the colloidal system will be stable. Generally speaking, particles with zeta potentials above 25 mV (positive or negative) are usually considered stable [41]. The zeta potential value of the Sunset Yellow/12-3-12 system displayed a positive potential near 38.8 mV. Hence, the highest colloid stability is predicted to be at Sunset Yellow/12-3-12 system. It may be attributed to the reason that the increase of localization of Sunset Yellow in vesicle surface leads to increase the surface charge of vesicle. So the increase of surface charge in the colloid formulation results in an increase in repulsive forces between colloidal particles since the stability of Sunset Yellow/12-3-12 colloidal system increases.

Table 5
The obtained potential from zeta potential measurements for dye-surfactant micelle (or vesicle).

	DTAB	12-3-12	12-6-12
Zeta potential (mV)	6.36	38.80	19.00

4. Conclusion

From the present study it is evident that most of the interaction between Sunset Yellow dye and cationic surfactants, in submicellar region, caused by electrostatic interaction lead to the formation of stable structure of closed packed dye–surfactant ion-pairs. These aggregates are the same as nonionic surfactant, which has a larger head group than surfactant alone. Therefore, they have different monolayer and micellar properties than the corresponding pure surfactants. However, the change in the UV–Vis spectra of Sunset Yellow is a result of dye-surfactant or dye aggregate. It seems that the charge density distribution and spacer length of the gemini surfactants has an excellent control on the kind of aggregations of dye. The results of binding constants and interaction parameters in micellar phase show that the power interaction of Sunset Yellow-surfactant follows the trend 12-3-12 > 12-6-12 > DTAB. The stronger interactions in oppositely charged dye-surfactant systems are reflected by higher Gibbs free energy and lower binding constants. In micellar region, the zeta potential data show that the solubilization capacity for gemini surfactants aggregates is larger than that of DTAB. Therefore, the mixed micelles are major aggregates in dye-surfactant solutions. Also, the maximum colloid stability is attributed to be at Sunset Yellow/12-3-12 system with highest surface charge on the vesicle and repulsive forces between colloidal particles.

Notation

A	the absorbance of dye in the presence of surfactant
A_0	the absorbance of dye in the absence of surfactant
A_{min}	minimum area per molecule
A	area per molecule
C	concentration
E	second order energy
$f_\pm$	mean activity coefficient
f_i	activity coefficient of ionic surfactants
G	Gibbs free energy
K	the binding constant
l	the light path of the cuvette
N_A	Avogadro's number

R	gas's constant
T	absolute temperature
X	mole fraction of cationic surfactant in mixed micelle
α	the mole fraction of surfactant in bulk solution
β	interaction parameter in the mixed aggregate
γ	surface tension
δ	the energy of σ NBOs
$\Gamma_{\max}$	surface excess

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