

NON-IONIC SURFACTANT SELF-ASSEMBLING PROMOTED BY DIFFERENT DYES IN AQUEOUS MEDIA

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The interactions of a non-ionic surfactant with anionic and cationic dyes in aqueous solution have been investigated in pre-micellar and micellar regions using spectrophotometric method. The critical micellar concentration value of the surfactant was increased by the addition of Rhodamine B. The surfactant interacted with the anionic dye and the corresponding equilibrium constant and partition coefficient have been calculated. In the case of the anionic dye, a more stable complex was formed, due to the hydrated ethylene oxide head groups of the surfactant, which are acting as positive charged groups. This investigation is important for water pollution abatement using microemulsion systems.

Keywords: dye-surfactant interactions, partition coefficient, micellar systems

1. Introduction

The study of interactions between surfactants and dyes in aqueous solutions has attracted significant interest in the recent years [1-4], due to their widespread applications and relatively complex behaviour. Surfactants are not only used for adsorption and fixation of dyes on substrate, but also for the removal of weak bound dye from the substrate *via* solubilisation process [5]. The applications of surfactants are usually based on their two basic features: the formation of microheterogeneous phases through self-assembly and their ability to change the surface tensions by adsorption at surfaces.

The most widely used method to investigate the properties of surfactants in order to form different phases through self-assembly is spectrophotometric method [6-19]. In pre-micellar region, monomers of surfactant interact with the dye molecules to form ion association complexes, while, in post-micellar region, dye molecules are incorporated into micelles [5]. These interactions are responsible for variations in the position and intensity of the absorption band [20].

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The changes in the tensioactive properties of surfactants in various media can be studied by stalagmometric method, as it is an easy and cheap technique.

The aim of the present study is to investigate the interactions of a non-ionic surfactant, polyoxyethylene 4-lauryl ether (Brij 30) with an anionic dye, Methyl orange (MO), and a cationic dye, Rhodamine B (Rh B), respectively. The surfactant/water partition coefficient of the dye was quantified by applying the mathematical models based on partition of the dye between the micellar and aqueous pseudo-phases [18]. This investigation is important for dyeing processes, chemical research (physical chemistry and biochemistry), as well as for new methods for water pollution abatement. The findings obtained in this study will be helpful in choosing the optimized conditions for extraction of different dyes from aqueous media by non-ionic surfactant/water/oil systems. Literature survey indicates that there are no studies on Brij 30 - MO/Rh B interactions in aqueous medium.

2. Experimental section

2.1. Materials

All chemicals were used as received without further purification or distillation: anionic dye Methyl Orange (MO) and cationic dye Rhodamine B (Rh B) were purchased from Sigma-Aldrich, non-ionic surfactant Brij 30 (polyoxyethylene 4-lauryl ether) was provided by Acros Organics. Solutions were prepared in distilled water. The chemical structures of dyes and surfactant used in this study are given in Fig. 1.

For surface tension analysis and spectroscopic study, aqueous solutions of dyes were prepared in distilled water, and then Brij 30 was added in the solution in concentrations corresponding to pre-micellar to post-micellar regions. All experiments were carried out at room temperature.

2.2. Methods

Stalagmometric method was used to determine the surface tension values of Brij 30/Dye/Water systems. From surface tension dependence on the surfactant concentrations, the critical micellar concentration (CMC) has been determined, while the equilibrium constant was calculated from the surface tension data in the pre-micellar region.

UV-VIS spectroscopy was used as an alternative technique for obtaining some preliminary information regarding compositional, structural and dynamic characteristics of self-assembled systems. Electronic spectra were recorded with UV-VIS spectrophotometer type V-670, Jasco. The micelle/water partition

coefficient was determined from the absorbance values of a series of solutions containing a fixed concentration of dye ($C_{\text{Dye}} = 0.01 \text{ mM}$) and different concentration of surfactants.

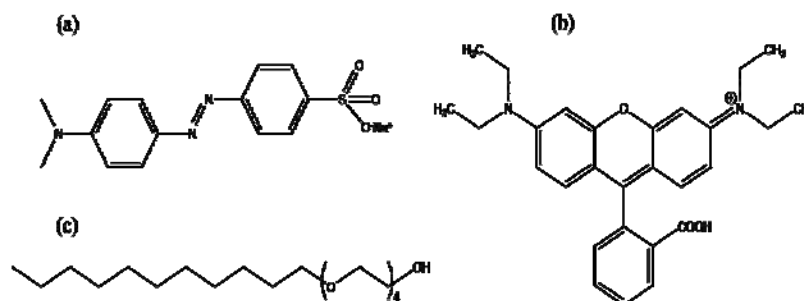


Fig. 1. Chemical structures of (a) Methyl orange (MO), (b) Rhodamine B (Rh B) and (c) polyoxyethylene 4-lauryl ether (Brij 30)

3. Results and discussion

3.1. Tensioactive properties of surfactant in aqueous media in absence/presence of different dyes

Surface tension measurements are used to estimate the CMC value for pure surfactant solution and mixtures of dye-surfactant. In the pure surfactant solutions, upon increasing surfactant concentration, the surface tension decreases linearly, then it remains constant for concentrations above CMC value. CMC value of Brij 30 in water was determined as 0.66 mM. As shown in Fig. 2, the surface tension of dye-surfactant mixture aqueous solutions is higher than the surface tension of pure surfactant solutions. CMC values of Brij 30 containing 0.01 mM dye were found to be 0.78 mM in the case of Rh B dye, and 0.68 mM when MO was used as dye. Generally, organic molecules or ions may influence CMC value of surfactant in various extents [21]. In the presented experiments, MO dye, with a quite linear and planer structure has minor influence on surfactant CMC, while Rh B, with a voluminous structure has a counteracting effect on surface tension, resulting in a higher CMC value for dye-surfactant mixture.

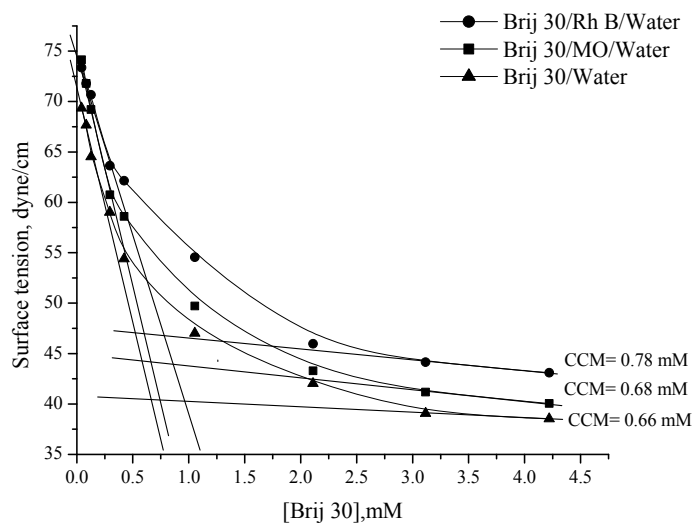


Fig. 2. The influence of dye on the tensioactive properties of the surfactant

The behavior of MO and Rh B in aqueous non-ionic surfactant media solutions with different concentrations was also studied, in order to establish if the dyes are surface-inactive in molecular and associated forms.

The calculated values of the surface tension for Brij 30/Dye/Water systems in pre-micellar and post-micellar regions are presented in Table 1. It can be noticed that the surface tension values are similar for a specific region and a specific chromophore. The calculated relative standard deviations have values smaller than 5%, which means that the dye concentration does not influence in a significant extent the tensioactive properties of the surfactant.

Table 1

Surface tension values for Brij 30/Dye/Water systems in pre-micellar and post-micellar regions

Dye	[Dye], mM	Pre-micellar region		Post-micellar region	
		Surface tension, dyne/cm	RSD %	Surface tension, dyne/cm	RSD %
MO	0.005	58.86	0.51	48.40	3.99
	0.05	58.34		48.40	
	0.5	58.86		45.13	
Rh B	0.005	59.91	2.87	50.03	5.19
	0.05	57.83		49.48	
	0.5	56.61		45.44	

3.2. Formation of microheterogeneous phases through surfactant self-assembling

The interactions of non-ionic surfactant (Brij 30) with anionic dye (MO) and cationic dye (Rh B), respectively, have been investigated by spectrophotometric method.

The effects of different Brij 30 concentrations on the absorption spectra of MO are shown in Fig. 3a, where the maximum absorption peak of the dye centered at 464 nm is observed. As the surfactant concentration gradually increases, the absorbance of MO initially decreases and then increases. Beyond the CMC value of surfactant, the maximum absorption peak of dye shows a hypsochromic shift from 464 nm to 414 nm, as the surfactant concentration increases, corresponding to the changes of the microstructure around the chromophore molecule.

The variation in the absorbance values of 0.01 mM Rh B as function of surfactant concentration is presented in Fig. 3b. Addition of non-ionic surfactant Brij 30 causes no peak shift, but only an intensity enhancement of the dye absorption. Brij 30 produces no perturbation in the visible spectra of the dye, and no other new band was observed. It means that no stable chemical complex is formed in solution.

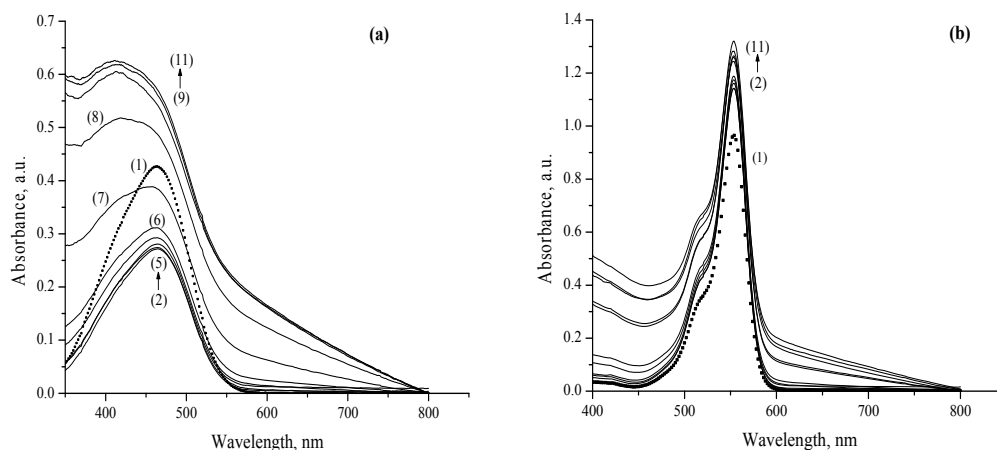


Fig. 3. Absorption spectra of (a) MO (0.01 mM) and (b) Rh B (0.01 mM) in the presence of various Brij 30 concentrations: [Brij 30] = (1) 0, (2) 0.042, (3) 0.084, (4) 0.127, (5) 0.295, (6) 0.422, (7) 1.055, (8) 2.110, (9) 2.850, (10) 3.116 mM and (11) 3.510 mM

The effect of the dye concentration on the absorption maximum values was also studied in the presence of the surfactant in pre-micellar and post-micellar regions (Fig. 4.). The corresponding maximum absorption value, λ_{\max} , of

Water/MO/Brij 30 (0.422 mM) systems in the monomer form is constant (around 463 nm) in pre-micellar region as it can be noticed from Fig. 4a. This demonstrates once again that the absorption maximum of MO remains at the same wavelength below the CMC values of surfactant concentrations. However, the maximum absorption wavelength of MO in post-micellar region ($[Brij\ 30] = 1.5\text{ mM}$) shows a bathochromic shift from 436 nm to 461 nm, as the dye concentration increases. This means that the micelles can incorporate all dye molecules at low dye concentrations and the saturation is reached by increasing the dye concentration.

In the case of Rh B, there are no changes in the absorption spectra below and beyond CMC of surfactant concentrations, as Fig. 4b shows. Indeed, the maximum absorption of the Water/Rh B/Brij 30 system has the same value (553 nm) in pre-micellar region as in post-micellar region.

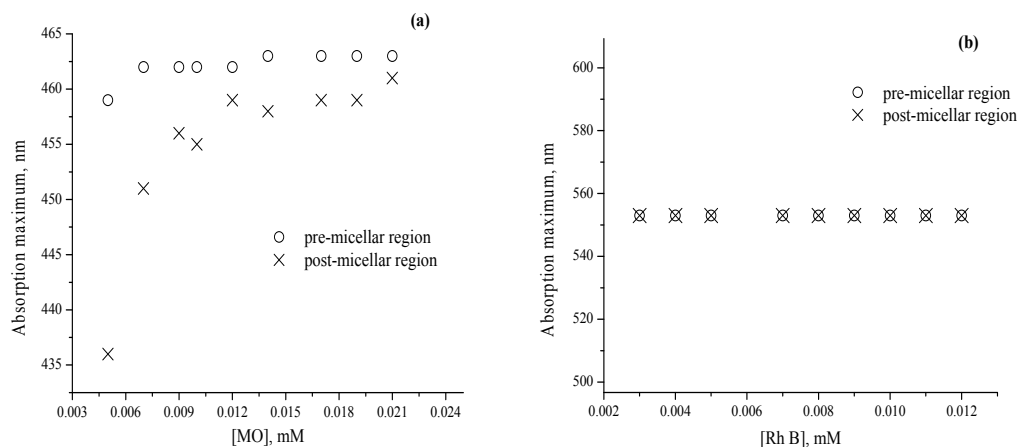


Fig. 4. Effect of MO (a) and Rh B (b) concentration on the absorption maximum values in presence of Brij 30 in pre-micellar and post-micellar regions

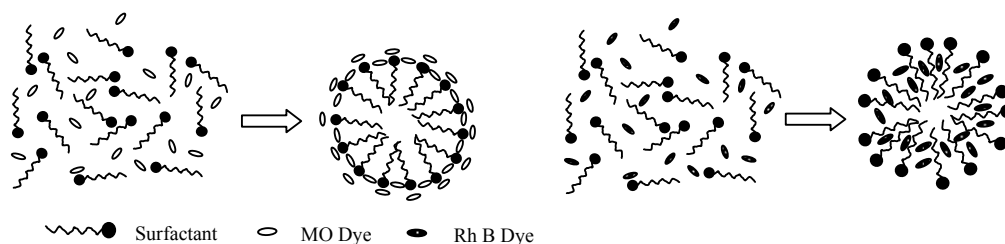


Fig. 5. Dynamic behavior in surfactant/dye/water systems

Some groups able to produce hydrogen bonds, such as –OH, can penetrate water clusters, producing only a small distortion of their shape. At the same time, the structure is not affected. The water solubility of the polyoxyethylene derivatives is mostly determined by the capacity of the ether oxygen to form weak hydrogen bonds with water. This forms a primary hydration layer that incorporates more water molecules leading to swelled micelles [22]. The bathochromic shift signifies that the MO (Fig. 4a) is incorporated into the micelle in the hydrophilic shell, between the hydrated ethylene oxide head groups.

Due to its quasilinear structure and hydration layer, MO can better align in the neighborhood of oxyethylenic head of surfactant. On the contrary, in the case of the voluminous molecules of Rh B no solvatochromic shift occurs (Fig. 4b), this fact pleading for the dye higher mobility and capacity to intercalate between the surfactant chains (Fig. 5).

3.3. Thermodynamic parameters

3.3.1. Determination of equilibrium constant

The values of the equilibrium constant K were obtained according to the methods previously described [4].

The equilibrium reaction for the binding of dye to the micelles can be written as:



and

$$K = \frac{[\text{Dye}(\text{Sf})_n]}{[\text{Dye}][\text{Sf}]^n} \quad (2)$$

where K is the equilibrium constant, by assuming $[\text{Dye}(\text{Sf})_n] = C_b$:

$$K = \frac{C_b}{(C_{\text{Dye}} - C_b)(C_{\text{Sf}} - n \cdot C_b)^n} \quad (3)$$

where C_{Dye} and C_{Sf} are the analytical concentrations of dye and surfactant solutions, respectively, and n is the number of surfactant molecules bound to the dye. Since the surface tension of solutions is directly proportional to the concentration, the equilibrium constant can be approximated by equation (4) where: Sf/Water - surfactant aqueous solution, Sf/Dye/Water - surfactant and dye aqueous solution, γ_c - surface tension of surfactant-dye complex, $\gamma_c = \gamma_{\text{Sf/Water}} - \gamma_{\text{Sf/Dye/Water}} + \gamma_{\text{Dye/Water}}$ - surface tension of dye; $\gamma_{\text{Sf/Dye/Water}}$ - surface tension of mixture surfactant-dye:

$$K = \frac{\gamma_C}{\gamma_{Dye/Water} \cdot \gamma_{Sf/Dye/Water}^n} \quad (4)$$

Based on stalagmometric measurements, the parameters n and K can be determined from equation (4):

$$\ln \gamma_C = \ln K \cdot \gamma_{Dye/Water} + n \cdot \ln \gamma_{Sf/Dye/Water} \quad (5)$$

The experimental data are represented in Fig. 6 and the corresponding parameters are $K=0.99$ and $n=2.5$. The linear regression coefficient obtained for this plot was 0.9918.

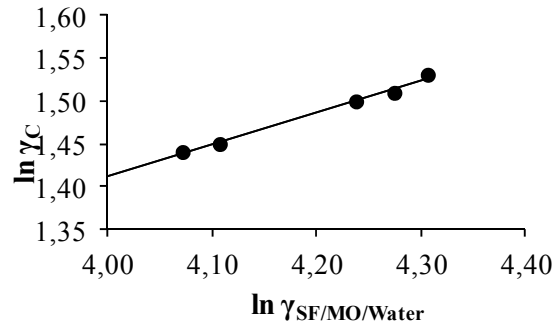


Fig. 6. Plot of $\ln \gamma_C$ versus $\ln \gamma_{SF/MO/Water}$ for the interaction of MO with Brij 30

3.3.2. Determination of partition coefficient

Partition coefficient, K_x , is an important parameter to determine the partition of the dye between the micellar and bulk water phases. K_x is defined according to the pseudo-phase model as [23,24]:

$$K_x = \frac{X_{Dye}^m}{X_{Dye}^w} \quad (6)$$

where X_{Dye}^m and X_{Dye}^w are the mole fractions of the dye in micellar and aqueous phase, respectively. They are related to the concentrations of species in the solubilization system:

$$X_{Dye}^m = \frac{n_{Dye}^m}{n_{Dye}^m + n_{Sf}^m} \quad (7)$$

$$X_{Dye}^w = \frac{n_{Dye}^w}{n_{Dye}^w + n_{Sf}^w + n_w} \quad (8)$$

where n_{Dye}^m , n_{Dye}^w , n_{Sf}^m and n_{Sf}^w represent the mole number of dye and surfactant, respectively, in micellar and monomeric states, and $n_w = 55.5 \text{ mol dm}^{-3}$ is the molarity of water. But:

$$n_{Dye}^m = C_{Dye}^m V \quad n_{Dye}^w = C_{Dye}^w V \quad (9)$$

$$n_{Sf}^m = C_{Sf}^m V \quad n_{Sf}^w = C_{Sf}^w V \quad (10)$$

By replacing n_{Dye}^m and n_{Dye}^w in Eq. (7) by Eq. (9), and n_{Sf}^m and n_{Sf}^w in Eq. (8) by Eq. (10), it can be obtained:

$$X_{Dye}^m = \frac{C_{Dye}^m}{C_{Dye}^m + C_{Sf}^m} \quad (11)$$

$$X_{Dye}^w = \frac{C_{Dye}^w}{C_{Dye}^w + C_{Sf}^w + n_w} \quad (12)$$

where C_{Sf}^m and C_{Sf}^w are the concentrations of surfactant in micellar and monomeric states. Denoting $K_c = K_x/n_w$ and assuming that under experimental conditions $C_{Dye}^w + C_{Sf}^w \ll n_w$, we get the equation:

$$K_c = \frac{C_{Dye}^m}{C_{Dye}^w (C_{Dye}^m + C_{Sf}^m)} \quad (13)$$

K_c is the partition constant in the units of $\text{mol}^{-1} \text{dm}^3 (\text{M}^{-1})$.

The fraction f of the associated dye may be defined as:

$$f = \frac{C_{Dye}^m}{C_{Dye}^m + C_{Dye}^w} \quad (14)$$

At a certain dye concentration, the fraction f is equal to zero in the non-micellar region up to CMC, and increases with the surfactant concentration above CMC. When surfactant concentration, C_{Sf} , tends to infinit, f approaches unity and all added dye should be solubilized in micelles.

The fraction f can be directly calculated from the experimental data, using Eq. (15):

$$f = \frac{\Delta A}{\Delta A^\infty} \quad (15)$$

where $\Delta A = A - A_w$ and $\Delta A^\infty = A^\infty - A_w$, A and A_w are the absorbance values of the dye in the presence and absence of the surfactant, A^∞ is the absorbance of the dye completely bound to the surfactant.

By using Eq. (14) and (15), Eq. (13) can be written in a linear form:

$$\frac{1}{\Delta A} = \frac{1}{\Delta A^\infty} + \frac{1}{K_c \Delta A^\infty (C_{Dye} + C_{Sf} - CMC)} \quad (16)$$

K_c was obtained from the intercept and slope of the plot of $1/\Delta A$ versus $1/(C_{Dye} + C_{Sf} - CMC)$, according to Eq. (16), using the absorbance values at the maximum absorption wavelength of the micelle-bound dye (at 414 nm), as shown in Fig. 7. The linear regression coefficient obtained for this plot is 0.9767.

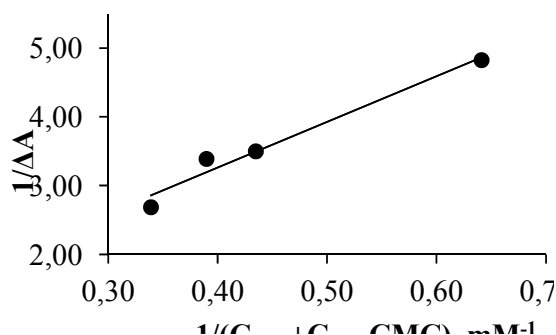


Fig. 7. Plot of $1/\Delta A$ versus $1/(C_{Dye} + C_{Sf} - CMC)$ for the interaction of MO with Brij 30

The calculated K_c and K_x values are $9 \times 10^{-5} \text{ M}^{-1}$ and 5×10^{-3} , respectively. These values are comparable with literature values previously reported for some anionic dye molecules bound to non-ionic surfactant micelles [14].

From Eq. (17), the standard Gibbs free energy change for the transfer of dye from bulk water phase to micellar phase can be obtained:

$$\Delta G^0 = -RT \ln K_x \quad (17)$$

The value of ΔG^0 is -4.02 kJ/mol, confirming the tendency of the dye to migrate towards the micellar phase.

The negative value obtained for ΔG^0 indicates that the partition process of MO between the micellar and the bulk water phases occur spontaneously.

4. Conclusions

The interactions between the ionic dyes and non-ionic surfactant molecules have been investigated, using the spectral shifts of the dye molecules as function of the surfactant concentration. The CMC value of the surfactant was influenced especially by the addition of Rh B and not so much by that of MO. Beyond the CMC value of surfactant concentrations, the maximum absorption peak of MO shows a bathochromic shift, as the surfactant concentration increases. This demonstrates that MO is incorporated into the micelle in the hydrophilic shell, between the ethylene oxide head groups.

The results showed that the absorbance value of Rh B increases with the addition of surfactant, and no stable chemical complex is formed. The calculated thermodynamic parameters revealed that MO-Brij 30 system formed a stable complex. The negative ΔG^0 value indicates that the partition process of MO between the micellar and the bulk water phases occur spontaneously.

These experiments provide useful data for applying the microemulsification technique for dyes pollution abatement from waste waters.

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