



## Dye–surfactant interaction in aqueous solutions

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### ABSTRACT

The interaction of four ionic dyes, C.I. Mordant Black 11, C.I. Mordant Black 17, C.I. Direct Yellow 50 and C.I. Basic Blue 9, with cationic and anionic surfactants was studied by absorption spectroscopy. The dyes interact strongly with oppositely charged surfactant in the premicellar concentration range and the appropriate values of constant of dye–surfactant complex formation were estimated. In addition, the most important factor affecting the number of dye particles solubilized in the surfactant micelle was its molecular mass.

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### 1. Introduction

Surfactant–dye associations are important not only in dyeing process but also in dye separation processes such as cloud point extraction (CPE) or micellar enhanced ultrafiltration (MEUF) [1,2]. The choice of surfactant type is crucial in dye separation by means of MEUF and it can be done on the basis of mutual interaction between dye and surfactant particles. Many techniques were used for qualitative and quantitative description of dye–surfactant interactions, i.e. potentiometry [3,4], conductometry [5,6], or ion selective electrodes [7,8]. The most often used method to investigate dye–surfactant interactions is spectrophotometry [9–14]. In the presence of surfactant new bands in the electronic absorption spectra of many dyes can appear and the stronger the mutual interaction between dye and surfactant the greater change is observed [13]. The changes of dye visible absorption spectra in the presence of surfactant at different concentrations result from equilibrium between surfactant monomers, micelles, dye aggregates, dye–surfactant premicellar complex and dye particles incorporated into the micelles [15,16].

In systems containing ionic dye and surfactant charged opposite to the dye electrostatic interactions appear. As a result of the attraction forces ionic pairs dye–surfactant are formed in the solution. Exemplary Fig. 1 presents the structure of complex formed between anionic dye Mordant Black 11 and cationic surfactant hexadecyltrimethylammonium bromide.

The aim of the work was to study dye–surfactant complex formation between opposite- and the same-charged dyes and surfactant particles by means of spectroscopic measurements.

### 2. Experimental

#### 2.1. Chemicals

Methylene blue (C.I. Basic Blue 9 (MB)), C.I. Mordant Black 11 (MB11), C.I. Mordant Black 17 (MB17) and C.I. Direct Yellow 50 (DY) were taken under investigation. Hexadecyltrimethylammonium bromide (CTAB) and sodium dodecylsulfate (SDS), both from Merck, Germany, were used as surfactants. The critical micelle concentrations (CMCs) in deionized water were equal to 0.335 and 2.39 g/L for CTAB and SDS, respectively. Deionized water from reverse osmosis was used as a solvent. The chemical structures of the chemicals are presented in Fig. 2.

#### 2.2. Spectral analysis

Absorption measurements were performed on a spectrophotometer Spekol 40, Analytic Jena, Germany. Visible spectra of each dye in two surfactant systems (with CTAB and with SDS) were recorded for wavelength ranged from 400 to 700 nm. The concentration of each dye was kept constant during the study and was equal to 50 mg/L for anionic dyes and 5 mg/L for MB. The surfactants' concentration was changed in the range of 0.025–5 in the CMC scale.

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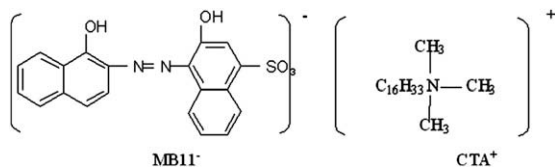


Fig. 1. Structure of MB11/CTAB complex (molar ratio equal to 1:1).

### 2.3. Calculations

Dye–surfactant complex formation constant ( $K$ ) was estimated for the premicellar surfactant concentrations. On the basis of literature data [17,18] authors established that 1:1 molecular complex is formed as a result of the interaction between the dye anion ( $D^-$ ) and surfactant cation ( $S^+$ ) (or dye cation and surfactant anion). Thus, complex formation can be represented by the equilibrium



with the equilibrium constant ( $K$ ) equal to

$$K = \frac{[S^+D^-]}{[S^+] \times [D^-]} \quad (2)$$

Values of  $K$  and  $\alpha$  were estimated using the least squares method. From the reaction balance (Eq. (2)) and the assumptions that (i) both dye and dye–surfactant complex absorb at considered wavelength and (ii) the absorbance occurs in accordance to the Bouguera–Lamberta–Beera rule the relation (3) was obtained

$$\Delta A = -\frac{C_{S0}C_{D0}}{\Delta A} \times \alpha^2 + (C_{S0} + C_{D0}) \times \alpha + \frac{\alpha}{K} \quad (3)$$

where  $\alpha$  denotes the difference between absorbance coefficient values of dye and dye–surfactant complex multiplied by an optical wavelength,  $\Delta A = A_0 - A$ , where  $A_0$  and  $A$  denote absorbance of the dye in water and surfactant solution, respectively,  $C_{S0}$  and  $C_{D0}$  stand for initial concentrations of surfactant and dye, respectively.

The standard free enthalpy of the dye–surfactant complex formation ( $\Delta G^0$ ) was calculated from values of  $K$  obtained from the equation

$$\Delta G^0 = -RT \ln K \quad (4)$$

The approximate number of dye molecules ( $n$ ) incorporated into a single micelle was estimated for the micellar surfactant concentrations (1–5 CMC). For calculations the following equations were used [19]:

$$n = \frac{[D_m]}{[m]} \quad (5)$$

and

$$[m] = \frac{[S] - CMC}{N_{ag}} \quad (6)$$

where  $D_m$  is the concentration of the dye solubilized in the micelle,  $m$  is the micelle concentration,  $S$  is the total surfactant concentration and  $N_{ag}$  is the mean surfactant aggregation number. For all the calculations the assumption that the mean surfactant aggregation number in the absence and presence of the dye is the same.  $N_{ag}$  at critical micelle concentration was equal to 80 [19] and 63 [20] for CTAB and SDS, respectively.

The concentration of the solubilized dye was calculated from the relationship

$$[D_m] = \frac{A_0 - A}{\varepsilon_0 - \varepsilon_m} \quad (7)$$

where  $\varepsilon_0$  and  $\varepsilon_m$  stand for molar absorbance coefficient calculated from absorbance value obtained for dye aqueous solution and surfactant solution, respectively.

## 3. Results and discussion

### 3.1. Spectral studies

In aqueous solutions methylene blue exists in cationic form. Fig. 3 presents the visible spectra of aqueous methylene blue solution at 5 mg/L for several SDS concentrations ranging from 0 to

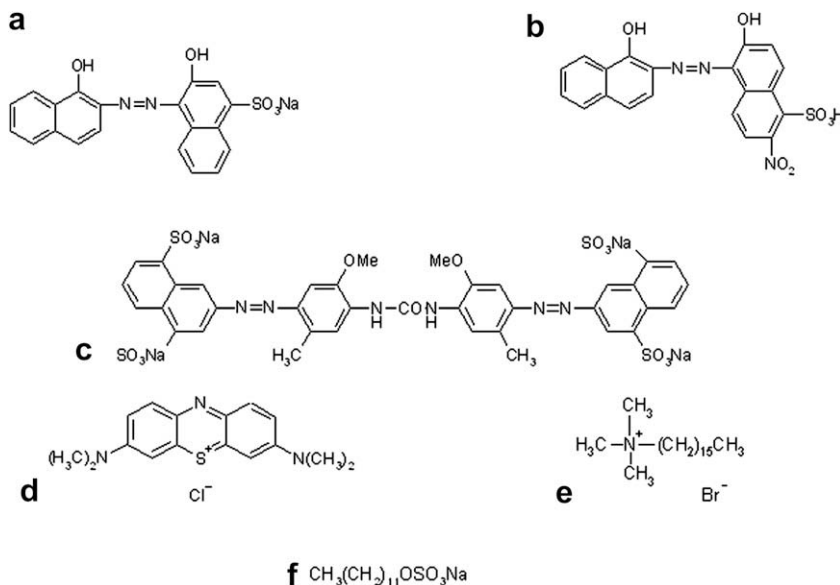
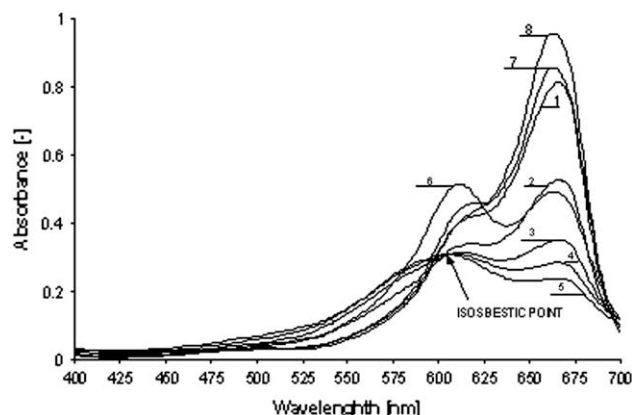


Fig. 2. Chemical structures of (a) (MB11) Mordant Black 11 (C.I. Black T (14645)), (b) (MB17) Mordant Black 17 (C.I. Black RSS (15705)), (c) (DY) Direct Yellow (C.I. Direct Yellow 50 (29025)), (d) (MB) Methylene Blue (C.I. Blue 9 (52015)), (e) hexadecyltrimethylammonium bromide (CTAB), (f) sodium dodecylsulfate (SDS).

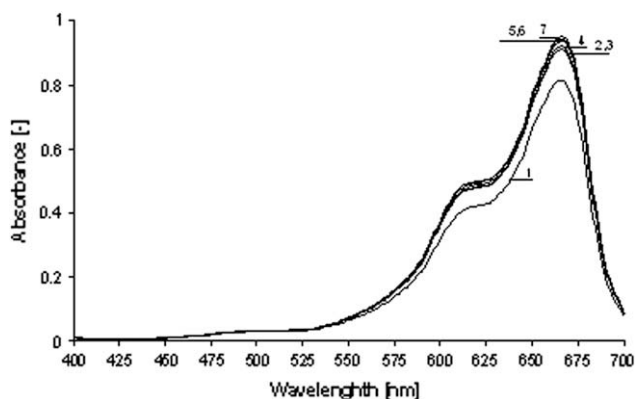


**Fig. 3.** Visible absorption spectra of Methylene Blue [5 mg/L] in water – 1 and in SDS solutions: [0.05 CMC] – 2, [0.1 CMC] – 3, [0.15 CMC] – 4, [0.25 CMC] – 5, [0.5 CMC] – 6, [0.75 CMC] – 7, [1 CMC] – 8.

1 CMC. In aqueous solution the dye exhibits a maximum absorption band at 660 nm (the band attributed to dye monomer) and a shoulder at 612 nm [21]. In the presence of increasing sodium dodecylsulfate concentration up to 0.025 CMC the absorbance of both bands decreased weakly and a new band at 610 nm appeared (hipsochromic shift). The new maximum may be attributed to dye dimerization in the presence of surfactant. The dimerization is a frequent phenomenon occurred also in high concentrated dye solution or in the presence of macromolecules, i.e. DNA [22], cyclodextrins [23] in the dye aqueous solution. Oppositely charged dye–surfactant complex formation decreases the repulsion forces, affects the hydrophobic interactions and van der Waals forces between the same-charged dye particles [24]. Such associates may induct premicellar surfactant aggregation and enhance the solubilization of the dye [25,26]. Dye aggregation at low surfactant concentration is typical of cationic dyes i.e. acridine orange, methylene blue, tionine, rhodamine, methyl violet [27,28].

At increasing SDS concentration (ranging 0.5–1 CMC) the intensity of absorption bands at 660 and 612 nm increase. Such a behavior can be treated as an evidence of premicellar surfactant aggregation and enhanced dye dimerization by greater amount of surfactant monomers present in the solution.

An isosbestic point in the spectra of methylene blue/SDS solutions is observed at 598 nm. The existence of the isosbestic point is connected with 1:1 MB–SDS complex formation. Formation of such complex between the particles of methylene blue and anionic surfactants is proposed also by Pramanik and Mukherjee [29].



**Fig. 4.** Visible absorption spectra of Methylene Blue [5 mg/L] in water – 1 and in CTAB solutions: [0.05 CMC] – 2, [0.1 CMC] – 3, [0.2 CMC] – 4, [0.5 CMC] – 5, [0.75 CMC] – 6, [1 CMC] – 7.

**Table 1**

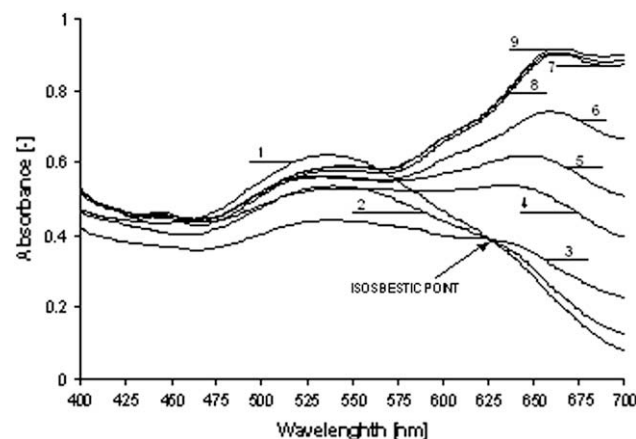
Values of the dye–surfactant complex formation constant ( $K$ ), standard free enthalpy of the complex formation ( $\Delta G^0$ ) and the model error (Err.)

Dye	CTAB			SDS		
	$K$ [–]	Err.	$-\Delta G^0$ [kJ/mol]	$K$ [–]	Err.	$-\Delta G^0$ [kJ/mol]
MB 11	$1.1 \times 10^5$	$2.02 \times 10^{-6}$	28.7	88	$2.55 \times 10^{-6}$	11.1
MB 17	$4.4 \times 10^5$	$2.50 \times 10^{-4}$	32.2	78	$1.03 \times 10^{-5}$	10.8
DY	$2.6 \times 10^4$	$6.73 \times 10^{-5}$	25.2	450	$2.37 \times 10^{-4}$	15.1
MB	760	$2.89 \times 10^{-6}$	16.4	$1.70 \times 10^3$	$9.93 \times 10^{-4}$	18.4

At SDS micellar concentrations the absorbance of methylene blue solutions does not change. It means that monomeric forms of the dye are solubilized in the surfactant micelles. The same relationship was observed for all the dyes taken under investigation.

Addition of cationic surfactant hexadecyltrimethylammonium bromide causes only a higher intensity of the dye absorption (Fig. 4). CTAB produces no perturbation in the visible spectra of the dye and any new band was observed. It means that the repulsion forces between the same-charged dye and surfactant particles were stronger than the hydrophobic and van der Waals interactions and no stable complex could be formed in the solution. However, on the basis of absorbance intensity changes the complex formation constant was calculated (Table 1).

Mordant Black dyes exist in anionic form in aqueous solution. The spectrum of MB11 in aqueous solution exhibits the absorption maximum ( $\lambda_{\max}$ ) at 540 nm (Fig. 5) and for MB17  $\lambda_{\max}$  is equal to 545 nm. Changes of absorption spectra observed for MB11 and MB17 in the presence of the same- and opposite charged surfactants were analogical, so in the present work only the figures for MB11 are shown. In the presence of CTAB, spectacular changes occurred in the spectra of these dyes. In the solutions containing MB11 and cationic surfactant CTAB at the concentration ranging from 0.025 to 1 CMC the intensity of the band at 540 nm diminished with the appearance of a new band. First, for the lowest surfactant concentrations the new band is observed at 640 nm and then, with increasing surfactant amount up to 1 CMC it moves to 660 nm (bathochromic shift). The initial decrease of the absorbance results from dye–surfactant complex formation. The intensity of the band gradually increases, as the CTAB concentration increased to 1 CMC. For the surfactant concentrations higher than CMC the intensity of the band stood constant. Such observations are according to a theory proposed by Shah et al. [30] that in the solutions containing surfactant at the concentration near CMC first an



**Fig. 5.** Visible absorption spectra of Mordant Black 11 [50 mg/L] in water – 1 and in CTAB solutions: [0.025 CMC] – 2, [0.05 CMC] – 3, [0.1 CMC] – 4, [0.15 CMC] – 5, [0.25 CMC] – 6, [0.5 CMC] – 7, [0.75 CMC] – 8, [1 CMC] – 9.

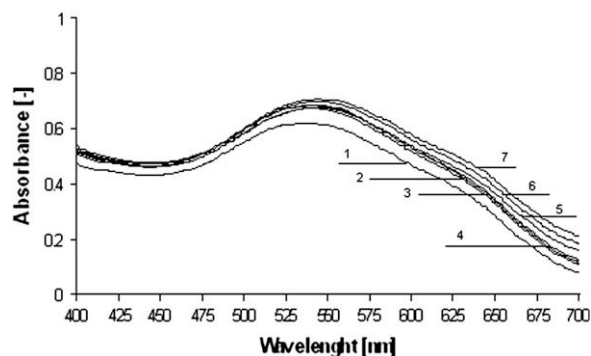


Fig. 6. Visible absorption spectra of Mordant Black 11 [50 mg/L] in water – 1 and in SDS solutions: [0.05 CMC] – 2, [0.1 CMC] – 3, [0.2 CMC] – 4, [0.5 CMC] – 5, [0.75 CMC] – 6, [1 CMC] – 7.

adhesion of ionic pairs on the surfaces of micelles formed in the system takes place and then dye particles are incorporated into the micelles. The observed bathochromic shift can also result from the interaction between aromatic rings present in the structure of the dye ( $\pi-\pi$  stacking) [31] and formation of dye J-aggregates (head-to-tail). Similar observation is presented by Karukstis et al. [32] for the azo dyes with hydroxyl and sulfonic groups in naphthyl ring.

At 625 nm the isosbestic point appears. It can be the indication that in the solution containing MB11 and CTAB 1:1 complex was formed as a result of sulfate group ionization.

Addition of anionic surfactant to MB11 solutions did not influence the spectral characteristic of the dye (Fig. 6). The value of  $\lambda_{\max}$  was constant regardless of the surfactant concentration. Only the absorption intensity increased slightly with increase of surfactant concentration.

Spectral characteristics of Mordant Black 17 in the presence of ionic surfactants CTAB or SDS were similar to those obtained for Mordant Black 11. The strong bathochromic shift was observed in the presence of cationic surfactant and isosbestic point appeared at 575 nm. In the solutions containing SDS only the increase of absorption intensity was observed at the constant position of the fundamental band.

Spectral characteristics of Direct Yellow with the addition of the cationic surfactant were similar to the spectrum of the dye in water. Any new band appeared, however, for low surfactant concentrations (0.025–0.075 CMC) a sharp decrease of the absorption intensity resulting from dye–surfactant complex formation was observed.

### 3.2. Calculation results

Table 1 presents calculated values of the dye–surfactant complex formation constant ( $K$ ), standard free enthalpy of the complex formation ( $\Delta G^0$ ) and the model error (Err.) for all the studied dye–ionic surfactant systems. Very low values of model error confirm the high accuracy of calculation method.

The comparison of the standard free enthalpy values of dye–surfactant complex formation in systems with CTAB and SDS indicated that the  $\Delta G^0$  is much higher, twofold or even more in all the systems containing anionic surfactant. Only in the case when MB is present in the solution i.e. in systems containing MB and CTAB or MB and SDS, the estimated values of  $\Delta G^0$  are very close to each other. Moreover, the important differences between  $K$  values estimated for CTAB–dye or SDS–dye complex can be observed. Thus, the results confirmed that the complexes formed in the systems containing cationic surfactant are much more stable and moreover their formation consumes less amount of energy.

Exemplary Fig. 7(a, b) shows the comparison of measured and calculated absorbance values for the systems DY–CTAB and MB11–SDS, respectively. The compatibility of the results is satisfactory not only for the opposite charged dye–surfactant system (Fig. 7(a)), but also for the system containing the same-charged particles (Fig. 7(b)).

Table 2 shows the experimental values of dyes' absorbance in the absence and presence of surfactant and calculated number of dye molecules solubilized in individual surfactant micelle. Presented data show that the most important factor affecting the amount of dye solubilization is the dye molecular weight. Mordant Black dyes have similar molecular weight equal to 416 and 463 g/mol for MB11 and MB17, respectively. Thus, for both of the dyes the approximate number of dye molecules incorporated into a single micelle of cationic surfactant was equal to 3. The same value was obtained by Awan and Shah [19] for hemicyanine dye (dimethylamino)stilbazolium butyl sulfonate of molecular weight 360 g/mol, solubilized in CTAB micelles.

The molecular weight of Direct Yellow is equal to 1016 g/mol and is over twice bigger than the molecular weight of Mordant Black type dyes. Thus, only one such a big particle can be solubilized in individual micelle of cationic surfactant. Similar results were presented in the work of Choi et al. [33]. The authors observed that dyes having smaller molecular weight are easily solubilized in surfactant micelles. However, the number of dye molecules solubilized in micelle of the same-charged surfactant in each case was smaller than 1. It means that electrostatic repulsion forces between the same-charged dye and surfactant molecules were stronger than other interactions present in the dye micellar solutions

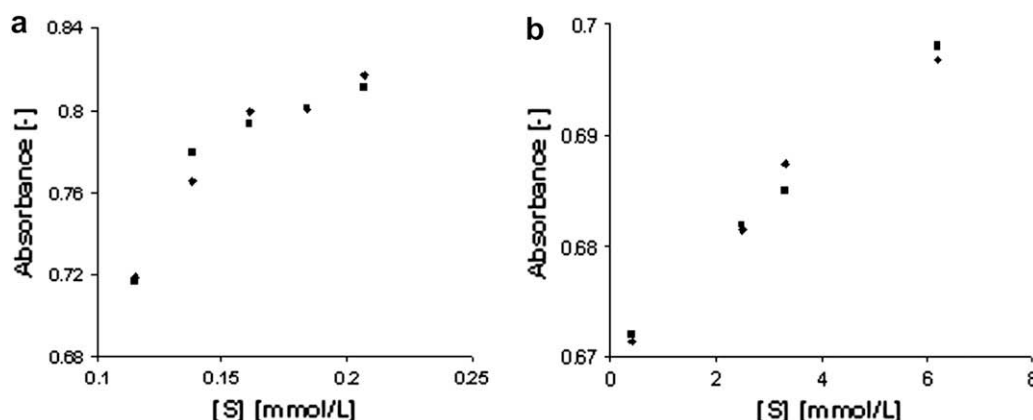


Fig. 7. Comparison of measured (◆) and calculated (■) absorbance values for two dye–surfactant systems: (a) DY–CTAB and (b) MB11–SDS.



**Table 2**

Values of the absorbance of the dye aqueous ( $A_0$ ) and surfactant (A) solutions and approximate number of dye molecules ( $n$ ) incorporated into a single micelle

Dye	Surfactant	$A_0$	A	$n$
MB11	CTAB	0.619	0.917	3
	SDS		0.699	0.25
MB17	CTAB	0.938	1.176	3
	SDS		1.059	0.25
DY	CTAB	0.696	0.963	1
	SDS		0.974	0.1
MB	CTAB	0.812	0.944	0.3
	SDS		0.977	2

(i.e. hydrophobic interactions, van der Waals forces), thus solubilization in such solutions was impossible.

Positively charged polar groups of CTAB particles interact with  $\text{SO}_3^-$  and aromatic rings present in particles of studied dyes. Thus, the dyes are localized in the near of hypothetic micelle surface.

The number of methylene blue molecules solubilized in micelles of oppositely charged surfactant sodium dodecylsulfate was equal to two. Lower molecular weight of MB (319 g/mol) than Mordant Black type dyes could suggest solubilization of higher number of particles. However, micellar sorption capacity of surfactant having the same length of hydrocarbon chain changes in the following direction: nonionic surfactant > cationic surfactant > anionic surfactant [34] and sodium dodecylsulfate hydrocarbon chain is shorter than the chain of the particle of cationic hexadecyltrimethylammonium bromide. Therefore, solubilization of two molecules of methylene blue per SDS micelle can be explained.

#### 4. Conclusions

The high values of complex formation constants estimated for the systems MB11–CTAB, MB17–CTAB, DY–CTAB and MB–SDS showed that the interactions between the oppositely charged dyes and surfactants are very strong. In the case when the same-charged dye and surfactant were used, it was found that the electrostatic repulsion forces were strong and the complex formation constant values were two or three order lower than in systems with opposite charged dyes and surfactants.

The number of dye molecules solubilized in surfactant micelle is mainly affected by the molecular weight of the dye. However, the type and chemical structure of surfactant and especially the length of hydrocarbon chain seem to be also very important parameters.

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