Dyes and Pigments 80 (2009) 201–205

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

# Dye–surfactant interaction in aqueous solutions

Małgorzata Bielska, Anna Sobczyńska, Krystyna Prochaska*

*Institute of Chemical Technology and Engineering, Poznan University of Technology, Pl. M. Sklodowskiej-Curie 2, 60-965 Poznan, Poland*

A R T I C L E I N F O

*Article history:*
Received 28 February 2008
Received in revised form 30 May 2008
Accepted 30 May 2008
Available online 7 June 2008

*Keywords:*
Dye–surfactant interaction
Ionic surfactants
Anionic dyes
Cationic dyes

A B S T R A C T

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.

## 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.

---

* Corresponding author. Tel.: +48 61 6653601; fax: +48 61 6653649.
*E-mail address:* Krystyna.Prochaska@put.poznan.pl (K. Prochaska).

0143-7208/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2008.05.009

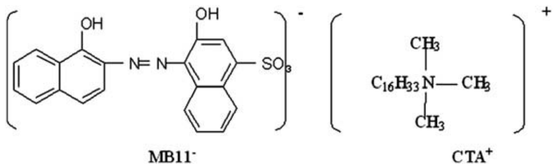

**Fig. 1.** Structure of MB11/CTAB complex (molar ratio equal to1:1).

### 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

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

with the equilibrium constant ($K$) equal to

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

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

$$\Delta A = -\frac{c_{S0}c_{C0}}{\Delta A}\times\alpha^2 + (c_{S0}+c_{B0})\times\alpha + \frac{\alpha}{K} \tag{3}$$

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

$$\Delta G^0 = -RT\ln K \tag{4}$$

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]:

$$n = \frac{[D_m]}{[m]} \tag{5}$$

and

$$[m] = \frac{[S]-\mathrm{CMC}}{N_{ag.}} \tag{6}$$

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

$$[D_m] = \frac{A_0 - A}{\varepsilon_0 - \varepsilon_m} \tag{7}$$

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

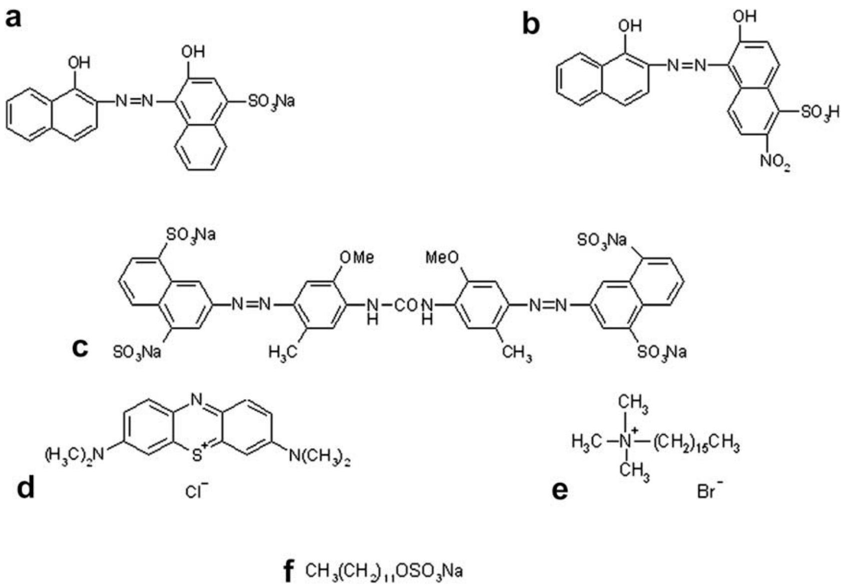

**Fig. 2.** Chemical structures of (a) (MB11) Mordant Black 11 (*C.I. Black T* (*14645*)), (b) (MB17) Mordant Black 17 (*C.I. Black RSS* (*15705*)), (c) (DY) Direct Yellow (*C.I. Direct Yellow 50* (*29025*)), (d) (MB) Methylene Blue (*C.I. Blue 9* (*52015*)), (e) hexadecyltrimethylammonium bromide (CTAB),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