



ORIGINAL ARTICLE

Specific interactions within micelle microenvironment in different charged dye/surfactant systems



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Abstract The interactions of two ionic dyes, Crystal Violet and Methyl Orange, with different charged surfactants and also with a nonionic surfactant were investigated using surface tension measurements and visible spectroscopy in pre-micellar and post-micellar regions. It was found that for the water dominant phase systems the dye was localized between the polar heads, at the exterior of the direct micelle shells for all the systems. For the oil dominant phase systems, in case of the same charged dye/surfactant couples, the dye was localized in the micelle shell between the hydrocarbon chain of the surfactant nearby the hydrophilic head groups while for nonionic surfactant and oppositely charged dye/surfactant, localization of dye was between the oxyethylenic head groups towards the interior of the micelle core. Mixed aggregates of the dye and surfactant (below the critical micellar concentration of cationic surfactant), dye-surfactant ion pair and surfactant-micelles were present. The values of equilibrium constants (for TX-114/MO and TX-114/CV systems were 0.97 and 0.98, respectively), partition coefficients between the micellar and bulk water phases and standard free energy (for the nonionic systems were -12.59 kJ/mol for MO and

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–10.97 kJ/mol for CV) were calculated for all the studied systems. The partition processes were exothermic and occurred spontaneously.

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1. Introduction

Studies of dye-surfactant interactions provide useful information for industrial applications, chemical research and dye separation processes (Bilski et al., 1997; Purkait et al., 2004). Dye-surfactant associations depend principally on the chemical structure of the compounds (Kartal and Akbas, 2005; Tehrani Bagha et al., 2007). Hydrophobic interactions, electrostatic interactions, hydrogen bonds, π -stacking and Van der Waals forces are typical examples of the intermolecular forces that dominate the interactions of dye molecules with surfactant aggregates (Naeem et al., 2000; Dezhmanah and Firouzi, 2012; Karukstis et al., 2010). In pre-micellar region, monomers of surfactant interact with the dye molecules to form ion association complexes, while, in post-micellar region, the dye molecules are likely to be localized at micelle surface. These interactions are responsible for changes in the position and intensity of absorption band in electronic spectra (Ghosh et al., 2012; Haq et al., 2014).

Despite the occurrence of many investigations of dye-surfactant systems and the behaviour of surfactant and dye mixtures, the mechanism underlying dye-surfactant interactions in surface films and micelles is not fully understood yet (Ghosh, 2001; Chakraborty et al., 2011; Ghosh et al., 2011; Muntaha and Khan, 2014; Kert and Simoncic, 2008). These studies may be applied in: (i) solubilization (Goddard and Ananthapadmanabhan, 1998) and photographic industries (Simoncic and Kert, 2002) where the dye should be localized inside the direct micelles; and (ii) dyes sensitized cells (Guo et al., 2013), nonlinear optical materials (Rao et al., 2002; Cyprych et al., 2015) and photosensitizer (Prakash, 2002) when the chromophore is intended to be placed in the hydrophilic shell of the surfactant micelles. Moreover, these dye-surfactant complexes find wide applications in extraction of dyes from wastewater using water-in-oil systems (Fleancu et al., 2013).

In the present investigation, the interactions of three different types of surfactants with cationic and anionic dyes have been thoroughly studied, given their intrinsic environmental and economic importance for dye removal from wastewater. Anionic dye Methyl Orange (MO) and cationic dye Crystal Violet (CV), respectively, being largely present in the dyeing process and rinsing effluents of the textile industries were selected as being representative for this study (Shah et al., 2013; Rahimi et al., 2010; Alqaragully, 2014).

The surfactants were chosen from three classes: cationic, anionic and nonionic surfactants in order to get complete information on the dye-surfactant complex formation between opposite- or the same-charged dye and surfactant molecules.

The surfactant and dye-surfactant aggregations were investigated by Ostwald stalagmometric method, while the dye-surfactant interactions were monitored by UV-VIS spectroscopy. The equilibrium constant, surfactant/water partition

coefficient and standard free energy change of dye transfer from bulk water to micellar phase were quantified as well.

Since the ternary water/surfactant/oil system is reported as a more efficient removal agent for different types of pollutants (Fleancu et al., 2013) and knowing that the dye microenvironment into the micelles is influenced by the oil addition (Mihaly et al., 2014), the influence of ethyl acetate (EtAc) on the preferential location of dye into the micelles was checked.

2. Experimental

2.1. Materials

Methyl Orange (MO), Crystal Violet (CV) dyes, nonionic surfactant, (1,1,3,3-tetramethylbutyl)phenyl-polyethylene glycol (Triton X-114, hereafter termed TX-114) and ethyl acetate (EtAc) were purchased from Sigma-Aldrich. Anionic surfactant sodiumdodecyl sulphate (SDS) was provided by Merck and cationic surfactant dodecyltrimethylammonium bromide (DTAB) was obtained from Alfa Aesar. All chemicals were used as received. Solutions were prepared in distilled water. The chemical structures of dyes and surfactants used in this work are presented in Fig. 1.

2.2. Methods

Surface tension measurements were carried out at 298.15 K by Ostwald stalagmometric method (method of counting drops) (Mihaly et al., 2007), which is often used to measure the relative surface tension $\frac{\sigma}{\sigma_0}$, i.e. to compare the surface tension of the tested liquid σ to surface tension of the standard liquid σ_0 . The formula for the relative surface tension is as follows:

$$\frac{\sigma}{\sigma_0} = \frac{n_0 \cdot d}{n \cdot d_0} \quad (1)$$

where n_0 – the number of drops of standard liquid, n – the number of drops of the test liquid, d_0 – density of the standard liquid, and d – density of the test liquid.

The critical micellar concentration (CMC) values were obtained from the surface tension dependence against the surfactant concentrations. Also, the binding equilibrium constants were calculated from the surface tension data in the pre-micellar region.

Absorbance measurements have been performed with UV-VIS spectrophotometer type V-670, Jasco. The micelle/water partition coefficients for dye-surfactant system were determined from the absorbance changes occurred as a result of the interaction between dye and surfactant molecules (Duman et al., 2012). The concentration of each dye was kept constant ($C_{Dye} = 0.01$ mM) and the concentration of surfactants was increasing during the experiments.

For surface tension analysis and spectroscopic study, different solutions have been used as presented in Table 1.

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