Available online at www.sciencedirect.com
ScienceDirect
Dyes and Pigments 76 (2008) 104–112
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Influence of the chemical structure of dyes and surfactants on their interactions in binary and ternary mixture

Barbara Simončič*, Mateja Kert

University of Ljubljana, Faculty of Natural Sciences and Engineering, Department of Textiles, Snežniška 5, 1000 Ljubljana, Slovenia

Received 8 August 2006; received in revised form 17 August 2006; accepted 17 August 2006

Abstract

The influence of the structures of both dye and surfactant on the strength of the intermolecular forces operating between dye anions and surfactant cations in the presence of nonionic surfactants has been studied using potentiometry. Two anionic azo dyes, C.I. Acid Orange 7 (AO7) and C.I. Acid Red 88 (AR88), two cationic surfactants, *n*-dodecyltrimethylammonium bromide (DTA) and *n*-hexadecyltrimethylammonium bromide (CTA) and two nonionic surfactants, 4-(1,1,3,3-tetramethylbutyl)phenyl polyoxyethylene(10)-ol, Triton X-100 (TX100), and polyoxyethylene(23)lauryl ether, Brij 35 (BR35), were used. From potentiometric measurements, the equilibrium constants, K_1 and κ_1, and the standard free energy change, ΔG_1^o, for the first association step of dye–surfactant and surfactant–surfactant complex formation in binary and ternary mixtures were calculated. The results show that the strength of dye–surfactant interactions, as well as the stability of the complex formed, increases with increasing hydrophobicity of surfactant and dye. The influence of the hydrophobicity of the anionic dye and cationic surfactant on their interactions is decreased in the solution of nonionic surfactant. At the same time, the presence of structural elements of the nonionic surfactants, which promotes an increase in the attractive forces between the cationic and nonionic surfactants, decreases the strength of the interactions between the cationic surfactant and the anionic dye.

Keywords: Anionic dye–cationic surfactant interactions; Structural effects; Influence of nonionic surfactant; Binary mixture; Ternary mixture; Potentiometry

1. Introduction

In aqueous solution, attractive forces between dyes and surfactants result in the formation of complexes of different size and stability. This phenomenon can be successfully applied to dyeing processes to help solve the problem of unlevel dyeing. In these systems, the surfactant acts as a levelling agent in the presence of dyes; the dye–surfactant attractive forces, which create a counterbalancing mechanism against dye–fibre attractive forces, control the adsorption of the dye on the fibre [1,2]. The literature shows that complex formation between the dye and surfactant decreases the velocity and the degree of dye exhaustion, which results in an increase in levelness [3–8]. The effectiveness of a surfactant as a levelling agent that functions by this mechanism depends on the strength of dye–surfactant interactions and the stability of the complex formed. If attractive forces between the dye and surfactant are very strong, and consequently the stability of the complex is very high, the breakdown of the complex is hindered even at higher temperatures. This results in a low degree of dye uptake by the fibre. Since the solubility of such a complex in water could strongly decrease, this could cause it to be precipitated. Conversely, if intermolecular forces are too weak, an unstable complex is formed in the solution, which results in an ineffective levelling action of the surfactant. Hence, the strength of dye–surfactant interactions and the stability of the complex are of great importance for level dyeing.

Dye–surfactant interactions are influenced by many factors, among which the structures of the dye and the surfactant are of paramount importance. Much research work is focused

---

* Corresponding author. Tel.: +386 1 200 32 31; fax: +386 1 200 32 70.
E-mail address: barbara.simoncic@ntf.uni-lj.si (B. Simončič).

0143-7208/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2006.08.012

on investigation into the influence of ionic activity and hydrophobicity of the dye and surfactant on their interactions in aqueous solution. These investigations are mainly carried out on binary dye–surfactant mixtures, which are relatively uncomplicated to study [9–22]. In contrast to these systems, ternary mixtures, which include two surfactants present in a dye solution, are very complex and therefore much more demanding to study. However, since many surfactants cause synergistic behaviour in mixtures, the technological importance of such systems is very high. Studies that deal with dye–surfactant interactions in ternary mixtures are, because of their complexity, very rare. In the literature, investigations into such systems are mainly qualitative [22–26]. The only quantitative investigation was presented in our previous studies [27,28] where the thermodynamics of an anionic dye and cationic surfactant in the presence of a nonionic surfactant was studied with a potentiometric method.

The aim of this work was to investigate the influence of the dye and surfactant structures on the strength of intermolecular forces between dye anions and surfactant cations as well as the stability of complex formed in the presence of nonionic surfactants of concentrations higher than critical micellar concentration (c.m.c.). We also discussed the influence of hydrophobic–hydrophilic balance (HLB) of the nonionic surfactant on the tendency of anionic dye–cationic surfactant complex formation. The results obtained in ternary mixtures are compared to those obtained in binary dye–surfactant and surfactant–surfactant mixtures under the same conditions.

2. Theory

The dye–surfactant and surfactant–surfactant complex formation process can be explained using the theoretical model proposed by Rossotti and Rossotti [29], which is widely used for a large number of systems, especially of diluted solutions. In this treatment, it is assumed that only mononuclear complexes are formed in solutions with the general formula B_qA_p, where $q = 1$ and $p = n$. In such a complex, A is the ligand and B is referred to as the central group. The formation of the complex can be described as a set of multiple equilibria:

$$A + B \overset{K_1}{\longleftrightarrow} BA \tag{1}$$

$$A + BA \overset{K_2}{\longleftrightarrow} BA_2 \tag{2}$$

…

$$A + BA_{(n-1)} \overset{K_n}{\longleftrightarrow} BA_n \tag{3}$$

where BA, BA_2, $BA_{(n-1)}$ and BA_n refer to complexes with different numbers of bound ligand A, n, and K_1, K_2, …, K_n are the corresponding stoichiometric equilibrium constants.

The extent of mononuclear complex formation can be expressed in terms of the degree of binding, β. In this case, the average number of ligand A bound to each central group B may be calculated from the relationships [29]:

$$\beta_B = \frac{m_A - m_{A,F}}{m_B} \tag{4}$$

where m_A is the total concentration of ligand A, m_B is the total concentration of central group B and $m_{A,F}$ is the concentration of free molecules of ligand A in solution.

Assuming that in studied solutions only mononuclear complexes can be formed, the total concentrations of A and B may be expressed as a sum of the free ligand or central group concentration and the concentrations of complexes of different sizes. Therefore, Eq. (4) can be converted into the form:

$$\beta_B = \frac{m_{AB} + 2m_{A_2B} + 3m_{A_3B} + \cdots + nm_{A_nB}}{m_{B,F} + m_{AB} + m_{A_2B} + m_{A_3B} + \cdots + m_{A_nB}} \tag{5}$$

where each mole of complex includes n mole of bound A. Moreover, according to the multiple equilibria (1)–(3), the concentrations of complexes in Eq. (5) may be expressed by the free ligand concentration and the equilibrium constants. Therefore, the degree of binding, β_B, can be written as:

$$\beta_B = \frac{K_1 m_{A,F} + 2K_1K_2 m_{A,F}^2 + \cdots + nK_1K_2\cdots K_n m_{A,F}^n}{1 + K_1 m_{A,F} + K_1K_2 m_{A,F}^2 + \cdots + K_1K_2\cdots K_n m_{A,F}^n} \tag{6}$$

In the case where two central groups B and C are present in the solution, it is considered that ligand A forms complexes with both species simultaneously. Therefore, the concentration of bound A consists of two contributions – the first due to binding of A to B and the second due to binding of A to C. According to this, the degree of binding of ligand A to central group B, β_B, in the presence of central group C can be calculated as follows:

$$\beta_B = \frac{m_A - m_{A,F} - \beta_C m_C}{m_B} \tag{7}$$

where $\beta_C m_C$ is equal to the concentration of ligand A bound to central group C. Since the binding process of A to C can be interpreted in the same way as that of A to B (multiple equilibria (1)–(3)), the degree of binding of ligand A to central group C, β_C, can be expressed as:

$$\beta_C = \frac{m_A - m_{A,F}}{m_C} \tag{8}$$

and

$$\beta_C = \frac{\kappa_1 m_{A,F} + 2\kappa_1\kappa_2 m_{A,F}^2 + \cdots + n\kappa_1\kappa_2\cdots\kappa_n m_{A,F}^n}{1 + \kappa_1 m_{A,F} + \kappa_1\kappa_2 m_{A,F}^2 + \cdots + \kappa_1\kappa_2\cdots\kappa_n m_{A,F}^n} \tag{9}$$

where κ_1, κ_2, …, κ_n are the stoichiometric equilibrium constants for formation of complexes between A and C of different sizes.

The complex formation process can also be presented graphically in the form of binding isotherms, where β_B or β_C are plotted against the concentration of free ligand, $\log m_{A,F}$.

For systems where the binding process of ligand A to central groups B or C increases progressively with increased ligand concentration, the equilibrium constants K_1 for BA complex formation and κ_1 for CA complex formation can be calculated from Eqs. (6)–(9) as follows [29,30]:

$$\lim_{m_{\mathrm{A,F}}\to 0}\frac{\beta_{\mathrm{B}}}{m_{\mathrm{A,F}}}=K_1;\quad \lim_{m_{\mathrm{A,F}}\to 0}\frac{\beta_{\mathrm{C}}}{m_{\mathrm{A,F}}}=\kappa_1 \tag{10}$$

If the values of $\beta_{\mathrm{B}}/m_{\mathrm{A,F}}$ and $\beta_{\mathrm{C}}/m_{\mathrm{A,F}}$ are plotted against $m_{\mathrm{A,F}}$, the values K_1 and κ_1 are obtained by extrapolating to zero free ligand A concentration.

From the values obtained for K_1 and κ_1 at different temperatures, the standard free energy change, ΔG_1^{o}, for the formation of BA and CA complexes in the first step of multiple equilibria (1) can be calculated as follows [31]:

$$\Delta G_1^o=-RT\ln K_1;\quad \Delta G_1^o=-RT\ln\kappa_1 \tag{11}$$

3. Experimental

3.1. Materials

We used two anionic azo dyes, C.I. Acid Orange 7 (AO7) and C.I. Acid Red 88 (AR88); two cationic surfactants, *n*-dodecyltrimethylammonium bromide (DTA) and *n*-hexadecyltrimethylammonium bromide (CTA) and two nonionic surfactants, 4-(1,1,3,3-tetramethylbutyl)phenyl polyoxyethylene(10)-ol, Triton X-100 (TX100) and polyoxyethylene(23)-lauryl ether, Brij 35 (BR35). The dyes and surfactants were all Aldrich Chemical Company commercial products. AO7 and AR88 were purified by repeated recrystallization from aqueous acetone solution and from *N*,*N*′-dimethylformamide-acetone. DTA and CTA were purified by three recrystallizations from acetone while TX100, BR35 and TW20 were used without further purification. Sodium dodecylsulphate (SDS), another Aldrich Chemical Company product was used for the preparation of the ion-exchange complex and was also purified by three recrystallizations from acetone. All solutions were prepared in double distilled water by weighing and expressed in molal concentrations. Chemical structures of dyes and surfactants are shown in Fig. 1.

3.2. Potentiometric method

Potentiometric measurements, based on the use of DTA- and CTA-selective membrane electrodes, were carried out in the following electrode cell:

$$\begin{aligned}&\mathrm{Ag}\,|\,\mathrm{AgCl}\,|\,\text{reference solution}:1\times10^{-4}\ \mathrm{mol/kg\ DTA(CTA)}\\&\quad+0.1\ \mathrm{mol/kg\ NaCl,}\,|\,\text{polymer membrane}\,|\,\text{test solution}\\&\quad\|\,\mathrm{KCl(satd.)}\,|\,\mathrm{Hg_2Cl_2}\,|\,\mathrm{Hg.}\end{aligned}$$

Ion-selective membrane electrodes were prepared using a well-known method [32] and constructed in our laboratory. The potentiometric method used was also described in detail in our previous publications [21,28].

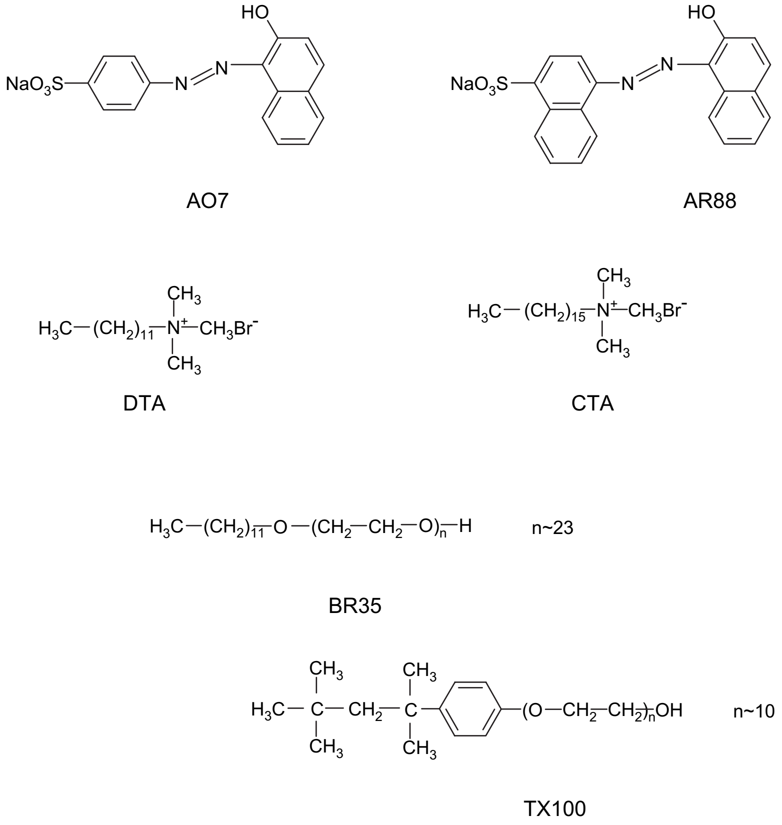

Fig. 1. Chemical structures of dyes and surfactants used.

The potentiometric measurements of e.m.f. (E) versus total concentration (m_S) of DTA or CTA were carried out in aqueous solutions with constant concentrations of 1.0×10^{-3}, 5.0×10^{-3}, 1.0×10^{-2} and 5.0×10^{-2} mol/kg TX100 or BR35 and 5.0×10^{-5}, 1.0×10^{-4}, 5.0×10^{-4} and 1.0×10^{-3} mol/kg AO7 or AR88 and in AO7/TX100, AR88/TX100, AR88/BR35 mixtures, in which the dye and surfactant concentrations mentioned above were used in combinations. All solutions contained 5.0×10^{-3} mol/kg NaBr. The temperatures used were 25 °C.

4. Results and discussion

Fig. 2 shows the plots of E versus log m_S of CTA in CTA/AO7/TX100 mixtures of different concentrations at 25 °C. As can be seen from the figure, the calibration curves which represent plots E versus m_S of CTA in water without AO7 and TX100, are linear over the concentration range of 2.0×10^{-6} to 1.3×10^{-4} mol/kg. In accordance with the Nernstian response [33], the slope of the linear plot was $+59.05 \pm 1.40$ mV/decade at 25 °C. All the titration curves, which represent plots of E versus log m_S of CTA obtained in the presence of AO7 and TX100, deviate from linearity over the whole concentration range measured. Since, this indicates that at any measured concentration of CTA the concentration of free surfactant cations, which can be detected by the CTA-selective electrode, is lower than the total concentration, m_S. The electrode is not sensitive to CTA bounded in dye–surfactant and surfactant–surfactant complexes.

Calibration curve was obtained below the c.m.c. of CTA, where linear behaviour is observed at any E measured value, the total CTA concentration, m_S, was got from the titration curve and the corresponding concentration, $m_{S,F}$ of free CTA cations from the calibration curve. The concentration of CTA cations from which the complexes were formed is equal to $m_S - m_{S,F}$. The same calculations were made for CTA in CTA/AR88/TX100 mixtures and for DTA in DTA/AR88, DTA/TX100, DTA/BR35, DTA/AR88/TX100, DTA/AR88/BR35 mixtures.

Since concentrations of free and bound CTA or DTA cations as a function of the total concentrations of CTA, DTA, AR88, AO7, TX100 and BR35 are obtained as a result of the potentiometric measurements, the degree of binding, β_B, of CTA and DTA to AR88 and AO7 in the absence and in the presence of nonionic surfactant can be calculated from Eqs. (4) and (7), and the degree of binding, β_C, of CTA and DTA to TX100 and BR35 from Eq. (8). In this treatment, it is assumed that cations of DTA and CTA are ligand A, anions of AR88 and AO7 are the central group B, and micelles of TX100 and BR35 are the central group C. According to this, the concentration m_C in Eq. (8) stands for the concentration of the TX100 and BR35 micelles and equals to:

$$m_C = \frac{m_N - \text{c.m.c.}}{\nu} \tag{12}$$

where m_N represents the stoichiometric concentration of nonionic surfactant and ν, its micellar aggregation number. In the literature, ν is equal to 136 for TX100 [34] and 40 for BR35 [35]. Some of the typical binding isotherms are shown in Figs. 3–5.

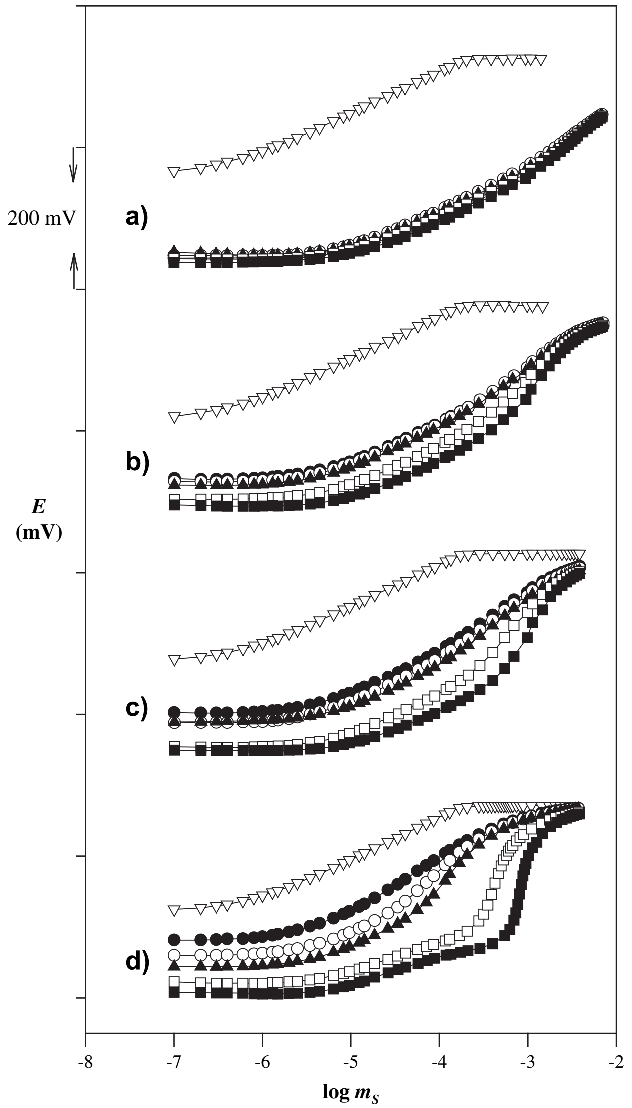

Fig. 2. Plots of e.m.f., E, of the cell versus the logarithm of the molal concentration, log m_S, of CTA in TX100 and AO7 mixtures of different concentrations at 25 °C. m_N of TX100: (a) 5.0×10^{-2} mol/kg; (b) 1.0×10^{-2} mol/kg; (c) 5.0×10^{-3} mol/kg; (d) 1.0×10^{-3} mol/kg. −▽−▽−, calibration curve; −●−●−, TX100; −○−○−, TX100 and 5.0×10^{-5} mol/kg AO7; −▲−▲−, TX100 and 1.0×10^{-4} mol/kg AO7; −□−□−, TX100 and 5.0×10^{-4} mol/kg AO7; −■−■−, TX100 and 1.0×10^{-3} mol/kg AO7.

The shapes of adsorption isotherms show that the degree of binding of cationic surfactant to anionic dye in a binary mixture differs considerably from the one obtained in the presence of nonionic surfactant under the same measuring conditions. Comparing the curves in Figs. 3–5 it can be established that they differ from one another in shape for different systems. Three different stages can be determined for the adsorption isotherm of binding surfactant cation to dye anion in binary mixture (Fig. 3). The early stage where the values of β_B increase progressively with the increase in the $m_{S,F}$ concentration, the middle stage where the values of β_B slightly change

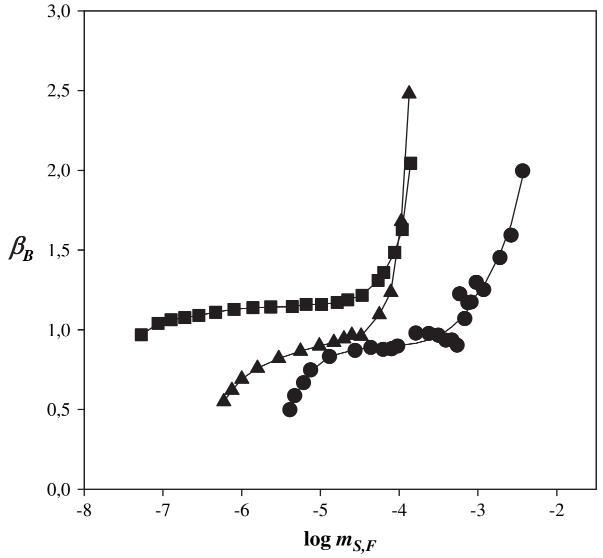

Fig. 3. Binding isotherms of CTA and DTA cations to AR88 and AO7 anions in binary mixtures at 25 °C. CTA: −■−■−, 1.0×10^{-4} mol/kg AR88; −▲−▲−, 1.0×10^{-4} mol/kg AO7. DTA: −●−●−, 1.0×10^{-4} mol/kg AR88.

with the increase in the $m_{S,F}$ concentration, and the final stage where the values of β_B start increasing dramatically with the increase in the $m_{S,F}$ concentration. In contrast to the values of β_B, the adsorption isotherms of binding surfactant cation to the micelle of nonionic surfactant are in constant increase with the increase in concentration of free surfactant ions in the solution (Fig. 4). Fig. 5 also shows that the adsorption isotherms of binding surfactant cation to dye anion in the presence of nonionic surfactant are more similar in shape to those obtained for the surfactant−surfactant interactions than to those obtained for the surfactant−dye interactions in binary mixtures. However, as far as values are concerned they are much lower.

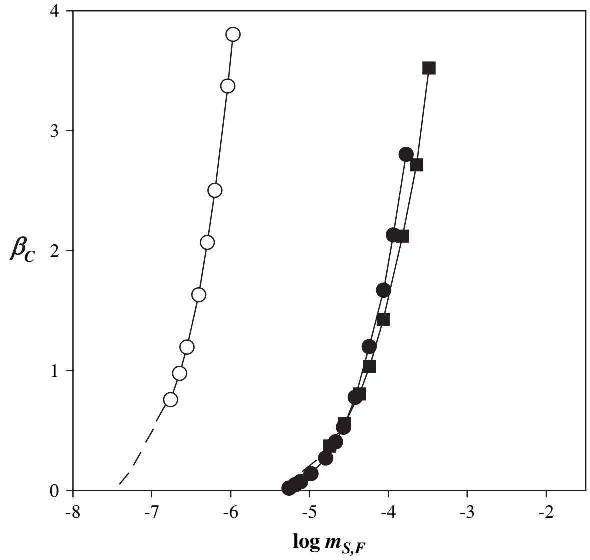

Fig. 4. Binding isotherms of CTA and DTA cations to TX100 and BR35 micelles in binary mixtures at 25 °C. CTA: −○−○−, 5.0×10^{-3} mol/kg TX100, DTA: −●−●−, 5.0×10^{-3} mol/kg TX100; −■−■−, 5.0×10^{-3} mol/kg BR35.

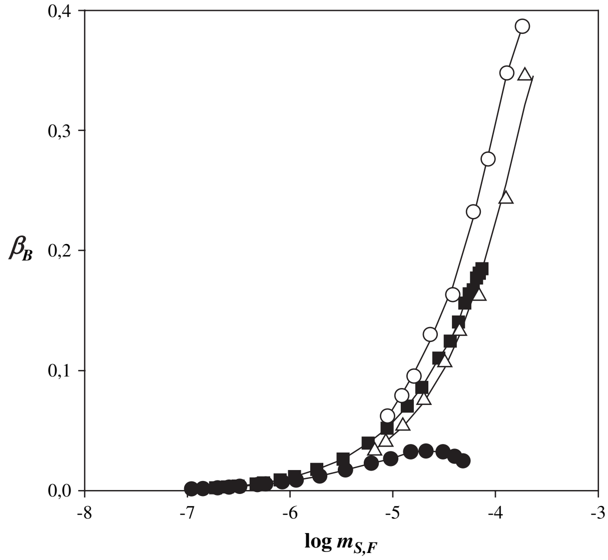

Fig. 5. Binding isotherms of CTA and DTA cations to AR88 and AO7 anions in TX100 or BR35 solutions at 25 °C. CTA: −●−●−, 5.0×10^{-3} mol/kg TX100 and 1.0×10^{-4} mol/kg AR88; −■−■−, 5.0×10^{-3} mol/kg TX100 and 1.0×10^{-4} mol/kg AO7. DTA: −○−○−, 5.0×10^{-3} mol/kg TX100 and 1.0×10^{-4} mol/kg AR88; −△−△−, 5.0×10^{-3} mol/kg BR35 and 1.0×10^{-4} mol/kg AR88.

As it is assumed in the theoretical model used [29], DTA and CTA binding process increases progressively with increased concentration, and the equilibrium constants K_1 for complex formation between DTA and AR88, CTA and AR88, and CTA and AO7, and κ_1 for complex formation between DTA and TX100, CTA and TX100, and DTA and BR35 (equilibrium 1) are determined from Eq. (10). Some of the typical plots of $\beta_B/m_{S,F}$ versus $m_{S,F}$ are shown in Fig. 6. Furthermore, from the values of K_1 and κ_1 the standard free energy change for complex formation is calculated using Eq. (11). The results are collected in Tables 1−3.

The results show that the strength of dye−surfactant interactions and the stability of complex formed, which in accordance with Eq. (11) increase with the increase in K_1 or κ_1 value and consequently with the decrease in ΔG_1^o value, increase with the increase in hydrophobicity of the surfactant and the dye (Fig. 7). In accordance with this, the ΔG_1^o values are the lowest in the case of interactions between CTA and AR88 whose hydrophobic groups are larger than those of DTA and AO7. Since the difference in ΔG_1^o values obtained for the CTA−AR88 and DTA−AR88 interactions is much higher than that between CTA−AO7 and CTA−AR88 it can be established that the extension of the hydrophobic chain of the surfactant by four C atoms has a greater influence on the increase of the strength of the interactions than the addition of the aromatic ring in the structure of the dye. The results are in keeping with the results obtained for the interactions between the dyes AR88 and AO7 and the surfactants dodecylpyridinium chloride, cetylpyridinium chloride and CTA which were established potentiometrically and spectrophotometrically [16,18,21].

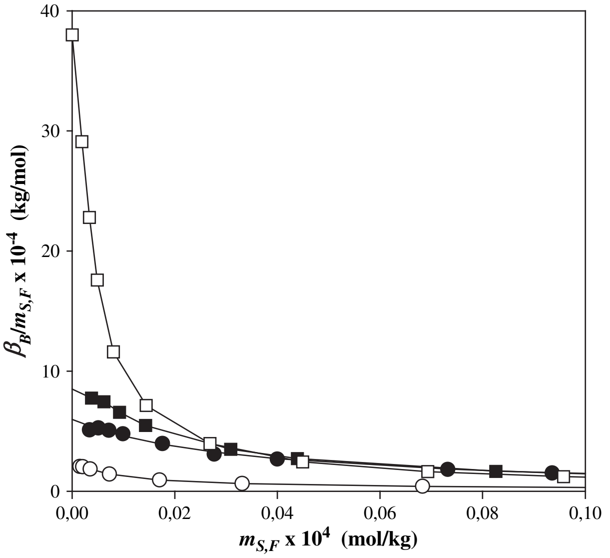

Fig. 6. Plots of values of $\beta_B/m_{S,F}$ versus the CTA free cation concentration $m_{S,F}$, obtained in AO7/TX100 mixtures of different concentrations at 25 °C. −○−○−, 5.0×10^{-3} mol/kg TX100 and 5.0×10^{-4} mol/kg AO7; −●−●−, 1.0×10^{-3} mol/kg TX100 and 5.0×10^{-5} mol/kg AO7; −■−■−, 1.0×10^{-3} mol/kg TX100 and 1.0×10^{-4} mol/kg AO7; −□−□−, 1.0×10^{-3} mol/kg TX100 and 5.0×10^{-4} mol/kg AO7.

The increase in the hydrophobicity of cation surfactant results in a considerable increase of the binding strength of the surfactant to the micelle of the nonionic surfactant (Fig. 8). Therefore, the $-\Delta G_1^o$ values for the formation of the CTA−TX100 complex are more than 10 kJ/mol higher than the values for the formation of the DTA−TX100 complex. The influence of the nonionic surfactant structure on the strength of the interactions is considerably less expressed than the influence of the cationic surfactant structure. Fig. 8 shows that the ΔG_1^o values for the binding of surfactant DTA to surfactants TX100 and BR35 are almost the same. Since the nonionic surfactants differ from one another in HLB values as well as in aggregation number, the results lead to the conclusion that the micelles of the nonionic surfactants, regardless of

Table 1
Association constant, K_1, and the standard free energy change, ΔG_1^o, of DTA−AR88, CTA−AR88 and CTA−AO7 complex formation at 25 °C

Surfactant	Dye	m_D (mol/kg)	$K_1 \times 10^{-5}$ (kg/mol)	ΔG_1^o (kJ/mol)
DTA[a]	AR88	5×10^{-5}	0.8	−28.0
		1×10^{-4}	1.3	−29.2
		5×10^{-4}	2.4	−30.7
		1×10^{-3}	3.0	−31.2
CTA	AR88	5×10^{-5}	125.0	−40.5
		1×10^{-4}	300.0	−42.7
		5×10^{-4}	500.0	−43.9
		1×10^{-3}	600.0	−44.4
	AO7	5×10^{-5}	6.5	−33.2
		1×10^{-4}	13.0	−34.9
		5×10^{-4}	19.0	−35.8
		1×10^{-3}	23.0	−36.3

[a] Results from Ref. [27].

Table 2
Association constant, κ_1, and the standard free energy change, ΔG_1^o, of DTA−BR35 and CTA−TX100 complex formation at 25 °C

Cationic surfactant	Nonionic surfactant	m_N (mol/kg)	$\kappa_1 \times 10^{-4}$ (kg/mol)	ΔG_1^o (kJ/mol)
DTA	TX100[a]	5×10^{-3}	2.3	−24.9
		1×10^{-2}	3.0	−25.6
		5×10^{-2}	3.7	−26.1
	BR35	5×10^{-3}	2.2	−24.8
		1×10^{-2}	2.3	−24.9
		5×10^{-2}	2.5	−25.1
CTA	TX100	1×10^{-3}	280.0	−36.8
		5×10^{-3}	450.0	−37.9
		1×10^{-2}	530.0	−38.4
		5×10^{-2}	460.0	−38.0

[a] Results from Ref. [27].

Table 3
Association constant, K_1, and the standard free energy change, ΔG_1^o, of DTA−AR88 complex formation in the presence of TX100 or BR35 and for CTA−AR88 and CTA−AO7 complex formation in the presence of TX100 at 25 °C

Cationic surfactant	Dye	Nonionic surfactant	m_N (mol/kg)	m_D (mol/kg)	$K_1 \times 10^{-3}$ (kg/mol)	ΔG_1^o (kJ/mol)
DTA	AR88	TX100[a]	5×10^{-3}	1×10^{-4}	7.1	−22.0
			1×10^{-2}	1×10^{-4}	4.2	−20.7
			5×10^{-2}	1×10^{-4}	1.6	−18.3
		BR35	5×10^{-3}	1×10^{-4}	5.5	−21.3
			1×10^{-2}	1×10^{-4}	3.3	−20.1
			5×10^{-2}	1×10^{-4}	0.6	−15.8
CTA	AR88	TX100	1×10^{-3}	5×10^{-5}	150.0	−29.5
				1×10^{-4}	350.0	−31.6
				5×10^{-4}	730.0	−33.4
				1×10^{-3}	1300.0	−34.9
			5×10^{-3}	5×10^{-5}	11.0	−23.0
				1×10^{-4}	12.0	−23.3
				5×10^{-4}	27.0	−25.3
				1×10^{-3}	68.0	−27.6
			1×10^{-2}	5×10^{-5}	5.7	−21.4
				1×10^{-4}	5.1	−21.1
				5×10^{-4}	8.1	−22.3
				1×10^{-3}	11.6	−23.2
			5×10^{-2}	5×10^{-5}	2.9	−19.7
				1×10^{-4}	0.9	−17.0
				5×10^{-4}	0.8	−16.6
				1×10^{-3}	1.4	−18.0
	AO7	TX100	1×10^{-3}	5×10^{-5}	58.0	−27.2
				1×10^{-4}	88.0	−28.2
				5×10^{-4}	380.0	−31.8
				1×10^{-3}	680.0	−33.3
			5×10^{-3}	5×10^{-5}	11.5	−23.2
				1×10^{-4}	12.5	−23.4
				5×10^{-4}	23.0	−24.9
				1×10^{-3}	45.0	−26.5
			1×10^{-2}	5×10^{-5}	2.1	−18.9
				1×10^{-4}	3.2	−20.0
				5×10^{-4}	5.5	−21.3
				1×10^{-3}	8.2	−22.3
			5×10^{-2}	5×10^{-5}	–	–
				1×10^{-4}	0.7	−16.2
				5×10^{-4}	0.6	−16.0
				1×10^{-3}	0.8	−16.5

[a] Results from Ref. [27].

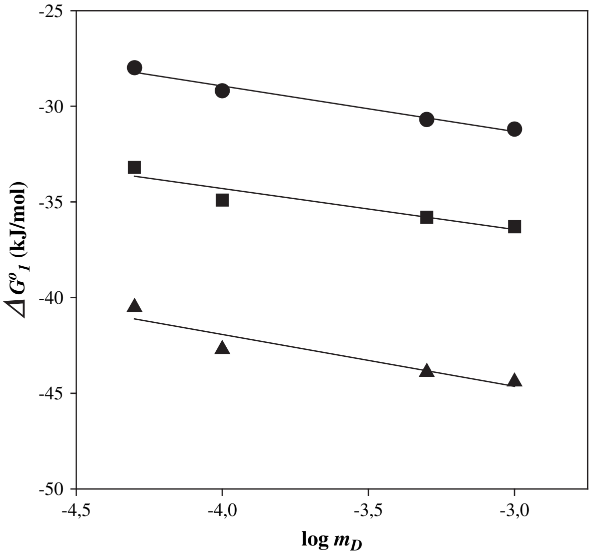

Fig. 7. Plots of ΔG_1^{o} versus the logarithm of dye concentration, log m_{D}, for the first step of the cationic surfactant–anionic dye complex formation at 25 °C. −●−●−, DTA–AR88; −■−■−, CTA–AO7; −▲−▲−, CTA–AR88.

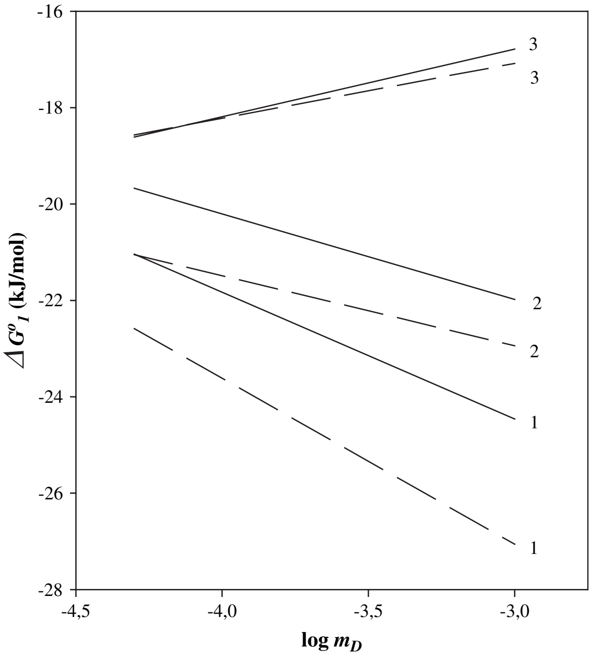

Fig. 9. Plots of ΔG_1^{o} versus the logarithm of dye concentration, log m_{D}, for the first step of the anionic dye–cationic surfactant complex formation in the presence of TX100 of different concentrations at 25 °C. —, DTA–AR88 (results from Ref. [27]), − −, CTA–AR88. m_{N} of TX100: 1 − 5.0×10^{-3} mol/kg, 2 − 1.0×10^{-2} mol/kg, 3 − 5.0×10^{-2} mol/kg.

their size and the ratio between the hydrophilic and hydrophobic groups, create a similar environment for the cationic surfactant binding in binary mixtures.

In ternary mixtures, the results presented in Figs. 9–11 show that the influence of the dye and the cationic surfactant structure on the strength of the dye–surfactant interactions in the presence of the nonionic surfactant TX100 is very similar to the one in binary mixtures. The strength of binding DTA and CTA surfactants to the AR88 and AO7 dyes is directly dependent on their hydrophobicity. Simultaneously, it was determined for all the studied systems that the tendency to form DTA–AR88, CTA–AR88 and CTA–AO7 complexes increases with the increase in the concentration of the AR88 or AO7 dye in a TX100 surfactant solution of the lowest concentration and that the increase in the TX100 surfactant

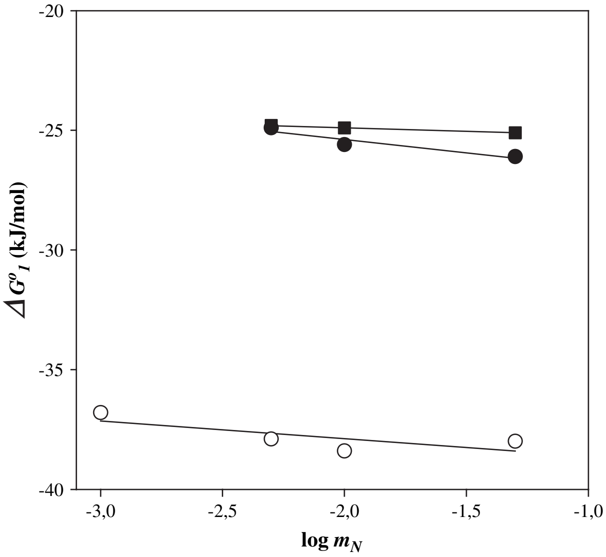

Fig. 8. Plots of ΔG_1^{o} versus the logarithm of nonionic surfactant concentration, log m_{N}, for the first step of the cationic surfactant–nonionic surfactant complex formation at 25 °C. −●−●−, DTA–TX100; −■−■−, DTA–BR35; −○−○−, CTA–TX100.

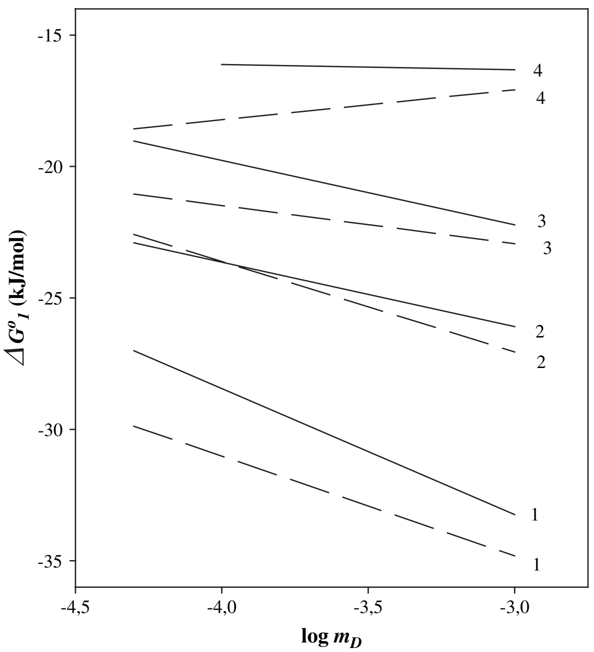

Fig. 10. Plots of ΔG_1^{o} versus the logarithm of dye concentration, log m_{D}, for the first step of the anionic dye–cationic surfactant complex formation in the presence of TX100 of different concentrations at 25 °C. —, CTA–AO7, − − CTA–AR88. m_{N} of TX100: 1 − 1.0×10^{-3} mol/kg, 2 − 5.0×10^{-3} mol/kg, 3 − 1.0×10^{-2} mol/kg, 4 − 5.0×10^{-2} mol/kg.

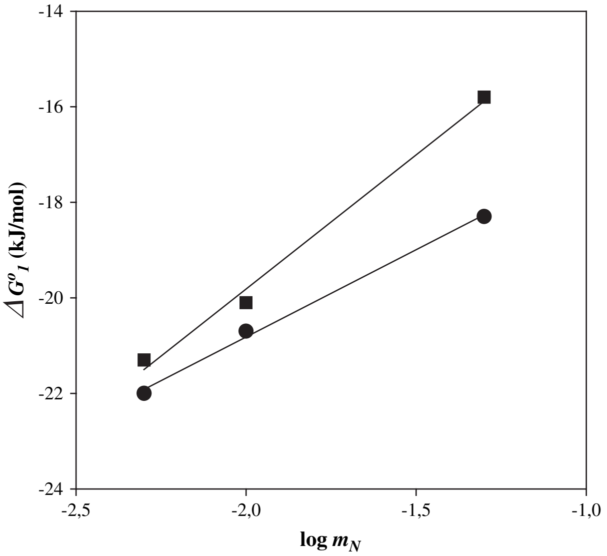

Fig. 11. Plots of ΔG^o_1 versus the logarithm of nonionic surfactant concentration, log m_N, for the first step of DTA–AR88 complex formation in the presence of nonionic surfactant at 25 °C. −●−●−, TX100; −■−■−, BR35.

concentration causes a decrease in the tendency to form complexes in spite of the increase in the concentration of AR88 or AO7 dye.

Fig. 9 shows that the strength of the CTA–AR88 interactions of all the studied TX100 concentrations is higher than that of DTA–AR88 which is in accordance with the results obtained in binary mixtures (Fig. 7). The presence of the TX100 surfactant influences the decrease in the difference in strength of the CTA–AR88 and DTA–AR88 interactions. The difference, which is most noticeable at the lowest TX100 concentration in the ternary mixtures, decreases with the increase in the TX100 concentration.

The strength of the interactions between the cationic surfactant and the anionic dye increases with the increase in the hydrophobicity of the dye (Fig. 10) even in the presence of the nonionic surfactant. The results show that the binding of the CTA surfactant to the AR88 dye is stronger than that to the AO7 dye regardless of whether it is performed in the absence or presence of the TX100 surfactant.

Fig. 11 shows that the strength of interactions between the DTA surfactant and the AR88 dye decreases with increased concentration of the nonionic surfactant, regardless of its structure. The decrease in the strength of the interactions with increasing concentration of the nonionic surfactant is slightly lower in the presence of TX100 than in the presence of BR35, from which it can be established that the DTA–AR88 interactions in the surfactant TX100 solution, especially with high concentrations of TX100, are stronger than in the surfactant BR35 solutions. This means that the structure of the nonionic surfactant influences the strength of the interactions between the cationic surfactant and the anionic dye. By comparing the chemical formulae of the TX100 and BR35 nonionic surfactants (Fig. 1), it can be seen that they differ from each other in the hydrophobic and hydrophilic groups. BR35 includes a straight-chain hydrophobic group and TX100, a branched one. The hydrophilic polyoxyethylene group of BR35 is much longer than that of TX100. These structural differences are directly reflected in the HLB value, which is lower for TX100 (13.5) than for BR35 (16.9). The comparison of the structure of the nonionic surfactants also shows that a higher HLB value of the BR35 surfactant derives primarily from the larger polyoxyethylene group in comparison with the TX100 surfactant, which has a polyoxyethylene group approximately half as long. The larger the polyoxyethylene group, the larger the partial negative charge in the oxygen bridges, allowing stronger charge transfer interactions between the cations of the DTA surfactant and the micelles of the BR35 nonionic surfactant in comparison with TX100. Since the attractive forces between DTA and the nonionic micelle create a counterbalancing mechanism against DTA–AR88 attractive forces, stronger interactions between the cationic and nonionic surfactants promote a decrease in the strength of the interactions between the cationic surfactant and the anionic dye. This result is unexpected, since in two-component surfactant–surfactant systems, the strength of DTA–TX100 and DTA–BR35 interactions is very similar. However, it should be stressed that in this consideration we assume that a micelle of the nonionic surfactant represents a central group to which the surfactant cation could be bound. According to this, the concentration of micellized nonionic surfactant is divided by the micellar aggregation number, ν, of the nonionic surfactant to obtain the concentration of micelles (Eq. (12)). Surprisingly, the results change significantly if the molecule of nonionic surfactant, bound to the micelle, is taken as a reacting entity and the concentration of micellized nonionic surfactant on a monomeric basis is taken into the observation. In this case, the values of κ_1 are ν times lower than those obtained on the micellar basis. If the values of κ_1 in Table 2 are expressed on the monomolecular basis, the DTA–BR35 interactions with $\kappa_1 = 587 \pm 37$ kg/mol are more than double those of DTA–TX100 interactions with $\kappa_1 = 220 \pm 50$ kg/mol. These results may explain the lower value of K_1 for DTA–AR88 interactions in the presence of BR35 than in the presence of TX100 in ternary mixtures. Nevertheless, additional studies of the influence of the nonionic surfactant structure on the anionic dye–cationic surfactant interactions will be carried out to investigate the structural effects in greater detail.

5. Conclusions

The dye–surfactant and surfactant–surfactant interactions in binary and ternary mixtures are discussed on the basis of the results of the potentiometric measurements. In the studied systems, the chemical structure of the anionic dyes and the cationic and nonionic surfactants affects their intermolecular attractive forces. The influence of the hydrophobicity of the dye and the cationic surfactant on the strength of the dye–surfactant interactions in the presence of the nonionic surfactant TX100 is very similar to that in binary mixtures. In a ternary mixture, the structure of the hydrophobic and hydrophilic groups of a nonionic surfactant influences the interactions between the cationic surfactant and the anionic dye. To explain the influence of the HLB value and the micellar aggregation number of the nonionic surfactant on the dye–surfactant interactions more precisely, additional investigations into the intermolecular interactions in ternary mixtures are required.

Acknowledgements

This work was supported by the Ministry of High Education, Science and Technology of Slovenia.

References

[1] Shore J, editor. Auxiliaries. Colorants and auxiliaries: organic chemistry and application properties, vol. 2. Society of Dyers and Colourists; 1990. p. 423–33.

[2] Datyner A. Surfactants in textile processing. New York; Basel: Marcel Dekker Inc.; 1983. p. 77–105.

[3] Navarro A, Cegarra J, Valldeperas J, Jocic D. Influence of oxyethylenated alkylamines in the dyeing of polyamide 66 fibres. Dyes and Pigments 2006;69(1–2):40–4.

[4] Yang J. Interaction of surfactants and aminoindophenol dye. Journal of Colloid and Interface Science 2004;274(1):237–43.

[5] Oakes J, Dixon S. Adsorption of dyes to cotton and inhibition by surfactants, polymers and surfactant–polymer mixtures. Coloration Technology 2003;119(6):315–23.

[6] Simončič B, Kert M. Influence of the surface active agent structure and composition on dye–textile substrate interactions. Tekstilec 2002; 45(11/12):327–33.

[7] Kim IS, Kono K, Takagishi T. Dyeing polyester fibers with 1,4-diaminoantraquinone in the presence of dialkyldimethylammonium bromide. Textile Research Journal 1997;67(8):555–62.

[8] Riva A, Cegarra J, Prieto R. Sorption of nonionic auxiliary products by wool and its influence on dyeing with acid dyes. Journal of the Society of Dyers and Colourists 1996;112(4):114–6.

[9] Khan MN, Sarwar A. Study of dye–surfactant interaction: aggregation and dissolution of yellowish in *N*-dodecyl pyridinum chloride. Fluid Phase Equilibria 2006;239(2):166–71.

[10] Akbaş H, Kartal Ç. Conductometric studies of the interaction of C.I. Reactive Orange 16 with cationic alkyltrimethylammonium bromide surfactants. Dyes and Pigments 2007;72(3):383–6.

[11] Gögtürk S. Effect of hydrophobicity on micellar binding of carminic acid. Journal of Photochemistry and Photobiology A: Chemistry 2005;169(2):115–21.

[12] Ghoreishi SM, Nooshabadi MS. Electromotive force studies about some dyes–cationic surfactants interactions in aqueous solutions. Dyes and Pigments 2005;65(2):117–23.

[13] Behera PK, Mohapatra S, Patel S, Mishra BK. Dye–surfactant interaction: solubilization of styryl pyridinium dyes of varying alkyl chain in alfa-olefinic sulfonate and linear alkyl benzene sulfonate solutions. Journal of Photochemistry and Photobiology A: Chemistry 2005; 169(3):253–60.

[14] Pereira RV, Gehlen MH. Fluorescence of acridinic dyes in anionic surfactant solution. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 2005;61(13–14):2926–32.

[15] Bhowmik BB, Ganguly P. Photophysical studies of some dyes in aqueous solution of Triton X-100. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 2005;62(4–5):808–13.

[16] Forte Tavčer P. Interactions between some anionic dyes and cationic surfactants with different alkyl chain length studied by the method of continuous variations. Dyes and Pigments 2004;63(2):181–9.

[17] Oakes J, Gratton P. Solubilisation of dyes by surfactant micelles. Part 1: Molecular interactions of azo dyes with nonionic and anionic surfactants. Coloration Technology 2003;119(2):91–9.

[18] Bračko S, Špan J. Conductometric investigation of dye–surfactant ion pair formation in aqueous solution. Dyes and Pigments 2000;45(2): 97–102.

[19] Simončič B, Špan J. A study of dye–surfactant interactions. Part 3. Thermodynamics of the association of C.I. Acid Orange 7 and cetylpyridinium chloride in aqueous solutions. Dyes and Pigments 2000; 46(1):1–8.

[20] Simončič B, Kovač F. A study of dye–surfactant interactions. Part 2. The effect of purity of a commercial cationic azo dye on dye–surfactant complex formation. Dyes and Pigments 1998;40(1):1–9.

[21] Simončič B, Špan J. A study of dye–surfactant interactions. Part 1. Effect of chemical structure of acid dyes and surfactants on the complex formation. Dyes and Pigments 1998;36(1):1–14.

[22] Jocić D. Conductivity measurement – a simple method for determining dye/surfactant interaction. Textile Research Journal 1995;65(7): 409–16.

[23] Kartal Ç, Akbaş H. Study on the interaction of anionic dye–nonionic surfactants in a mixture of anionic and nonionic surfactants by absorption spectroscopy. Dyes and Pigments 2005;65(3):191–5.

[24] Oakes J, Gratton P, Dixon S. Solubilisation of dyes by surfactant micelles. Part 3. A spectroscopic study of azo dyes in surfactant solutions. Coloration Technology 2003;119(5):301–6.

[25] Bhattacharya SC, Das HT, Moulik SP. Quenching of fluorescence of 2-anthracene sulphonate by cetylpyridinium chloride in micellar solutions of Tweens, Triton X-100, sodium dedecylsulphate (SDS) and cetyltrimethylammonium bromide (CTAB). Journal of Photochemistry and Photobiology A: Chemistry 1993;71(3):257–62.

[26] Uchiyama H, Tokuoka Y, Abe M, Ogino K. Solubilization of oil-soluble azo dye by anionic–nonionic mixed surfactants in aqueous solution, II. Journal of Colloid and Interface Science 1989;132(1):88–93.

[27] Simončič B, Kert M. Thermodynamics of anionic dye–cationic surfactant interactions in cationic–nonionic surfactant mixtures in comparison with binary systems. Dyes and Pigments 2006;71(1):43–53.

[28] Simončič B, Kert M. A study of anionic dye–cationic surfactant interactions in mixtures of cationic and nonionic surfactants. Dyes and Pigments 2002;54(3):221–37.

[29] Rossotti FJC, Rossotti H. The determination of stability constants: and other equilibrium constants in solution. New York: McGraw-Hill Book Company; 1961.

[30] Klotz IM. Introduction to biomolecular energetics: including ligand–receptor interactions. Orlando: Academic Press; 1986.

[31] Moore WJ. Physical chemistry. London: Longman Scientific and Technical; 1972.

[32] Cutler SG, Meares P, Hall DG. Surfactant-sensitive polymeric membrane electrodes. Journal of Electroanalytical Chemistry 1977;85(1):145–61.

[33] Morf WE. The principles of ion-selective electrodes and of membrane transport. Budapest: Akademiai Kiado; 1981.

[34] Bhattacharya SC, Das H, Moulik SP. Visible and fluorescence spectral studies on the interaction of safranine T with surfactant micelles. Journal of Photochemistry and Photobiology A: Chemistry 1993; 74(2–3):239–45.

[35] Le Maire M, Champeil P, Møller JV. Interaction of membrane proteins and lipids with solubilizing detergents. Biochimica et Biophysica Acta – Biomembranes 2000;1508(1–2):86–111.