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The influence of nonionic surfactant structure on the thermodynamics of anionic dye–cationic surfactant interactions in ternary mixtures

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Abstract

Anionic dye–cationic surfactant interaction was measured in a solution of a nonionic surfactant with a concentration greater than the critical micelle concentration using potentiometry. Two azo dyes namely, C.I. Acid Red 88 and C.I. Acid Orange 7, the cationic surfactant dodecyltrimethylammonium bromide and seven nonionic surfactants were studied. The use of ion-selective membrane electrodes for potentiometric titrations and the theoretical model chosen enabled two constants to be established: (i) the association constant, K_1, for the first association step in the formation of a complex between the anionic dye and cationic surfactant in the solution of the nonionic surfactant and (ii) the association constant, κ_1, for the first association step in the formation of the cationic surfactant–micelle of the nonionic surfactant complex. The thermodynamic parameters ΔG_1^0, ΔH_1^0, and ΔS_1^0 for these two steps were determined. The tendency to form dye–cationic surfactant complexes in a micellar solution of the nonionic surfactant decreases as the hydrophile–lipophile balance of the nonionic surfactant increases. This finding is in contrast to that obtained for the interactions between cationic and nonionic surfactants under the same conditions. An increase in the hydrophile–lipophile balance of the nonionic surfactant also reduced the ΔH_1^0 and ΔS_1^0 values for complex formation; the formation of the dye–cationic surfactant complexes in ternary mixtures is an entropy-driven process, regardless of nonionic surfactant structure.

Keywords: Anionic dye; Cationic surfactant; Nonionic surfactant; Surfactant mixture; Thermodynamics; Potentiometry; Influence of the structure

1. Introduction

Mixtures of surfactants have a great technological significance in the dyeing of textiles because they assure more even dyeing of textile substrates. Usually, mixtures of surfactants are compounds of ionic and nonionic surfactants, where the concentration of ionic surfactants is lower than the critical micelle concentration (c.m.c.) and the concentration of nonionic surfactants is higher than c.m.c. Ionic surfactants can be either dye-substantive or fibre-substantive [1]. A surfactant is dye-substantive when it carries a charge opposite to that of the dye and, as a result, complexes between surfactant ions and dye ions are formed. Complexes thus formed reduce dye adsorption at low temperatures and, therefore, enable uniform distribution of dye between and within fibres. However, the strength of complexes should not be so strong so that they are prohibited from falling apart at higher temperatures; otherwise, an insufficient bath exhaustion could occur. The addition of an ionic surfactant to the solution of an ionic dye with the opposite charge often leads to the formation of insoluble complexes, manifested as precipitates. Precipitation can be prevented by adding either an amount of the ionic surfactant exceeding the stoichiometric amount or by adding a nonionic surfactant at a concentration higher than c.m.c. to the solution. The first addition will result in a formation of complexes involving more ions of surfactant to each dye ion, whilst the second addition will cause solubilisation of formed complexes into the micelles of a nonionic surfactant.

Fibre-substantive surfactants carry the same charge as dye ions. They compete with dye ions for free fibre sites. If dye ions have greater affinity for fibres than surfactant ions, then dye ions will displace surfactant ions during dyeing and

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bind to the functional groups of fibres. Understanding both the working mechanism of surfactants as levelling agents and the influence of different factors (the structure of both the dye and the surfactant, the temperature of the system, the addition of nonionic surfactant into the mixture of dye and surfactant) on the strength of dye–surfactant interactions contributes to a more rational use of surfactants as levelling agents in dyeing.

The scientific literature contains a series of studies about dye–surfactant interactions [2–17] and surfactant–surfactant interactions [18–26] in binary mixtures. Studies of ionic dyes–ionic surfactants interactions in the presence of micelles of nonionic surfactant in the solutions are very rare [14–16,27–30]. Most of the ternary mixture studies are qualitative [27–29] and only a few of them are quantitative [14–16,30]. More recently, studies on the solubilisation of polycyclic hydrocarbons into mixed micelles composed of ionic and nonionic surfactants [31–35] have been gaining ground.

To date, no research into the influence of the hydrophile–lipophile balance (HLB) value of nonionic surfactants on anionic dye–cationic surfactant interactions has been published. Therefore, the influence of branching and the length of both the hydrophilic and hydrophobic groups of nonionic surfactants on the thermodynamics of anionic dye–cationic surfactant interactions has been studied by potentiometry within the framework of our research. Thermodynamic functions, the standard free energy change, the standard enthalpy change and the standard entropy change, for the first association step of the surfactant–surfactant complex formation in a binary mixture and the first association step of dye–surfactant complex formation in a ternary mixture, have been calculated and compared to those obtained in our previous research where the anionic dye–cationic surfactant interactions were studied in a binary mixture [15]. It is assumed that the presence of a nonionic surfactant with a concentration higher than c.m.c. in the solution of an anionic dye and a cationic surfactant influences the strength of the anionic dye–cationic surfactant interactions.

2. Experimental

2.1. Materials

Two anionic dyes, C.I. Acid Red 88 (AR88) and C.I. Acid Orange 7 (AO7), cationic surfactant *N*-dodecyltrimethylammonium bromide (DTAB), and seven nonionic surfactants of different structures – Brij 30 (BR30), Brij 35 (BR35), Brij 56 (BR56), Brij 58 (BR58), Brij 700 (BR700), Tween 20 (TW20) and Triton X-100 (TX100) – were used in this research. The anionic surfactant sodium dodecylsulphate (SDS), one of the components of a carrying complex, was used during the preparation of the ion-selective membrane electrode (ISE). Structural formulae of dyes and surfactants are given in Fig. 1. All substances are Aldrich Chemical Co. products. Anionic dyes AR88 and AO7 were purified via three recrystallizations from an *N*,*N*′-dimethylformamide/acetone mixture. Surfactants DTAB and SDS were purified by means of three recrystallizations from acetone. Nonionic surfactants, which were in the form of highly concentrated liquid, paste or granule, were not purified any further.

2.2. Potentiometric method

Potentiometric titrations were carried out by means of a galvanic cell and by using ISE, including the DTAB–SDS carrying complex, which assures that the membrane will be sensitive to free DTAB cations and free SDS anions. The composition of the electrode cell was as follows:

$\mathrm{Hg} \mid \mathrm{Hg_2Cl_2} \mid \mathrm{KCl_{(satd.)}} \parallel$ test solution | polymer membrane | 1.0×10^{-4} m DTAB in 0.1 m NaCl (inner reference solution) | AgCl | Ag

ISE was created by our lab following previously published procedures [36]. Measurements of e.m.f., E, versus the total concentration, m_S, of DTAB were carried out in the aqueous solutions of nonionic surfactants BR30, BR35, BR56, BR58, BR700, TW20 and TX100, mixtures of AR88 dye and the above mentioned nonionic surfactants, and mixtures of AO7 dye and nonionic surfactants BR56, BR58 and BR700. The concentration of nonionic surfactants was 5.0×10^{-3} mol/kg (a concentration higher than c.m.c.) and the concentration of dyes was 1.0×10^{-4} mol/kg in all the studied solutions. All solutions were prepared in double distilled water, containing 5.0×10^{-3} mol/kg NaBr. Since solutions were prepared by weighing, the concentrations are expressed in molal concentrations. Measurements of E versus the logarithm of the molal concentration, $\log m_S$, of DTAB were carried out at pH 6 at four different temperatures, i.e., 15, 25, 35 and 45 °C.

2.3. Spectrophotometry

The visible absorption spectra of dye–nonionic surfactant solutions were recorded at 25 °C on a Varian Cary 1E UV–Visible Spectrophotometer using 1 cm cells. The dye concentrations were 5.0×10^{-5} mol/kg for both AR88 and AO7. The surfactant concentrations were 5.0×10^{-3} mol/kg for nonionic surfactants BR56 and BR700, and 1.0×10^{-4} and 1.0×10^{-3} mol/kg for the cationic surfactant DTAB.

3. Results and discussion

Figs. 2 and 3 show plots of E versus $\log m_S$ of DTAB in 5.0×10^{-3} m solutions of nonionic surfactants BR30, BR56 and BR700 at 15, 25, 35 and 45 °C, a mixture of 5.0×10^{-3} m BR56 and 1.0×10^{-4} m AO7, and a mixture of BR56–AR88 of the same concentrations at 25 °C. It can be seen from both the figures that calibration curves, obtained at a titration of 5.0×10^{-3} m aqueous solution of NaBr with surfactant DTAB, are linear over the concentration range of 8.0×10^{-6} to 7.0×10^{-3} mol/kg. In compliance with the Nernstian response [37], the slope of a linear plot was +56.7 mV/decade at 15 °C, +58.6 mV/decade at 25 °C, +60.5 mV/decade at 35 °C and +62.4 mV/decade at 45 °C. It is evident from the figures that the calibration curves deviate from linearity at both very low and very high DTAB concentrations in the solution. Deviation at a very low DTAB

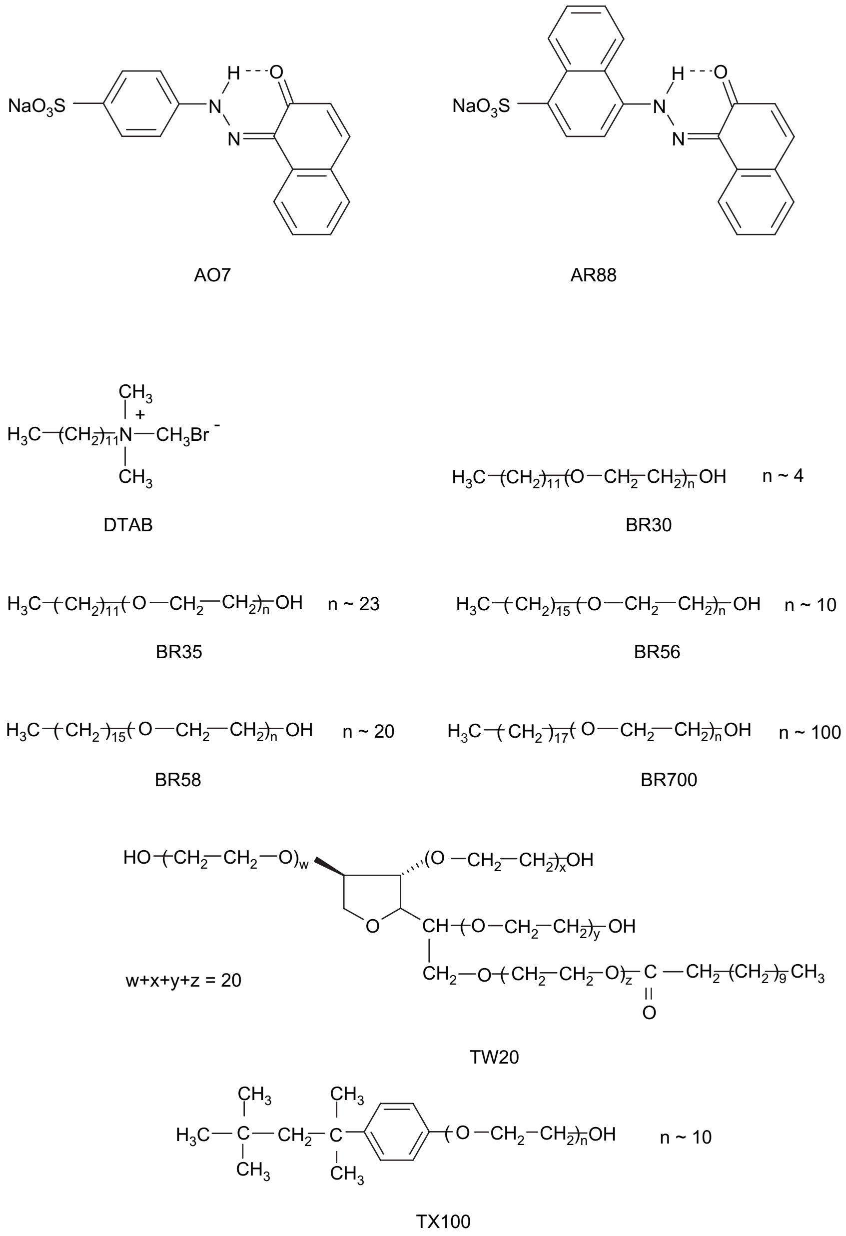

Fig. 1. Chemical structures of the used dyes and surfactants.

concentration is the consequence of the limit of detection of the ISE, while the deviation from linearity at DTAB concentrations higher than c.m.c. is the consequence of DTAB micellization. Figs. 2 and 3, representing titration curves of DTAB–BR30, DTAB–BR56, DTAB–BR700, DTAB–BR56–AO7 and DTAB–BR56–AR88 studied systems, show that the titration curves deviate from linearity over the whole concentration range measured. They lie below the calibration curve, which means that at any measured concentration of DTAB the concentration of free cations, $m_{S,F}$, of DTAB detected by ISE is lower than the total concentration, m_S. The reason for that was ascribed to the binding of DTAB cations to a nonionic surfactant and to an anionic dye, since DTAB ions bound into a complex are not perceived by the ISE.

Since calibration curves are linear over the studied concentration range, the total concentration, m_S, of DTAB at any measured value E could be read from the titration curve and the corresponding concentration, $m_{S,F}$, of free DTAB cations from the calibration curve. Accordingly, the concentration of DTAB cations bound to a nonionic surfactant or a dye, is equal to $(m_S - m_{S,F})$.

To be able to analyse the results obtained in the ternary mixture of a dye and two surfactants, it is necessary to consider all interactions which can occur between the species in such complex system, regardless of their tendency and strength. These interactions are presented in the following equilibrium reactions:

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

$$nN \leftrightarrow M \tag{2}$$

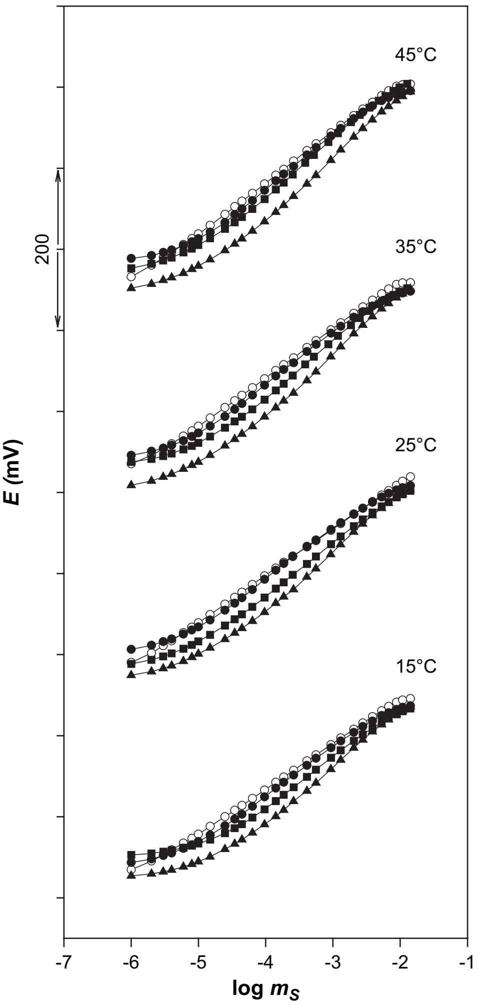

Fig. 2. Plots of e.m.f., E, of the cell versus the logarithm of the molal concentration, log m_S, of DTAB in 5.0×10^{-3} mol/kg solution of BR30, BR56 and BR700 at different temperatures. —○—: calibration curve, —●—: BR30, —■—: BR56, —▲—: BR700.

$$S^{+} + M \leftrightarrow MS^{+} \tag{3}$$

$$D^{-} + M \leftrightarrow MD^{-} \tag{4}$$

$$DS + M \leftrightarrow MSD \tag{5}$$

where S^{+} and D^{-} refer to the free DTAB cation and the free AR88 or AO7 anion, N and M are a molecule and a micelle of a nonionic surfactant, and DS, MS^{+}, MD^{-}, and MSD are complexes formed between different species in the mixture. Based on our spectrophotometric and potentiometric measurements, we can assume that the binding of the dyes AR88 and AO7, or of the surfactant DTAB, to free molecules of the studied nonionic surfactants is negligible in the studied systems.

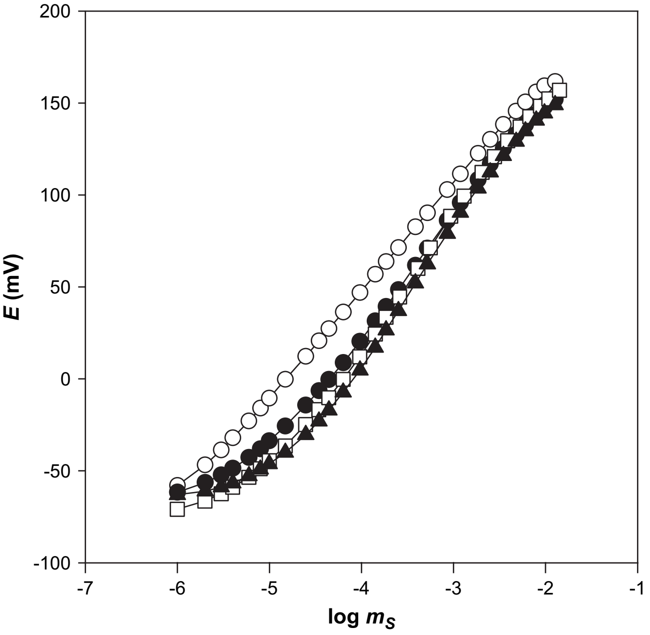

Fig. 3. Plots of e.m.f., E, of the cell versus the logarithm of the molal concentration, log m_S, of DTAB in mixtures of BR56–AO7 and BR56–AR88 at 25 °C. —○—: calibration curve, —●—: 5.0×10^{-3} mol/kg BR56, —□—: 5.0×10^{-3} mol/kg BR56 and 1.0×10^{-4} mol/kg AO7, —▲—: 5.0×10^{-3} mol/kg BR56 and 1.0×10^{-4} mol/kg AR88.

Although the existence of DS and MS^{+} complexes in the mixture could be determined potentiometrically, the results of our previous work [14] show that the potentiometric method is not suitable for studying the dye–nonionic surfactant micelle (MD^{-}) interactions. Therefore, to detect if MD^{-} complexes exist in the studied systems, the visible spectra of the AR88 and AO7 solutions were recorded in the presence of the studied nonionic surfactants. Fig. 4 shows the absorption spectrum of a 5.0×10^{-5} m AR88 solution with an

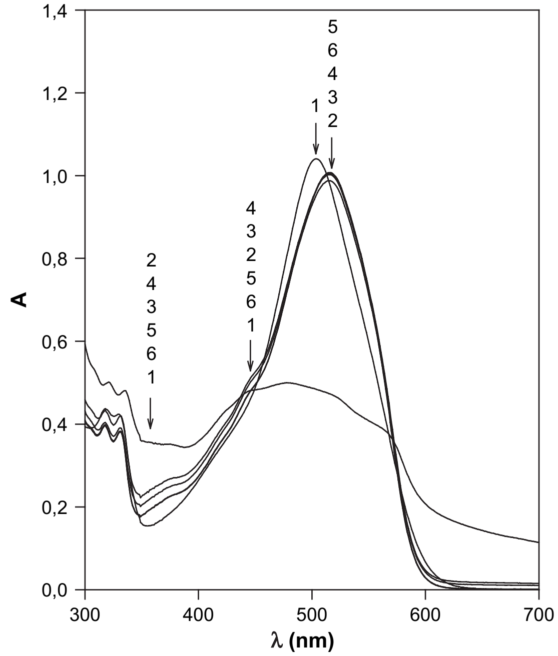

Fig. 4. The visible absorption spectra of AR88 with and without the presence of different surfactants in 5.0×10^{-3} mol/kg NaBr at 25 °C. Concentration of AR88: 5.0×10^{-5} mol/kg, concentration of DTAB: 1.0×10^{-4} mol/kg, concentration of BR56 and BR700: 5.0×10^{-3} mol/kg. (1) AR88, (2) AR88 + DTAB, (3) AR88 + BR56, (4) AR88 + BR56 + DTAB, (5) AR88 + BR700, (6) AR88 + BR700 + DTAB.

absorption maximum at 504 nm. All the dye spectra obtained in BR56 and BR700 solutions of the concentrations above the c.m.c. cause the decrease in absorbance with batochromic spectral shift at 516 nm. Furthermore, all spectra pass through two isosbestic points at 460 and 575 nm. All these support the formation of a 1:1 complex between AR88 and a Brij micelle in the absence of DTAB. The existing interactions between AO7 and the nonionic micelles of BR56 and BR700 are evident in Fig 5. One isosbestic point at 440 nm and the appearance of an absorption peak at 520 nm can be detected in all dye spectra obtained in BR56 and BR700 solutions, which confirms the dye–surfactant interactions. These spectra are very similar to those obtained in the TX100 solution and were presented in our previous work [14]. These results revealed that the structure of nonionic surfactants does not significantly affect the spectra. In this study, the influence of dye tautomerism on the dye–surfactant complex formation was not examined in greater detail. But with respect to Oakes et al. [10,11,29], it should be stressed that the azo–hydrazone tautomeric equilibrium of the dye strongly influences the location of the solubilised dye in a nonionic micelle. According to these studies, both AR88 and AO7 adopt the hydrazone tautomeric form in aqueous media. As water is replaced by less polar solvents, a progressive shift to shorter wavelengths indicates a shift in the azo–hydrazone tautomeric equilibrium more to the azo form [38]. This phenomenon was obtained for both the studied dyes, since the spectrum of AR88 in BR56 or BR700 solutions exhibits a peak at 440 nm (Fig. 4) and the spectrum of AO7 in BR56 or BR700 solutions exhibits a peak at 430 nm (Fig. 5). From the proportion of dye in the azo form, which may be estimated from the ratio of the peak intensity at 430 nm to that at 485 nm for AO7 and the ratio of the peak intensity at 440 nm to that at 504 nm for AR88 [38], it can be concluded that in the solution of nonionic surfactant, the azo character of both dyes is very small. This suggested that AR88 and AO7 are located in a more hydrophilic environment in the nonionic micelles.

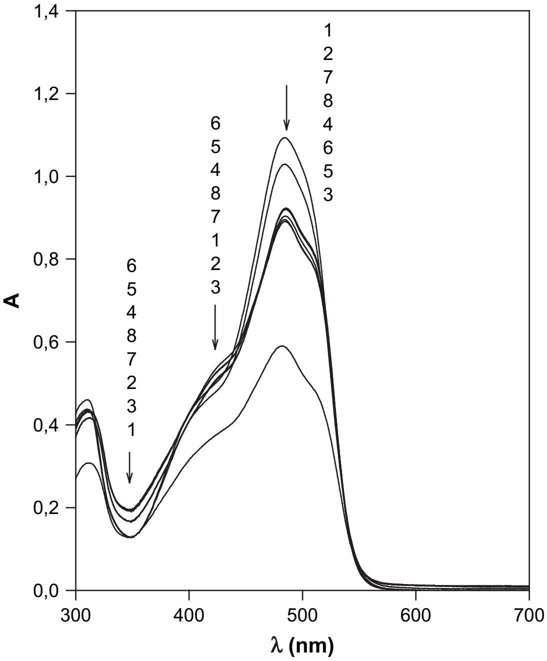

Fig. 5. The visible absorption spectra of AO7 with and without the presence of different surfactants in 5.0×10^{-3} mol/kg NaBr at 25 °C. Concentration of AO7: 5.0×10^{-5} mol/kg, concentration of DTAB: 1.0×10^{-4} mol/kg, concentration of DTAB1: 1.0×10^{-3} mol/kg, concentration of BR56 and BR700: 5.0×10^{-3} mol/kg. (1) AO7, (2) AO7 + DTAB, (3) AO7 + DTAB1, (4) AO7 + BR56, (5) AO7 + BR56 + DTAB, (6) AO7 + BR56 + DTAB1, (7) AO7 + BR700, (8) AO7 + BR700 + DTAB.

To discuss the formation of DS, MS$^+$ complexes in equilibrium, Eqs. (1) and (3), in a quantitative manner, it is necessary to introduce an appropriate theoretical model, taking into account all its assumptions and simplifications. According to our previous research [14–16], dye–surfactant and surfactant–surfactant interactions could be sufficiently described using the theoretical model by Rossotti and Rossotti [39], which is widely used for a large number of systems, especially those of diluted solutions. In this treatment, it is assumed that only monomolecular complexes with the general formula C_qL_p can be formed in diluted solutions. In a monomolecular complex CL_p, where $q = 1$ and $p = n$, C represents the central group to which n numbers of ligand L can be bound. In compliance with this model, the binding of the ligand to the central group can be illustrated in a set of multiple equilibria, describing the stepwise binding of the ligand to the central group:

$$\mathrm{L} + \mathrm{C} \overset{K_1}{\rightleftarrows} \mathrm{CL} \quad K_1 = \frac{m_{\mathrm{CL}}}{m_{\mathrm{L,F}} m_{\mathrm{C,F}}} \tag{6}$$

$$\mathrm{L} + \mathrm{CL} \overset{K_2}{\rightleftarrows} \mathrm{CL}_2 \quad K_2 = \frac{m_{\mathrm{CL}_2}}{m_{\mathrm{L,F}} m_{\mathrm{CL}}} \tag{7}$$

$$\mathrm{L} + \mathrm{CL}_{n-1} \overset{K_n}{\rightleftarrows} \mathrm{CL}_n \quad K_n = \frac{m_{\mathrm{CL}_n}}{m_{\mathrm{C,F}} m_{\mathrm{CL}_{n-1}}} \tag{8}$$

where CL, CL_2 and CL_n are complexes with a different number, n, of the bound ligand, L, and K_1, K_2, and K_n, are the corresponding stoichiometric equilibrium constants, and $m_{\mathrm{L,F}}$, and $m_{\mathrm{C,F}}$, are concentrations of free ions of the ligand or central group and m_{CL}, m_{CL_2} and $m_{\mathrm{CL}_{n-1}}$ are concentrations of the complexes.

In using the theoretical model for studying the formation of DS, MS$^+$ complexes, it was assumed that AR88 or AO7 anions and the molecule of a nonionic surfactant BR30, BR35, BR56, BR58, BR700, TW20 or TX100, bound to the micelle, represent the central group, while the DTAB cation represents the ligand. The average number of ligands, L, bound to the central group, C, can be expressed as a ligand number, β_{C}, and calculated from the following equation:

$$\beta_{\mathrm{C}} = \frac{m_{\mathrm{L,B}}}{m_{\mathrm{C}}} = \frac{m_{\mathrm{L}} - m_{\mathrm{L,F}}}{m_{\mathrm{C}}} \tag{9}$$

where $m_{\mathrm{L,B}}$ is the concentration of bound ions of the ligand, m_{L} is the total concentration of ligand, L, and m_{C} is the total concentration of a central group.

If the concentration of a ligand in Eq. (9) is expressed as a sum of the free ligand concentration and the concentration of ligands bound to the complex, where each mole of a complex includes n moles of bound ligand, then Eq. (9) can be expressed as:

$$\beta_{\mathrm{C}} = \frac{m_{\mathrm{CL}} + 2m_{\mathrm{CL_2}} + 3m_{\mathrm{CL_3}} + \ldots + nm_{\mathrm{CL}_n}}{m_{\mathrm{C,F}} + m_{\mathrm{CL}} + m_{\mathrm{CL_2}} + m_{\mathrm{CL_3}} + \ldots + m_{\mathrm{CL}_n}} \tag{10}$$

In compliance with equilibria Eqs. (6)–(8), the concentration of complexes in Eq. (10) can be expressed as a product between the equilibrium constant and the free ligand concentration. Therefore, Eq. (10) can be expressed as:

$$\beta_{\mathrm{C}} = \frac{K_1 m_{\mathrm{L,F}} + 2K_1K_2 m_{\mathrm{L,F}}^2 + 3K_1K_2K_3 m_{\mathrm{L,F}}^3 + \ldots + nK_n m_{\mathrm{L,F}}^n}{1 + K_1 m_{\mathrm{L,F}} + K_1K_2 m_{\mathrm{L,F}}^2 + K_1K_2K_3 m_{\mathrm{L,F}}^3 + \ldots + K_n m_{\mathrm{L,F}}^n} \tag{11}$$

In ternary mixtures, where two central groups are present, the surfactant can be bound on both of them simultaneously. In that case, the degree of binding of a ligand L to a central group C in the presence of a central group C′ can be calculated in the following manner:

$$\beta_{\mathrm{C}} = \frac{m_{\mathrm{L}} - m_{\mathrm{L,F}} - \beta_{\mathrm{C'}} m_{\mathrm{C'}}}{m_{\mathrm{C}}} \tag{12}$$

where the term $\beta_{\mathrm{C'}} m_{\mathrm{C'}}$ is equal to the concentration of a ligand bound to the central group C′. The degree of binding of a ligand L to the central group C′ can be calculated from the following equation:

$$\beta_{\mathrm{C'}} = \frac{m_{\mathrm{L}} - m_{\mathrm{L,F}}}{m_{\mathrm{C'}}} \tag{13}$$

Since the process of binding of ligand L to the central group C′ is identical to the binding of ligand L to the central group C, the degree of binding of ligand L to the central group C′ can, in accordance with equilibria Eqs. (6)–(8), be expressed as:

$$\beta_{\mathrm{C'}} = \frac{\kappa_1 m_{\mathrm{L,F}} + 2\kappa_1\kappa_2 m_{\mathrm{L,F}}^2 + 3\kappa_1\kappa_2\kappa_3 m_{\mathrm{L,F}}^3 + \ldots + n\kappa_n m_{\mathrm{L,F}}^n}{1 + \kappa_1 m_{\mathrm{L,F}} + \kappa_1\kappa_2 m_{\mathrm{L,F}}^2 + \kappa_1\kappa_2\kappa_3 m_{\mathrm{L,F}}^3 + \ldots + \kappa_n m_{\mathrm{L,F}}^n} \tag{14}$$

where $\kappa_{1,}\ \kappa_{2,}\ \kappa_3 \ldots \kappa_n$ are stoichiometric equilibrium constants of complex formation between the ligand L and the central group C′. If the molecule of a nonionic surfactant, N, bound to the micelle, M, represents a central group C′ in the studied systems, then the total concentration of the central group, $m_{\mathrm{C'}}$, is equal to: (m_{N} − c.m.c.), where m_{N} is the concentration of a nonionic surfactant.

The process of complex formation between a ligand and a central group can be graphically presented as binding isotherms, where the values of β_{C} and $\beta_{\mathrm{C'}}$ are shown versus the logarithm of the molal concentration of free ligand, log $m_{\mathrm{L,F}}$. In the case of systems where binding of ligand L to central groups C and C′ rises progressively with the increasing ligand L concentration, the stoichiometric equilibrium constant, K_1, for the CL complex formation and the stoichiometric equilibrium constant, κ_1, for C′L complex formation, can be calculated from the following equations:

$$\lim_{m_{\mathrm{L,F}} \to 0} \frac{\beta_{\mathrm{C}}}{m_{\mathrm{L,F}}} = K_1; \quad \lim_{m_{\mathrm{L,F}} \to 0} \frac{\beta_{\mathrm{C'}}}{m_{\mathrm{L,F}}} = \kappa_1 \tag{15}$$

According to Eq. (15), the values of K_1 and κ_1 can be obtained by an extrapolation of the curves of $\beta_{\mathrm{C}}/m_{\mathrm{L,F}}$ and $\beta_{\mathrm{C'}}/m_{\mathrm{L,F}}$ versus $m_{\mathrm{L,F}}$ to the zero free ligand concentration ($m_{\mathrm{L,F}} = 0$). In the systems studied, the values of κ_1 corresponding to MS^+ complex formation are presented in Table 1, and the values of K_1 corresponding to DS complex formation in the presence of micelles of a nonionic surfactant are presented in Table 2. From the values of K_1 and κ_1, obtained at different temperatures, the thermodynamic functions, the standard free energy change, ΔG_1^0, the standard enthalpy change, ΔH_1^0, and the standard entropy change, ΔS_1^0 for the first association step of DS and MS^+ complex formation are calculated from the following equations [40]:

$$\Delta G_1^0 = -RT \ln K_1; \quad \Delta G_1^0 = -RT \ln \kappa_1 \tag{16}$$

$$\frac{\mathrm{d} \ln K_1}{\mathrm{d}T} = \frac{\Delta H_1^0}{RT^2}; \quad \frac{\mathrm{d} \ln \kappa_1}{\mathrm{d}T} = \frac{\Delta H_1^0}{RT^2} \tag{17}$$

Table 1
Association constant, κ_1, and thermodynamic functions of MS^+ complex formation for different studied systems at different temperatures, T

Nonionic surfactant	HLB[b]	T (°C)	$\kappa_1 \times 10^{-2}$ (kg/mol)	ΔG_1^0 (kJ/mol)	ΔH_1^0 (kJ/mol)	ΔS_1^0 (J/mol K)
BR30	9	15	1.25	−11.6	−2.4	30.4
		25	0.75	−10.7		
		35	1.1	−12.0		
		45	1.0	−12.2		
BR35	17	15	4.15	−14.4	3.4	62.3
		25	4.25	−15.0		
		35	5.35	−16.1		
		45	4.45	−16.1		
BR56	12	15	3.25	−13.8	−6.4	26.9
		25	3.95	−14.8		
		35	4.0	−15.3		
		45	2.4	−14.5		
BR58	16	15	5.50	−15.1	−6.5	30.5
		25	6.95	−16.2		
		35	4.5	−15.6		
		45	4.75	−16.3		
BR700	18	15	9.30	−16.4	0.1	57.7
		25	10.0	−17.1		
		35	10.4	−17.8		
		45	9.2	−18.0		
TW20	16	15	3.5	−14.0	−2.5	40.3
		25	3.9	−14.8		
		35	3.45	−15.0		
		45	3.25	−15.3		
TX100[a]	13	15	1.32	−11.7	5.2	58.9
		25	1.69	−12.7		
		35	1.40	−12.7		
		45	1.76	−13.7		

Nonionic surfactant concentration, m_{N}, is 5.0×10^{-3} mol/kg.

[a] The results, calculated on micellar basis, have already been presented in Ref. [15].

[b] Values obtained from Sigma–Aldrich online catalogue.

Table 2
Association constant, K_1, and thermodynamic functions of DTAB–AR88 and DTAB–AO7 complex formation in the presence of a nonionic surfactant at different temperatures, T

Dye	Nonionic surfactant	T (°C)	$K_1 \times 10^{-3}$ (kg/mol)	ΔG_1^0 (kJ/mol)	ΔH_1^0 (kJ/mol)	ΔS_1^0 (J/mol K)
AR88	BR30	15	41.0	−25.4	9.2	121.5
		25	74.0	−27.8		
		35	55.0	−28.0		
		45	67.0	−29.4		
	BR35	15	8.0	−21.5	−12.1	32.5
		25	7.5	−22.1		
		35	3.6	−21.0		
		45	6.1	−23.0		
	BR56	15	11.0	−22.3	−4.7	60.1
		25	9.25	−22.6		
		35	6.0	−22.3		
		45	10.5	−24.5		
	BR58	15	9.0	−21.8	−6.0	54.3
		25	5.0	−21.1		
		35	13.0	−24.3		
		45	5.0	−22.5		
	BR700	15	4.0	−19.9	−0.4	68.6
		25	6.2	−21.6		
		35	3.2	−20.7		
		45	4.9	−22.5		
	TW20	15	5.5	−20.6	0.4	74.4
		25	10	−22.8		
		35	5.0	−21.8		
		45	7.0	−23.4		
	TX100[a]	15	8.5	−21.7	−0.3	73.5
		25	7.1	−22.0		
		35	7.0	−22.7		
		45	8.5	−23.9		
AO7	BR56	15	7.5	−21.4	−2.1	67.0
		25	7.7	−22.2		
		35	6.4	−22.4		
		45	7.3	−23.5		
	BR58	15	5.8	−20.7	−9.1	41.0
		25	5.4	−21.3		
		35	5.7	−22.1		
		45	3.8	−21.8		
	BR700	15	2.3	−18.5	2.4	73.0
		25	2.4	−19.3		
		35	3.2	−20.7		
		45	2.3	−20.5		

Dye concentration, m_D, is 1.0×10^{-4} mol/kg, and nonionic surfactant concentration, m_N, is 5.0×10^{-3} mol/kg.

[a] The results have already been published in Ref. [15].

$$\Delta S_1^0 = \frac{\Delta H_1^0 - \Delta G_1^0}{T} \tag{18}$$

According to van't Hoff Eq. (17), if ΔH_1^0 is assumed to be constant with temperature, it follows that:

$$\ln K_1 = -\frac{\Delta H_1^0}{RT} + \frac{\Delta S_1^0}{R}; \quad \ln \kappa_1 = -\frac{\Delta H_1^0}{RT} + \frac{\Delta S_1^0}{R} \tag{19}$$

Therefore, a plot of the natural logarithm of K_1 or κ_1 versus the reciprocal temperature gives a straight line. The slope of the line is equal to minus the standard enthalpy change divided by the gas constant, $-\Delta H_1^0/R$ and the intercept is equal to the standard entropy change divided by the gas constant, $\Delta S_1^0/R$. van't Hoff plots are presented in Fig. 6 and the calculated values of the thermodynamic functions are collected in Tables 1 and 2.

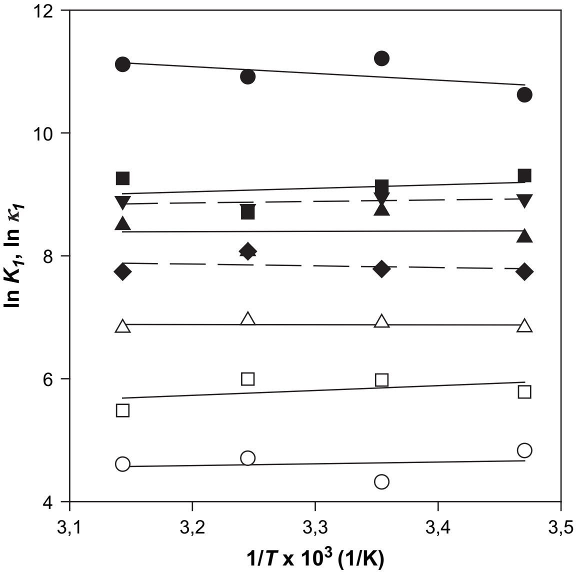

Fig 6. Plots of $\ln K_1$ and $\ln \kappa_1$ versus $1/T$ for DS complex formation in solutions of nonionic surfactants and for MS^+ complex formation in binary mixtures. —●—: DTAB–AR88 in BR30, —■—: DTAB–AR88 in BR56, —▲—: DTAB–AR88 in BR700, – –▼– –: DTAB–AO7 in BR56, – –◆ – –: DTAB–AO7 in BR700, —○—: DTAB–BR30, —□—: DTAB–BR56, —△—: DTAB–BR700.

It can be seen from Tables 1 and 2 that the values of κ_1 are much lower than the values of K_1. This means that the strength of interactions between a cationic surfactant and a molecule of a nonionic surfactant bound to the micelle was weaker than the strength of interactions between a cationic surfactant and an anionic dye in a solution of nonionic surfactant. In compliance with this observation, in all the studied solutions it was noticed that the values of ΔG_1^0 for DS complex formation are lower than those obtained for MS^+ complex formation.

The results presented in Table 1 show that the strength of MS^+ complex formation is strongly influenced by the structure of a nonionic surfactant, where the length and the shape of hydrophobic hydrocarbon (HC) chain and hydrophilic polyoxyethylene (POE) group affect the surfactant–surfactant interactions. Binding of DTAB to a nonionic surfactant was the strongest in the solution of BR700, which includes 100 POE units, and was the weakest in the solution of BR30 with 4 POE units. Furthermore, in the case of nonionic surfactants with HC chains of the same length, binding of DTAB was stronger to BR35 with 23 POE units than to BR30 with 4 POE units; it was also stronger to BR58 with 20 POE units than to BR56 with 10 POE units. These results reveal that the increase of POE units in the hydrophilic group of nonionic surfactant enhanced the MS^+ complex formation. On the other hand, the strength of interactions is also dependent on the branching of both hydrophilic and hydrophobic chains of a nonionic surfactant. Among nonionic surfactants with comparable hydrophobic chains, DTAB formed weaker interactions with TW20 consisting of a branched voluminous hydrophilic chain with 20 POE units than it did with BR35 consisting of a straight hydrophilic chain containing 23 POE units. Branching of the hydrophobic chain of a nonionic surfactant has an influence on the strength of MS^+ interactions that is very similar to that of the branching of a hydrophilic chain. With the same number of POE units, DTAB formed stronger interactions with BR56, containing a straight hydrophobic chain, than with TX100, whose hydrophobic group is branched. These results indicate that the branching of hydrophilic or hydrophobic groups of the nonionic surfactant hindered the binding of surfactant cation into the MS^+ complex. Consequently, the strength of MS^+ interactions increased in the following order: BR30 < TX100 < BR56 < TW20 < BR35 < BR58 < BR700. This sequence is not directly related with the HLB values of nonionic surfactants, which increase in the following order: BR30 < BR56 < TX100 < BR58 = TW20 < BR35 < BR700. However, a comparison of the results reveals that the strength of surfactant–surfactant interactions is generally connected to the HLB value of the nonionic surfactant, since it is weak in a solution of a nonionic surfactant with a low HLB value, and strongly increases in the presence of a nonionic surfactant with a high HLB value.

The results presented in Table 2 show that the strength of DS complex formation in the solution of a nonionic surfactant strongly depends on the structure of the nonionic surfactant and the dye. The lowest values of ΔG_1^0 for DS complex formation were noticed for the mixture consisting of DTAB, AR88, and BR30, indicating the strongest interactions, while the highest ΔG_1^0 values (and therefore the weakest interactions) were determined for the mixture of DTAB, AO7, and BR700. According to this, the strength of DTAB–AR88 interactions increased in the following order: BR700 < BR35 < TW20 < BR58 < TX100 < BR56 < BR30, and increased for DTAB–AO7 interactions in the following order: BR700 < BR58 < BR56. These results reveal that the strength of DS interactions was decreased by increasing the HLB value of a nonionic surfactant, which, surprisingly, correlates much better to the HLB value than that of MS^+ interactions. This phenomenon was obtained for both the studied dyes. In the case of the above order, it can be seen that the tendency for DTAB–AR88 complex formation was higher in the presence of BR30 than BR35, and complex formation was also higher in the presence of BR56 than BR58, which is just opposite to that observed for MS^+ interactions. The branching of a hydrophilic or hydrophobic chain of a nonionic surfactant had a weaker influence on the strength of DS interactions in comparison to MS^+ interactions in a binary mixture. It can also be seen from Table 2 that DTAB formed stronger interactions to AR88 than to AO7, irrespective of a nonionic surfactant structure. These results reveal that AR88, whose structure includes one more aromatic ring than AO7, formed stronger attractive interactions with DTAB. The same findings have been observed while studying CTA–AR88 and CTA–AO7 interaction strength in TX100 solution at 25 °C [16]. To conclude, the results presented in Tables 1 and 2 show that the increase of the strength of MS^+ interactions causes a reduction in the strength of DS interactions. In ternary mixtures, the stronger the binding of DTAB to the micelle of a nonionic surfactant the weaker the binding of DTAB to the dye anion, and vice versa (see also Fig. 6).

The values of ΔH_1^0 presented in Tables 1 and 2 are between +10 and −12 kJ/mol. These values are much higher than those of ΔH_1^0 for DTAB–AR88 complex formation in the absence of nonionic surfactants, which were equal to -42.0 ± 0.6 [15], indicating that the MS^+ as well as DS complex formation in solutions of nonionic surfactants was much less exothermic than that of DS complexes in a binary mixture. Furthermore, it should be stressed that by using the van't Hoff equation, the values of ΔH_1^0 and ΔS_1^0 were determined indirectly, which could have resulted in some experimental error. Irrespective of this, the results presented in Fig. 7 reveal that the HLB value of a nonionic surfactant significantly influenced the ΔH_1^0 value. While the increase of the HLB value caused the increase of ΔH_1^0 for MS^+ complex formation, it resulted in decreased ΔH_1^0 values for DS complex formation.

Tables 1 and 2 demonstrate that the values of ΔS_1^0 for both MS^+ and DS complex formations are high and positive compared to those obtained for the DTAB–AR88 binary mixture, whose values are low and negative [15]. The results presented in Fig. 8 reveal that the value of ΔS_1^0 increased with increasing HLB values of a nonionic surfactant in the MS^+ system, while it decreased in the DS system. Accordingly, the highest ΔS_1^0 value was obtained for DTAB–AR88 interactions in a solution of BR30, which was related to the lowest ΔS_1^0 value obtained for DTAB–BR30 interactions. The nature of interactions between DTAB surfactant and AR88 dye in the solution of BR30 is endothermic ($\Delta H_1^0 > 0$), with high positive values of ΔS_1^0, indicating that the DTAB–AR88 complex formation is an entropy-driven process. Taking our previous findings into consideration, we can conclude that for both MS^+ and DS complex formation, the stronger the interactions between species, the lower the ΔG_1^0 value and the higher the ΔH_1^0 and ΔS_1^0 values.

High positive values of ΔS_1^0 for DS complex formation in a solution of nonionic surfactants, which are much higher

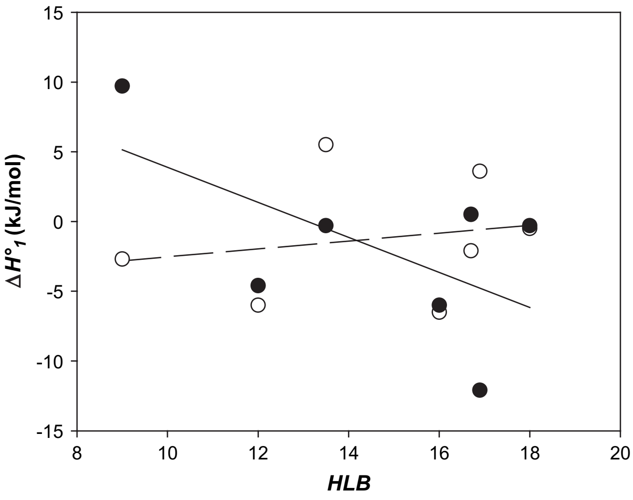

Fig 7. ΔH_1^0 for MS^+ complex formation (○) and for DS complex formation (●) versus the HLB values of nonionic surfactants. — — —: regression line through ○, ——: regression line through ●.

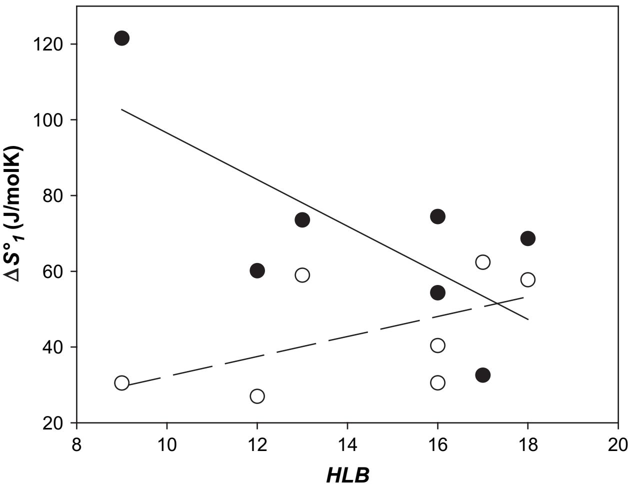

Fig 8. ΔS_1^0 for MS$^+$ complex formation (○) and for DS complex formation (●) versus the HLB values of nonionic surfactants. — — —: regression line through ○, ——: regression line through ●.

than those obtained for DS interactions in binary mixtures [15], reveal that not only the intermolecular forces but also the surrounding is very different for both DS complexes. Namely, a positive value of ΔS_1^0 is the consequence of a disruption of the hydrophobically structured water molecules around the dye and surfactant molecules when DS complex formation takes place. The positive ΔS_1^0 value seen here indicates that hydrophobic interactions play the main role for DS interactions in the presence of a nonionic surfactant, and that these interactions are much less important in binary mixtures. This finding is confirmed by spectra presented in Figs. 4 and 5, where the shape of DTAB–AR88 and DTAB–AO7 spectra changed significantly when BR56 or BR700 was added into the solution, and became very similar to those obtained for AR88 and AO7 in solutions of nonionic surfactants. Following this observation, it can be concluded that in addition to the equilibrium reactions (1) through (4), reaction (5) took place in the ternary mixtures where DS complexes were solubilised in the micelles of nonionic surfactants.

4. Conclusions

Taking into consideration the results obtained, the following can be concluded:

- The structure of a nonionic surfactant plays an important role during the association process between an anionic dye and a cationic surfactant in ternary mixtures.
- The tendency to form DS complexes in ternary mixtures decreases with increasing HLB value of a nonionic surfactant. By increasing the length of a POE unit in the hydrophilic chain of a nonionic surfactant, the strength of DS interactions in ternary mixture decreases, while the branching of a hydrophilic or hydrophobic chain of a nonionic surfactant has a weaker influence on the strength of dye–surfactant interactions.
- The increase of the HLB value of a nonionic surfactant resulted in decreased ΔH_1^0 and ΔS_1^0 values for DS complex formation. Consequently, the stronger the interactions between species, the lower the ΔG_1^0 value and the higher the ΔH_1^0 and ΔS_1^0 values.
- The formation of DS complexes in the presence of nonionic surfactants is entropy-controlled irrespective of the structure of a nonionic surfactant, which enables the conclusion that DS complexes were solubilised in the micelles of nonionic surfactants.

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References

[1] Datyner A. Surfactants in textile processing. New York: Marcel Dekker Inc.; 1983.

[2] 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.

[3] Akbaş H, Kartal Ç. C.I. Reactive Orange 16-dodecylpyridinium chloride interactions in electrolytic solutions. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 2006;65(3): 95–9.

[4] Bračko S, Špan J. Anionic dye–cationic surfactant interactions in water–ethanol mixed solvent. Dyes and Pigments 2001;50(1): 77–84.

[5] Dutta RK, Bhat SN. Interaction of Methyl Orange with submicellar cationic surfactants. Bulletin of the Chemical Society of Japan 1993;66(9):2457–60.

[6] 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.

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

[8] Ghoreishi SM, Behpour M, Ghafari Farsani A. Study of interaction between a cationic surfactant and two anionic azo dyes by ion-selective electrode technique and spectrophotometry. Dyes and Pigments 2007;74(3):585–9.

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

[10] 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.

[11] Oakes J, Gratton P. Solubilisation of dyes by surfactant micelles. Part 2: molecular interactions of azo dyes with cationic and zwitterionic surfactants. Coloration Technology 2003;119(2):100–7.

[12] 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.

[13] 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.

[14] 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.

[15] 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.

[16] Simončič B, Kert M. Influence of the chemical structure of dyes and surfactants on their interactions in binary and ternary mixture. Dyes and Pigments 2008;76(1):104–12.

[17] Tunç S, Duman O. Investigation of interactions between some anionic dyes and cationic surfactants by conductometric method. Fluid Phase Equilibria 2007;251(1):1–7.

[18] Chatterjee S, Sen PK, Das K, Bhattacharya SC. Mixed micellization of ionic and nonionic surfactants in aqueous solution. Journal of Dispersion Science and Technology 2006;27(5):751–9.

[19] Bakshi MS, Sachar S. Influence of hydrophobicity on the mixed micelles of Pluronic F127 and P103 plus cationic surfactant mixtures. Colloids and Surfaces A: Physicochemical and Engineering Aspects 2006;276(1–3):146–54.

[20] Desai TR, Dixit SG. Interaction and viscous properties of aqueous solutions of mixed cationic and nonionic surfactants. Journal of Colloid and Interface Science 1996;177(2):471–7.

[21] Gharibi H, Sohrabi B, Javadian S, Hashemianzadeh M. Study of the electrostatic and steric contributions to the free energy of ionic/nonionic mixed micellization. Colloids and Surfaces A: Physicochemical and Engineering Aspects 2004;244(13):187–96.

[22] Razavizadeh BM, Mousavi-Khoshdel M, Gharibi H, Behjatmanesh-Ardakani R, Javadian S, Sohrabi B. Thermodynamic studies of mixed ionic/nonionic surfactant systems. Journal of Colloid and Interface Science 2004;276(1):197–207.

[23] Shirahama K, Nishiyama Y, Takisawa N. Binding of *N*-alkylpyridinium chlorides to nonionic micelles. Journal of Physical Chemistry 1987;91(23):5928–30.

[24] Simončič B, Papež V. Potentiometric study of intermolecular interactions in cationic–nonionic mixed surfactant systems. Textile Research Journal 2000;70(5):454–9.

[25] Varade D, Mody S, Ankleshwaria H, Bahadur P. Mixed surfactant systems. Part I: micelle formation from mixtures of polyoxyethylene *t*-octylphenol and cationic surfactants. Tenside Surfactant Detergents 2003;40(1):46–51.

[26] Kert M, Simončič B. Influence of the nonionic surfactant structure on surfactant–surfactant interactions. Tekstilec 2007;50(1–3):35–49.

[27] Akbaş H, Kartal Ç. Spectrophotometric studies of anionic dye–cationic surfactant interactions in mixture of cationic and nonionic surfactants. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 2005;61(5):961–6.

[28] Akbaş H, Kartal Ç. Erratum to "Spectrophotometric studies of anionic dye–cationic surfactant interactions in mixture of cationic and nonionic surfactants". Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 2006;65(5):1241–2.

[29] 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.

[30] Bhattacharya SC, Das HT, Moulik SP. Quenching of flourescence 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.

[31] Zhou W, Zhou L. Solubilization of pyrene by anionic–nonionic mixed surfactants. Journal of Hazardous Materials 2004;109(1–3):213–20.

[32] Zhao B, Zhu L, Li W, Chen B. Solubilization and biodegradation of phenantrene in mixed anionic–nonionic surfactant solutions. Chemosphere 2005;58(1):33–40.

[33] Zhou W, Zhu L. Solubilization of polycyclic aromatic hydrocarbons by anionic–nonionic mixed surfactant. Colloids and Surfaces A: Physicochemical and Engineering Aspects 2005;255(1–3):145–52.

[34] Paria S, Yuet PK. Solubilization of naphthalene by pure and mixed surfactants. Industrial and Engineering Chemistry Research 2006;45(10):3552–8.

[35] Dar AA, Rather GM, Das AR. Mixed micelle formation and solubilization behaviour toward polycyclic aromatic hydrocarbons of binary and ternary cationic–nonionic surfactant mixtures. Journal of Physical Chemistry B 2007;111(12):3122–32.

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

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

[38] Oakes J, Batchelor SN, Dixon S. Azo dye location in textiles: a novel UV–vis approach. Coloration Technology 2005;121(5):237–44.

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

[40] Moore WJ. Physical chemistry. London: Longman Scientific and Technical; 1992.