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# Thermodynamic investigation of the interaction between Mono-schloroTriazinyl (MCT) Reactive Dyes and cetylpyridinium chloride in aqueous solution

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# ABSTRACT

he interactions of two synthetic triazinyl reactive dyes (Mono-schloroTriazinyl reactive dyes with the cationic surfactant Nhexadecylpyridinium chloride were studied using a conductometric method at 25, 30, 35, 40 and 45 °C. The equilibrium constants and other thermodynamic parameters for the ion pair formation were calculated on the basis of a theoretical model using the data obtained by conductometry. The results showed that the equilibrium constants and the negative standard free energy difference values for all systems decreased by increasing the temperature. According to the thermodynamics data, the formation of ion pair between the dye and the surfactant were revealed to be an enthalpy-driven process which is highly dependent on the temperature and the structures of dyes for both investigated systems. Therefore, both long range and short range interactions are responsible for the formation of the ion pair. The importance of long range electrostatic forces is basically to bring the dye anion and the surfactant cation close enough to drive short range interactions whose contribution represents the major part of the standard free enthalpy difference for the formation of anionic dye- cationic surfactant ion pair. Prog. Color Colorants Coat. 8 (2015), 237-245 © Institute for Color Science and Technology.

#### 1. Introduction

Dyes and surfactants are two important classes of organic compounds with wide industrial uses. In order to design desirable dye-surfactant systems for industrial applications, it is essential to understand the nature of the interactions between them. Studies in this area are still important and interesting for the theory and technology of dyeing in textile and printing technologies [1, 2] or analytical applications [3].

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Investigation of dye interaction with surfactant aqueous solutions can give useful information about the mechanisms according to which surfactants operate as leveling agents and establish thermodynamics and kinetics of dyeing process and finishing of textile material.

Various techniques such as spectrophotometry [4-8], membrane selective electrode [9], polarography [10], potentiometry [11, 12], voltammetry [10] and conductometry [13-19] have been applied for this purpose. Spectrophotometry and voltammetry are more expensive equipments. Conductometric method is easy to perform to investigate the interactions between molecules. For this reason, conductometric method was preferred in this study.

Reactive dyes are attached to suitable fibers via covalent bond. They are known for their bright colors and very good to excellent light and wash fastnesses; however, their resistance to chlorine bleach is poor [20].

Quaternary ammonium salt is one of the major components of cationic surfactant. These compounds are widely used as disinfectants due to having positively charged quaternary nitrogen. They inflict on microbes via a variety of detrimental effects, including damage to cell membranes, denaturation of proteins and disruption of the cell structure [21]. During inactivation of bacterial cells, the quaternary ammonium group remains intact and retains its antibacterial ability as long as the compound is attached to textiles [22].

The purpose of this study was to investigate the interaction of two synthetic triazinyl reactive dyes with two or more functional groups of the same or of different types, whilst altering the position or substituents in the dye molecule with Nhexadecylpyridinium chloride (CPC) cationic surfactant by conductometric method. The influence of temperature and dye structure (the effect of functional groups) on ion pair formation is observed.

# 2. Experimental

# 2.1. Materials and method

Mono-s-chloroTriazinyl (MCT) reactive dyes (D<sub>1</sub> and D<sub>II</sub>) were synthesized and purified according to the Nmethod previously described [23]. hexadecylpyridinium chloride (CPC) was Sigma chemical and used without further purification. The chemical structure of dyes and surfactant used in this study are given in figure 1. All solutions were prepared in deionized water. The concentration of D<sub>I</sub> and D<sub>II</sub> was constant at 0.05 mM for all solutions during the experiments. The temperature of all solutions was maintained constant at desired temperature with a fluctuation of  $\pm$  0.1 °C by circulating thermostated water through the jacket of sample container.

The conductance measurements of solutions were performed with Mi 170 bench conductivity meter (Martini conductometer) using a dip type cell of 0.99 cm<sup>-1</sup> cell constant. The specific conductivity of deionized water was measured before each series of measurements at each temperature. Then the specific conductivity of exact volume and known concentrations of D<sub>I</sub> and D<sub>II</sub> solutions (0.05 mM) were measured. Binary mixtures of dye/surfactant were prepared by keeping the dye concentration constant and increasing the surfactant concentration. Then the specific conductivity of each solution was measured. The uncertainty of the measurements was  $\pm 0.01 \mu \text{Scm}^{-1}$ . The specific conductivity of surfactant alone was also measured at the concentration that is exactly the same as that in the binary mixtures. Measurements were made at 25.0, 30.0, 35.0, 40.0, and 45.0 °C.



Figure 1: The chemical structures of D<sub>I</sub>, D<sub>II</sub> and CPC.

#### 3. Results and discussion

 $D_I$  and  $D_{II}$  with three sulfonate groups were reacted with the studied cationic surfactant with dye to surfactant mole ratio of 1:3.

The specific conductances of D<sub>I</sub>-CPC, and D<sub>II</sub> -CPC mixtures at different temperatures are shown in Figures 2 and 3, respectively. If there were no interaction between CPC and dye in the solution, the experimentally measured conductance of the mixed solution would be the sum of the conductivities of individual dye ions and surfactant ions in the solution. Figures 2 and 3 show that the measured conductances of D<sub>I</sub>-CPC and D<sub>II</sub>-CPC mixtures are lower than the sum of specific conductivities of individual dye andindividual CPC molecule. The decrease in the measured values can be explained by the formation of a non-conducting or a less-conducting specie in the solution. Furthermore, the specific conductance would increase linearly withconcentration of added surfactant. As can be seen from the figures, the specific conductance curve deviates from linearity at certain concentration of surfactant and certain temperature. This indicates that a non-conducting or a less-conducting species has been formed in the solution. However, the deviation of measured values from linearity decreased with increasing the temperature from 25 to 45 °C which caused a decrease in the formation of non-conducting or less-conducting species for all studied systems. At a given dye concentration for each temperature, the deviation from the theoretical values increased in the order of D<sub>I</sub>-CPC > D<sub>II</sub>-CPC.

This trend may be explained by the structure of the dye molecules. Both DI and DII dyes are anionic molecules containing three sulfonate groups making both dyes electrostatic interactions with CPC cationic surfactant. It seems that the electrostatic interaction between oppositely charged dye and surfactant molecules has a major role in consequent electrostatic interactions.



Surfactant Concentration (mol.dm<sup>-1</sup>)

Figure 2: Specific conductivity of D<sub>I</sub>-CPC mixture in aqueous solution as a function of the CPC concentration at 15 °C (□), 25 °C (■),35 °C (O) and 45 °C (●), Solid lines show the sum of the conductivities of individual species in the solution, dashed lines show the measured conductivity of dye-surfactant mixtures.



Figure 3: Specific conductivity of D<sub>II</sub>-CPC mixture in aqueous solution as a function of the CPC concentration at 15 °C (□), 25 °C (■),35 °C (O) and 45 °C (●), Solid lines show the sum of the conductivities of individual species in the solution, dashed lines show the measured conductivity of dye-surfactant mixtures.

According to  $D_I$  dye molecular structure, it can be seen that the anionic molecule has hydrophobic centers that make it suitable for both electrostatic and hydrophobic interactions with CPC cationic surfactant. The  $D_{II}$  dye with CPC cationic complex formation can be explained by the long range electrostatic. However, short range hydrophobic forces do not make the formation of dye/surfactant complex. According to DII dye molecular structure, it has a positive nitrogen center containing alkyl group and a benzyl group connected to the nitrogen center as seen from figure 1, where there is an electrostatic repulsion between  $D_{II}$ dye (positive nitrogen center) and cationic surfactant molecule.

For this reason, hydrophobic interactions effective for the formation of non-conductive or less-conductive complex in  $D_{II}$  –surfactant system as in  $D_I$  -surfactant system do not occur between  $D_{II}$  dye and surfactant system.

The equilibrium constants were calculated by using a theoretical model based on the deviation from linear behavior. This model is based on the comparison between the measured conductivity of the dyesurfactant mixture and a theoretical straight line that represents the sum of the specific conductivities of the dye and the surfactant [25-27].

If a non-conducting complex  $DS_3$  forms between dye  $D^{3-}$  and surfactant  $S^+$  molecules, the equilibrium interaction can be written as:

$$D^{3-} + 3S^+ \to DS_3 \tag{1}$$

and surfactant molecules in the solution, the measured conductance would be given by Eq. 2.

$$10^{3} \kappa = C_{D} 3\lambda_{Na^{+}} + C_{D}\lambda_{D^{3-}} + 3C_{S}\lambda_{S^{+}} + 3C_{S}\lambda_{Cl^{-}}$$
(2)

where  $C_D$  and  $C_S$  are the molar concentrations of the dye and surfactant, respectively, and  $\lambda_{Na}^{+}$ ,  $\lambda_D^{3-}$ ,  $\lambda_S^{+}$ , and  $\lambda_{Cl}^{-}$  are the equivalent conductances of Na<sup>+</sup>, D<sup>3-</sup>,S<sup>+</sup> and Cl<sup>-</sup> ions, respectively.

It can be seen from Figures 2 and 3 that the measured conductance of the dye-surfactant mixtures was lower than the sum of the specific conductivities of

the individual dye and the individual surfactant molecule. The formation of a non-conducting dye– surfactant complex causes a decrease in the concentration of free ions:

$$10^{3}\kappa = (C_{\rm D} - C_{\rm DS_{3}})\lambda_{\rm D^{3-}} + C_{\rm D}3\lambda_{\rm Na^{+}} + (C_{\rm S} - C_{\rm DS_{3}})3\lambda_{\rm S^{+}} + 3C_{\rm S}\lambda_{\rm C}$$
(3)

Where  $C_{DS3}$  is the concentration of the nonconducting dye–surfactant complexes. By subtracting Eq. (3) from Eq. (2), Eq. (4) is obtained:

$$10^{3} \Delta \kappa = C_{DS_{3}} (\lambda_{D^{3-}} + 3\lambda_{S^{+}})$$
(4)

where  $\Delta \kappa$  is the difference between the theoretical and measured conductance at a given surfactant concentration.

Based on the Kohlrausch's law in dilute solution, Eq. (4) is given as:

$$10^{3}\kappa = C_{DS_{3}}(\lambda^{0}_{D}{}^{3-} + 3\lambda^{0}_{S}{}^{+}) \approx C_{DS_{3}}(\Lambda^{0}_{D}{}^{S_{3}})$$
(5)

Where  $\Lambda^{o}_{DS3}$  is the equivalent conductance of the dye-surfactant ion pair at infinite dilution and can be obtained for both systems by plotting the equivalent conductance  $\Lambda$  versus  $C^{1/2}$  according to the Kohlrausch equation:

$$\Lambda = \Lambda^0 - b\sqrt{C} \tag{6}$$

Where  $\Lambda$  is molar conductivity of the solution at concentration C and b is a constant.  $\Lambda^{\circ}$  value of a salt can be calculated from the intercept of a graph by plotting  $\Lambda$  versus C<sup>1/2</sup> [28]. Typical  $\Lambda$  versus C<sup>1/2</sup> plots for calculating the  $\Lambda^{\circ}$  values of DI, DII as a dye and CPC as a surfactant are shown in Figures 4 and 5, respectively. Calculated  $\Lambda^{\circ}$  values for dyes and surfactant are given in Table 1.  $\Lambda^{\circ}_{DS3}$  values determined from  $\Lambda^{\circ}$  values of dyes, surfactant and NaCl are listed n Table 1.



Figure 4: Λ<sub>C</sub> vs C<sup>1/2</sup> graph for the determination of molar conductivity of D<sub>1</sub> at infinite dilution at (15 °C (□), 25 °C (■), 35 °C (O) and 45 °C (●)



Figure 5: Λ<sub>c</sub> vs C<sup>1/2</sup> graph for the determination of molar conductivity of D<sub>II</sub> at infinite dilution at (15 °C (□), 25 °C (■), 35 °C (O) and 45 °C (●)

**Table 1:** molar conductances (S cm<sup>2</sup> mol<sup>-1</sup>) at infinite dilution in water for dyes (D<sub>I</sub>, D<sub>II</sub>), surfactant (CPC) and complex (DS<sub>3</sub>)

T(°C)	$\Lambda^{o}_{DI}$	$\Lambda^{o}_{D11}$	$\Lambda^{o}_{CPC}$	$\lambda^{o}_{S^{+}}$	$\Lambda^{o}_{DI (CPC)3}$	$\Lambda^{o}_{DII (CPC)3}$
15.0	525.94	210.23	78.90	17.49	459.10	143.39
25.0	651.30	263.47	98.40	22.05	567.15	179.32
35.0	785.91	321.69	118.90	26.69	678.09	213.87
45.0	931.90	384.09	138.80	31.3	800.35	252.54

The equilibrium constant for the reaction (Eq. (1)) of complex formation is given by Eq. (7).

$$K = \frac{C_{DS_3}}{(C_D - C_{DS_3})(C_S - 3C_{DS_3})^3}$$
(7)

The values for equilibrium constants (K), which are obtained using this method, are shown in Table 2; the numbers represent the average values.

When the equilibrium constants for both dye systems are compared, the equilibrium constant for the DI-CPC system is higher than those for DII-CPC system. This situation is in accordance with Traube's rule [29]. Both surfactant and dye molecules have a strong polar group. In aqueous solutions, these molecules dissociate into ions and there are electrostatic attractive interactions between opposite charged ions (long range interaction). Furthermore, there is hydrophobic interaction between non-polar part of the surfactant and other short range attractive forces. A larger value of K for DI-CPC in comparison with DII-CPC implicates that there is an electrostatic repulsion between the positive nitrogen center of DII dye and cationic surfactant molecule.

The free energy difference,  $\Delta G^{\circ}$ , enthalpy difference,  $\Delta H^{\circ}$ , and the entropy difference,  $\Delta S^{\circ}$ , of binding processes for the complex formation DI and

DII at different temperatures can be calculated using Eqs. (8)-(10), respectively, [28] from the K values in Table 2.

$$\Delta G^0 = -RT LnK \tag{8}$$

$$\Delta H^{0} = \frac{\partial (\Delta G^{0} / T)}{\partial (1 / T)}$$
(9)

$$\Delta S^0 = \frac{(\Delta H^0 - \Delta G^0)}{T} \tag{10}$$

It can be seen from Eq. (9) that if  $\Delta G^{\circ}/T$  is plotted against 1/T, the slope of the curve at any temperature is equal to  $\Delta H^{\circ}$  at that temperature. But, it is assumed that  $\Delta H^{\circ}$  does not depend on the temperature in the measured temperature range; a plot of  $\Delta G^{\circ}/T$  versus 1/T should be a straight line with a slope equal to  $\Delta H^{\circ}$ . The thermodynamics parameters are listed in Table 2. Formation of ion pairs, in fact, means the aggregation of two species to form one species resulting in increasing the order of the system which is reflected as a negative value of  $\Delta S^{\circ}$ .

system	T(°C)	K(M <sup>-2</sup> )	$\Delta G^{\circ} (KJmol^{-1})$	∆H° (KJmol <sup>-1</sup> )	$\Delta S^{\circ} (Jmol^{-1}K^{-1})$
D <sub>I</sub> -CPC	15.0	5.78×10 <sup>13</sup>	-75.92		-43.94
	25.0	$1.74 \times 10^{13}$	-75.57	-88.57	-43.61
	35.0	5.25×10 <sup>12</sup>	-75.04		-43.41
	45.0	1.73×10 <sup>12</sup>	-74.54		-44.13
D <sub>II</sub> -CPC	15.0	3.04×10 <sup>12</sup>	-68.86		-35.89
	25.0	$1.07 \times 10^{12}$	-68.65	-79.19	-36.36
	35.0	4.22×10 <sup>11</sup>	-68.08		-36.06
	45.0	1.35×10 <sup>11</sup>	-67.82		-35.75

**Table 2:** The values of  $K_{\Delta} G^{\circ}$ ,  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  for D<sub>I</sub>-CPC and D<sub>II</sub>-CPC complex formations.

# 4. Conclusions

Conductometric method was applied successfully for the investigation of dye–surfactant systems.  $D_I$  and  $D_{II}$ formed a non-conducting or a less-conducting species with CPC surfactant. The equilibrium constants for the process of dye-surfactant complex formation were calculated by this method. Standard free energy difference values confirmed the spontaneity of the complex formation process. Increase of temperature lead to a decrease in the equilibrium constant values for both systems studied. The equilibrium constant value for the association of dye-surfactant system was higher for D<sub>I</sub>-CPC system than D<sub>II</sub>-CPC. It may be concluded from these results that electrostatic forces played important roles in dye–surfactant complex formation. The formation of dye–surfactant complex results in decreasing the system's order, so it can be considered as an enthalpy-driven reaction under the influence of both hydrophobic and electrostatic interactions. The amount of ion pairs forming through the process is highly dependent on the physical conditions and the structure of the dyes (e.g. charge density). In addition, the results show that the tendency to form dye–surfactant complex decreases with increasing temperature in the range of 15- 45°C.

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