PROGRESS
IN COLOR, COLORANTS AND COATINGS

available online @ www.pccc.icrc.ac.ir
*Prog. Color Colorants Coat. 4(2011), 121-128*

Ministry of Science, Research and Technology
Institute for Color Science and Technology

# Aggregation of an Anionic Azo Dye with Conventional Cationic Surfactants in Premicellar Region

**S. Javadian*[1], F. Hooshmand[2] and A. Asadzadeh Shahir[3]**
[1]. Assistant Professor, Department of Physical Chemistry, Tarbiat Modares University, P.O. Box: 14115-117, Tehran, Iran.
[2]. M. Sc., Department of Physical Chemistry, Payame Noor University, Urmiah Branch, Urmiah, Iran.
[3].M. Sc., Department of Physical Chemistry, Tarbiat Modares University, P.O. Box: 14115-117, Tehran, Iran.

ARTICLE INFO

Article history:
Received: 30-05-2011
Revised: 3-12-2011
Accepted: 1-1-2012
Available online:1-1-2012

Keywords:
Congo Red
Cationic surfactant
Dye- surfactant ion pair
Conductometry
Job's method.

## ABSTRACT

*The interaction of Congo Red (CR) with a series of Alkyl trimethyl ammonium bromide ($C_nTAB$), N-hexadecyl pyridinium bromide (CPB) and N-hexadecyl pyridinium chloride (CPC) were investigated using conductometry and UV-Vis spectroscopy technique. Job's method was used to determine the stoichiometric ratio of dye and surfactant in ion pairs. The equilibrium constant and other thermodynamic parameters for the ion pair formation were calculated on the basis of a theoretical model using the data obtained by conductometry. It was found that an increase in temperature reduces the tendency for ion pair formation as equilibrium constants decrease with increasing temperature. The results showed that as the chain length of the $C_nTAB$ molecule in Dye/$C_nTAB$ systems was increased, the equilibrium constants were significantly increased. Therefore, the short range as well as long range interactions is responsible for the formation of the ion pair. The importance of long range electrical forces is basically to bring the dye anion and the surfactant cation close enough to enable the action of short range interactions whose contribution represents the major part of the standard free energy change for the formation of the anionic dye–cationic surfactant ion pair. The reaction between the dye and the surfactants was revealed to be an enthalpy-driven reaction which is highly dependent on the temperature and the structures of both dye and the surfactant. Prog. Color Colorants Coat. 4(2011), 121-128. © 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] For this purpose, various

---

*Corresponding author: javadian_s@modares.ac.ir techniques such as spectrophotometry [4, 5], polarography [6], tensiometry [7, 8], potentiometry by means of surfactant selective electrodes [9] and conductometry [10-13] have been applied. Among various dye/surfactant mixtures, oppositely charged systems have been studied widely compared to the others because of their benefits to understand the contributions of both electrostatic and hydrophobic interactions. These investigations have shown the formation of some species such as dye-surfactant ion pairs and salts [1, 4, 15], induced dye aggregates [16], dye-rich micelles [17] and surfactant-rich micelles with solubilized dye monomers [7, 8, 17] for oppositely charged systems.

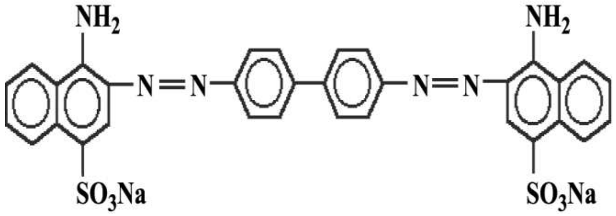
In the present study, the ion pair formation between an anionic azo dye, Congo Red (CR), and conventional cationic surfactants with different chain lengths, head groups and counter ions has been studied. Congo Red (CR) is a carcinogenic benzidine-based anionic diazo dye (Scheme 1), which comes in the effluents of textile industries during the dyeing and the rinsing processes. Despite its wide industrial use in combination with surfactants, there are very few reports on investigation of the interactions in CR/surfactant mixtures [18-22] Tehrani-bagha et al. have studied the interaction of CR with some cationic surfactants and found that a stronger interaction occurs for gemini surfactants compared to the conventional ones under the influence of both electrostatic and hydrophobic forces at concentrations far below the CMC (critical micelle concentration), which makes them more efficient dye leveling and fixing agents [23]. Ion pairs are formed in all oppositely charged dye/surfactant mixtures at concentrations far below the CMC of corresponding surfactants resulting in a change in physical properties of the solution such as specific conductivity. Therefore, we have employed the conductometry technique to investigate the ion pair formation at different temperatures. In the present study, we examine dye-surfactant interactions in which the cationic surfactant is comprised of a tetradecyl and hexadecyl chain and a range of head groups, in combination with different counter-ions. Congo Red (CR) was used as the anionic dye. By using cationic surfactants with different head groups and counter ions, we could study the effects of head group type and counter ion on the dye-surfactant interactions. In addition, the variation of alkyl chain length provides a quantitative molecular-level understanding of the contribution of non-electrostatic interactions to ion pair formation.

## 2. Experimental

### 2.1. Materials and method

Congo Red (CR), hexadecyl trimethyl ammonium bromide (CTAB) and tetradecyl trimethyl ammonium bromide (TTAB) were obtained from Merck (Germany). N-hexadecyl pyridinium bromide (CPB) and N-hexadecyl pyridinium chloride (CPC) were purchased from Sigma (USA). All solutions were prepared using double-distilled water. The concentration of CR 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 ±0.1 K by circulating thermostated water through the jacket of sample container. Equimolar solutions (0.05 mM) of dye and surfactants were mixed in various volume fractions to obtain Job's plots.

A JENWAY 4510 Conductivity meter was employed to measure the specific conductivity of the solutions. The electrode was first rinsed so that the specific conductivity of distilled water was measured up to 1-2 $\mu Scm^{-1}$. Stock solution of 0.05 mM CR was first prepared and then, concentrated stock solution of surfactants was also prepared using this CR solution. 50 ml of CR solution was placed in sample vessel. Certain volumes of concentrated surfactant solution were injected to the solution and stirred for 5 minutes, then the electrode was plunged in the solution and released to equilibrate for 10 minutes and finally the specific conductivity was recorded. Three successive measurements were done for each injection at a controlled constant temperature.



**Scheme 1.** Molecular structure of Congo Red (M.W. = 696.68 g/mol).

The uncertainty of the measurements was ±0.01 µS $cm^{-1}$. Visible absorption spectra were recorded with a Shimadzu 2100 UV-Vis spectrophotometer (Shimadzu, Japan) using a matched pair of glass cuvettes with 1 cm optical path length.

## 3. Result and discussion

The specific conductance values of dye-cationic surfactant mixture in aqueous solution were measured as a function of the surfactant concentration in the temperature range of 298.0-313.0 K. As it is obvious from Figure 1, with primary addition of surfactant, the specific conductivity of the solution is increased linearly as well as its increase with temperature. In this region, there is no ion pair formation between CR and the surfactant molecules, the measured conductance values would be expected to be the sum of conductivities of the individual ions in the solution [10, 12]. As can be observed from Figure 1, specific conductance curve deviates from linearity at certain concentration of surfactant and at certain temperature. This indicates that the components interact to form corresponding ion pairs. In our previous work, we demonstrated the ion pair formation between CR and surfactant molecules using UV-Vis spectroscopy and surface tension methods [24, 25]. These ion pairs are probably less-conductive or non-conductive species since the specific conductivity of the solution deviates from the linearity and varies as another line with a smaller slope. This deviation from linearity is the basis of our theoretical model to determine the thermodynamical parameters of ion pair formation, as it has been used in some previous works [10-12], since the amount of the deviation is attributed to the amount of formed ion pairs. The formation of dye-surfactant ion pairs can be illustrated by following equilibriums:

$$D^{2-} + S^{+} \leftrightarrow DS^{-} \qquad K_1 \qquad (1)$$

$$DS^{-} + S^{+} \leftrightarrow DS_2 \qquad K_2 \qquad (2)$$

$$DS_{n-1}^{+(n-3)} + S^{+} \leftrightarrow DS_n^{+(n-2)} \qquad K_n \qquad (3)$$

where $S^{+}$, $D^{2-}$ and $DS_n^{+(n-2)}$ refer to the free surfactant cation, the free CR anion and complexes with different numbers of surfactant cations (n), respectively. $K_1$, $K_2$, … and $K_n$ are the corresponding stoichiometric equilibrium constants. The method of continuous variations (Job's method) was used to determine the stoichiometry of ion pairs as it has been employed in some previous works [26, 27].

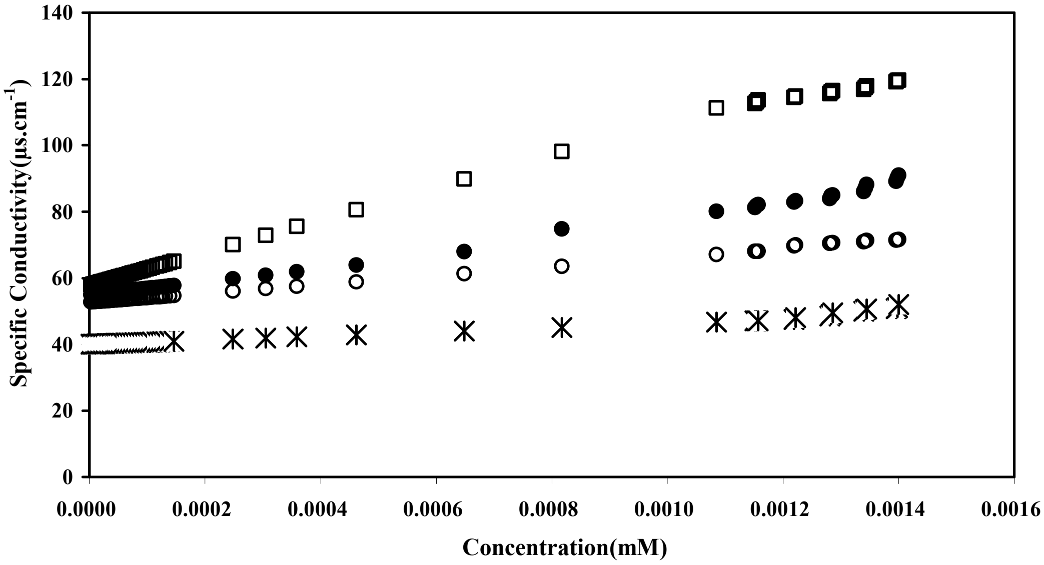


**Figure 1:** Specific conductance vs. the concentration, $C_t$ for CTAB solution in the presence of 0.05 mM Congo Red at various temperatures: (*)298K; (○) 303K; (•)308K ; (□) 313K.

To obtain a Job's plot, various volume fractions of equimolar solutions of dye and surfactant are mixed and the corrected absorbances of these mixtures (ΔE) are plotted versus the volume fraction of the surfactant solution(X). According to the Beer-Lambert law, if no interaction occurs between the dye and the surfactant, the total absorbance of the mixture ($E_{theo}$) will be equal to the sum of their individual absorbances:

$$E_{theo} = \varepsilon_S C_S^0 X_S + \varepsilon_D C_D^0 (1 - X_S) \tag{4}$$

where $\varepsilon_S$ and $\varepsilon_D$ are the molar extinction coefficients of the surfactant and the dye, $C_S^0$ and $C_D^0$ are concentrations of stock solutions of the surfactant and the dye, respectively, which are equal to each other ($C_S^0 = C_D^0$). The formation of $D_mS_n$ complexes makes the solution absorbance to satisfy following relation:

$$E_{\exp} = \varepsilon_S C_S + \varepsilon_D C_D + \varepsilon_{D_mS_n} C_{D_mS_n} \tag{5}$$

$\varepsilon_{D_mS_n}$ is the molar extinction coefficients of the complex and $C_S$, $C_D$, and $C_{D_mS_n}$ are the concentration of the species in the mixture. By calculating the amount of $E_{theo}$ and measuring the amount of $E_{\exp}$, the corrected absorbance can be obtained for all mixtures and plotted vs. $X_s$:

$$\Delta E = E_{\exp} - E_{theo} \tag{6}$$

The minimum or maximum of this plot corresponds to the stoichiometric ratio of dye and the surfactant in the complexes.

Appearance of a minimum in volume fractions of X≈0.5 implies 1:1 stoichiometric ratio for CR-cationic surfactant ion pairs (Figure 2). According to job's approach, it is assumed that only $DS^-$ complexes are formed in the studied mixtures. When there is no interaction between dye and surfactant molecules, the conductance of the solution is, in fact, the sum of conductances of individual ions in the solution:

$$10^3\kappa = C_D.2\lambda_{Na^+} + C_D.\lambda_{D^-} + C_S.\lambda_{S^+} + C_S.\lambda_{X^-} \tag{7}$$

where $C_D$ and $C_S$ are the concentration of CR and the surfactant, respectively. X is Br or Cl ions and λ is the equivalent conductance of corresponding ion. As the ion pairs form, the concentration of free dye and surfactant ions decrease by $C_{DS^-}$:

$$\begin{aligned} 10^3\kappa' = {} & C_D.2\lambda_{Na^+} + (C_D - C_{DS^-})\lambda_{D^-} + \\ & (C_S - C_{DS^-})\lambda_{S^+} + C_S.\lambda_{X^-} \end{aligned} \tag{8}$$

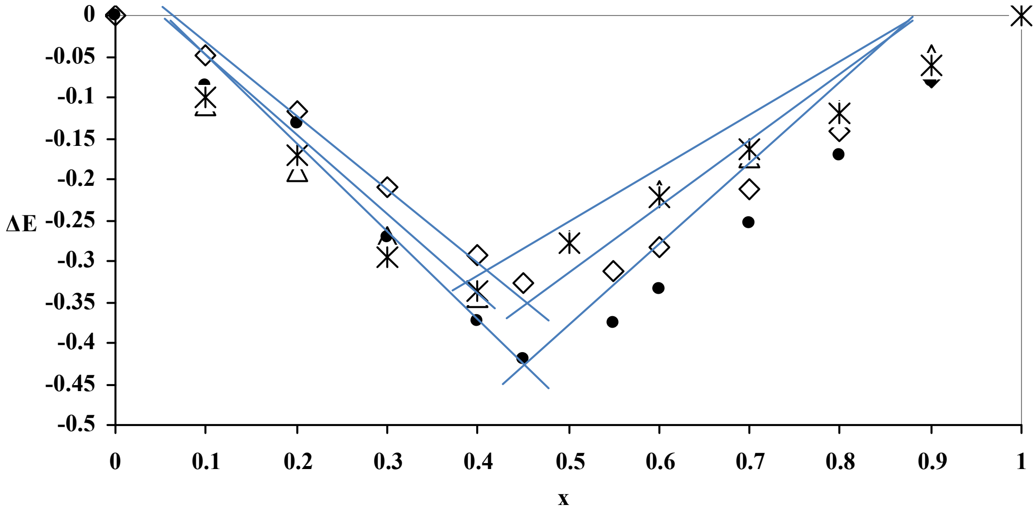


**Figure 2:** Plots of Job's method for: CTAB/CR (□), TTAB/CR (•), CPB/CR (*) and CPC/CR (Δ) mixtures. equimolar solutions (0.05 mM) of Congo Red and surfactants were used.

Subtraction of Eq. (7) from Eq. (8) gives Eq. (9):

$$10^3\Delta\kappa = C_{DS^-}.(\lambda_{D^-} + \lambda_{S^+}) \tag{9}$$

Based on the Kohlrausch's law in dilute solution:

$$\lambda^\circ_{D^-} + \lambda^\circ_{S^+} \approx \Lambda^\circ_{DS^-} \tag{10}$$

So Eq. (9) can be rewritten as:

$$10^3\Delta\kappa \approx C_{DS^-}.\Lambda^\circ_{DS^-} \tag{11}$$

where $\Lambda^\circ_{DS^-}$ is the equivalent conductance of ion pairs at infinite dilution and can be obtained for all systems by plotting the equivalent conductance $\Lambda$ versus $C^{1/2}$ according to the Kohlrausch equation:

$$\Lambda = \Lambda^\circ - b\sqrt{c} \tag{12}$$

$\Lambda$ is obtained from the slope of conductometry plots according to the Eq. (12):

$$\kappa = (10^3.\Lambda) \times c \tag{13}$$

The values obtained for $\Lambda^\circ_{DS^-}$ are listed in Table 1. From conductometry plots, $\Delta\kappa$ can be obtained for each surfactant concentration and thus, $C_{DS^-}$ is obtainable from Eq. (11). Knowing the value of $C_{DS^-}$ for each surfactant concentration, the equilibrium constant of ion pair formation can be calculated by following equation:

$$K = \frac{C_{DS^-}}{(C_D - C_{DS^-})(C_S - C_{DS^-})} \tag{14}$$

In these systems, the K values corresponding to DS$^-$ complex formation are presented in Table 2. From the K values obtained at different temperatures, the thermodynamic parameters, the standard free energy change, $\Delta G^\circ$, the standard enthalpy change, $\Delta H^\circ$, and the standard entropy change, $\Delta S^\circ$ for the first association step of DS$^-$ complex formation are calculated from the following equation [15-17].

$$\Delta G^\circ = -RT\ln K \tag{15}$$

$$\Delta H^\circ = [\frac{\partial(\Delta G^\circ/T)}{\partial(1/T)}]_P \tag{16}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \tag{17}$$

It can be seen from Eq. (16) 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 $\Delta S^\circ$.

**Table 1:** Equivalent conductance of formed ion pairs at infinite dilution in water at various temperatures.

| T (K) | Equivalent conductance (S cm$^2$mol$^{-1}$) | | | |
|---|---|---|---|---|
| | $\Lambda^\circ_{CTAB-CR}$ | $\Lambda^\circ_{TTAB-CR}$ | $\Lambda^\circ_{CPC-CR}$ | $\Lambda^\circ_{CPB-CR}$ |
| 298 | 335.77 | 360.19 | 199.08 | 110.09 |
| 303 | 338.71 | 382.96 | 201.31 | 112.17 |
| 308 | 343.01 | 399.08 | 202.97 | 113.86 |
| 313 | 345.42 | 402.51 | 205.13 | 113.98 |

**Table 2:** The thermodynamic parameters obtained for various systems at different temperatures.

| Ion pair | T (K) | K $\times 10^{-5}$ ($dm^6\ mol^{-2}$) | $\Delta G^o$ ($kJ\ mol^{-1}$) | $\Delta H^o$ ($kJ\ mol^{-1}$) | $\Delta S^o$ ($J\ mol^{-1}\ K^{-1}$) | CMC [a] (mM) |
|---|---|---|---|---|---|---|
| **CTAB-CR** | 298 | 22.63 | -36.25 | -39.32 | -10.32 | 1.00(0.36) |
| | 303 | 19.46 | -36.72 | | -8.54 | |
| | 308 | 16.73 | -36.69 | | -8.54 | |
| | 313 | 10.2 | -36.00 | | -10.62 | |
| **TTAB-CR** | 298 | 18.76 | -35.78 | -48.42 | -42.39 | 3.48(1.27) |
| | 303 | 11.11 | -35.29 | | -43.01 | |
| | 308 | 9.64 | -35.28 | | -42.65 | |
| | 313 | 7.35 | -35.15 | | -42.39 | |
| **CPC-CR** | 298 | 9.72 | -34.15 | -23.02 | -37.35 | 1.00(0.30) |
| | 303 | 7.59 | -34.33 | | -37.06 | |
| | 308 | 7.03 | -34.47 | | -37.16 | |
| | 313 | 6.24 | -34.72 | | -37.39 | |
| **CPB-CR** | 298 | 9.82 | -34.18 | -48.78 | -48.99 | 0.96(0.32) |
| | 303 | 5.79 | -33.64 | | -49.63 | |
| | 308 | 5.34 | -33.77 | | -48.74 | |
| | 313 | 3.75 | -33.39 | | -49.15 | |

[a] Data taken from Ref.[19]. The CMC values in parentheses were obtained in the presence of dye.

The reduced entropy is caused by the loss of the rotational and translational entropy that accompanies the ion pair formation. In spite of this order decrease, a negative value of free standard energy changes indicates that the ion pair formation is a thermodynamically-feasible process. In addition, a negative value of the standard enthalpy changes shows that this reaction is exothermic, and thus, is an enthalpy-driven reaction because of the existence of strong attractive interactions between the components. These observations are also in good agreement with previous findings for other systems [10, 11, 28].

By increasing the temperature, the equilibrium constant gets smaller in all systems (standard free energy changes become less negative), indicating a decrease in ion pair formation because the molecular motion of both CR and the surfactant molecules rises with temperature. The results presented in Table 2 show that the strength of $DS^-$ complex formation is strongly influenced by the structure of the cationic surfactant. Furthermore, a larger value of K for CTAB-CR in comparison with TTAB-CR implicates the importance of hydrophobic interactions as well as electrostatics in ion pair formation since the increase in the chain length of the surfactant leads to stronger hydrophobic interactions between CR and Alkyl chain resulting in an increase in the K value of ion pair formation. The increase of the dye/surfactant interaction by increasing the hydrophobicity of the components has been reported for a lot of similar systems in the literature [29-31].

As the head group of the surfactant changes from alkylammonium to pyridinuim ring in CPC and CPB, delocalization of positive charge [32] of the head group occurs and the electrostatic attraction between the head group and sulfonate groups of CR becomes weakener, so the ion pair formation decreases and the K gets smaller values. Moreover, replacement of the surfactant counterion from $Br^-$ in CPB to $Cl^-$ in CPC causes an increase of the ion pair formation. This phenomenon is originated from the size difference between the ions. A larger size of $Br^-$ makes its hydration difficult, so these ions are preferred rather than $Cl^-$ ions to bind to the surfactant molecules. As a result, freedom of the surfactant molecules to interact with CR molecules is lowered. All of these observations confirm that the interaction between dyes and the surfactants is highly influenced by physical conditions of their medium and the structural properties of both components. These results are in agreement with the previous reports in the literature [10, 24-26].

## 4. Conclusions

Job's method of continuous variations demonstrated that only $DS^-$ complexes are formed in the studied mixtures. The formation of $DS^-$ complexes results in decreasing the system's order so it is 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 physical conditions and structure of the dyes and the surfactants such as chain length, head group and counterion. By increasing the length in the hydrophobic chain or the charge density of headgroup of a cationic surfactant, the strength of dye-surfactant interaction increases. In addition, the results show that the counter ion has no significant effect on dye-surfactant interaction.

The tendency to form $DS^-$complexes decreases with increasing temperature in the range of 298.0-313.0 K.

## 5. References

1. B. Gohain, P. M. Saikia, S. Sarma,S. N. Bhat, R. K.Dutta, Hydrophobicity-induced deprotonation of dye in dye-submicellar surfactant systems, *Phys. Chem. Chem. Phys.*, 4(2002), 2617-2620.
2. K. M. Chen, L. H. Lin, C. F. Wang, M. C. Hwang, Interactions between new multi-anionic surfactants and direct dyes and their effects on the dyeing of cotton fabrics, *Colloids Surf., A*, 356(2010), 46-50.
3. N. Zaghbani, A. Hafiane, M. Dhahbi, Separation of methylene blue from aqueous solution by micellar enhanced ultrafiltration, *Sep. Purif. Technol.*, 55(2007), 117-124.
4. S. Göktürk, M. Tunçay, Spectral studies of safranin-O in different surfactant solutions, *Spectrochim. Acta, Part A*, 59(2003), 1857-1866.
5. L. García-Río, P. Hervella, J. C. Mejuto, M. Parajó, Spectroscopic and kinetic investigation of the interaction between crystal violet and sodium dodecylsulfate, *Chem.Phys.*, 335(2007), 164-176.
6. A. Navarro,F.Sanz, Chemical Interaction between Nonionic Surfactants and an Acid Dye, *J. Colloid Interface Sci.*, 237(2001), 1-5.
7. B. Gohain,R. K. Dutta, Premicellar and micelle formation behavior of dye surfactant ion pairs in aqueous solutions: Deprotonation of dye in ion pair micelles, *J. Colloid Interface Sci.*, 323(2008), 395-402.
8. B. Gohain, B. Boruah, P. M. Saikia, R. K. Dutta, Premicellar and micelle formation behavior of aqueous anionic surfactants in the presence of triphenylmethane dyes: protonation of dye in ion pair micelles, *J. Phys. Org. Chem.*, 23(2010), 211-219.
9. B. Simončič, M. Kert, A study of anionic dye-cationic surfactant interactions in mixtures of cationic and nonionic surfactants, *Dyes Pigm.*, 54(2002), 221-237.
10. H. Akbaş, Ç. Kartal, Conductometric studies of the interaction of C. I. Reactive Orange 16 with cationic alkyltrimethylammonium bromide surfactants, *Dyes Pigm.*, 72(2007), 383-386.
11. S. Tunç, O. Duman, Investigation of interactions between some anionic dyes and cationic surfactants by conductometric method, *Fluid Phase Equilib.*, 251(2007), 1-7.
12. A. A. Rafati, S. Azizian, M. Chahardoli, Conductometric studies of interaction between anionic dyes and cetylpyridinium bromide in water-alcohol mixed solvents, *J. Mol. Liq.*, 137(2008), 80-87.
13. M. Nasiruddin Khan, A. Sarwar, Study of dye-surfactant interaction: Aggregation and dissolution of yellowish in N-dodecyl pyridinum chloride, *Fluid Phase Equilib.*, 239(2006), 166-171.
14. P. Mukerjee, K. J. Mysels, A re-evaluation of the Spectral Change Method of Determining Critical Micelle Concentration, *J. Am. Chem. Soc.*, 77(1955), 2937-2943.
15. J. C. Micheau, G. V. Zakharova, A. K. Chibisov, Reversible aggregation, precipitation and re-dissolution of rhodamine 6G in aqueous sodium dodecyl sulfate, *Phys. Chem. Chem. Phys.*, 6(2004), 2420-2425.
16. R. T. Buwalda, J. B. F. N. Engberts, Aggregation of dicationic surfactants with methyl orange in aqueous solution, *Langmuir*, 17(2001), 1054-1059.
17. B. Gohain, S. Sarma, R. K. Dutta, Protonated dye-surfactant ion pair formation between neutral red and anionic surfactants in aqueous submicellar solutions, *J. Mol. Liq.*, 142(2008), 130-135.
18. S. Chatterjee, D. S. Lee, M. W. Leeand, S. H. Woo, Congo red adsorption from aqueous solutions by using chitosan hydrogel beads impregnated with nonionic or anionic surfactant, *Bioresour. Technol.,* 100(2009), 3862-3868.
19. M. K. Purkait, S. S. Vijay, S. D. Gupta, S. De, Separation of congo red by surfactant mediated cloud point extraction, *Dyes Pigm.*, 63(2004), 151-159.
20. M. K. Purkait, S. Dasgupta, S. De, Determination of design parameters for the cloud point extraction of congo red and eosin dyes using TX-100, *Sep. Purif. Technol.,* 51(2006), 137-142.
21. S. Chatterjee, S. Chatterjee, B. P. Chatterjee, A. K.

Guha, Adsorptive removal of congo red, a carcinogenic textile dye by chitosan hydrobeads: Binding mechanism, equilibrium and kinetics, *Colloids Surf., A*, 299(2007), 146-152.

22. W. U. Malik, P. Chand, Physico-chemical studies on the binding of dyes with surfactants: II. Polarography of surfactant-dye mixtures, *J. Electroanal. Chem. Interfacial Electrochem.*, 22(1969), 69-74.
23. A. R. T. Bagha, H. Bahrami, B. Movassagh, M. Arami, F. M. Menger, Interactions of gemini cationic surfactants with anionic azo dyes and their inhibited effects on dyeability of cotton fabric, *Dyes Pigm.*, 72(2007), 331-338.
24. M. Rashidi-Alavijeh, S. Javadian, H. Gharibi, M. Moradi, A. Tehrani-Bagha, A. A. Shahir, Intermolecular interactions between a dye and cationic surfactants: Effects of alkyl chain, head group, and counterion, *Colloids Surf., A,* 380(2011), 119-127.
25. A. A. Shahir, M. Rashidi-Alavijeh, S. Javadian, J. Kakemam, A. Yousefi, Molecular interaction of Congo Red with conventional and cationic gemini surfactants, *Fluid Phase Equilib.*, 305(2011), 219-226.
26. P. Forte-Tavcer, Interaction between some anionic dyes and cationic surfactants with different alkyl chain length studied by the method of continuous variations, *Dyes Pigm.,* 63(2004), 181-189.
27. S. Gokturk, M. Tuncay, Dye surfactant interactionin the premicellar region, *J. Surfactants Deterg.,* 6(2003), 325-330.
28. W. J. Moore, Physical chemistry, Longman Scientific and Technical, London, 1992.
29. B. Simoncic, J. Span, A study of dye-surfactant interactions, part 1: effect of chemical structure of acid dyes and surfactants on the complex formation, *Dyes Pigm.*, 36(1998), 1-14.
30. K. K. Karukstis, D. A. Savin, C. T. Loftus, N. D. D'Angelo, Spectroscopic Studies of the Interaction of Methyl Orange with Cationic Alkyltrimethyl ammonium Bromide Surfactants, *J. Colloid Interface Sci.*, 203(1998), 157-163.
31. S. Alehyen, F. Bensejjay, M. El. Achouri, L. Pérez, M. Infante, Study of the Interaction Between Methyl Orange and Mono and bis-Quaternary Ammonium Surfactants, *J. Surfactants Deterg.,* 13(2010), 225-231.
32. H. Gharibi, B. Sohrabi, S. Javadian, M. Hashemian-zadeh, Study of the electrostatic and steric contributions to the free energy of ionic/nonionic mixed micellization, *Colloids Surf., A,* 244(2004), 187-196.