PROGRESS
IN COLOR, COLORANTS AND COATINGS

available online @ www.pccc.icrc.ac.ir
Prog. Color Colorants Coat. 7(2014), 39-48

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

Conductometric Studies of the Interaction of Acid Green 25 with Cationic Alkyltrimethyl Ammonium Bromid Surfactants

H. Dezhampanah[1*], B. Ghalami Choobar[2], R. Ansari[3] and R. Firouzi[4]

[1] Assistant Professor, Laboratory of Physical Chemistry, Department of Chemistry, Faculty of Science, University of Guilan, P. O. Box 41335-1914, Rashat, Iran.

[2] Associate Professor, Laboratory of Physical Chemistry, Department of Chemistry, Faculty of Science, University of Guilan, P. O. Box 41335-1914, Rashat, Iran.

[3] Associate Professor, Laboratory of Physical Chemistry, Department of Chemistry, Faculty of Science, University of Guilan, P. O. Box 41335-1914, Rashat, Iran.

[4] Ph. D. Student, Laboratory of Physical Chemistry, Department of Chemistry, Faculty of Science, University of Guilan, P. O. Box 41335-1914, Rashat, Iran.

ARTICLE INFO

Article history:
Received: 25-09-2012
Final Revised: 11-03-2013
Accepted: 09-04-2013
Available online: 11-04-2013

Keywords:
Cationic surfactants
Anionic dye
Ion pair
Equilibrium constant
Conductometry

ABSTRACT

The interactions between an anionic dye, Acid Green 25 (AG) and the two cationic surfactants tetradecyltrimethyl ammonium bromide (TTAB), and hexadecyltrimethyl ammonium bromide (CTAB) in aqueous solutions far below the CMC are studied using the conductometric method at different temperatures. The equilibrium constants and other thermodynamic functions for the process of dye-surfactant ion pair formation were calculated using the conductometric data. The results showed that the surfactant with the longer hydrophobic chain had a stronger tendency to associate with the dye and the equilibrium constant was considerably higher than those measured for the surfactant with the shorter hydrophobic chain. These results indicate that short range, non-electrostatic interactions have a significant influence on dye - surfactant ion pair formation as well as long range electrostatic forces. Prog. Color Colorants Coat. 7(2014), 39-48. © Institute for Color Science and Technology.

1. Introduction

Surfactants are widely used in households and as industrial cleaners, in cosmetics, research laboratories and as wetting, dispersing and leveling agents for improving dyeing processes by increasing the solubility, stabilizing the dispersed state and promoting a uniform distribution of the dye in the textile. In the dyeing process, many surfactants have been used as leveling agents and/or dispersing agents [1, 2]. Surfactants present in the dye bath are responsible for a considerable change in the state of the dye in solution, predominately caused by interactions between the dye and the surfactant. In order to design desirable dye-surfactant systems, it is

---

*Corresponding author: h.dpanah@guilan.ac.ir essential to understand the nature of the interactions between them [3]. In the last few decades, many investigations have been made on the interactions between surfactants and water soluble dyes in order to acquire information about dye-surfactant associations [4–10].

Although the interaction between dyes and surfactants has been reported in many papers, studies in this area are still important and interesting for improving the dyeing process from theoretical, technological, ecological and economical points of view. The investigations into the behavior of different dyes in aqueous surfactant solutions can give useful information for understanding the thermodynamics and kinetics of the dyeing process and the finishing of textile material. UV-Vis spectroscopy, conductometry and surfactant selective electrodes are among the most widely used measurement methods for studying in this area [6, 8, 11–13]. Conductometer is a cheap equipment and conductometric method is also easy to investigate the interactions between molecules. For these reasons, conductometric method was preferred to use in this study.

There are also several studies about the affect of organic and inorganic solutes on the interaction between dyes and micelles [5, 6, 14], but to date very few studies have been made on the influence of temperature on the interaction between dyes and surfactants [2, 9, 13, 15].

Various parameters including the charge and the alkyl tail length of the surfactants as well as the type and the position of the substituents in the aromatic ring of the dye molecules, can affect the interactions between the surfactant and the dye molecules. Surfactants contain both hydrophobic and hydrophilic part in their structure. The dye solutions properties such as electrical conductivity and absorption spectrum are changed by the addition of small amounts of surfactant with varying the medium of the solution. The changes as a function of surfactant concentration in the measured quantities indicate a significant variation in the nature of the solution [3]. When the charge of the surfactant is opposed to that of the dye, the attractive forces between the dye and surfactant molecules lead to dye–surfactant complex formation in the solution [16].

The purpose of this study was to investigate the interactions of cationic surfactants; tetradecyltrimethyl ammonium bromide (TTAB), hexadecyltrimethyl ammonium bromide (CTAB) with anionic dye; Acid Green 25 (AG) by conductometric method. The influence of temperature and surfactant structure (the effect of alkyl chain length of surfactant) on ion pair formation is examined with this method.

2. Experimental

2.1. Materials

Tetradecyltrimethyl ammonium bromide (TTAB), hexadecyltrimethyl ammonium bromide (CTAB) and Acid Green 25 (AG) were Sigma chemicals and were used without further purification. Ultra pure water, obtained by deionising distilled water using a Milli-Q Reagent Grade water system, was used for praparing solutions for all physical measurements.

2.2. Method

The conductance measurements of solutions were performed with Metrohm 712 digital conductometer using a dip type cell with cell constant of 0.99 cm^{-1}. The specific conductivity of deionized water was measured before the each series of measurement at each temperature. Then the specific conductivity of an exact volume and known concentration of AG solution (10^{-4} M) was measured. Binary mixtures of dye/surfactant were prepared by keeping the dye concentration constant while increasing the surfactant concentration. Then the specific conductivity of each solution was measured. The uncertainty of the measurements was ±0.01 $\mu S\ cm^{-1}$. The specific conductivity of the surfactant alone was also measured at the concentration that is exactly the same as in the binary mixtures. Measurements were made at 25.0, 30.0, 35.0, 40.0, and 45.0 ºC. The temperature of solutions was kept within the range of ± 0.1 ºC.

3. Results and discussion

AG with two sulfonate groups is reacted with the studied cationic surfactants in 1:2 ratio (Figure 1). The specific conductances of AG –TTAB, and CTAB mixtures at different temperatures were shown in Figures 2 and 3, respectively. If there were no interaction between AG and surfactants in the solution, the experimentally measured conductance of the mixed solution should be the sum of the conductivities of the individual AG ions and the surfactant ions in the solution [17].

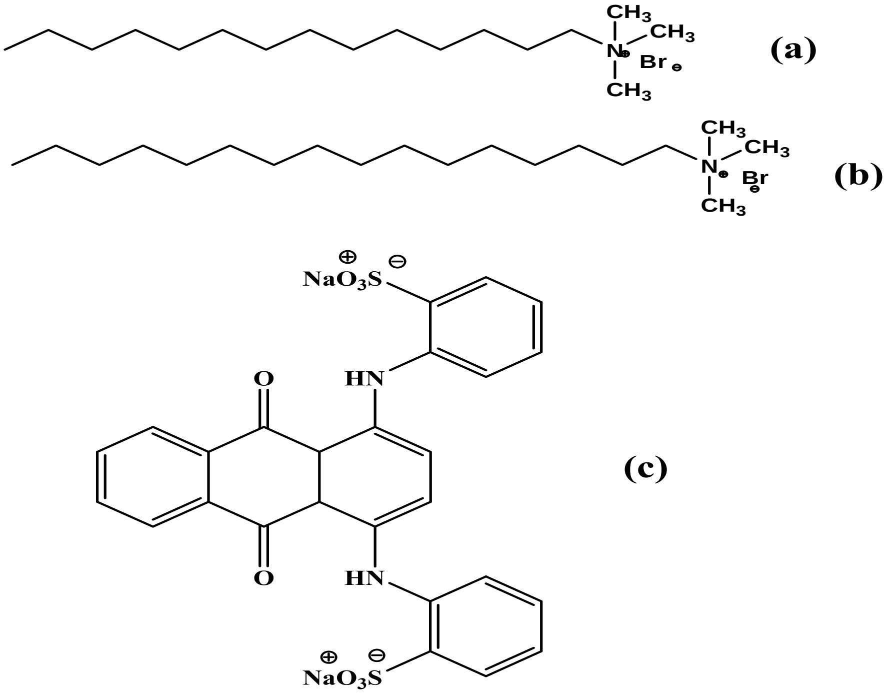

Figure 1: The chemical structure of TTAB (a), CTAB (b), AG (c).

Figures 2 and 3 show that the measured conductances of the AG – surfactant mixtures are lower than the sum of the specific conductivities of the individual AG and the individual surfactant molecule.

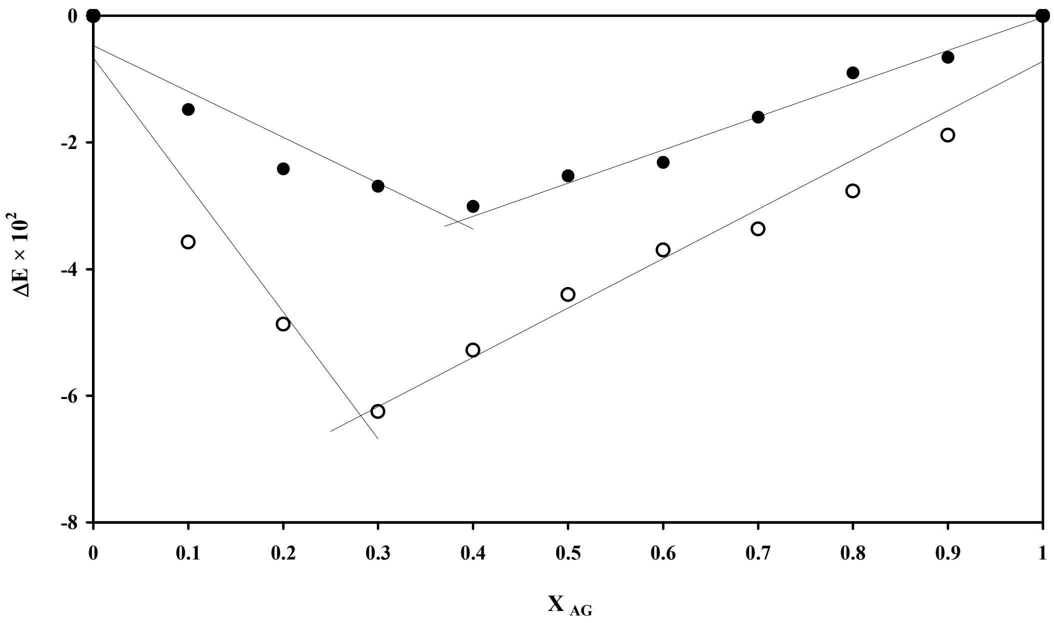

Figure 2: Plots of Job's method for:AG/ CTAB (○), AG/ TTAB (●) mixtures. Equimolar solutions (0.1mM) of Acid Green and surfactants were used.

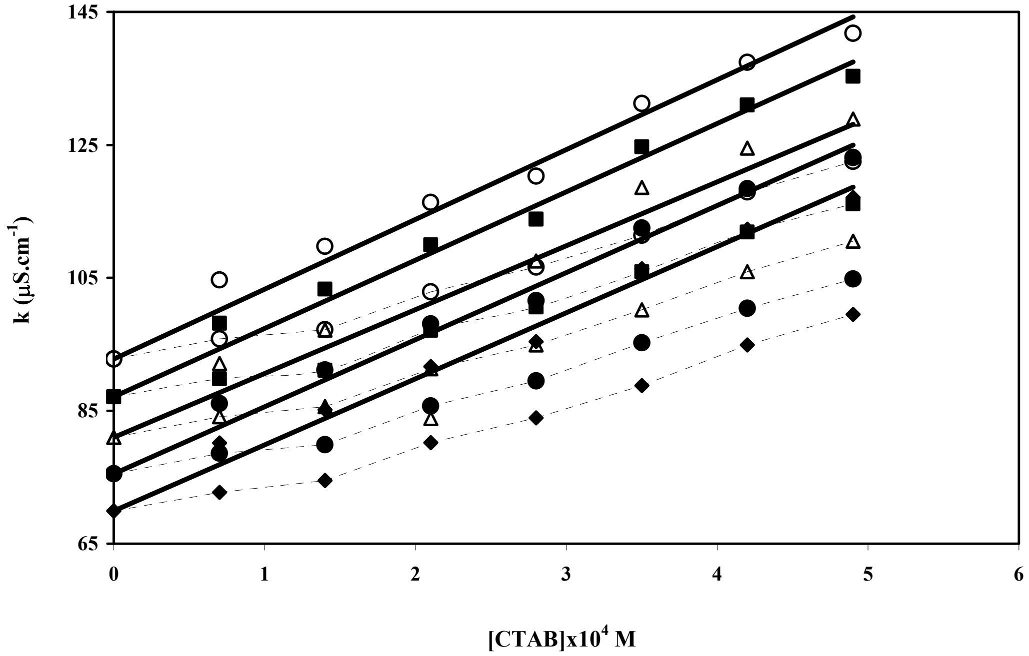

Figure 3: Specific conductivity of AG – CTAB mixture in aqueous solution as a function of the CTAB concentration at 25 °C (◆), 30 °C (●), 35 °C (△), 40 °C (■)and 45 °C (○) Solid lines show the sum of the conductivities of individual species in the solution, dashed lines show the measured conductivity of dye–surfactant mixtures.

The decrease in the measured values can be explained by the formation of a non-conducting or a less-conducting species in the solution. Furthermore, the specific conductance would increase linearly with increasing the concentration of added surfactant. As can be seen from the figures, specific conductance curve deviates from linearity at certain concentration of the surfactant and at a certain temperature. This indicates that a non-conducting or a less-conducting species forms in the solution. However, the deviation of measured values from linearity decreased with increasing the temperature. From the figures, it can also be observed that at 40°C, the measured conductance for the AG-TTAB and AG-CTAB mixtures increases linearly. This indicates that there are no nonconducting or less-conducting species in the solutions at this temperature.

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 dye-surfactant mixture and a theoretical straight line that represents the sum of the specific conductivities of the dye and the surfactant [10,11,13].

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:

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

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

$$DS_{n-1}^{+(n-3)} + S^{+} \longleftrightarrow DS_n^{+(n-2)} \qquad K_3 \qquad (3)$$

where S^+, D^{2-} and $DS_n^{+(n-2)}$ refer to the free surfactant cation, the free AG anion and complexes with different numbers of surfactant cations (n), respectively. K_1, K_2, …, 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 employed in previous works [18, 19].

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:

$$E_{theo} = \varepsilon_D C_D^o X_D + \varepsilon_S C_S^o (1 - X_D) \qquad (4)$$

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

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

$\varepsilon_{D_mS_n}$ 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 is obtained for all mixtures and can be plotted versus X_s-:

$$\Delta E = E_{exp} - E_{theo} \qquad (6)$$

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~0.35 (fraction of AG) implies 1:2 stoichiometric ratio for AG-cationic surfactant ion pairs (Figure 2). According to job's approach, it is assumed that only DS_{2-} complexes are formed in the studied mixtures. The conductance of the solution is, in fact, the sum of conductances of individual ions in the solution.

If a non-conducting complex formation DS_2 occurs between dye D^{2-} and surfactant $2S^+$ molecules, the equilibrium interaction for this case can be written as:

$$D^{2-} + 2S^+ \longleftrightarrow DS_2 \qquad (7)$$

If there was no interaction between the dye and the surfactant molecules in the solution, the measured conductance would be given by Eq. 8.

$$10^3 \kappa = C_D \cdot 2\lambda_{Na^+} + C_D \lambda_{D^{2-}} + 2C_S \lambda_{S^+} + 2C_S \lambda_{Br^-} \qquad (8)$$

where C_D and C_S are the molar concentrations of the dye and the surfactant, respectively and λ_{Na+}, $\lambda_{D^{n-}}$, λ_{S+}, and λ_{Br-} are the equivalent conductances of the ions Na^+, D^{2-}, S^+ and Br^-.

It is evident from Figures 3 and 4 that there are interactions between the dye and the surfactants. This interaction decreases the concentration of free ions in the solution and Eq. (8) can be written as:

$$10^3 \kappa = (C_D - C_{DS_2})\lambda_{D^{2-}} + C_D \cdot 2\lambda_{Na^+} + (C_S - C_{DS_2})2\lambda_{S^+} + 2C_S \lambda_{Br^-} \qquad (9)$$

where C_{DS_2} is the concentration of the non-conducting dye–surfactant complex. By subtracting Eq. (9) from Eq. (8), Eq. (10) is obtained:

$$10^3 \Delta\kappa = C_{DS_2}(\lambda_{D^{2-}} + 2\lambda_{S^+}) \qquad (10)$$

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

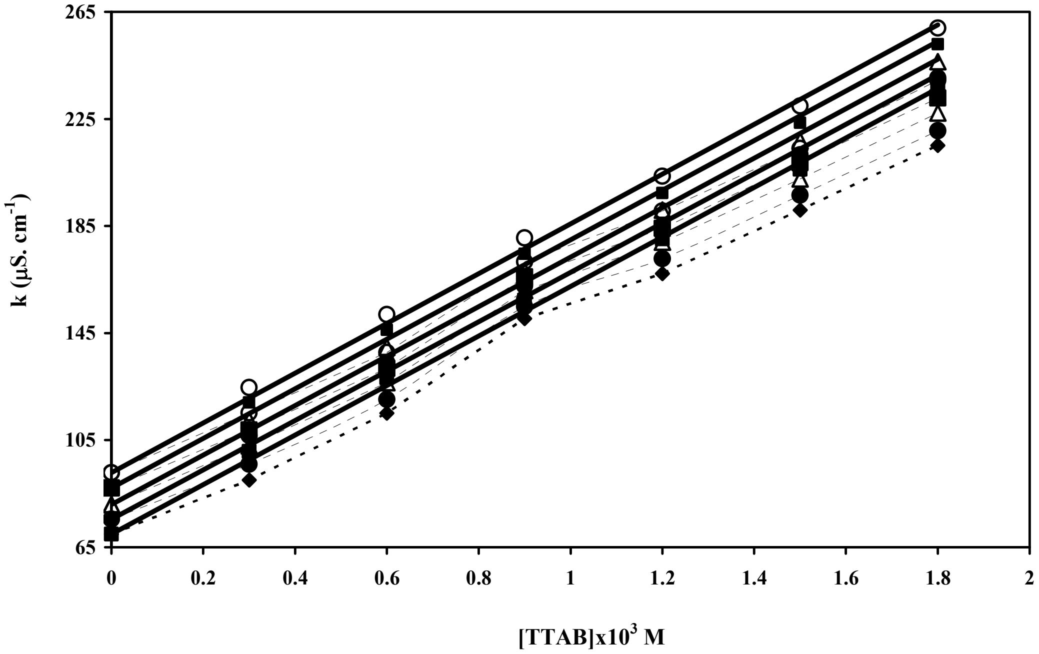

Figure 4: Specific conductivity of AG – TTAB mixture in aqueous solution as a function of the TTAB concentration at 25 °C (◆), 30 °C (●),35 °C (∆), 40 °C (■)and 45 °C (O) Solid lines show the sum of the conductivities of individual species in the solution, dashed lines show the measured conductivity of dye–surfactant mixtures.

Based on the Kohlrausch's law in dilute solution, Eq. (10) is given as:

$$10^3 \Delta\kappa = C_{DS_2}(\lambda^o_{D^{2-}} + 2\lambda^o_{S^+}) \approx C_{DS_2}\Lambda^o_{DS_2} \qquad (11)$$

Where $\Lambda^o_{DS_2}$ is the equivalent conductance of the dye–surfactant ion pair at infinite dilution and can be obtainned for any system by plotting the equivalent conductance Λ versus $C^{1/2}$ according to the Kohlrausch equation:

$$\Lambda = \Lambda^o - b\sqrt{C} \qquad (12)$$

where Λ is molar conductivity of the solution at concentration C and b is a constant. Λ^o value of a salt can be calculated from the intercept of a graph by plotting Λ versus $\sqrt{C}$. Λ is obtained from the slope of conductometry plots according to the Eq. (13):

$$\kappa = (10^3 \Lambda) \times C \qquad (13)$$

The $\Lambda^o_{DS_2}$ values were determinated experimentally by measuring the specific conductivities of the surfactants TTAB and C TAB as well as the dye; these values are shown in Table 1. By using Eq. (11), we can estimate ion pair concentration at each concentration of dye and surfactant.

Table 1: Equivalent conductances (S cm^2 mol^{-1}) at infinite dilution in water for dye (AG), surfactants (TTAB and CTABA) and the complex (DS$_2$).

T(°C)	Λ^o_{AG}	Λ^o_{TTAB}	$\Lambda^o_{AG\,(TTAB)2}$	$\lambda^o_{S+(TTAB)}$	Λ^o_{CTAB}	$\Lambda^o_{AG\,(CTAB)2}$	$\lambda^o_{S+(CTAB)}$
25.0	665.0	112.4	633.3	34.3	168.0	744.6	89.9
30.0	669.0	114.1	607.4	25.8	190.0	759.3	101.7
35.0	670.0	115.8	581.0	18.4	210.0	769.5	112.4
40.0	677.0	118.2	564.8	14.3	224.0	776.3	120.1
45.0	685.0	118.7	544.0	4.7	246.0	798.6	131.9

The equilibrium constant for the reaction of complex formation (Eq. 1) is given by Eq. (14).

$$K = \frac{C_{DS_2}}{(C_D - C_{DS_2})(C_S - 2C_{DS_2})^2} \qquad (14)$$

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

When the equilibrium constants for both surfactant systems are compared, the equilibrium constant for the dye-CTAB systems is higher than those of dye-TTAB systems. This situation is in accordance with Traube's rule [20]. 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. The CTAB molecules have a longer aliphatic chain compared TTAB molecule. Furthermore, a larger value of K for CTAB-AG in comparison with TTAB-AG 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 AG and Alkyl chain resulting in an increase in the K value of ion pair.

3.2. Thermodynamic parameters for the binding and partition processes

The free energy (ΔG^o), the enthalpy (ΔH^o), and the entropy (ΔS^o) changes which belong to the binding processes for the interactions of AG with TTAB and CTAB at different temperatures can be calculated using Eqs. (15)–(17), respectively, [21] from the K values in Table 2.

$$\Delta G^\circ = -RT \ln K \qquad (15)$$

$$\Delta H^\circ = \frac{\partial(\Delta G^\circ / T)}{\partial(1/T)} \qquad (16)$$

$$\Delta S^\circ = \frac{(\Delta H^\circ - \Delta G^\circ)}{T} \qquad (17)$$

According to Eq. (16), a plot of $\Delta G^o/T$ versus 1/T gives a straight line (van't Hoff plot) and the slope of this line is equal to ΔH^o.

Table 2: The values of K ; ΔG^{o}; ΔH^{o} and ΔS^{o} for AG-TTAB and CTAB complex formations.

System	T(^{O}C)	K(M^{-2})	ΔG^{O} (kJmol $^{-1}$)	ΔH^{O} (kJmol $^{-1}$)	ΔS^{O} (Jmol $^{-1}$K^{-1})
AG-TTAB	25.0	2.87×10^{6}	-36.84	5.28	142.35
	30.0	3.05×10^{6}	-37.61		142.55
	35.0	3.11×10^{6}	-38.29		142.43
	40.0	3.21×10^{6}	-38.99		142.39
	45.0	3.34×10^{6}	-39.71		142.39
AG-CTAB	25.0	3.98×10^{7}	-43.36	12.38	188.56
	30.0	4.32×10^{7}	-44.29		188.51
	35.0	4.77×10^{7}	-45.27		188.65
	40.0	5.11×10^{7}	-46.19		188.56
	45.0	5.51×10^{7}	-47.12		188.54

The calculated standard thermodynamic parameters of the interaction of AG in the aqueous ionic surfactant systems (viz., ΔG^{o}, ΔH^{o} and ΔS^{o}) are given in Table 2 for the binding processes at various temperatures. The van't Hoff plots for the interaction of AG with premicellar of TTAB and CTAB in aqueous solution are shown in Figure 5.

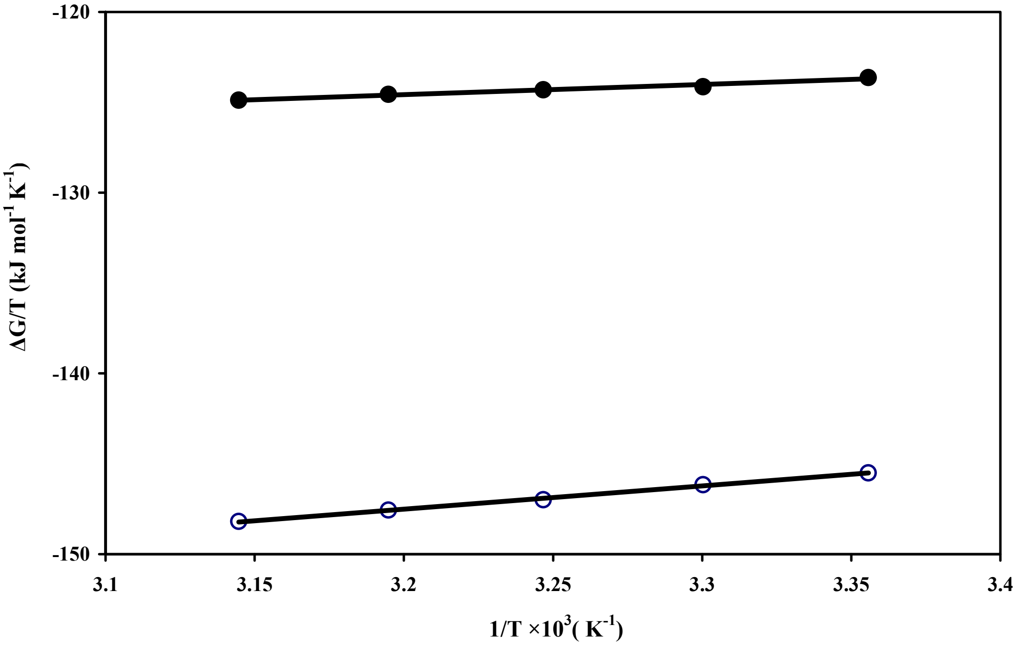

Figure 5: Plot of $\Delta G^{\circ}/T$ versus $1/T$ for the binding of AG to the submicellar of TTAB (●) and CTAB (○), respectively.

From the data obtained in Table 2 it is evident that all ΔG^o values are negative for both surfactants. The negative ΔG^o values indicate that the binding process of AG to the TTAB and CTAB occur spontaneously. The CTAB molecules have a larger ΔG^o compared to TTAB surfactant. The ΔG^o decreases with decreasing alkyl chain length of the surfactants as well as with decreasing the alkyl chain length of CTAB to TTAB. The calculated ΔH^o values are given in Table 2. The positive ΔH^o values indicate that binding processes are endothermic.The ΔH° decreases with decreasing alkyl chain length of the surfactants as well as with decreasing the molecular weight of CTAB to TTAB. This indicates weaker interaction between the low alkyl chain length with a dye by lower hydrophobicity. The standard entropy changes, ΔS° are positive and higher in the presence of the dye. ΔS° also increased with the chain length of the surfactant indicating a correlation of the strength of the interaction with hydrophobic interaction. The observed positive entropy changes may be due to mixing and a more disordered water structure in the dye-surfactant system compared to the free dye and surfactants in solutions. Thus, the large negative free energy changes in the systems result from the positive entropy changes in the system and are an entropy-driven reaction.

4. Conclusions

Acid Green 25 forms a non-conducting ion pair with Tetradecyltrimethyl ammonium bromide (TTAB), hexadecyltrimethyl ammonium bromide (CTAB) at certain temperatures. In this paper, we introduced one method for calculating the equilibrium constant of interactions between the dye and the surfactants. With this method, the equilibrium constant can be determined from the conductance measurements. The determination of K is very simple with this method and the value of K can give us essential data about the strength of the interaction between the dye and the surfactant. The formation of dye-surfactant ion pair is a consequence of mutual influences of long range electrostatic force and short range hydrophobic interactions. The increase of the hydrophobicity of surfactant increases the tendency to associate. Since the equilibrium constant was higher in the case of the surfactant with the longer aliphatic chain, this indicates that hydrophobic effects are important for dye-surfactant ion pair formations. Thermodynamic parameters, ΔG^o and ΔH^o indicate that binding process of AG to the submisellar of the all surfactants are spontaneous and endothermic. The favorable free energy changes of the binding process arise from the large positive entropy changes.

Acknowledgment

We gratefully acknowledge the Research Council of University of Guilan for supporting this work.

5. References

1. H. W. Gao, Y. Qian, Z. J. Hu, Tetraiodophenol-sulfonphthalein as a spectral substitute to characterize the complexation between cationic and anionic surfactant, *Dyes Pigm.,* 279(2004), 244-252.
2. M. Abe, T. Kasuya, K. Ogino, Thermodynamics of surfactant-dye complex formation in aqueous solutions. Sodium alkyl sulfates and azo oil dye systems, *Colloid. Polym. Sci.,* 266(1988), 156-163.
3. M. N. Khan, A. Sarwar, Study of dye-surfactant interaction: aggregation and dissolution of yellowish in *N*-dodecylpyridinium chloride, *Fluid Phase Equilib.,* 239(2006), 166-171.
4. M. E. Diaz Garcia, A. Sanz-Medel, Dye-surfactant interactions: a review, *Talanta,* 33(1986), 255-264.
5. P. F. Tavcer, J. Span, Dye-surfactant interactions studied using Job's method, *Text. Res. J.*, 69(1999), 278-284.
6. N. Hashemi, G. Sun, Intermolecular interaction between surfactants and cationic dyes and effect on antimicrobial properties, *Ind. Eng. Chem. Res.,* 49(2010), 8347-8352.
7. J. Yang, Interaction of surfactants and aminoindophenol dye, *J. Colloid Interface Sci.,* 27(2004), 237-243.
8. V. Kubicek, K. Nemcova, Study of the interaction phenomena of cetyl-trimethyl-ammonium bromide, cetylpyridinium chloride and benzethonium chloride with C.I. Acid Orange 52 and picric acid by two

spectral methods, *Dyes Pigm.,* 68(2006), 183-189.

9. O. Yazdani, M. Irandoust, J. B. Ghasemi, Sh. Hooshmand, Thermodynamic study of the dimerization equilibrium of methylene blue, methylene green and thiazole orange at various surfactant concentrations and different ionic strengths and in mixed solvents by spectral titration and chemometric analysis, *Dyes Pigm.,* 92(2012), 1031-1041.
10. B. Simoncic, M. Kert, Influence of the chemical structure of dyes and surfactants on their interactions in binary and ternary mixture, *Dyes Pigm.,* 76(2008), 104-112.
11. D. Jocic, Conductivity measurement-a simple method for determining dye/surfactant interaction. *Text. Res. J.*, 65(1995), 409-416.
12. N. Zaghbani, M. Dhahbi, A. Hafiane, Spectral study of eriochrome Blue Black R in different cationic surfactant solutions, *Spectrochim. Acta, Part A,* 79(2011), 1528-1531.
13. B. Simoncic, J. Span, 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 Pigm.,* 46(2000), 1-8.
14. S. Bracko, J. Span, Anionic dye-cationic surfactant interactions in water-ethanol mixed solvent, *Dyes Pigm.,* 50(2001), 77-84.
15. B. Simoncic, M. Kert, Thermodynamics of anionic dye-cationic surfactant interactions in cationic nonionic surfactant mixtures in comparison with binary systems, *Dyes Pigm.,* 71(2006), 43-53.
16. B. Simončič, F. Kovač, A study of dye-surfactant interactions, part 2 the effect of purity of a commercial cationic azo dye on dye-surfactant complex formation, *Dyes Pigm.,* 40(1998), 1-9.
17. S. Tunc, O. Duman, Investigation of interactions between some anionic dyes and cationic surfactants by conductometric method, *Fluid Phase Equilib.*, 25(2007), 1-7.
18. 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.
19. S. Gokturk, M. Tuncay, Dye surfactant interactionin the premicellar region, *J. Surfactants Deterg.,* 6(2003), 325-330.
20. A. W. Adamson, Physical chemistry of surface, John Wiley and Sons, 3rd ed., New York, 1976.
21. G. W. Castellan, Physical chemistry, the Benjamin/Cummings Publishing Company, Inc., California, 1983.