

Thermodynamic Study of the Interaction Between C.I. Reactive Red180 with Cationic Gemini Surfactant in Aqueous Solution†

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Interactions between Reactive Red 180 and cationic gemini surfactant solutions were investigated by means of electrical conductivity measurements at different temperatures ranging from 298.15 to 323.15 K. Gemini surfactant of the type *N,N'*-didecyl-*N,N,N',N'*-tetramethyl-*N,N'*-ethanediy-diammonium dibromide referred as (10-2-10) was synthesized in our laboratory. It was observed that a decrease in the measured specific conductance of dye-gemini surfactant mixtures was caused by the formation of nonconducting or less conducting dye-surfactant associates. The aggregation of surfactant and dye takes place at a surfactant concentration far below the critical micelle concentration of the individual surfactant. The long-range electrostatic forces and short-range hydrophobic interactions are very important factors at the dye-surfactant aggregation in aqueous solutions. From conductivity data for dyes-gemini surfactant interaction such as micellar ionization degree, counterion binding, equilibrium constant and thermodynamic parameters of interaction were calculated. Thermodynamic parameters of interaction indicate that interaction of dye-(10-2-10) is enthalpy driven.

Key Words: Cationic gemini surfactant, Reactive dye, Ionization degree, Association constant, Thermodynamic parameters.

INTRODUCTION

In recent years, the dimeric surfactants known as Gemini surfactants have generated attention in the academic and various industrial applications¹⁻⁴. These surfactants have two hydrophilic head group and two hydrophobic groups per molecule, separated by a covalently bonded spacer. There is a growing interest to study of gemini surfactants because of their different molecular structure with respect to monomeric surfactants and their superior properties for special purposes⁵⁻⁷. Gemini surfactants show bioactivity as disinfectants and are used in skin care formulations, antipollution protocols, analytical separations, nanoscale technology and as paint additives. In particular, gemini surfactants have critical micelle concentrations (CMC) that are up to two orders of magnitude lower than critical micelle concentrations of corresponding single chain surfactants⁸⁻¹¹. Different methods were used to investigate the dye-surfactant interactions but most widely used are UV-VIS spectroscopy, conductometry and potentiometry (using surfactant selective electrodes)¹²⁻¹⁵. The aggregation phenomenon of oppositely-charged dyes with surfactant molecules involves contributions from both repulsive interactions between the surfactant head groups and attractive interactions between the hydrocarbon tails. In our previous studies, by

spectrophotometric method we were concerned with an anionic dye (RO16)-surfactants (anionic, cationic and non-ionic surfactants) interaction in mixture of ionic and non-ionic surfactants. We also discussed optimum conditions for surfactants and temperatures used in colour fastness of anionic dye^{16, 17}. In addition in the other studies, conductometry was used to understand the interactions between dyes-surfactant and to calculate the equilibrium constants and other thermodynamics¹⁵. In present study, we determined the critical micelle concentration values of *N,N'*-didecyl-*N,N,N',N'*-tetramethyl-*N,N'*-ethanediy-diammonium dibromide in aqueous solutions in presence of Reactive Red 180 using the conductometric technique. To obtain thermodynamic information on the process, the critical micelle concentration values of surfactants in a temperature range are used.

EXPERIMENTAL

Anionic dye: The anionic azo dye, Reactive Red 180 (RR-180, commercial product, gift from DyStar, Istanbul, Turkey) was used without further purification. It exhibits a maximum absorption band (1.878) at 540 nm and 298 K. Its chemical structure is shown in **Scheme-I**.

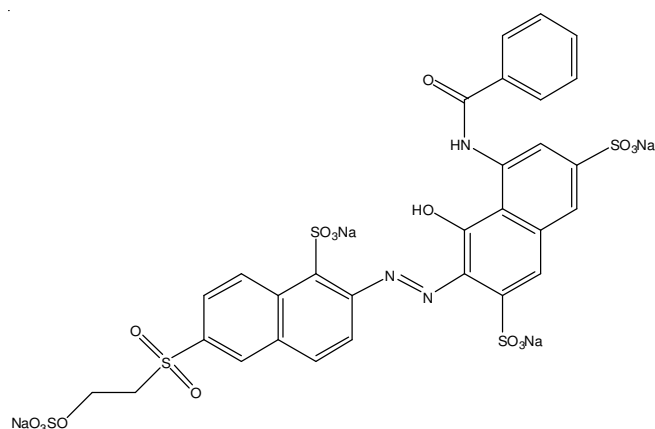
Cationic surfactant: *N,N'*-didecyl-*N,N,N',N'*-tetramethyl-*N,N'*-ethanediy-diammonium dibromide (10-2-10) were

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TABLE-1
VARIOUS MICELLIZATION AND THERMODYNAMIC PARAMETERS OF (10-2-10)
SURFACTANT SOLUTIONS AT DIFFERENT TEMPERATURES

Temperature (K)	CMC (mmol/L)	(α)	ΔG_{mic}^0 (kJmol ⁻¹)	ΔH_{mic}^0 (kJmol ⁻¹)	$T\Delta S_{mic}^0$ (kJmol ⁻¹)	Equilibrium constant (K)
298.15	6.63	0.20	-58.2	-48.1	10.1	1.57×10^6
303.15	6.65	0.22	-58.3	-49.7	8.5	1.07×10^6
308.15	6.67	0.26	-57.4	-51.3	6.0	0.54×10^6
313.15	6.69	0.31	-55.9	-53.0	3.0	0.21×10^6
318.15	6.70	0.34	-55.4	-54.6	0.7	0.13×10^6
323.15	6.71	0.39	-53.8	-56.3	-2.5	0.05×10^6

synthesized from 1-bromo decane (97 %, Fluka), *N,N,N',N'*-tetramethylethylene diamine (98 %, Fluka) and purified in our laboratory as described by Zana¹⁸. The yield of the reaction was almost quantitative, 97 %. The purities were checked *via* nuclear magnetic resonance. The ¹H NMR spectra were recorded in with a Varian Mercury Plus 300 MHz spectrometer and the ¹³C spectra were recorded at 75 MHz.



Scheme-I: Reactive Red 180 (RR180)

Preparation of solutions: Using critical micelle concentration values, which were found for pure surfactant solution, a certain total concentration (1.0×10^{-1} M) was selected. At this selected concentration, micellization was present for all surfactant solutions and so, stock solutions were prepared at this concentration. As dye concentration, 1.0×10^{-4} M concentration value which exhibits a maximum absorption 1.878 at 540 nm was found from calibration curve and this dye concentration was hold constant in all cases.

Conductometric measurements: The conductometric measurements of the solutions were performed by using a WTW Terminal 740 (cell constant = 0.485 cm^{-1}) with a temperature sensor. Conductometric measurements were carried out at six different temperatures (298.15 to 323.15 K). All solutions were prepared with double distilled water in an all-glass distillation apparatus. Specific conductivity of this water was in the range of $(1-2) \times 10^{-6} \text{ S cm}^{-1}$.

RESULTS AND DISCUSSION

Critical micelle concentration: Fig. 1 shows the dependence of specific conductance on the (10²-10) concentration in presence of RR180 at different six temperatures ranging from 298.15 to 323.15 K. The increase of conductivity with concentration, which is observed for diluted solution, is a direct result of the increasing number of free ions in solution.

Conductivities of the systems decrease suddenly at a certain concentration and then increase linearly again. This indicates that the associates (non-conducting or less-conducting species) occurred in the systems. The critical micelle concentration values found from Fig. 1 (Table-1). To comparison with pure water, the various micellization and thermodynamic parameters of (10-2-10) surfactant solutions at different temperatures are given Table-2 (which it was taken from our previous study)⁹. It can be seen from Tables 1-2 and Fig. 1 data that the presence of Reactive Red 180 delays the micellization process and this suggests that dye-surfactant interactions exist in all the studied solutions. According to Reactive Red 180 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 (10-2-10) gemini surfactants. It seems that at first, electrostatic interaction between oppositely charged dye and surfactant molecules of micelles have a major role for consequent hydrophobic interaction and dye penetration and distribution between micelle and water phase.

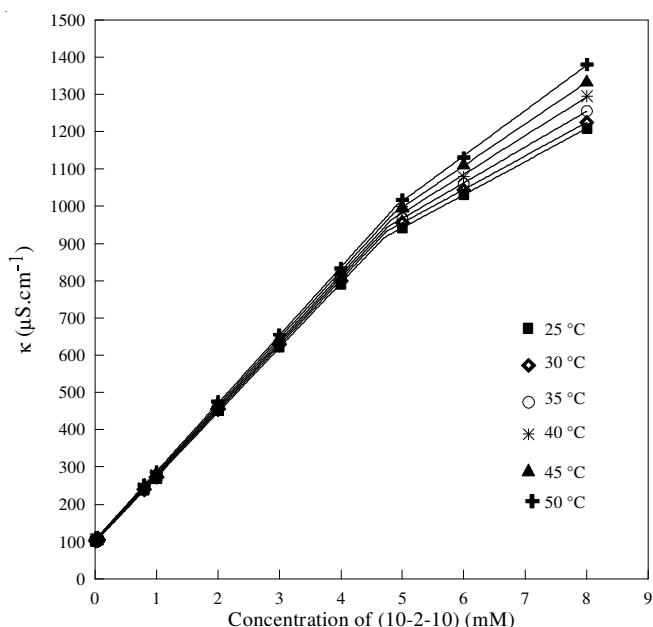


Fig. 1. Plot of specific conductivity against (10-2-10) concentration in RR180-(10-2-10) solutions at different six temperatures

Micelle ionization degree (α): As observed for the studied surfactants, the conductances of surfactants were found to be increased at different rates prior to and after the critical micelle concentration in pure water. The pre-micellar slope (S_1) was always higher than the post-micellar slope (S_2) and

TABLE-2
VARIOUS MICELLIZATION AND THERMODYNAMIC PARAMETERS OF (10-2-10) + C.I.
REACTIVE RED 180 SURFACTANT SOLUTIONS AT DIFFERENT TEMPERATURES

Temperature (K)	CMC (mmol/L)	(α)	ΔG_{mic}^0 (kJmol ⁻¹)	ΔH_{mic}^0 (kJmol ⁻¹)	$T\Delta S_{mic}^0$ (kJmol ⁻¹)	Equilibrium constant (K)
298.15	4.70	0.50	-46.5	-47.6	-1.1	140.3×10^6
303.15	4.74	0.51	-46.8	-49.1	-2.3	115.9×10^6
308.15	4.76	0.54	-46.1	-50.6	-4.5	65.2×10^6
313.15	4.80	0.58	-44.8	-52.1	-7.3	28.7×10^6
318.15	4.85	0.61	-44.0	-53.7	-9.7	16.8×10^6
323.15	4.90	0.66	-42.1	-55.2	-13.1	6.39×10^6

their ratios were used for the evaluation of the values of micelle ionization degree, α , as $\alpha = S_2/S_1 = (d\kappa/dC)_{C > CMC} / (d\kappa/dC)_{C < CMC}$ ^{19,20}. The values of both in pure water and in dye mixed solutions are given in Tables 1 and 2. It can be seen from figures that the presence of dye results in a less abrupt change in conductivity in going from the pre-micellar surfactant concentration range to the post micellar surfactant concentration range, as compared to that in pure water. So that the degree of micelle ionization, α , increases in the presence of Reactive Red 180.

Effect of temperature on the critical micelle concentration and α of (10-2-10)-RR180 solutions: Fig. 2 depicts representative plots of κ against the concentration of (10-2-10) in presence Reactive Red 180 at all six temperatures. It can be seen from Tables 1 and 2 that the presence of RR180 causes an increase in the critical micelle concentration of 10-2-10, Br⁻ gemini surfactant. An increase in the temperature can influence the critical micelle concentration of surfactant by two opposite ways. First one is by decreasing the dehydration of hydrophilic head group and this favours the micellization. Second, by disrupting the water structure surrounding the hydrophobic groups and this does not favour micellization. Here it seems that the second effect predominates over the first in the studied temperature range. The micelle ionization degree describes the number of counter ions not bound to the micelle. It can be seen that as the temperature varied from 298.15 to 323.15 K, α values increased from 0.20 to 0.39 for (10-2-10) gemini cationic surfactant and from 0.50 to 0.66 for 10-2-10-RR180 solution. The values of α both in pure water and in RR180 solution are larger at higher temperature. Thus the degree of counterion binding to micelles β ($\beta = 1 - \alpha$) shows a trend to decrease with increase in temperature, suggesting that the binding of counterions to micellar surface is an exothermic process. So, the counterion binding is caused by an electrostatic interaction between opposite charges²¹.

Thermodynamics of micellization: The thermodynamic parameters can be calculated from the temperature dependence of the critical micelle concentration and a value. The standard Gibbs free energies of micellization (ΔG_{mic}^0), the standard enthalpy change ΔH_{mic}^0 and the entropy change ΔS_{mic}^0 were calculated using the below relations, which were derived for the charged phase separation model of micellization²² and summarized in Tables 1 and 2.

$$\Delta G_{mic}^0(\text{dimer}) = (3-2\alpha) RT \ln X_{CMC}$$

$$\Delta H_m^0 = -2RT^2(1.5 - \alpha) \left(\frac{d(\ln X_{CMC})}{dT} \right)_p - \ln X_{CMC} \left(\frac{d\alpha}{dT} \right)_p$$

$$\Delta S_m^0 = \frac{\Delta H_m^0 - \Delta G_m^0}{T}$$

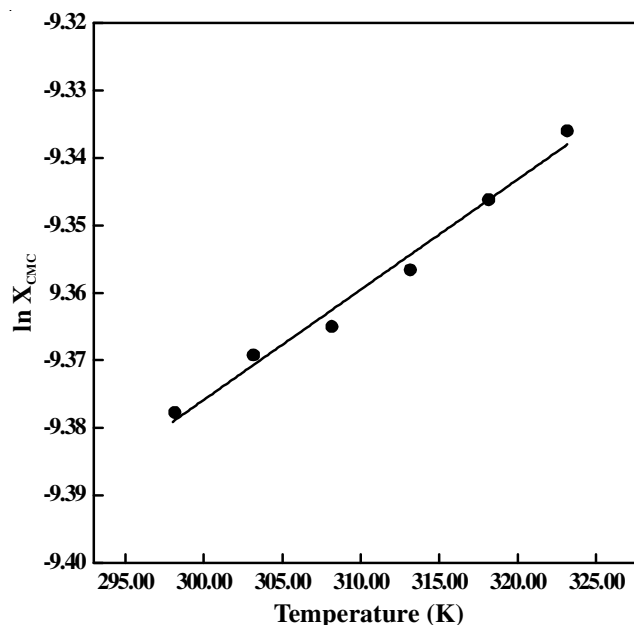


Fig. 2. Plot of $\ln X_{CMC}$ versus temperature for RR180- (10-2-10) solutions

It can be seen from the tables that, Gibbs energy values were found to be negative in all the systems. This reveals that the process of micellization is a spontaneous process. ΔG_{mic}^0 values become less negative in the presence of RR180. It can also be seen that ΔG_{mic}^0 values decrease with increasing

temperature in all cases. The values of $\left(\frac{d(\ln X_{CMC})}{dT} \right)_p$ was

obtained from the slope of a plot of $\ln X_{CMC}$ versus temperature and the plot was shown in the Fig. 2 for RR180-(10-2-10) mixtures. Also, the change of ionization degree versus temperature was shown in Fig. 3. It is evident that the enthalpy of the micellization is to be an exothermic in all cases and slightly decreases with increasing temperature. The values of negative enthalpy indicate that the London dispersion forces have a major importance for the micellization process. These forces are the main attractive force in the micelle formation^{22,23}. The values of ΔS_{mic}^0 were found to be positive which decreased with the increase in temperature for (10-2-10) in pure water. Also, the entropies of micellization in the presence of RR180 were found to be negative and become more negative with the rise of in temperature (Table-2). This implies that the presence of RR180 causing an effective decrease in the degree of randomness of the system. As the temperature increased, the hydrogen bonds diminished and so the entropy effect decreased. When the temperature increased the size of iceberg decreased due to melting and so less energy was required to break up the three-dimensional water structure. From the thermodynamic

data it is evident that equilibrium constants values, K , for RR180-(10-2-10) systems are smaller than that of (10-2-10) systems; the K values for (10-2-10) were found between 1.57×10^{10} - 4.97×10^8 in water and between 1.40×10^8 - 6.39×10^6 in presence of the Reactive Red 180 over the temperature range 298.15 K to 323.15 K, respectively. Also, equilibrium constants, K gradually decreased with increasing temperature in all cases. According to our thermodynamic results, the interaction between RR180 and - (10-2-10) is an enthalpy-driven process. It is known that the value of (ΔG°_{mic}) is the sum of the the enthalpic (ΔH°_{mic}) and entropic ($-\Delta S^{\circ}_{mic}$) contribution. The negative values of ΔG°_{mic} are mainly due to the negative ΔH°_{mic} values. When the temperature increased, entropic contribution also increased and process becomes enthalpy- entropy controlled. (Enthalpic contribution is 5 times larger than the entropic contribution at 323.15 K).

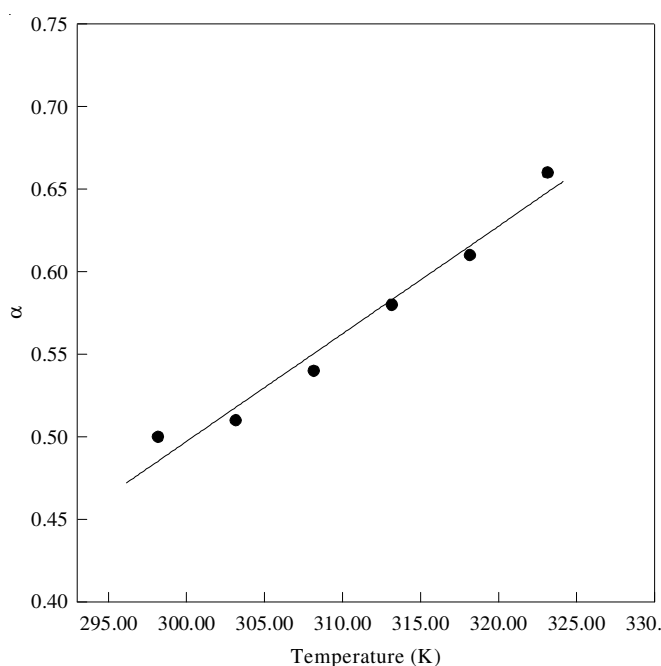


Fig. 3. Plot of ionization degree versus temperature for RR180-(10-2-10) solutions

Conclusion

(1) Micellization process of (10-2-10) is delayed in the presence of Reactive Red 180.

(2) The values of Gibbs energies of micellization (ΔG°_{mic}) show that the micellization process becomes less favourable as the temperature increases.

(3) The values of ΔH°_{mic} show that the association of the RR180-(10-2-10) is exothermic and spontaneous at all the studied cases.

(4) To main contribution to ΔG°_{mic} comes from the enthalpy term and so process is a enthalpy driven process. With the increase in temperature, enthalpic contribution increases and process becomes enthalpy-entropy controlled.

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