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Investigation of Interactions between Sodium Dodecyl Sulfate and Crystal Violet in Aqueous Solution

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To study the interactions between the anionic surfactant sodium dodecyl sulfate in presence of cationic dye crystal violet and effect of increasing temperature on these interactions, both surface tension and conductometric techniques were used. The surface tension and the specific conductance values of dye-surfactant mixtures decreased when proportion of dye increased in the mixtures, in respect of the temperature. Furthermore, the results revealed that the critical micelle concentrations (CMC) have reflected a tendency towards decreasing in the values with increasing in both the proportion of the dye in the surfactant solutions and in the temperatures. Moreover, the interactions of dye-surfactant are spontaneous based on the negative values of standard Gibbs free energy changes of micelle formation (ΔG°_{mic}), for all systems. Significantly, the positive values of standard enthalpy micelle formation (ΔH°_{mic}), revealed that the interactions of dye-surfactant system are endothermic. Additionally, the entropy change of micellization formation (ΔS°_{mic}), is positive.

Keywords: Conductivity, Crystal violet, Micellization, Sodium dodecyl sulfate, Surface tension.

INTRODUCTION

The surfactants have been used as emulsifier, detergents and foaming agents in higher scale. Furthermore, due to their size to lower the surface tension, it is used as auxiliaries in most textile finishing processes such as washing, wetting, dispersing, dyeing and finishing. It has tendency to aggregate in solutions into several supramolecular structures like micelles and bilayers due to the amphiphilic nature [1-5].

Dyes consist of complex unsaturated aromatic compounds. It has unique properties due to the dual significant portions, chromophore and auxochrome. Chromophores have conjugated systems with resonating electrons. However, auxochromes are affecting the colour of the chromophore through the substituting of withdrawing electron [6]. Crystal violet is well-known dye that it is hygienic, antibacterial and antifungal. On the industrial level, it is used to dye paper and prepare printing inks [7].

There are several studies related to interactions between surfactants and dyes. To explain the mechanisms of dyeing and finishing processes, it is essential to know how surfactants and dyes interact in aqueous solutions [8]. Currently, surfactants are in extreme use as dispersing, wetting and leveling agents through dyeing processes. When the surfactants exist in a dye bath, it will causes an interaction between both dye and surfactant ions in the solution, which result in obvious largely modify in the status of dye. It is well known that both ionic surfactants and dyes have charged groups, therefore the interactions between them are relatively difficult and have different types of intermolecular forces. Remarkable modifications in the solution have been observed through the changes in surfactant concentration as function in the measured quantities [9]. A complex of dye-surfactant form in the solution. The reason behind it is the attractive forces between dye and surfactant molecules, which have opposite charges [10].

The interactions between dyes and surfactants can be understood through many techniques, like potentiometry [10,11], voltammetry [12], spectrophotometry [13-16], conductometry [9,17] and surface tension [15,17,18]. Each technique has it is own uses, advantages and disadvantages. For example, in the potentiometric methods, surfactant-selective membrane electrodes were used. Consequently, to investigate the interactions between dye and surfactant, preparation of surfactant-selective electrodes should be done. Furthermore, an exact concentration and pH ranges is required to these electrodes to work, which result of disadvantages of potentiometric methods. Meanwhile, spectrophotometry and voltammetry are more expensive apparatus. Conductometer and tensiometer are economy equipment. Moreover conductometric and surface tension method is simple to examine the interactions between molecules. As a result, conductometric and surface tension techniques were chosen to use in this work.

The purpose of this study is to investigate the interactions between cationic dye crystal violet and an anionic surfactant sodium dodecyl sulfate (SDS), as well as to examine the effect of increasing the proportion of the dye in the surfactant solutions and the impact of increasing temperature on these interactions. Both conductometric and surface tension techniques were implemented to confirm the dye-surfactant interactions. In order to calculate the critical micelle concentrations (CMC) values, a series of conductance and surface tension measurements were performed at five different temperatures, at pure surfactant and at different proportion of the dye in the surfactant solutions. The critical micelle concentrations are calculated to identify the interactions between dye and surfactant, to determine the thermodynamic functions.

EXPERIMENTAL

The cationic dye crystal violet or gentian violet, tris(4-(dimethylamino)phenyl)methylium chloride, $C_{25}N_3H_{30}Cl$, C.I. number (42555) was obtained from Research-Lab Fine Chem Industries® and used without further purification. The anionic surfactant sodium dodecyl sulfate (SDS), $CH_3(CH_2)_{11}OSO_3Na$, was obtained from Panreac®. The chemical structure of dye and surfactant used in this study are given in Fig. 1.

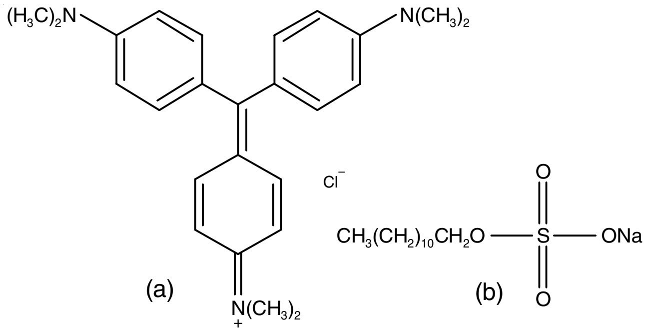

Fig. 1. Molecular structure of (a) crystal violet, (b) sodium dodecyl sulfate

Preparation of solutions: All stock solutions of dye and surfactant were prepared in doubly distilled water. Stock solution of dye was 1 × 10^{-3} M (407.979 g/mol, 0.407979 g). Stock solution of surfactant was 1 × 10^{-2} M (288.372 g/mol, 2.8837 g). 0, 5, 10, 15 % (v/v) of dye-surfactant solutions were prepared above and below the critical micelle concentration of surfactant, in order to correct determination of critical micelle concentration. These solutions are placed on a constant temperature water bath before measurements at 293.15, 303.15, 313.15, 323.15 and 333.15 K.

The electrical conductivity was measured with a conductometer model Mettler-Toledo from SevenGo Duo pro™ and the conductivity cell was calibrated with KCl solution in the appropriate concentration range. The cell constant was 0.10 cm^{-1}. Surface tension measurements were done by applying du Nouy ring method using a Sigma 700 from Attention® model tensiometer and platinum ring. Water bath Lauda CS-C20 Circulating Bath. Control accuracy is ± 0.01 °C.

RESULTS AND DISCUSSION

Surface tension measurements: Fig. 2 shows the variation of surface tension (γ) (mN m^{-1}) for sodium dodecyl sulfate solutions in the absence and presence of 5, 10, 15 % dye as a function of the natural logarithm of free surfactant concentration ln [SDS], in respect of the temperature. The surface tension of surfactant was measured for a range of concentrations above and below critical micelle concentration and the critical micelle concentration values were determined at sharp break point (Table-1). As can be observed from Fig. 2, the surface tension decreased when the surfactant concentrations increased for the pure surfactant aqueous solutions. This is a common behaviour revealed by surfactants in solution and is used to determine their purity and critical micelle concentrations, since critical micelle concentration is characteristic phenomena for each pure surfactant [1].

TABLE-1
THERMODYNAMIC PARAMETERS FOR CRYSTAL VIOLET-SODIUM DODECYL SULFATE MIXTURE, USING CONDUCTANCE AND SURFACE TENSION METHODS

Crystal violet (%)	Temp. (K)	Conductance technique					Surface tension technique				
		CMC × 10^3 (M)	$\Delta G°_{mic}$ (kJ mol^{-1})	$\Delta H°_{mic}$ (kJ mol^{-1})	$\Delta S°_{mic}$ (kJ mol^{-1} K^{-1})	$T.\Delta G°_{mic}$ (kJ mol^{-1})	CMC × 10^3 (M)	$\Delta G°_{mic}$ (kJ mol^{-1})	$\Delta H°_{mic}$ (kJ mol^{-1})	$\Delta S°_{mic}$ (kJ mol^{-1} K^{-1})	$T.\Delta G°_{mic}$ (kJ mol^{-1})
0	293.15	6.00	-12.469	1.143	0.0464	13.612	6.409	-12.308	3.715	0.0547	16.024
	303.15	5.95	-12.915	1.222	0.0466	14.138	6.097	-12.854	3.973	0.0555	16.827
	313.15	5.90	-13.363	1.304	0.0468	14.668	6.097	-13.278	4.240	0.0559	17.517
	323.15	5.80	-13.836	1.389	0.0471	15.225	5.380	-14.038	4.515	0.0574	18.553
	333.15	5.60	-14.361	1.476	0.0475	15.838	5.248	-14.541	4.798	0.0581	19.340
5	293.15	5.800	-12.552	1.215	0.0470	13.766	5.799	-12.552	2.501	0.0513	15.053
	303.15	5.750	-13.002	1.299	0.0472	14.300	5.799	-12.980	2.674	0.0516	15.654
	313.15	5.600	-13.499	1.386	0.0475	14.885	5.656	-13.473	2.854	0.0521	16.327
	323.15	5.600	-13.930	1.476	0.0477	15.406	5.248	-14.105	3.039	0.0531	17.143
	333.15	5.400	-14.462	1.569	0.0481	16.031	5.118	-14.611	3.230	0.0536	17.840
10	293.15	5.600	-12.637	2.286	0.0509	14.923	5.517	-12.674	1.786	0.0493	14.460
	303.15	5.600	-13.068	2.445	0.0512	15.513	5.380	-13.169	1.910	0.0497	15.079
	313.15	5.500	-13.546	2.609	0.0516	16.155	5.248	-13.668	2.038	0.0502	15.707
	323.15	5.300	-14.078	2.778	0.0522	16.857	5.118	-14.172	2.170	0.0506	16.343
	333.15	4.900	-14.731	2.953	0.0531	17.684	4.992	-14.680	2.307	0.0510	16.987
15	293.15	5.500	-12.681	2.358	0.0513	15.039	5.118	-12.856	0.714	0.0463	13.571
	303.15	5.500	-13.114	2.521	0.0516	15.635	4.992	-13.358	0.764	0.0466	14.122
	313.15	5.350	-13.618	2.690	0.0521	16.309	4.992	-13.798	0.815	0.0467	14.614
	323.15	5.200	-14.129	2.865	0.0526	16.995	4.992	-14.239	0.868	0.0468	15.107
	333.15	4.800	-14.788	3.045	0.0535	17.834	4.868	-14.749	0.923	0.0470	15.672

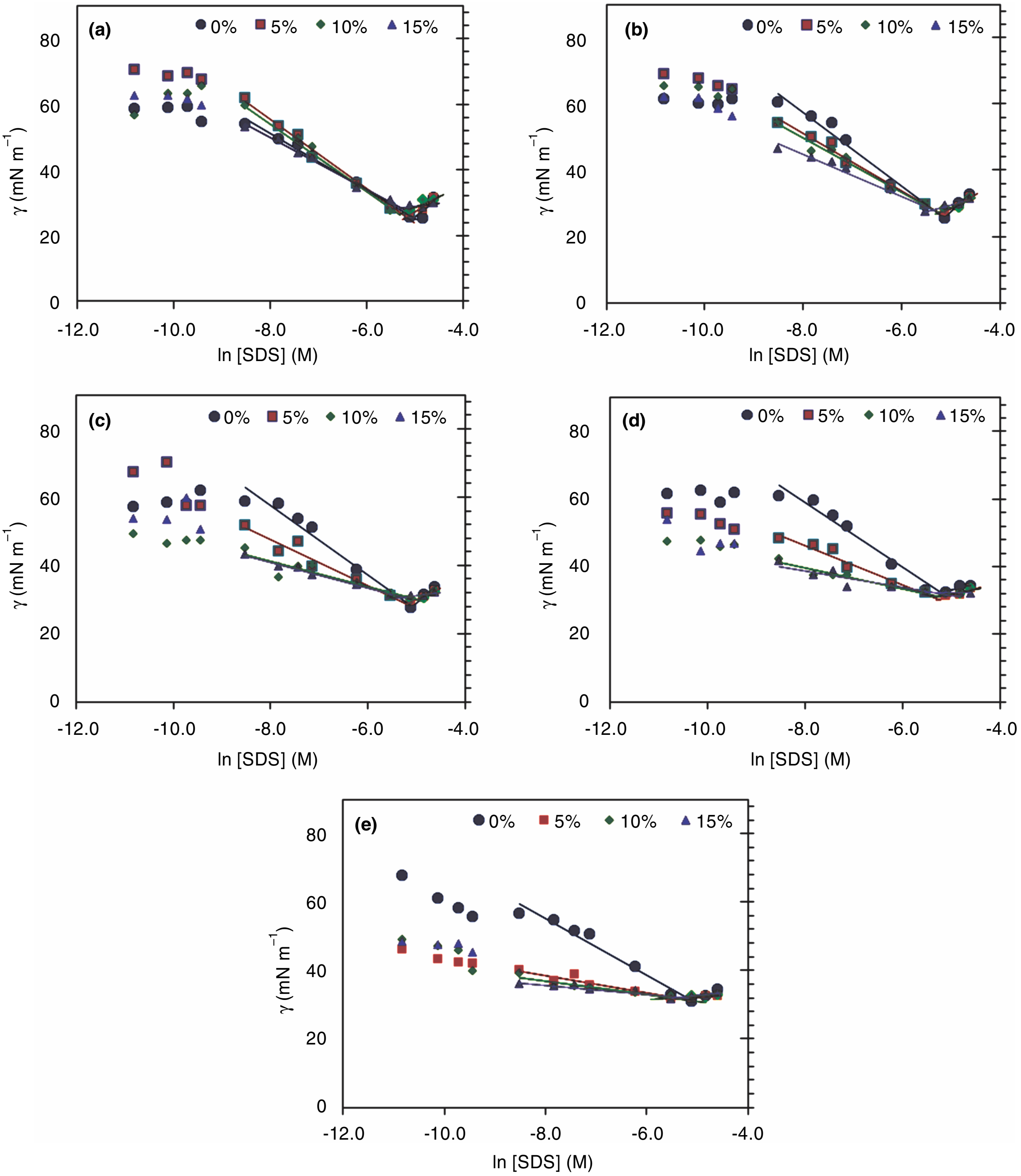

Fig. 2. Surface tension (γ) (mN m^{-1}) against ln concentration (M) of (0, 5, 10, 15 % crystal violet-sodium dodecyl sulfate) mixture at different temperatures (a) 293.15, (b) 303.15, (c) 313.15, (d) 323.15 and (e) 333.15 K

Moreover, a difference of surface tension performance of the surfactant solutions in the existence of the dye. As can be observed in Fig. 2, the surface tension of surfactant decreased when the dye concentrations increased in the solutions, it might be a result of the higher hydrophobicity of the complexes between dye and surfactant, which shaped rapidly under ionic and electrostatic interactions [19].

The data in Table-1 indicated that over the whole temperature range the critical micelle concentration values decreased as the temperature increased. This behaviour can be elaborated as a result of two contradicts effects; first effect is the hydration of the head group and the other effect is structured water molecules surrounding the hydrophobic alkyl chain. The increase in temperature produces a decrease in the hydration of the head group and an increase in the breakdown of the structured water molecules surrounding the hydrophobic alkyl chain. The first favours micelle formation and therefore decrease in the critical micelle concentration happen, while the second does not [20]. So, the first effect is dominant based on the decreasing of critical micelle concentration values.

Conductivity measurements: The crystal violet dye is reacted with the studied anionic surfactant in various proportion of dye (0, 5, 10 and 15). The specific conductances of dye-surfactant mixtures at 293.15, 303.15, 313.15, 323.15 and 333.15 K were shown in Fig. 3, respectively. If there were no interactions between the crystal violet and sodium dodecyl sulfate in the solution, the experimentally measured conductance of the mixed solution must be the sum of the conductivities of the individual ions of dye and surfactant in the solution [21]. Fig. 3 shows that the measured conductances of the mixtures between dye and surfactant are lower than the sum of the specific conductivities of the individual dye and surfactant molecule.

The specific conductance curve deviated from linearity at certain concentration of surfactant and at certain temperature (Fig. 3). This indicates that the components interacted to form corresponding ion pairs. These ion pairs maybe less-conductive or nonconductive species since the specific conductivity of the solution deviated from the linearity and varied as another line with a smaller slope [19,22].

Furthermore, the specific conductance values of the dye-surfactant mixtures decreased when the proportion of dye increased in the mixtures in respect of the temperature (Fig. 3). The decrease was attributed to the formation of a non-conducting or a less-conducting species in the solution [23]. This behaviour is due to interionic attraction. At low proportion of

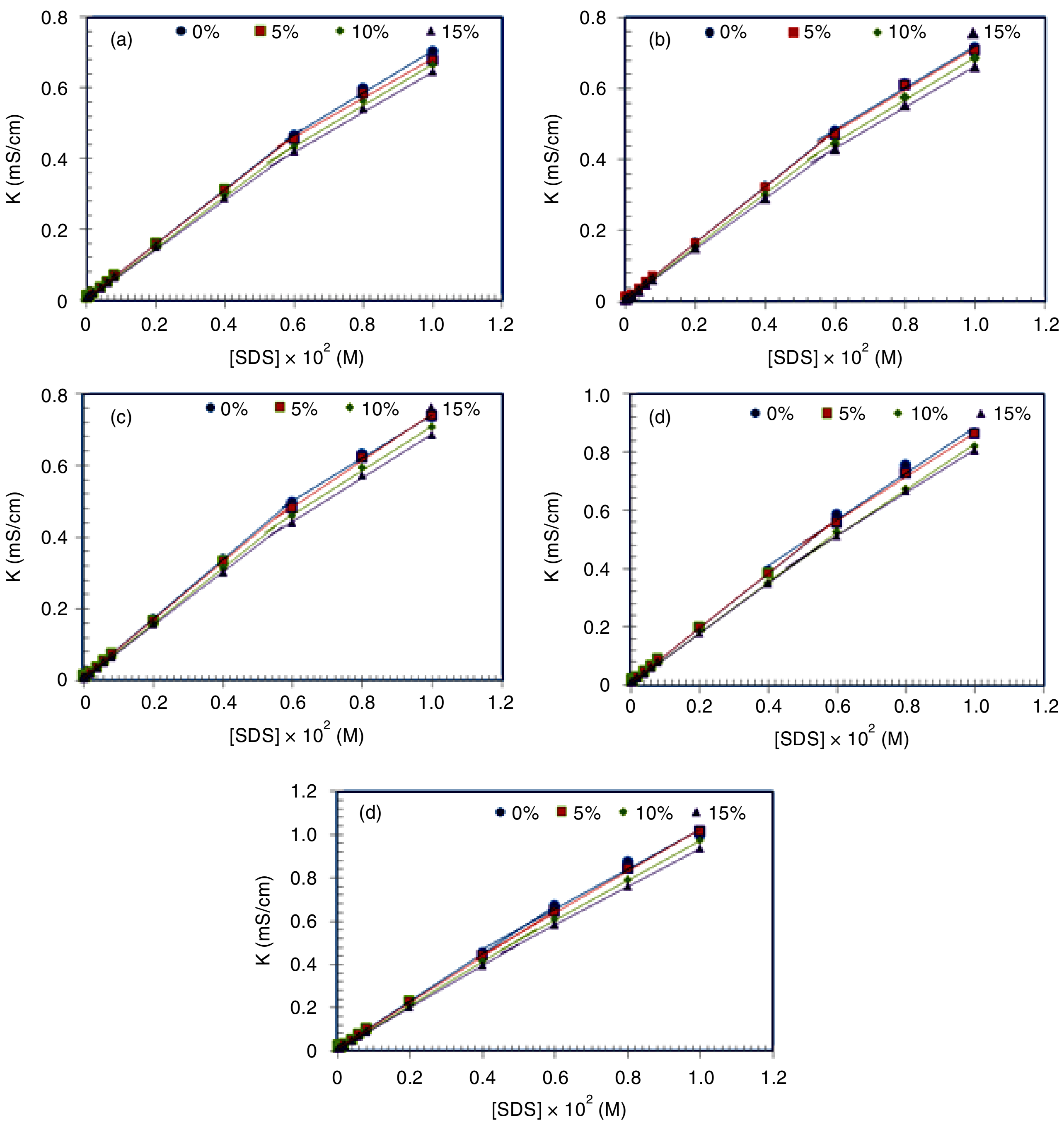

Fig. 3. Specific conductance (κ) (mS cm^{-1}) vis. concentration (M) of (0, 5, 10, 15 % crystal violet-sodium dodecyl sulfate) mixture at different temperatures (a) 293.15, (b) 303.15, (c) 313.15, (d) 323.15 and (e) 333.15 K

dye, the ions were relatively far apart. So, they exerted little influence upon one another. As proportion of dye is increased, the ions come closer to each other. The attraction between ions resulted in a decrease of their speeds and consequently in the specific conductance of the solution.

Table-1 showed the values of the critical micelle concentrations in aqueous solutions at various temperatures. For a given system, critical micelle concentration values decrease with increasing the temperature. The increase in the critical micelle concentration with respect to temperature is usually analyzed in two ways. First, the degree of hydration of the hydrophilic head groups decreased (when temperature increased), which favours micellization (and thereby decreased the critical micelle concentration). Second, as the temperature increases, the water structure around the hydrophobic group is gradually destroyed, which is unfavourable for micellization and then an increase in the critical micelle concentration happens [24,25]. Therefore, it is assumed that the dominant effect is the dehydration of the hydrophilic head groups which results in decreasing critical micelle concentration values.

The result obtained from the measurements of critical micelle concentration corresponded with those previously obtained from surface tension measurements in all system as shown in Table-1. Consequently, coincide results of conductometric and surface tension techniques confirmed the interactions between dye and surfactant and the effect of increasing the proportion of dye and the temperatures.

Thermodynamics measurements: The standard Gibbs free energy changes, of micelle formation per mole (ΔG°_{mic}), is given by:

$$\Delta G^{o}_{mic} = RT \ln CMC \tag{1}$$

whereas R and T are the gas constant and absolute temperature, respectively. The standard enthalpy micelle formation (ΔH°_{mic}), can be obtained from the temperature variation of critical micelle concentration by applying Gibbs-Helmholtz equation to eqn. 1:

$$\Delta H^{o}_{mic} = -RT^2 \frac{d \ln CMC}{dT} \tag{2}$$

Obviously the entropy of micelle formation can be determined from the Gibbs free energy and the enthalpy of micelle formation as given in equation below:

$$\Delta S^{o}_{mic} = \frac{(\Delta H^{o}_{mic} - \Delta G^{o}_{mic})}{T} \tag{3}$$

The values of Gibbs free energy of micellization are negative in all cases studied, as shown in Table-1, indicating spontaneous micelle formation. Moreover, results revealed that the values of Gibbs free energy of micellization become slightly more negative as the temperature increased, reflecting that the dehydration of surfactant molecules is predominant factor in the formation of micelles at higher temperature [26].

Obviously, enthalpy of micellization (ΔH°_{mic}) is positive and slightly dependent on temperature and becomes more positive as the proportion of dye increased. The positive values signifying that the complex formation processes of dye-surfactant system are endothermic [23].

In the temperatures range studied, the entropy change of micellization formation ΔS°_{mic} is positive and becomes more positive as the temperatures increased. Two aspects can be explained the increase in entropy of micelle formation in an aqueous solution; the first aspect, the system "order" would be increased; after the formation of iceberg of the water molecules surrounding the solute (surfactant) molecules, then the micellization process by removing the surfactant molecules from the aqueous medium to the micelle, would surely increase the entropy of the system simply owing to the rupture of iceberg [27], second, the degree of rotational freedom of the hydrophobic chain of surfactant molecules in the non-polar interior of the micelle is much larger than that in the aqueous medium [28]; in other words, the configurationally entropy of hydrophobic chain of surfactant molecules is increased when the surfactant molecules are removed from the aqueous solution to the micelle.

Conclusion

The interactions between the dye and surfactant were investigated by using both conductometric and surface tension techniques. The critical micelle concentration (CMC) revealed a tendency for decreasing with increasing in proportion of dye in mixture solutions, as well as increasing in temperature, for all mixture compositions system. Furthermore, the critical micelle concentration values were in agreement with measured specific conductivity and surface tension techniques. The Gibbs free energy of micellization ΔG°_{mic} was negative in all cases; which meant that the interactions of dye-surfactant were spontaneous and became more negative with increased both the proportion of dye and temperature. The positive values of signified that the complex formation processes of dye-surfactant system were endothermic. Over the whole temperature range, the entropy change of micellization formation is positive and becomes more positive as the temperatures increased.

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