



Thermodynamics of Micellization and Adsorption Behaviour of Anionic Surfactant as Effected by Mixed Organic/Aqueous Media

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Received: 14 August 2015;

Accepted: 24 September 2015;

Published online: 5 December 2015;

AJC-17678

Surfactants being surface-active agents have a number of industrial, medicinal and other applications. The study of surfactants in polar non-aqueous solvents and their mixture with water is a rather limited but new and emerging field. The interactions of alcohols with water can be interesting as it provides a miscible solvent in all ratios as well as polarity can be changed to required level easily. Thus, the work can be applied to improve the bioavailability of drugs. For the purpose we have investigated the micellization behaviour of sodium dodecyl sulfate, an anionic surfactant in mixed organic/aqueous solutions as a function of its concentrations using different techniques like surface tension, conductance and laser light scattering. The results obtained reveal a dramatic change in the critical micelle concentration of surfactants. The thermodynamic parameters of micellization and adsorption have also been calculated from the data obtained.

Keywords: Critical micelle concentration, Sodium dodecyl sulphate, Micellization, Dielectric constant.

INTRODUCTION

The micelle formation in the aqueous solution is known to be affected by organic additives and several studies have been carried out to find out the effect of such compounds on the critical micelle concentration (CMC) of the surfactants. A special attention has been paid in the last decade over the incorporation or solubilization of alcohols, which play an important role in the preparation of micro emulsions [1-8]. In addition to the importance of the theoretical study, the effects of alcohol on the CMC and thermodynamic parameters of surfactants in non-aqueous solutions also have industrial as well as medicinal applications [9,10]. Amphiphilic molecules are the class of surfactants characterized by two moieties, one of which has affinity for aqueous solvent, known as hydrophilic or polar region and the other of which is antipathetic to it, is known as hydrophobic or non-polar region [3]. Most industrial and domestic processes using chemicals involve contact between a liquid and a solid where the solid needs wetting. This is exactly the function of surfactant, however, there are many products which can easily substrates better than water *e.g.* alcohols, hydrocarbons *etc.* [1,5]. If the concentration of these amphiphilic molecules is increased above certain limit then micelles is formed the threshold concentration at which micellization process begins is known as critical micelle concentration (CMC) [5,11-15].

The amount of work done on the physical and chemical properties and aggregation behaviour of surfactants in a mixture of water and polar solvents as compared to mixture of water and polar non-aqueous solvents is rather limited. However, there have been few systematic investigations on the correlation of solvent properties and surfactant aggregation and to follow the change in surfactant aggregation behaviour with the gradual and/or complete exchange of water by a polar solvent is even rare [16]. The objective of this study was to investigate the influences of ethanol on aggregation behaviour of surfactant and to identify the interactions at molecular level between surfactant and the ethanol by obtaining free energy of the system involved in this process. These results will be utilized to investigate the thermodynamic behaviour of the system by using the simple models/thermodynamic relationships. It is hoped that the results will be useful to understand the impact of ethanol over the micellization behaviour of surfactants.

EXPERIMENTAL

Sodium dodecyl sulfate (SDS) was obtained from Acros Organics USA. Ethanol was purchased from Fisher Chemical New Jersey USA. Deionized water used for preparation of samples having conductance 0.9 $\mu\text{S/cm}$.

Surface tension measurement: Surface tension measurements of sodium dodecyl sulfate solutions and solvent were

performed using TE 3 LAUDA Tensiometer, supplied by LAUDA, Germany. These measurements were made at different temperatures (298 to 318 K) and as a function of sodium dodecyl sulfate concentration. The solvent used was a mixture of varying concentration of ethanol in water. The instrument was connected to Ecoline Circulation Thermostat Model E 015T, Germany, to keep the temperature constant up to ± 0.01 °C. Before each measurement the ring was washed with dilute hydrochloric acid followed by deionized water. Then the ring was heated in alcohol flame in order to dry it and remove the adsorbed impurities.

Conductance measurement: The conductance of sodium dodecyl sulfatesolutions and solvent was measured by InoLab Cond.720 conductivity meter as a function of concentration at different temperatures (298 to 318 K). The instrument was connected to Ecoline Circulation Thermostat Model E 015T, Germany, to keep the temperature constant to ± 0.01 °C through the jacketed glass cell used.

Laser light scattering measurement: The aggregation behaviour of sodium dodecyl sulfate in water and water/organic solvent was studied by static and dynamic laser light scattering techniques. The measurement was made at different concentrations while temperature was kept constant. Before laser light scattering measurements, all samples were filtered using a filter of 0.02 and 0.25 mL pore size for the solvent and solution, respectively. Instrument used for the purpose was DAWN EOS/QELS supplied by Wyatt, USA, with helium-neon laser of 632.8 nm wavelength as light source. A cylindrical cell (SV) of 2 cm diameter was used for the purpose.

Differential scanning calorimetric measurement: High-sensitivity differential scanning calorimeter (DSC) was employed to determine the enthalpy of surfactant. For this purpose Perkin Elmer Diamond Differential Scanning Calorimeter Pyris-1 was used to carry out measurements. In order to control the thermal history of samples and to obtain reproducible DSC curves a strict experimental protocol was respected. Solutions were introduced into aluminum pans and left until thermal equilibrium was established before the temperature scan was started. Then the consecutive scans at a rate of 10 °C/min in the temperature range 0-100 °C were carried out, beginning with cooling followed by heating and then again cooling. Between each consecutive scans the samples were equilibrated by giving delay time. From these scans only the last two scans in cooling and heating mode were recorded to obtain reproducible data concerning peaks.

Fourier transform infrared (FTIR) analysis: FTIR spectrum of sodium dodecyl sulfate was recorded in solid form, using FTIR spectrophotometer obtained from company Bruker TENSOR27, Switzerland.

RESULTS AND DISCUSSION

Surface tension measurement: The results obtained from the surface tension measurement of sodium dodecyl sulfate in aqueous and mixed aqueous/organic (ethanol/water mixture) media in the temperature range 298-318 K are plotted as a function of its concentration (Figs. 1-4). It was observed that the surface tension plot showed a typical trend expected for such systems [17]. The plot of surface tension can be divided

into three parts. In the first part of the plot the surface tension decreases slowly until it reaches to a point, we call as critical association concentration of the surfactant (CAC), with further increase in the concentration the surface tension decreases sharply and ultimately leads to a minimum value of surface tension which shows the adsorption of surfactant at the air-water interface and then becomes constant. This point is called critical micelle concentration (CMC). Further increase in concentration of the surfactant does not alter the surface tension; however, it can increase size and change the shape of micelles [17-20].

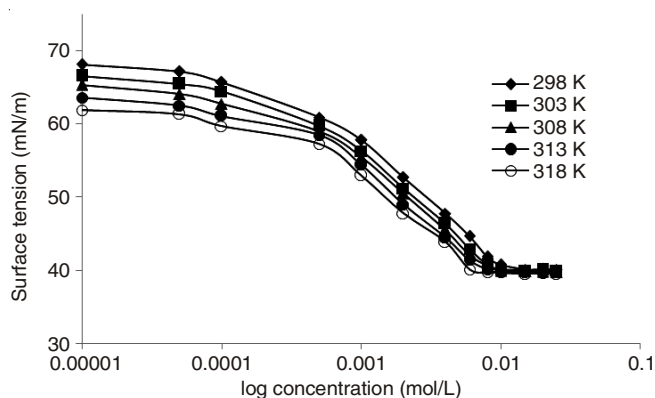


Fig. 1. Surface tension of SDS in water measured at different temperatures

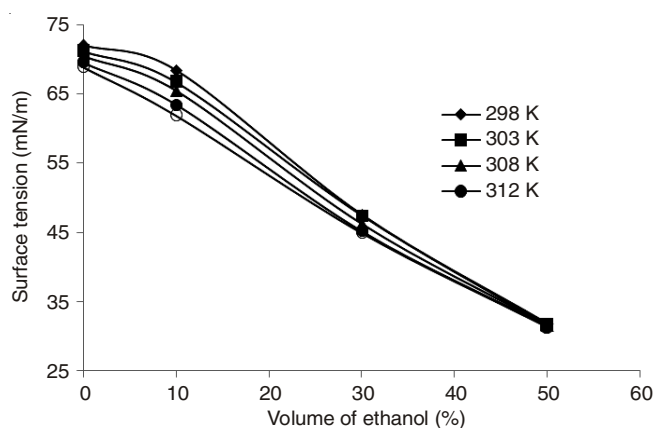


Fig. 2. Surface tension of water-ethanol mixture measured at different temperatures

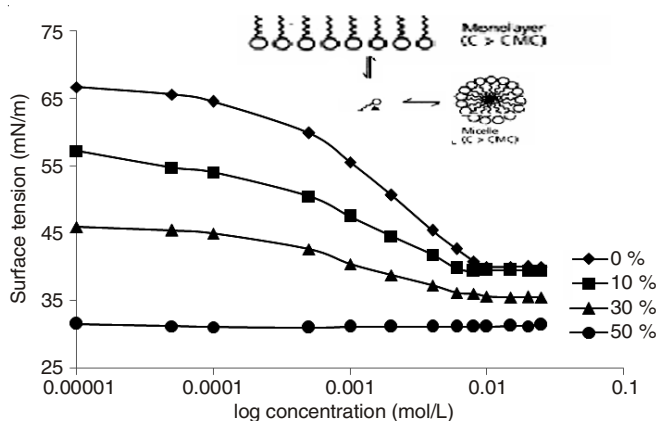


Fig. 3. Surface tension of SDS measured in different ethanol ratio at 303 K

Such behaviour of surfactant can be explained on the fact that at low concentration the surfactant molecules are present in molecular level and coexist in equilibrium with monolayer at the air-water interface. When the solution concentration was increased then the adsorption of surfactant at the interface increased and thus reduction in the surface tension of surfactant [20]. This phenomenon has been discussed by Taylor *et al.* [20]. Further addition of surfactant only leads to further accumulation of surfactant at the air-water interface and micellization, hence the surface tension decreases drastically [17,19,20]. While the surface tension of SDS solution in both water and ethanol/water mixture measured at different temperatures exhibited a similar trend for all temperatures and the surface tension was decreased with increase in temperature. With the increase in temperature the solvent-solute interactions changed and resulted in decrease in the surface tension. It can be noted that the extent of decrease in surface tension with temperature, decreases with the increase in surfactant concentration, which is due to the reason that at high concentration region ($C > \text{CMC}$) the surface tension is not much sensitive to surfactant concentration [20-23].

Surface activity of sodium dodecyl sulfate in the presence of ethanol: The surface tension of sodium dodecyl sulfate (SDS) measured as a function of ethanol contents showed that it decreases with the increasing ethanol contents. This can be explained in the way that by the increasing ethanol content the average interaction between molecules of solvent (hydrogen bonding) decreases, which would make the surface tension of the mixed solvents less (Fig. 2) [16,22]. The surface tension of SDS measured in different volume percent of ethanol in water is plotted (Fig. 3) as a function of its concentration. The results show that the surface tension decreases with the increase in concentration of SDS in usual manner and showing two abrupt changes in surface tension corresponding to CAC and CMC of SDS. Fig. 3 also shows that the CAC and CMC of SDS are decreasing with increase in ethanol content. The addition of ethanol to aqueous solution of SDS reduces the surface tension up to large extent in dilute system and the impact is diminished in higher concentration of SDS and the CAC and CMC remains almost the same. Further addition of ethanol (ethanol/water, 50/50) reduces the surface tension of the system up to the extent that there seems to be no effect of SDS concentration over the surface tension. It means that the

structure of the water is disrupted up to maximum level and hence further addition of SDS neither can increase the amount of molecules at the surface nor change the structure.

The CMC of SDS and γ_{cmc} (surface tension at CMC) decrease with the addition of the ethanol to the aqueous solution of SDS (it follows both the co-solvent and co-surfactant effect). This trend can be due to variation in the solvent properties. For example dielectric constant which is one of the most important parameters of the solvent with reference to solubility of the solute and solute solvent interactions increases or decreases with the addition of ethanol. The dielectric constant of the solution decreases as the ethanol content increases, which in turn influences the various charge effects such as counter ion dissociation and hence the size and shape of the micelle.

Conductance measurement: The conductance of SDS in water and water/ethanol system measured at different temperatures and different ethanol ratio are shown in Figs. 5 and 6. The data shows a smooth increase in conductance with concentration of SDS up to CMC. However, after CMC the slope of the curves of conductance *versus* concentration decreases. This is due to micellization of the SDS as the micellization process increases, the size of the available species and hence reduces the conductance. Another reason which supports the above phenomenon is that SDS is a weak electrolyte so concentration of SDS has great impact on its dissociation. When we increase the concentration, dissociation decreases and equilibrium is shifted towards molecular stage, therefore, the rate of change in conductance with concentration decreases. However with increase in temperature kinetic energy of molecules increases and allows certain molecules of the compound to dissociate resulting in an increase in conductance. Fig. 6 also indicates that the conductance decreases with the increase in contents of ethanol. Ethanol deteriorates the quality of water as a solvent due to its low dielectric constant therefore, due to addition of ethanol dissociation of molecules decreases and hence the conductance decreases. In Figs. 5 and 6, two linear segments of the plots, which correspond to the pre-micellar and micellar regions of the surfactant, can be seen and the CMC was obtained from the intersection of straight lines of these two regions [14,19,24,25], which are comparable with the surface tension technique.

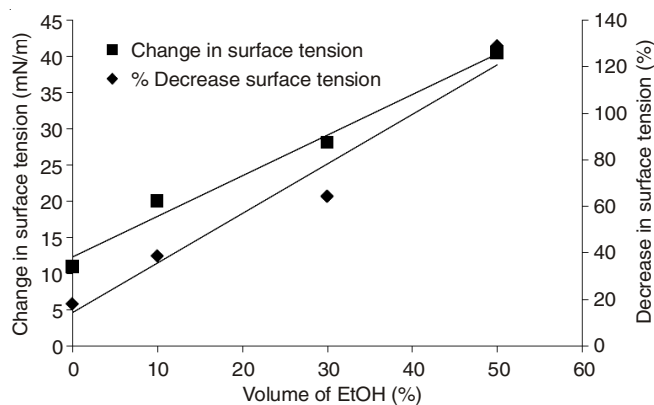


Fig. 4. Per cent decrease and change in surface tension of SDS solution as a function of volume percent of ethanol

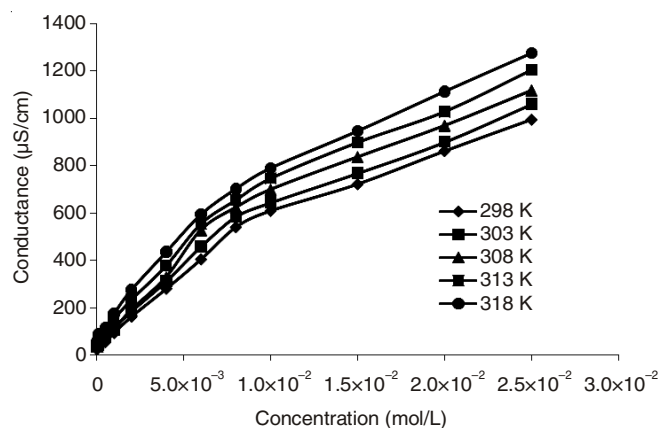


Fig. 5. Conductance measurement of SDS in water as a function of concentration measured at different temperatures

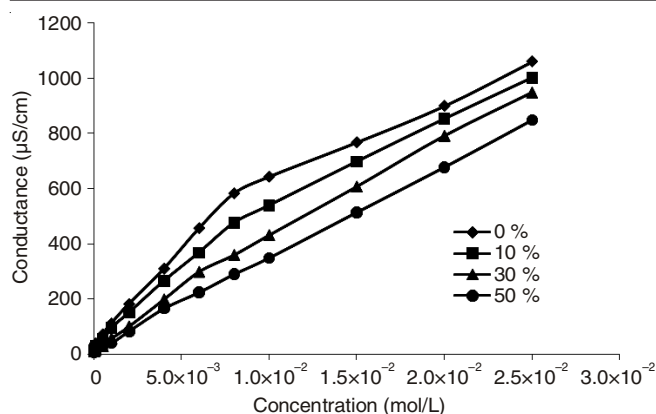


Fig. 6. Conductance measurement of SDS in different ethanol ratio at 303 K

The degree of counter ion binding (β) was evaluated from the slope ratios of the post-micellar (S_2) and pre-micellar (S_1) regions of the surfactant as [26]:

$$\beta = \frac{S_2}{S_1} \quad (1)$$

The values of counter ion binding are plotted in Fig. 7.

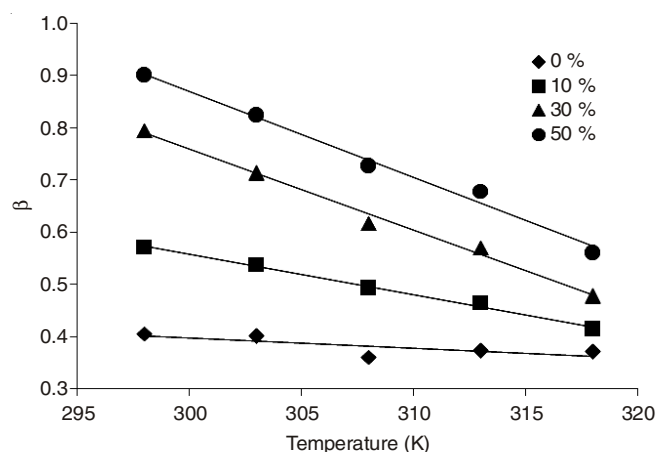


Fig. 7. Degree of counter ion binding as a function of temperature measured at different ethanol ratio

Light scattering: The hydrodynamic radius (R_H) values obtained through dynamic light scattering for SDS are plotted in Fig. 8. It can be observed that in SDS lower concentration, the R_H value is small and not much affected by the increase in SDS concentration. R_H values increases very fast when the SDS concentration reaches to CMC value due to micelle formation. When the concentration of SDS is further increased than the size of micelle *i.e.* its aggregation number increases. This phenomena leads to a sharp change in the micelle size and hence, the rate of change of micelle size decreases with the concentration, when compared to the first part. This can be explained on the basis that when the concentration of SDS is increased than saturation occurs and hence its rate decreases. From Fig. 8, it is concluded that the addition of micelle leads to confirmation changes rather than the size of micelle [27-29].

Fig. 8 also shows that the size of micelle for specific SDS concentrations with increasing alcohol concentration reduces when the alcohol concentration is increased. This can be

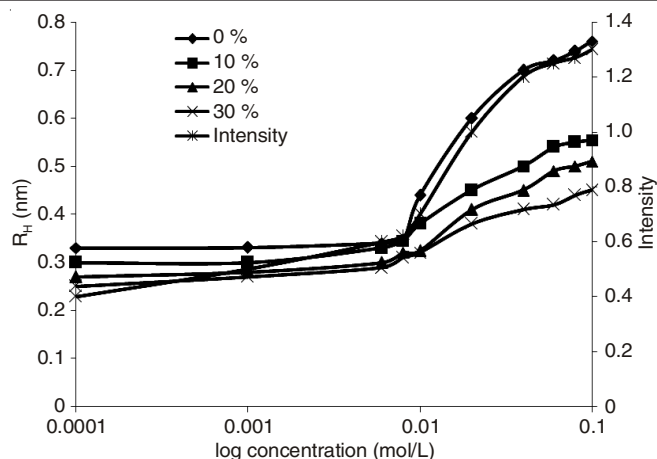


Fig. 8. Hydrodynamic radius as a function of concentration of surfactant measured at different ethanol ratio

explained on the basis that when alcohol is added to SDS solution, its hydrophobicity increases and hence, micelle size decreases. Critical micelle concentration obtained through this technique is comparable.

Calorimetry: The results obtained from differential scanning calorimetry (DSC) are shown in Figs. 9 and 10. The observed peaks illustrate the behaviour of surfactant crystals and its solution in aqueous/organic mixture. Their respective profiles are similar in the heating as well as cooling mode. Fig. 9 showed a single and sharp peak in the heating mode corresponding to the melting/Kraft point of SDS crystals. In the cooling mode similar peak is observed but with high amplitude and position shifted towards lower temperature. Fig. 10 showed two peaks, one corresponding to the melting of crystals which is small and broad followed by second single and sharp endothermic peak corresponding to the micellization of surfactant in alcohol. Similar two peaks observed in cooling mode with higher amplitude than heating. However depending on the sign of thermal gradient, the observed temperatures of the peaks differ by about 15 K between heating and cooling. The enthalpy change calculated by instrument is endothermic which supports our enthalpy change calculated by applying formula (eqn. 16) which also indicated endothermic process;

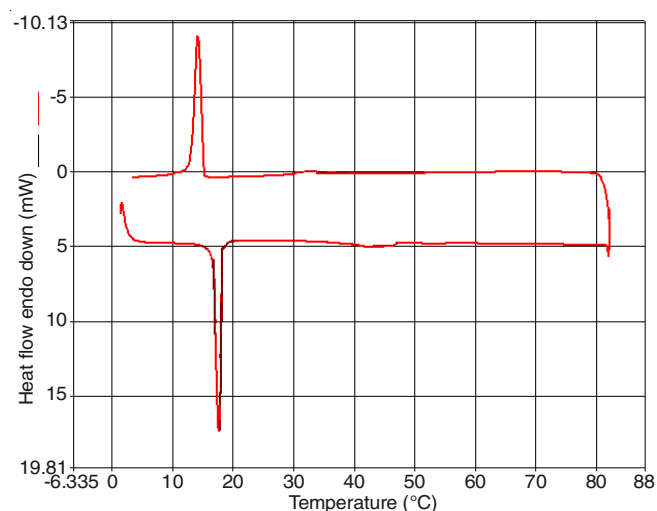


Fig. 9. DSC curve of surfactant recorded in heating and cooling mode at a scanning rate of 10 °C/min

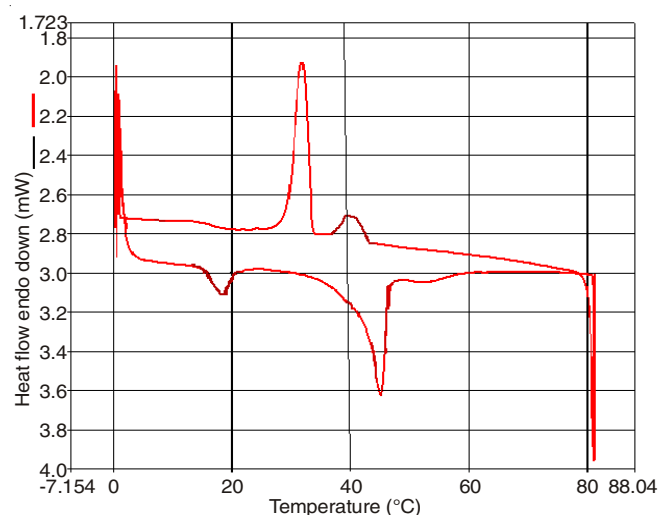


Fig. 10. DSC curve of surfactant in mixed aqueous/organic solution recorded in heating and cooling mode at a scanning rate of 10 °C/min

this means that micellization process of SDS in aqueous/organic mixture is endothermic in nature [28,29].

FTIR analysis: The spectrum in Fig. 11 shows two strong sharp characteristic absorption peaks due to C-H stretch at 2916 and 2850 cm^{-1} . The strong sharp absorption peak at about 1217 cm^{-1} is due to SO_4 and absorption band at 1081 cm^{-1} is due to C-O stretch. Multiple absorption peaks at 1468 and 994-632 cm^{-1} are again due to C-H bending of methyl and methylene groups. Thus it can be concluded from the spectra that the sample is SDS.

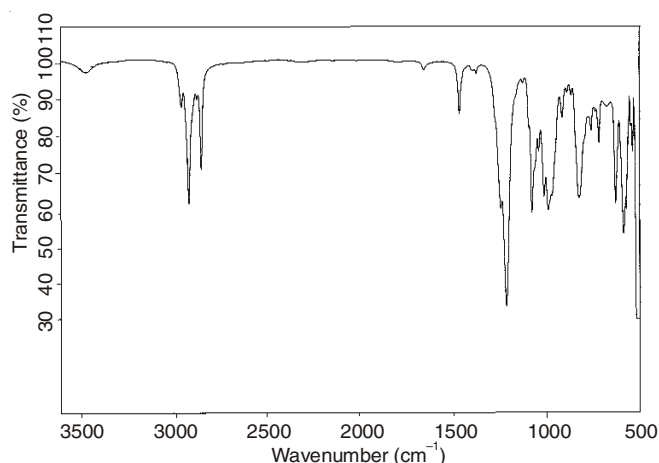


Fig. 11. FTIR spectrum of SDS in solid form

Critical micelle concentration and thermodynamic parameters: The process of micelle formation in aqueous solution occurs when the concentration of free amphiphiles reaches the critical micelle concentration (CMC).

This process of the clustering of low molecular weight surfactant molecules to form micelles can be represented by the following reaction [4]:



where “n” is the degree of aggregation, “p” is the number of counter ion binding to the micelle and “z” is the charge of the micelle.

$$z = n - p \quad (2)$$

It can also be represented as the fraction ionized;

$$\alpha = n - p/n \quad (3)$$

As we know:

$$n - p = z \quad (4)$$

So,

$$\alpha = z/n \quad (5)$$

Mass action model

Now, considering above reaction and applying law of mass action to it we get following results:
The equilibrium constant for this reaction is [3-5].

$$K = X_{\text{mic}} / X_s^n X_{\text{Cl}}^p \quad (6)$$

whereas X_{mic} , X_s^n , X_{Cl}^p are the concentrations respectively. The well known thermodynamic result can be applied to the eqn. 5 to determine ΔG° which is the standard Gibbs free energy change [3-5],

$$\Delta G^\circ = -RT \ln (K) \quad (7)$$

$$\Delta G^\circ = -RT (\ln X_{\text{mic}} - n \ln X_s - p \ln X_{\text{Cl}}) \quad (8)$$

If we define $\Delta G_{\text{mic}}^\circ$ as the standard Gibbs free energy change of micellization per mole of amphiphile *i.e.*;

$$\Delta G_{\text{mic}}^\circ = \Delta G^\circ/n$$

Then

$$\Delta G_{\text{mic}}^\circ = -RT(1/n \ln X_{\text{mic}} - n/n \ln X_s - p/n \ln X_{\text{Cl}}) \quad (9)$$

$$\Delta G_{\text{mic}}^\circ = RT(n/n \ln X_s + p/n \ln X_{\text{Cl}} - 1/n \ln X_{\text{mic}}) \quad (10)$$

$$\Delta G_{\text{mic}}^\circ = RT[(1 + p/n) \ln X_{\text{cmc}} - 1/n \ln X_{\text{mic}}] \quad (11)$$

The second term on the right can be neglected because it is very smaller than the first term at CMC due to the high value of “n”. Thus the above equation becomes;

$$\Delta G_{\text{mic}}^\circ = RT(1 + p/n) \ln X_{\text{cmc}} \quad (12)$$

Considering $n = 0$ for ionic micelles the above equation will become;

$$\Delta G_{\text{mic}}^\circ = RT \ln X_{\text{cmc}} \quad (13)$$

The CMC values expressed in molarity units can be converted into mole fractions by dividing [CMC] by the molar concentrations of water = 55.6 mol L^{-1} .

So the above equation will become;

$$\Delta G_{\text{mic}}^\circ = RT \ln [X_{\text{cmc}} / 55.6 \text{ mol L}^{-1}] \quad (14)$$

Eqn. 14 can be used to evaluate $\Delta G_{\text{mic}}^\circ$ from the available CMC values.

Thermodynamics of micellization: According to the mass-action model different thermodynamic parameters of micellization that is the cmc, γ_{cmc} , $\Delta G_{\text{mic}}^\circ$, $\Delta H_{\text{mic}}^\circ$ and $\Delta S_{\text{mic}}^\circ$ can be calculated using temperature-dependent values of CMC (Figs. 12 and 13, Table-1). It is clear from the data that the critical micelle concentration, CMC, of surfactant SDS in all volume ratios of ethanol/water decreases with increase in temperature as depicted in Fig. 12. This decrease in the CMC of SDS with temperature increase is possibly due to more

TABLE-1
THERMODYNAMICS PARAMETERS OF MICELLIZATION OF SDS IN EtOH-H₂O MIXTURE AT DIFFERENT TEMPERATURES

Volume per cent of ethanol	Temp. (K)	γ_{cmc} (mN/m)	π_{cmc} (mN/m)	ΔG_{mic}° (kJ/mol)	ΔH_{mic}° (kJ/mol)	ΔS_{mic}° (kJ/mol K ⁻¹)
0	298	41.24	34.26	-21.74	9.604	0.1052
	303	40.06	33.05	-22.22	9.603	0.1050
	308	39.73	33.14	-22.99	9.602	0.1058
	313	39.60	32.76	-23.45	9.603	0.1056
	318	39.45	32.06	-23.89	9.604	0.1053
10	298	39.54	28.91	-22.21	10.419	0.1095
	303	39.46	27.30	-22.84	10.396	0.1097
	308	39.38	26.11	-23.28	10.419	0.1094
	313	39.31	24.13	-23.96	10.404	0.1098
	318	38.04	23.85	-24.47	10.413	0.1097
30	298	36.32	11.27	-22.52	29.689	0.1752
	303	35.66	11.77	-23.24	29.696	0.1747
	308	35.64	10.56	-24.32	29.700	0.1754
	313	35.42	09.78	-24.86	29.697	0.1743
	318	35.21	09.75	-25.36	29.687	0.1731

Estimated uncertainties: 1 % in γ_{cmc} , 3 % in π_{cmc} .

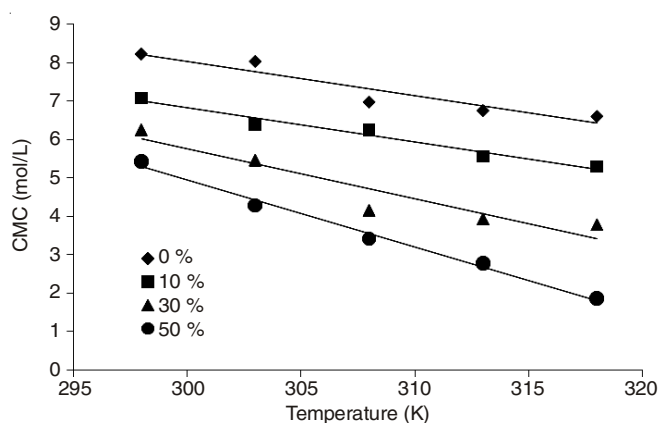


Fig. 12. CMC of SDS measured in water/ethanol mixture as a function of temperature

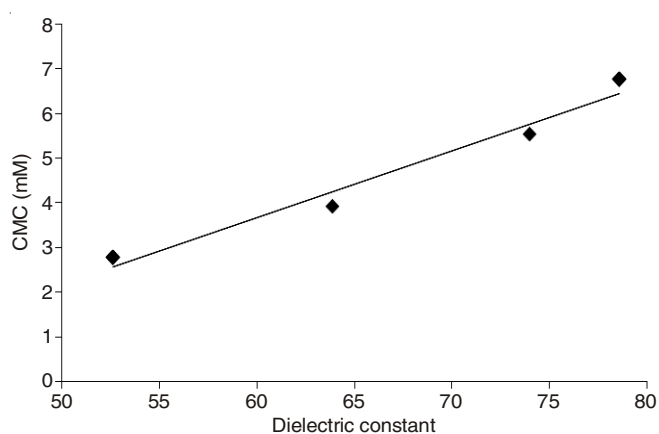


Fig. 13. CMC of SDS measured in water/ethanol mixture as a function of dielectric constant

hydrophobicity and dehydration of the monomers. However the effect of temperature on CMC is complex, temperature increase causes decreased hydration of the hydrophilic group, which favours micellization. However, temperature increase also causes disruption of the structured water around the hydrophobic groups which opposes micellization. It seems that the first effect is dominant in the temperature range studied [3,6,19,23,30].

This decrease in CMC may be due to the reason that with the increase in temperature the free energy of the system is affected in two ways *i.e.* the G_1 , the hydrophobic portion of free energy and G_2 , the electrostatic portion of free energy. Due to this overall change in free energy, the CMC decreases [6].

Decrease in the CMC on addition of alcohol as shown in Fig. 13 may result from the penetration of alcohol molecules into the micelle [31]. An increase in the ethanol content in ethanol -water mixed solvent cause a decrease of dielectric constant of the solvent and, thereby increases of attractive interactions. With the addition of ethanol the co-solvent molecules at the micelle-solution interface lower repulsion between the hydrophilic head groups due to increase in the ionic strength on the bulk phase [30].

Results obtained for free energy of micellization are tabulated in Table-1 as a function of temperature at different volume concentration of ethanol. ΔG_{mic}° values of SDS in water and mixed ethanol/water system are negative and become more negative with increase in temperature, which indicate that the micellization process is spontaneous in nature and become more spontaneous with increase in temperature. From table values it is clear that also with the increase in ethanol content the negative value of ΔG_{mic}° increases which shows that the micelle formation become more spontaneous in ethanol-water system. But the values are less negative than their corresponding ΔG_{ads}° values, indicating that work has to be done in transferring the surfactant from the surface to the micellar stage through the solution [3,19,32].

On the other hand, the enthalpy of micellization can be calculated by applying the Gibbs-Helmholtz equation as follows [4].

$$\Delta H_{mic}^{\circ} = [\partial(\Delta G_{mic}^{\circ}/T)/\partial(1/T)] \quad (15)$$

Using eqn. 13 as the expression of ΔG_{mic}° , eqn. 15 would become as follows:

$$\Delta H_{mic}^{\circ} = R[\partial \ln CMC/\partial(1/T)] \quad (16)$$

In the enthalpy of micellization from the Gibbs-Helmholtz relation, the term $[\partial \ln CMC/\partial(1/T)]$ was calculated from the

slope of the tangent to a plot of $\ln \text{CMC}$ versus $1/T$ at a particular temperature [4]. A less prominent change in $\Delta H_{\text{mic}}^\circ$ values, with changing the temperature was observed, while an increase in the enthalpy was observed with increase in ethanol content (Table-1). $\Delta H_{\text{mic}}^\circ$ is positive at all ethanol ratios, this indicates the endothermic nature of micellization [19,24].

Once $\Delta G_{\text{mic}}^\circ$ and $\Delta H_{\text{mic}}^\circ$ have been obtained, the entropy of the micellization process can be estimated from the relation as follows [4].

$$\Delta S_{\text{mic}}^\circ = \Delta H_{\text{mic}}^\circ - \Delta G_{\text{mic}}^\circ / T \quad (17)$$

The values obtained from eqn. 17 are presented in Table-1. A less prominent change in $\Delta S_{\text{mic}}^\circ$ values was observed with changing temperature. It increases with increase in ethanol contents. The entropy of micellization is positive in all ethanol ratios indicating greater disorder/randomness in the system upon micellization of surfactants in water. The positive value of entropy also suggests that the process of micellization is favoured by entropy gain.

Thermodynamics of adsorption: The surface excess concentration (Γ) of surfactant at the air-water interface as compared to that in the bulk was calculated from the slope of linear portion of linear part of surface tension against $\log C$ curves from Gibbs adsorption equation which is as follows [16,23,32].

$$\partial \gamma = \sum_i \Gamma_i \partial \mu_i \quad (18)$$

where, $\partial \gamma$ = change in surface tension, Γ_i = surface excess concentration of 'i', ' μ_i ' = change in chemical potential of 'i'

$$\partial \gamma = RT \partial \ln a_i \quad (19)$$

At equilibrium, a_i = activity of 'i' in bulk phase = mole fraction $\times$ activity coefficient.

Therefore,

$$\partial \gamma = -RT \sum_i \Gamma_i \partial \ln a_i \quad (20)$$

$$\partial \gamma = -RT \sum_i \Gamma_i \partial \ln C \quad (21)$$

where C = molar concentration of surfactant in bulk.

At constant temperature

$$\Gamma = \frac{-1}{2.303RT} \left(\frac{\partial \gamma}{\partial \log C} \right)_T \quad (23)$$

Knowing Γ , area per molecule at the interface can be calculated by using the following equation [23].

$$a = \frac{1 \times 10^{20}}{N\Gamma} \quad (24)$$

The values of different thermodynamic parameters of adsorption at air-water interface are presented in Table-2. It can be seen from the values that surface excess concentration and the surface area at air-water interface have regular trends with temperature. The surface excess concentration is an effective measure of the Gibbs adsorption at air-water interface. An increase in the surface excess concentration and decrease in the area per molecule values means greater number of monomers can be located at the air/water interface [19,32].

Using the free energy of micellization and surface excess concentration, the standard free energy of adsorption $\Delta G_{\text{ads}}^\circ$ was calculated as [18],

TABLE-2
THERMODYNAMICS PARAMETERS OF ADSORPTION OF SDS
IN EtOH-H₂O MIXTURE AT DIFFERENT TEMPERATURES

Volume per cent of ethanol	Temp. (K)	$\Gamma \times 10^{-5}$ (mol/cm ²)	a_{min} (Å ²)	$\Delta G_{\text{M}}^\circ$ (kJ/mol)	$\Delta G_{\text{ads}}^\circ$ (KJ/mol)
0	298	4.20	3.95	-	-103.29
	303	4.37	3.80	-	-97.79
	308	4.91	3.38	-	-90.52
	313	5.15	3.22	-	-87.01
	318	5.46	3.04	-	-82.63
10	298	3.72	4.47	-0.47	-99.99
	303	3.72	4.46	-0.63	-96.17
	308	4.90	3.39	-0.28	-76.51
	313	5.06	3.28	-0.51	-71.66
	318	5.17	3.21	-0.59	-70.65
30	298	1.61	10.33	-0.78	-92.62
	303	2.14	7.77	-1.02	-78.35
	308	2.24	7.43	-1.33	-71.57
	313	2.77	6.01	-1.41	-60.23
	318	2.82	5.89	-1.47	-59.95

Estimated uncertainties: 3 % in γ and a_{min} , 5 % in $\Delta G_{\text{M}}^\circ$.

$$\Delta G_{\text{ads}}^\circ = \Delta G_{\text{mic}}^\circ - \frac{\pi_{\text{cmc}}}{\Gamma} \quad (25)$$

The values of $\Delta G_{\text{ads}}^\circ$ are negative in ethanol-water mixture (Table-2) which indicates the spontaneous nature of adsorption process.

The effect of a co-solvent or additive on the micellization process can be determined from the free energy of transfer, $\Delta G_{\text{M}}^\circ$, which we have calculated by using the following equation [30].

$$\Delta G_{\text{M}}^\circ = (\Delta G_{\text{mic}}^\circ)_{\text{co-solvent+water}} - (\Delta G_{\text{mic}}^\circ)_{\text{water}} \quad (26)$$

The values are listed in Table-2. The negative values of $\Delta G_{\text{trans}}^\circ$ indicate that the micellization process is more favourable in ethanol-water mixture [25,30,33].

Enthalpy-entropy compensation phenomenon for micelle formation: The compensation between the $T\Delta S_{\text{mic}}^\circ$ and $\Delta H_{\text{mic}}^\circ$ values (Fig. 14) is shown for the micellization of SDS in different EtOH-H₂O mixtures at 303 K. For a large number of aqueous systems, the entropy and enthalpy quantities are known to obey the linear relationship known as the enthalpy-entropy compensation effect. The compensation phenomenon exists in micellization process of surfactants too. In general, this phenomenon between the enthalpy change and the entropy change in various processes can be written as follows [24].

$$\Delta H_{\text{mic}}^\circ = \Delta H_{\text{m}}^{\circ*} - T_c \Delta S_{\text{mic}}^\circ \quad (27)$$

According to the viewpoint of Lumry and Rajender [31] for a compensation phenomenon, micellization can be described as divided into a "solvation" part and a "chemical" part. The slope of the compensation plot (T_c), which is known as the compensation temperature provides a measure of the solvation part of micellization. The intercept, $\Delta H_{\text{mic}}^\circ$ gives information on the solute-solute interactions and stands for an index of the effectiveness of the chemical part of the micelle formation. In eqn. 27, $\Delta H_{\text{mic}}^\circ$ is independent of the entropy change, as $T_c \Delta S_{\text{mic}}^\circ$ is proportional to $\Delta H_{\text{mic}}^\circ$.

Value of $\Delta H_{\text{mic}}^\circ$ obtained from Fig. 14, is found to be 20.19 kJ mol⁻¹ from the intercept of the plot of $\Delta H_{\text{mic}}^\circ$ against $T\Delta S_{\text{mic}}^\circ$ [30,31].

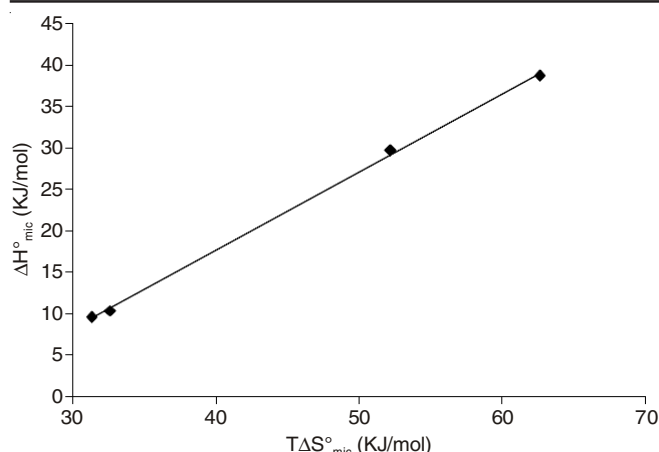


Fig. 14. ΔH°_{mic} against $T\Delta S^{\circ}_{mic}$ for the micellization of SDS measured in different EtOH-H₂O mixtures

ACKNOWLEDGEMENTS

One of the authors, Miss Ayesha Niazi is thankful to HEC for financial support under indigenous Ph.D. Fellowship Program and Hi-Tech Research Lab, Gomal University for providing equipment to carry out research activities.

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