

## Effect of Biologically Significant Metal Complex Additives on the Micellar Properties of SDS

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### Abstract

The effect of some biologically significant transition metal complexes such as  $[\text{Fe}(\text{bpy})\text{Cl}_4]$   $[\text{bpy}-\text{H}]$ ,  $[\text{Co}(\text{bpy})(\text{phen})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ,  $[\text{Fe}(\text{PDCl}_4)[\text{PD}-\text{H}]$ ,  $[\text{Cu}(\text{L})(\text{NO}_3)_2]$ ,  $[\text{Cu}(\text{phen})_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  and  $[\text{Cu}(\text{PD})(\text{phen})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  ( $\text{L}=3,14$ -diethyl-2,6,13,17-tetraazatricyclo(16,4,0<sup>7,12</sup>)docosane,  $\text{bpy}=2,2'$ -bipyridine,  $\text{PD}=1,10$ -phenanthroline-5,6-dione,  $\text{phen}=1,10$ -phenanthroline) on the critical micelle concentration (CMC) of an anionic surfactant, sodium dodecyl sulfate (SDS) were studied by conductance measurement method. The investigation was performed in the additives concentration ranging from  $2.0 \times 10^{-4}$  M to  $8.0 \times 10^{-4}$  M and at temperature ranging from 20°C to 35°C with an interval of 5°C. Different micellar parameters such as CMC, degree of counter ion dissociation ( $\alpha$ ), degrees of counter ion binding ( $f$ ), binding constant ( $K_b$ ) as well as thermodynamic parameters were determined using the conductivity data.

**Keywords:** Surfactant; Sodium dodecyl sulphate; Micellization; Critical micelle concentration; Hydrophobic interaction.

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### 1. Introduction

The behavior of surfactants in aqueous solution is determined by their tendency to move their hydrophobic part away from the solution and their hydrophilic part towards the solution. This dual tendency is responsible for adsorption of surfactants at interfaces and for the formation of such aggregates as micelles. The hydrophobic part of the aggregate forms the core of the micelle, while the polar head groups are located at the micelle–water interface in contact with and hydrated by a number of water molecules [1-3].

Surfactants have applications in many areas, including detergent, food industries, pharmaceuticals, enhanced oil recovery, meteorological processes for concentrating ores, solubilization of water insoluble dyes, hydrocarbons, analytical chemistry and a number of biological and environmental systems [4-8].

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Many research groups are at present working on the characterization of the micelles of different classes of surfactants. Special attention has been paid to study the physico-chemical properties of surfactant micelles like the CMC, aggregation number and micellar shapes, free energy and enthalpy of micellization, effect of added electrolytes, organic compounds on the micellar structures etc.

Kim *et al.* [9] has derived a new equation on the basis of  $\Delta G_0 = -RT \ln K$ , to explain the linear behavior of the enthalpy of micellization with temperature, and the Gibbs-Helmholtz relation. It described the dependence of CMC ( $X_{CMC}$ ) on temperature and has yielded excellent fitting results for various surfactant systems. The new equation resulted in the linear behavior of the entropy of micellization with temperature and accounts for the compensation phenomena observed for the micellization in aqueous solutions, along with the linear dependence of the enthalpy of micellization on temperature.

Lindmann *et al.* [10] has observed the influence of temperature and pressure and found very weak dependence of these parameters on the CMC for a number of (cataionic and anionic) surfactants. Noudeh *et al.* [11] has studied the temperature effect on the CMC over a wide range of temperature for different non-ionic surfactants such as, polyoxyethylene sorbitan fatty acid esters (polysorbate). We have reported the effect of some biologically important compounds on the micellar properties of anionic surfactants, SDS by conductance measurement method and calculated different thermodynamic micellar parameters [12]. We found that the CMC value decreased in the following order.

calcium oxalate < calcium fluoride < calcium chloride < calcium acetate

Ponganis *et al.* [13] interpreted the turbidity observed in aqueous solutions of SDS containing  $[\text{Cu}(\text{phen})_2]^+$  (phen=1,10-phenanthroline) below the CMC occurred from ion pair formation between the metal chelate ion and the polar head groups of the surfactant anions. Meisel *et al.* [14] compared the absorption spectra of  $[\text{Ru}(\text{bpy})_3]^{2+}$  (bpy=2,2'-bipyridine) in aqueous SDS solutions with those in aliphatic alcohols and observed evidence that  $[\text{Ru}(\text{bpy})_3]^{2+}$  interacted with the hydrocarbon part rather than the polar head group of SDS. Sumio *et al.* [15] has studied the interaction of SDS with Fe(II) chelate and concluded that the association complexes are formed mainly by the hydrophobic interaction between the groups of the metal chelate and the hydrocarbon parts of surfactant anions.

Furthermore, Oladega *et al.* [16] studied the binding of some Fe(II) complexes with cetyl trimethyl ammonium bromide (CTAB) and SDS and concluded that any of the surfactants increased the predominance of hydrophobic interaction over electrostatic interaction in the evaluation of the micelle.

A number of heterocyclic ligands such as phen, bpy and 1,10-phenanthroline-5,6-dione (PD) are versatile molecule with applications in organic and biological chemistry. Transition metal complexes containing heterocyclic ligands have been of considerable interest in terms of structural chemistry, catalysis and biological functions. They are

known to possess potential activities in the areas of biological, clinical, analytical, catalytic, microbial, insecticidal, antibiotic, growth factors, food additive, tumor inhibitor, cell division etc. [17-19].

Recently we have reported on synthesis, structural, spectroscopy as well as biological activities of metal complexes containing macrocyclic and phendione ligands [20-22]. In the present work, our aim is to study the interactions of  $[\text{Fe}(\text{bpy})\text{Cl}_4]$  [bpy-H],  $[\text{Co}(\text{bpy})(\text{phen})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ,  $[\text{Fe}(\text{PDCl}_4)]$ [PD-H],  $[\text{Cu}(\text{L})(\text{NO}_3)_2]$ ,  $[\text{Cu}(\text{phen})_2] \text{Cl}_2 \cdot 2\text{H}_2\text{O}$  and  $[\text{Cu}(\text{PD})(\text{phen})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  complexes with anionic surfactant SDS and to reveal the effect of these complexes on the micellar properties of SDS by the measurement of specific conductance, the most widely used method to locate the CMC's of ionic surfactants.

## 2. Experimental

All reagents used for experiment were of analytical grade. SDS, potassium chloride, potassium hydroxide, potassium bromide, sodium hydroxide, sodium chloride, magnesium sulphate, potassium permanganate, cobalt nitrate, copper nitrate, ferric Chloride, copper chloride, bpy and phen (Merck, Germany) were used as supplied. The solvents methanol, ethanol, diethyl ether, dichloromethane and acetone were dried before used according to standard methods. The complexes  $[\text{Fe}(\text{bpy})\text{Cl}_4]$ [bpy-H],  $[\text{Co}(\text{bpy})(\text{phen})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ,  $[\text{Fe}(\text{PDCl}_4)]$ [PD-H],  $[\text{Cu}(\text{PD})(\text{phen})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ,  $[\text{Cu}(\text{L})(\text{NO}_3)_2]$  and  $[\text{Cu}(\text{phen})_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  were synthesized according to the method reported in the literature [20, 23-24].

### 2.1. Method

All the solutions were prepared with double distilled water obtained by distilling alkaline solution of potassium permanganate. SDS solutions of specific concentrations were prepared from 50 mM stock solution by appropriate dilution in double distilled water. The conductivity of the solutions of SDS was measured with a digital conductivity meter (Model: DDS-307, China) equipped with a platinum black electrode (Model: DJS-1C Platinum Black with cell constant =1.0). The meter was calibrated and the cell constant was kept constant in the experimental temperature with 0.01M KCl solutions (specific conductance =  $1.55 \times 10^3 \mu\text{S cm}^{-1}$  at 30°C) at regular time intervals and the electrode was cleaned with distilled water after each measurement. The cell constant was kept constant at 1.0 throughout the work. The CMC of SDS was determined by measuring specific conductance of solutions of particular concentrations of the complexes kept in a plastic beaker by dipping the electrode in solutions. The temperature of the system was kept constant within  $\pm 0.1^\circ\text{C}$  with the aid of a digital thermostat (Clifton, Nickel Electro, England).

### 3. Results and Discussions

#### *Interaction of metal complexes with SDS*

The variation in CMC of SDS in the presence of different concentration of various metal complexes is illustrated in Fig. 1.

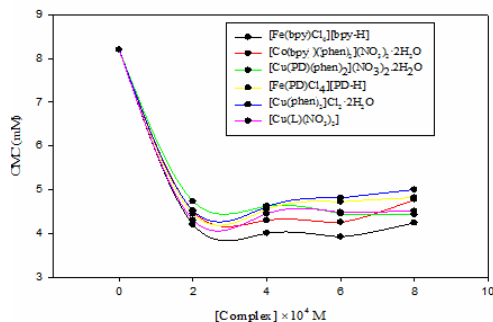


Fig. 1. Variation in CMC of SDS (mM) against concentration of different transition metal complexes at 30°C temperature.

It is observed from Fig. 1 that as the concentration of metal complexes is increased gradually, there is a sharp decrease in CMC values from 8.20 mM. However, it has been found that in some cases the CMC of SDS at first decreased to some value and then increased as the concentration of the metal complexes became higher. This might be due to the fact that the increase of concentration of the metal complexes increases the dielectric constant of water and at lower concentration of the metal complex micellization is influenced by an increase in the dielectric constant of the water [25-27]. Oladega *et al.* [16] showed that the positive charge on  $[\text{Fe}(\text{phen})_3]^{2+}$  made it least hydrophobic than the cyano neutral complexes. According to them the CMC is changed with increasing hydrophobicity according to the following order.

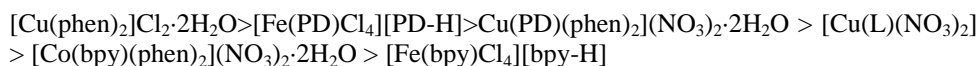


They also established that hydrophobic interaction lowered the CMC more than electrostatic interaction. In a similar fashion the presence of four  $\text{Cl}^-$  ion in the  $[\text{Fe}(\text{bpy})\text{Cl}_4][\text{bpy-H}]$  complex made it more hydrophobic than  $[\text{Co}(\text{bpy})(\text{phen})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  metal complex and so the decrease of CMC of SDS by  $[\text{Fe}(\text{bipy})\text{Cl}_4][\text{bipy-H}]$  metal complex is greater than by  $[\text{Co}(\text{bpy})(\text{phen})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  complex. Esan *et al.* [28] has showed that the binding of the Fe(II) complexes with CTAB is essentially hydrophobic but strong interaction of quaternary ammonium head group with  $\pi$ -electron system of aromatic groups of the ligands in the Iron(II) complex is also important. Corrin *et al.* [29] showed that an increase in the concentration of the electrolytes progressively contracted the electrical double layer around the micelle and in

the process stabilized the micelle. This resulted in a reduction in CMC of the surfactant. Lindman *et al.* [30] showed that an increase in the electrolyte level might not increase the amount of counter ions bound in the Stern layer of the micelle. Thus the greater decrease in CMC of SDS by  $[\text{Co}(\text{bpy})(\text{Phen})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  complex than the neutral complex  $[\text{Cu}(\text{L})(\text{NO}_3)_2]$  might be due to the counter ion binding of the  $[\text{Co}(\text{bpy})(\text{phen})]^{2+}$  complex ion to the dodecyl sulphate ion which decreased the repulsion between the negative charge of the head group of SDS and thereby favored micellization.

The association of the metal complexes to pre-micellar aggregates is fundamentally considered as hydrophobic interaction. The hydrophobic interaction occurred between the hydrophobic tail of SDS and bulky ligand of metal complexes has predominance over the electrostatic interaction and the hydrophobic interaction is related to the type of ligand involved.

The macrocyclic ligand, L=3,14-diethyl-2,6,13,17-tetraazatricyclo(16,4,0,<sup>7,12</sup>)docosane present in the neutral complex,  $[\text{Cu}(\text{L})(\text{NO}_3)_2]$  could have higher hydrophobic character than the mixed ligand PD and phen containing complexes of  $[\text{Cu}(\text{PD})(\text{phen})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  which in turn has lower effect than  $[\text{Fe}(\text{PD})\text{Cl}_4][\text{PD}-\text{H}]$  and  $[\text{Cu}(\text{phen})_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  complexes respectively. Thus the predicted order of decrease in CMC of SDS by these complexes is in the following order.



### 3.2. Thermodynamics of metal complexes-SDS systems

A clear understanding of the process of micellization is necessary for rational explanation of the effects of structural and environmental condition on the value of CMC and for predicting the effects of CMC on the variation of new structural and environmental condition. The interaction of metal complexes at different temperatures with an interval of 5°C ranging from 20 to 35°C in the absence and presence of  $6.0 \times 10^{-4}$  M concentration of metal complexes in aqueous solution and the variation in CMC values are illustrated in Fig. 2. It is obvious from the Fig. 2 that as the temperature is increased the CMC of SDS in the presence of different metal complexes decreased gradually.

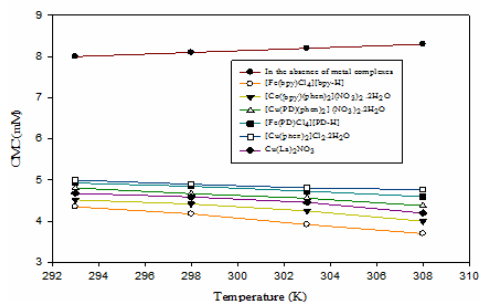


Fig. 2. Variation in CMC of SDS in the absence and presence of metal complexes at different temperature.

***Determination of thermodynamic parameters for metal complexes-SDS systems***

The micellization,  $\Delta G_{mic}^0$ , free energy change of micellization,  $\Delta H_{mic}^0$ , enthalpy change of micellization and  $\Delta S_{mic}^0$ , entropy change of micellization were calculated according to the following equations. The free energy of micellization was calculated using the following equation [31].

$$\Delta G_{mic}^0 = (1+f) RT \ln CMC \quad (1)$$

where,  $f$ , the degree of counter ion binding and the value of  $\alpha$  is known as the degree of counter ion dissociation, was calculated from the ratio of the slope of the straight lines at post-micellar to pre-micellar regions and the values of  $f$  were calculated by subtracting the values of  $\alpha$  from unity.

The binding constant ( $K_b$ ) was derived from the following relation.

$$\Delta G_{mic}^0 = 2.303RT \log K_b \quad (2)$$

From Van't Hoff equation

$$\log K_b = \Delta H_{mic}^0 / -2.303RT \quad (3)$$

A plot of  $\log K_b$  versus  $1/T$  gives a straight line of slope  $\Delta H_{mic}^0 / -2.303R$  from which the value of  $\Delta H_{mic}^0$  was calculated.

The values of  $\Delta S_{mic}^0$  can be calculated from the values of  $\Delta G_{mic}^0$  and  $\Delta H_{mic}^0$  by using the following equation.

$$\Delta G_{mic}^0 = \Delta H_{mic}^0 - T\Delta S_{mic}^0 \quad (4)$$

The calculated values of  $\alpha$ ,  $f$  and  $\log K_b$  by using Eq. 1 are listed in Tables 1 to 6.

Table 1. Calculated values of degree of ionization ( $\alpha$ ), degree of counter ion binding ( $f$ ), binding constant ( $K_b$ ) for the micellization of SDS in the presence of [Fe(bpy)Cl<sub>4</sub>] [bpy-H] complex.

Temperature/K	[Fe(bpy)Cl <sub>4</sub> ] [bpy-H] complex		
	$\alpha$	$f$	$\log K_b$
293	0.442	0.558	3.68
298	0.435	0.565	3.72
303	0.431	0.569	3.78
308	0.425	0.575	3.83

Table 2. Calculated values of degree of ionization ( $\alpha$ ), degree of counter ion binding ( $f$ ), binding constant ( $K_b$ ) for the micellization of SDS in the presence of [Co(bpy)(phen)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O complex.

Temperature/K	[Co(bpy)(phen) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O complex		
	$\alpha$	$f$	log $K_b$
293	0.540	0.460	3.42
298	0.490	0.510	3.55
303	0.478	0.522	3.61
308	0.460	0.540	3.69

Table 3. Calculated values of degree of ionization ( $\alpha$ ), degree of counter ion binding ( $f$ ), binding constant ( $K_b$ ) for the micellization of SDS in the presence of [Cu(PD)(phen)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O.

Temperature/K	[Cu(PD)(phen) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O		
	$\alpha$	$f$	log $K_b$
293	0.550	0.450	3.36
298	0.526	0.474	3.43
303	0.517	0.483	3.47
308	0.502	0.498	3.53

Table 4. Calculated values of degree of ionization ( $\alpha$ ), degree of counter ion binding ( $f$ ), binding constant ( $K_b$ ) for the micellization of SDS in the presence of [Fe(PD)Cl<sub>4</sub>][PD-H] complex.

Temperature / K	[Fe(PD)Cl <sub>4</sub> ][PD-H] complex		
	$\alpha$	$f$	log $K_b$
293	0.403	0.597	3.68
298	0.385	0.615	3.74
303	0.365	0.635	3.80
308	0.345	0.655	3.87

Table 5. Calculated values of degree of ionization ( $\alpha$ ), degree of counter ion binding ( $f$ ), binding constant ( $K_b$ ) for the micellization of SDS in the presence of [Cu(phen)<sub>2</sub>]Cl<sub>2</sub>·2H<sub>2</sub>O complex.

Temperature / K	[Cu(phen) <sub>2</sub> ]Cl <sub>2</sub> ·2H <sub>2</sub> O complex		
	$\alpha$	$f$	log $K_b$
293	0.635	0.365	3.14
298	0.624	0.376	3.18
303	0.615	0.385	3.21
308	0.605	0.395	3.24

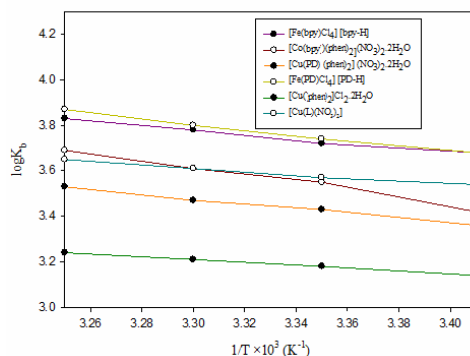
Table 6. Calculated values of degree of ionization ( $\alpha$ ), degree of counter ion binding ( $f$ ), binding constant ( $K_b$ ) for the micellization of SDS in the presence of  $[\text{Cu}(\text{L})(\text{NO}_3)_2]$  complex.

Temperature / K	[Cu(L)(NO <sub>3</sub> ) <sub>2</sub> ] complex		
	$\alpha$	$f$	$\log K_b$
293	0.480	0.520	3.54
298	0.475	0.525	3.57
303	0.466	0.534	3.61
308	0.430	0.538	3.65

It is obvious from Tables 1 to 6 that as the temperature is increased the values of  $f$  increased. This is because as the temperature is increased there would be a decrease in the hydrated radius of the counter ions, which resulted in an increase in the value of  $f$ . As a result, the CMC of SDS in the presence of all the metal complexes decreased with the increase of temperature as represented in Fig. 2.

### 3.4. Determination of enthalpy of micellization for metal complexes-SDS System

Using the Van't Hoff equation 3 a plot of  $\log K_b$  against  $1/T$  for all of the metal complexes will give straight lines with slope  $\Delta H_{mic}^0 / -2.303R$  as shown in Fig. 3. The value of  $\Delta H_{mic}^0$  was calculated from the value of this slope. Thus other thermodynamic parameters were calculated by using Eq. 4.

Fig. 3. Variation of  $\log K_b$  as a function of  $1/T$ .

The calculated values of  $\Delta G_{mic}^0$ ,  $\Delta H_{mic}^0$  and entropy of micellization,  $T\Delta S_{mic}^0$  are (using Eq. 4) given in Tables 7 to 12.



Table 7. Thermodynamic parameters in  $\text{kJmol}^{-1}$  for  $[\text{Fe}(\text{bpy})\text{Cl}_4][\text{bpy-H}]$  complex in aqueous solution.

Temperature/K	[Fe(bpy)Cl <sub>4</sub> ][bpy-H] complex		
	$-\Delta G_{\text{mic}}^0$ (kJ/mole)	$\Delta H_{\text{mic}}^0$ (kJ/mole)	$T\Delta S_{\text{mic}}^0$ (kJ/mole)
293	20.64		38.97
298	21.24		39.57
303	21.90	18.33	40.23
308	22.58		40.91

Table 8. Thermodynamic parameters in  $\text{kJmol}^{-1}$  for  $[\text{Co}(\text{bpy})(\text{phen})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  complex in aqueous solution.

Temperature/K	[Co(bpy)(phen) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O complex		
	$-\Delta G_{\text{mic}}^0$ (kJ/mole)	$\Delta H_{\text{mic}}^0$ (kJ/mole)	$T\Delta S_{\text{mic}}^0$ (kJ/mole)
293	19.20		50.79
298	20.28		51.87
303	20.94	31.59	52.53
308	21.77		53.36

Table 9. Thermodynamic parameters in  $\text{kJmol}^{-1}$  for  $[\text{Cu}(\text{PD})(\text{phen})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  complex in aqueous solution.

Temperature / K	[Cu(PD)(phen) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O		
	$-\Delta G_{\text{mic}}^0$ (kJ/mole)	$\Delta H_{\text{mic}}^0$ (kJ/mole)	$T\Delta S_{\text{mic}}^0$ (kJ/mole)
293	18.85		38.75
298	19.60	19.90	39.50
303	20.14		40.04
308	20.83		40.73

Table 10. Thermodynamic parameters in  $\text{kJmol}^{-1}$  for  $[\text{Fe}(\text{PD})\text{Cl}_4][\text{PD-H}]$  complex in aqueous solution.

Temperature/K	[Fe(PD)Cl <sub>4</sub> ][PD-H] complex		
	$-\Delta G_{\text{mic}}^0$ (kJ/mole)	$\Delta H_{\text{mic}}^0$ (kJ/mole)	$T\Delta S_{\text{mic}}^0$ (kJ/mole)
293	20.67		43.35
298	21.32		44.00
303	22.05	22.68	44.73
308	22.81		45.49

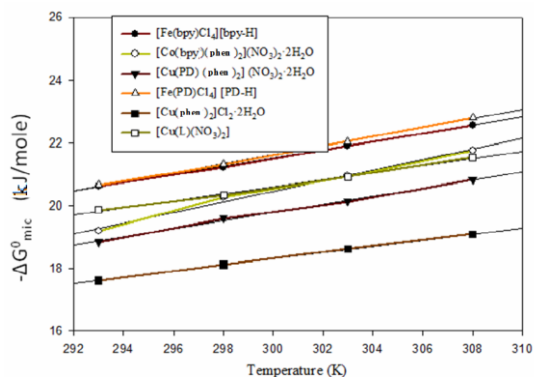
Table 11. Thermodynamic parameters in  $\text{kJmol}^{-1}$  for  $[\text{Cu}(\text{phen})_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  complex in aqueous solution.

Temperature/K	[Cu(phen) <sub>2</sub> ]Cl <sub>2</sub> ·2H <sub>2</sub> O complex		
	$-\Delta G^0_{mic}$ (kJ/mole)	$\Delta H^0_{mic}$ (kJ/mole)	$T\Delta S^0_{mic}$ (kJ/mole)
293	17.62		29.56
298	18.13		30.07
303	18.62	11.94	30.56
308	19.10		31.04

Table 12. Thermodynamic parameters in  $\text{kJmol}^{-1}$  for  $\text{Cu}(\text{La})_2\text{NO}_3$  complex in aqueous solution.

Temperature/K	[Cu(L)(NO <sub>3</sub> ) <sub>2</sub> ] complex		
	$-\Delta G^0_{mic}$ (kJ/mole)	$\Delta H^0_{mic}$ (kJ/mole)	$T\Delta S^0_{mic}$ (kJ/mole)
293	19.86		33.16
298	20.34		33.64
303	20.92	13.30	34.22
308	21.55		34.85

The values of  $\Delta G^0_{mic}$  for different metal complex-SDS systems are plotted against temperature as shown in Fig. 4. It is clear from the Fig. 4 that the negative values of  $\Delta G^0_{mic}$  increased with the increase of temperature i.e. as the temperature increased the formation of micelle became more spontaneous as reported in the literature [27]. The values of  $\Delta S^0_{mic}$  and  $\Delta H^0_{mic}$  in the presence of these complexes are found to be positive. As shown in the Tables 7 to 12  $T\Delta S^0_{mic}$  has higher value than  $\Delta H^0_{mic}$ . This contributed to the negative value of  $\Delta G^0_{mic}$ . This confirmed that the micellization process is actually entropy driven.

Fig. 4. Variation in free energy of micellization with temperature in the presence of various metal complexes at  $6.0 \times 10^{-4}$  M concentration.

#### 4. Conclusion

The CMC values of SDS were found to decrease exponentially from 8.20 mM to 3.92, 4.25, 4.30, 4.43, 4.44 and 4.52 mM in the presence of [Fe(bpy)Cl<sub>4</sub>][bpy-H], [Co(bpy)(phen)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, [Cu(L)(NO<sub>3</sub>)<sub>2</sub>], Cu(PD)(phen)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, [Fe(PD)Cl<sub>4</sub>][PD-H] and [Cu(Phen)<sub>2</sub>]Cl<sub>2</sub>·2H<sub>2</sub>O complexes respectively as the concentration of the metal complexes were increased from  $2.0 \times 10^{-4}$  M to  $8.0 \times 10^{-4}$  M at 30°C. The CMC of SDS was also found to decrease gradually as the temperature was increased from 20°C to 35°C in the presence of these metal complexes. The increase of temperature decreased the radius of the hydrated counter ions and so the repulsion between closely packed head groups was reduced. Consequently, the value of counter ion binding was increased which favored the micelle formation. Furthermore, the values of thermodynamic parameters ( $-\Delta G_{mic}^{\circ}$ ,  $\Delta H_{mic}^{\circ}$  and  $T\Delta S_{mic}^{\circ}$ ) for these metal-SDS systems showed an increasing trend with the increase of temperature and also the micellization was actually driven by change in entropy of the system.

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