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Spectroscopic Study of Interactions of Metal Complexes, Metal Salts and Amino Acids with Anionic Surfactant Sodium Dodecyl Sulphate (SDS) Using Surfactant-Solute-PAN Dye Ternary Systems

M. A. Subhan[*1], M. M. Rana[1], P. Sarker[2], M. A. Rahman[3]

[1]Department of Chemistry, Shah Jalal University of Science and Technology, Sylhet 3114, Bangladesh

[2]Square Pharmaceuticals Ltd., Bangladesh

[3]Department of Chemistry, Comilla University, Comilla. Bangladesh

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Abstract

The study of micellar behavior of SDS in presence of additives such as metal (Fe, Cu, Co, Zn) phendione complexes, calcium salts and amino acids in aqueous solutions in surfactant-solute-1-(2-pyridylazo)-2-naphthol(PAN) dye ternary systems were carried out by measuring the absorbance of PAN at 470 nm. The complexes $[Fe(phendione)_3](ClO_4)_2 \cdot 2H_2O$, $[Co(phendione)_3](ClO_4)_2 \cdot 3H_2O$, and $[Cu(phendione)_2](ClO_4)_2 \cdot 2H_2O$, decreased the CMC value of SDS from 8 mM to 0.70 mM, 0.40 mM, and 1.0 mM, respectively. In presence of calcium salts ($CaCl_2$, CaF_2, calcium acetate, calcium oxalate$\cdot H_2O$) the CMC of SDS decreased. The study of interaction of amino acids with anionic surfactant SDS provides important information about protein-surfactant and peptide-surfactant interaction in aqueous environment. In the present study glycine, L-alanine, L-valine, L-histidine, L-leucine, L-lysine have been used as additives in SDS aqueous solution which also decreased the CMC of SDS. The thermodynamic parameters for each series were obtained from absorbance versus concentration curves. Among the series more negative values for ΔG^0_{mic} of SDS are observed for the metal complexes. Amino acids series as well as metal salts show similar negative values for ΔG^0_{mic} of SDS. Negative values of ΔG^0_{mic} indicated that the process of micellization is thermodynamically favorable.

Keywords: Micellar behavior; PAN dye; Metal complexes; Surfactant; Thermodynamic parameters.

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1. Introduction

Surfactants have multipurpose applications in many areas, including detergent, food industries, pharmaceuticals, enhanced oil recovery, meteorological processes for

* *Corresponding author:* subhan-che@sust.edu

concentrating ores, solubilization of water insoluble dyes, hydrocarbons in analytical chemistry and a number of biological and environmental systems [1–5]. The formation of micelles by ionic and non-ionic surfactants is a well-established fact. In last few years, extensive structural, kinetic and thermodynamic studies have been performed on surfactant–water systems including the effect of additives on micellization [1–5]. Surfactants are capable of arranging themselves into organized molecular assemblies known as micelles. The concentration above which micelles form is called the critical micelle concentration (CMC). It is a well-established fact that the CMC of a surfactant is an extremely important parameter in view of its importance in the determination and optimization of various characteristic properties of micelles used in many pharmaceutical, biotechnological and chemical processes. As a result, detailed investigation of their behavior in aqueous solution and in presence of additives has recently attracted the attention of many investigators. For a couple of years, interests have been grown to reveal the nature of the interactions between metal chelate and different types of surfactants.

Many metal ions play very vital roles in biological processes in the human body. They are found either at the active sites or as structural components of a good number of enzymes. Cobalt is known to be a central element of metabolically important biomolecule, such as vitamin B_{12} and therefore its bio-specification in biological fluids constitutes a theme worthy of chemical and biological perusal. A number of heterocyclic ligands such as 1,10-phenanthroline(phen), 2,2'-bipyridine(bipy) 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. [6–8]. Metal such as calcium is essential for living organisms, in particular in cell physiology, where movement of the calcium ion into and out of the cytoplasm functions as a signal for many cellular processes. As a major material used in mineralization of bone, teeth and shells, calcium is the most abundant metal by mass in many animals. Calcium chloride ($CaCl_2$) is used in ice removal and dust control on dirt roads, in conditioner for concrete, as an additive in canned tomatoes, and to provide body for automobile tires. Calcium acetate is used as a food additive, as a stabilizer, buffer and sequestrant, mainly in candy products under the number E263. It also neutralizes fluoride in water. In kidney disease, blood levels of phosphate may rise (called hyperphosphatemia) leading to bone problems. Calcium acetate binds phosphate in the diet to lower blood phosphate levels. Major constituent of human kidney stones, calcium oxalate is also found in beer stone, a scale that forms on containers used in breweries. Calcium oxalate is also used in the manufacture of ceramic glazes.

The interaction between surfactant and proteins has been under investigation for a long time [9]. The study on the effect of amino acid on the properties of surfactant may provide the important information for interaction between surfactant and protein. Amino acids are important biological-active substances and basic structural units of proteins. A

large proportion of our cells, muscles and tissues are made up of amino acids. They carry out many crucial biological functions, such as giving cells their structure, in the transport and the storage of nutrients, etc. Medicals and clinical positive effects of amino acids include: rheumatoid arthritis, diabetes, fat-burning, skin treatment, reduce hair, cholesterol, etc. [10-13]. The standard amino acid glycine is used to synthesize porphyrins used in red blood cells. Leucine is a major component of the subunits in ferritin, astacin, and other "buffer" proteins. Many factors influence the interactions between surfactants and amino acids. Most industrial, biological, pharmaceutical and cosmetic systems contain surfactants and proteins/amino acids as their major ingredient. Thus the interaction between amino acid and surfactants has drawn much attention in recent years. Although, a number of studies have been looked at amino acid–surfactant interactions, the mechanism in general not well understood. Therefore, in order to understand the mechanism of interaction between surfactants and amino acids, it is important to determine the CMC of the surfactants correctly. Considering all the vital role of surfactants in industrial, biological, pharmaceutical, food industry and other chemical processes, we have been interested in studying the interaction of biologically important metal (Fe, Co, Cu, Zn) phendione complexes, metal salts and amino acids with anionic surfactant sodium dodecyl sulphate (SDS) by UV-Visible spectroscopic method.

2. Experimental

2.1. *Materials*

Sodium dodecyl sulfate (SDS), 1-(2-pyridylazo)-2-naphthol (PAN), cobalt chloride hexahydrates, copper nitrate dihydrates, ferrous ammonium sulfate, Zinc chloride, potassium bromate, sodium perchlorate, sulfuric acid and 1,10-phenanthroline (phen), pentane, calcium chloride, calcium fluoride, calcium acetate monohydrate, calcium oxalate monohydrate, glycine, L-alanine, L-valine, L-hstidine, L-leusine, L-lysine were purchased from Merck, Germany, and used without further purification.

2.2. *Synthesis of ligand, 1,10-phenanthroline-5,6-dione(phendione)*

Phendione was synthesized according to a new and convenient synthetic method developed by Ren Hua Zheng *et.al* [14] and characterized by IR, UV-Vis and melting point.

2.3. *Synthesis of $[Fe(phendione)_3](ClO_4)_2{\cdot}2H_2O$*

3.2 molar equivalent of phendione in ethanol was added to 1 equivalent of ferrous ammonium sulfate dissolved in water. The formation of the complex was apparent by the immediate formation of a reddish solution. The mixture was allowed to stir at room temperature for 30 min and the complex was precipitated as a red solid by the addition of

saturated aqueous $NaClO_4$. The complex was collected, washed with water and dried. Because this material as well as other complexes adsorbed very strongly on alumina and silica gel. Recrystallization from acetonitrile/ether was used for purification. The complexes $[Co(phendione)_3](ClO_4)_2 \cdot 3H_2O$, and $[Cu(phendione)_2](ClO_4)_2 \cdot 2H_2O$, were synthesized using same synthetic route reported on literature [15].

2.4. *UV-Visible method for the determination of CMC of SDS*

One of the simplest methods for CMC determination is to measure the absorbance PAN, a water-insoluble organic dye at 470 nm.

2.5. *Experimental procedure*

The following stock solutions were prepared and used for the experiments. 100 mL of 1.6×10^{-3} M solution of PAN in pentanes (0.040 g PAN). 500 mL of 8.0×10^{-3} M SDS aqueous solution (1.15 g SDS). 100 mL each of 0.001 M aqueous solutions were prepared for the following metal complexes $[Fe(phendione)_3](ClO_4)_2 \cdot 2H_2O$, $[Co(phendione)_3](ClO_4)_2 \cdot 3H_2O$, $[Cu(phendione)_2](ClO_4)_2 \cdot 2H_2O$, and $[Zn(phendione)_2](ClO_4)_2$. 100 mL 0.01 M solution of calcium chloride, calcium fluoride, calcium oxalate monohydrate, and calcium acetate monohydrate and 100 mL 0.01 M solution of glycine, L-alanine, L-valine, L-histidine, L-leucine, and L-lysine were prepared and during the respective experiments.

The SDS solutions of concentrations ranging from 1×10^{-4} M to 3.0×10^{-3} M were prepared by diluting 8 mM SDS. To each microlab vial 5 mL of an SDS solution and 3 mL of complex solution were added. Ten drops of the PAN solution in pentanes were added to each vial. The container was gently swirled and the pentane was allowed to evaporate for 20 min. The absorbance of each solution at 470 nm was measured using the UV-visible spectrometer. The same procedure was followed to determine the CMC of the SDS in presence of the $[Fe(phendione)_3](ClO_4)_2 \cdot 2H_2O$, $[Co(phendione)_3](ClO_4)_2 \cdot 3H_2O$, $[Cu(phendione)_2](ClO_4)_2 \cdot 2H_2O$ complexes, calcium salts and amino acids.

3. Results and Discussion

The measurement of the absorbance of PAN-SDS solution as a function of SDS concentration allows determining the CMC of SDS solution. Specifically, below the CMC the dye does not dissolve in the aqueous surfactant solution, and the absorbance of the solution remains low [16]. At the CMC, a sudden rise in the solution's absorbance is observed, as the dye is encapsulated in micelles and is dissolved in solution [16]. Above the CMC, the absorbance of the solution increases linearly with increasing concentration. The plot of absorbance against the concentration of SDS shows that the CMC occurs at the concentration where the two lines intersect, or where the flat absorption line starts to increase suddenly.

3.1. *Effect of metal complexes on the micellar properties of SDS*

The CMC of SDS in presence of metal complexes was determined by measuring the absorbance of PAN-SDS-complex solution at various concentration of SDS at 25°C temperature. The UV-visible spectrum SDS-complex-PAN solution shows the variation of absorbance with the concentration of SDS (Fig. 1).

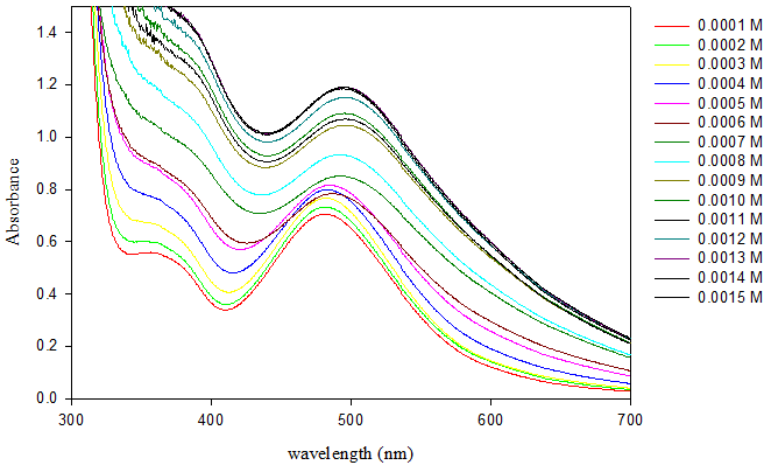
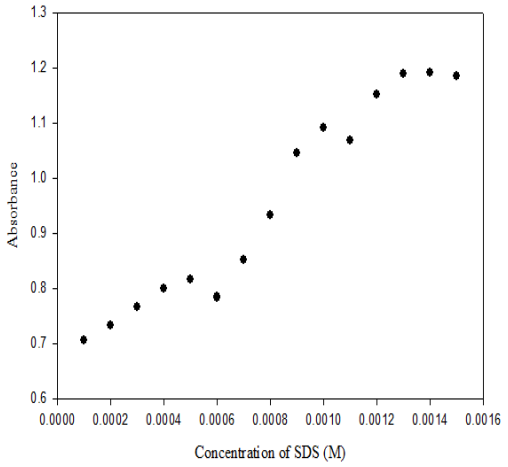
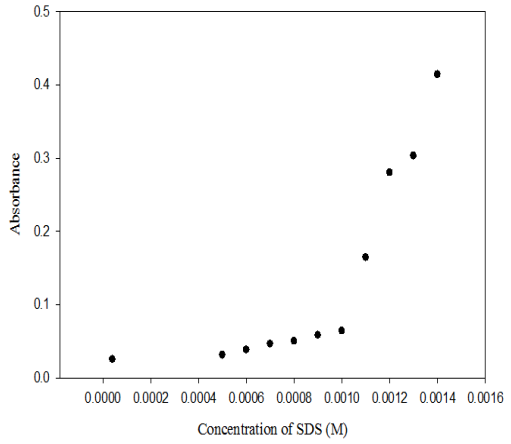


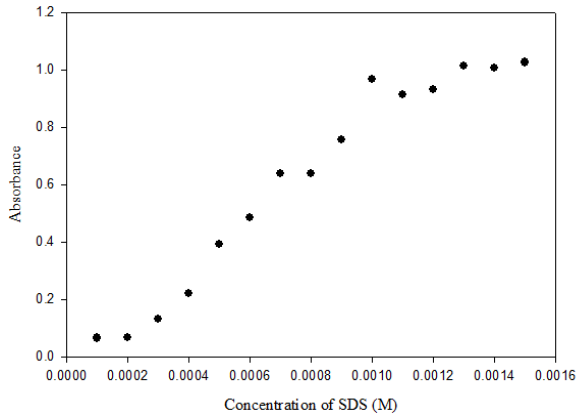
Fig. 1. UV-Visible spectrum of SDS-PAN-complex in aqueous solution.



(a) $[Fe(phendione)_3](ClO_4)_2 \cdot 2H_2O$



(b) $[Cu(phendione)_2](ClO_4)_2 \cdot 2H_2O$



(c) $[Co(phendione)_3](ClO_4)_2 \cdot 3H_2O$

Fig. 2. Absorbance vs. concentration curve SDS-PAN-metal complexes in aqueous solution.

The absorbance vs. concentration graph (Fig. 2(a)) shows a sharp increase of absorbance at concentration 0.70 mM indicating the CMC of SDS and this can be ascribed as the concentration at which micelles begin to form and the raise in absorbance can be attributed to the encapsulation of dye into the micelles core. So it can be inferred that the presence of $[Fe(phendione)_3](ClO_4)_2 \cdot 2H_2O$ complex causes a decrease in the CMC value of SDS from 8 mM to 0.70 mM. Similarly the $[Co(phendione)_3](ClO_4)_2 \cdot 3H_2O$ and $[Cu(phendione)_2](ClO_4)_2 \cdot 2H_2O$ complexes in PAN-SDS aqueous solution has an effect of lowering the CMC values of SDS. The presence of complexes $[Fe(phendione)_3](ClO_4)_2 \cdot 2H_2O$, $[Co(phendione)_3](ClO_4)_2 \cdot 3H_2O$, and $[Cu(phendione)_2](ClO_4)_2 \cdot 2H_2O$ in PAN-SDS aqueous solution lower the CMC value of SDS from 8 mM to 0.70 mM, 0.40 mM, and 1.0 mM, respectively. All these complexes are ionic and provide ionic species (ClO_4^- and metal ion) in aqueous solution which attract the ionic head group of surfactant resulting in lessening of the repulsion among them that favor the micelle formation at relatively low concentration [17]. These results are consistent with the reports on the effect of metal complexes on the CMC of anionic surfactant in solution; one is that the effect is similar to that of a simple cation of the same charge [18]. The association of the metal complexes to pre-micellar aggregates is fundamentally considered as hydrophobic interaction. The hydrophobic interaction occurs 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.

Tachiyashiki *et al.* [19] have commented that the interaction of the Fe(II) complexes with CTAB is predominantly hydrophobic and also mentioned a strong interaction of quaternary ammonium head group with π-electron system of aromatic groups of the ligands in the iron(II) complex is also quite significant. *Oldega et al.* [20] observed that the positive charge on $[Fe(phen)_3]^{2+}$ makes the complexes less hydrophobic than the cyano

neutral complexes. According to them the CMC with increasing hydrophobicity is in the following order:

$$[Fe\ (4,\ 7\text{-}Me_2phen)_2(CN)_2] < [Fe(phen)_2(CN)_2] < [Fe(phen)_3]^{2+}$$

They reported that hydrophobic interaction is more significant and lowers CMC more than electrostatic interaction. Hence it can be inferred that both electrostatic and hydrophobic interactions are responsible for the decrease of CMC due to the addition of metal complexes with phendione ligand. It has been found that the orders of decrease in CMC of SDS by the following complexes followed the order $[Fe(bpy)Cl_4][bipy\text{-}H] < Cu(PD)(phen)_2](NO_3)_2\cdot 2H_2O < Cu(La)_2NO_3 < [Co(bpy)(phen)_2](NO_3)_2\cdot 2H_2O < [Fe(PD)Cl_4][PD\text{-}H] < [Cu(Phen)_2]Cl_2\cdot 2H_2O$ [21]. Thus it is clear from the above discussion that $[Fe(bpy)Cl_4][bpy\text{-}H]$ metal complex has more hydrophobic character than that of $[Co(bpy)(phen)_2](NO_3)_2\cdot 2H_2O$ and so the decrease of CMC of SDS is greatest for $[Fe(bpy)Cl_4][bpy\text{-}H]$ and then $[Co(bpy)(phen)_2](NO_3)_2\cdot 2H_2O$. The greater decrease in CMC by $[Co(bpy)(phen)_2](NO_3)_2\cdot 2H_2O$ than $Cu(La)_2NO_3$ complex might be due to the greater hydrophobicity of the mixed metal complex of cobalt containing bi-pyridine and 1,10-phenanthroline ligand. In our present case the greatest decrease in CMC of SDS was observed for $[Co(phendione)_3](ClO_4)_2\cdot 3H_2O$ then $[Fe(phendione)_3](ClO_4)_2\cdot 2H_2O$ and $Cu(phendione)_2](ClO_4)_2\cdot 2H_2O$ complexes, respectively in PAN-SDS aqueous system.

3.2. *Effect of calcium chloride, calcium fluoride, calcium oxalate, calcium acetate on the micellar properties of SDS*

To determine the effect of CaF_2 on the micellar properties of SDS the UV-Visible spectrum of SDS-PAN-CaF_2 solution was recorded at 25°C temperature (Fig. 3). The absorbance of various solutions was plotted against the concentration SDS and the CMC was determined from the breaking point of the curve.

The graphs in Fig. 4 show the variation of absorbance of SDS-PAN-calcium salts in aqueous solution at 470 nm with the concentration of SDS. It can be inferred from the figure that the CMCs of SDS in presence of calcium fluoride, calcium oxalate monohydrate, calcium acetate monohydrate, calcium chloride were found 2.0 mM, 2.0 mM, 1.8 Mm, 1.8 mM, respoectively. The CMC of SDS was calculated from the absorbance vs. [SDS] graph. At lower concentration of SDS the absorbance of PAN solution remains lower and shows a steady increase as concentration of SDS gradually increases. At a certain point there is a sharp increase in absorbance and this corresponding point can be referred to the CMC of SDS and from this point micelle starts forming and the insoluble dye gradually become soluble in the micelle core hence shows the raise in absorbance. Thus the raise in absorbance can be attributed to the encapsulation of dye into the micelles core and above CMC the absorbance again become steady after a certain point. The CMC lowering effect of the metal salts is due to the electrostatic interaction of the ionic head groups of SDS and counter ions. Ionic surfactants are dissociated into ionic surface active molecules and counters ion when they dissolved in water. The degree of

binding of these counter ions to micelles or surface active part in surfactant molecules significantly influences the surface chemical properties of surfactant such as CMC, micellar size etc. [22]. It is well known that the adsorption of counter ions at the micellar surface reduces the electrostatic repulsion between the ionic head groups of the surfactant thus permits aggregation of surfactant molecules [20,23] and reduce CMC of the surfactant. The CMC of SDS in presence of calcium chloride, calcium fluoride, calcium oxalate monohydrate, calcium acetate monohydrate is found to decrease from 1.8, 2.0, 2.0, and 1.8 mM as the addition of salts facilitates micellization. The reason for that trend is that these salts ($CaCl_2$, CaF_2, $Ca(CH_3COO)_2{\cdot}H_2O$ and $CaC_2O_4{\cdot}H_2O$) are ionic and produces Ca^{2+} as counter ion in aqueous solution. These metal ions are adsorbed at the micellar surface reducing the electrostatic repulsion between ionic groups as follows: attraction between Na+ and DS^- would decrease (i.e.,diminished ion association), Na^+-Na^+ repulsion would decrease, and DS^--DS^- repulsion would decrease. The decrease in electrostatic repulsion between DS^--DS^- would allow micellization to take place at lower SDS concentration because one opposing factor of the phenomenon is now weaker and hence the hydrophobic interactions may dominate [24,25] that facilitate micelle formation. Do-Hoon Kim *et al.* [26] showed the effect of addition of cesium and sodium ion to SDS solution significantly decreases its CMC as well as the surface tension of water. Meisel *et al.* [27] also showed that the metal chelate ion interacted with the hydrocarbon part rather than the polar head group of SDS.

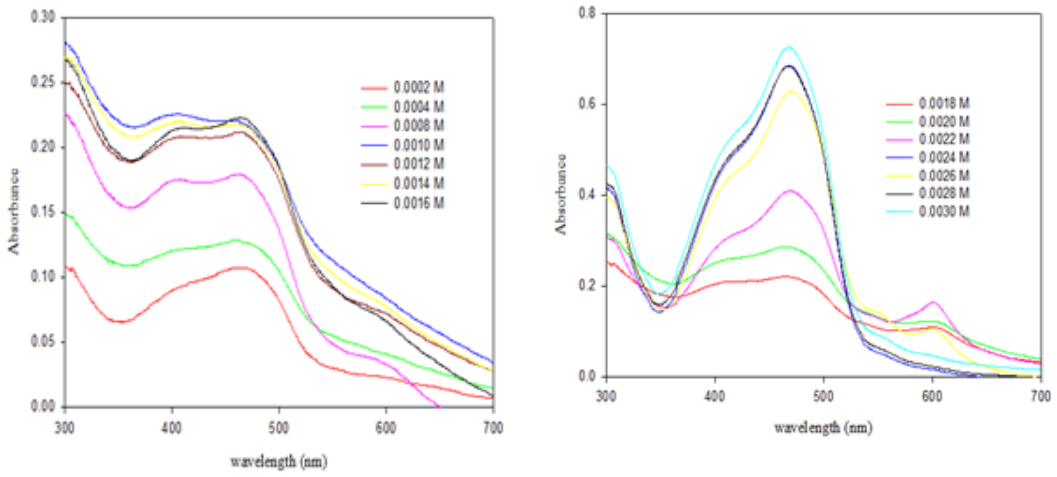
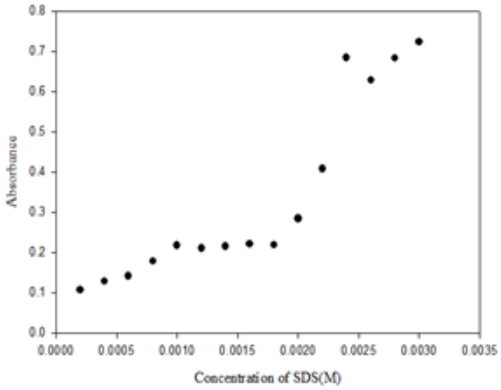
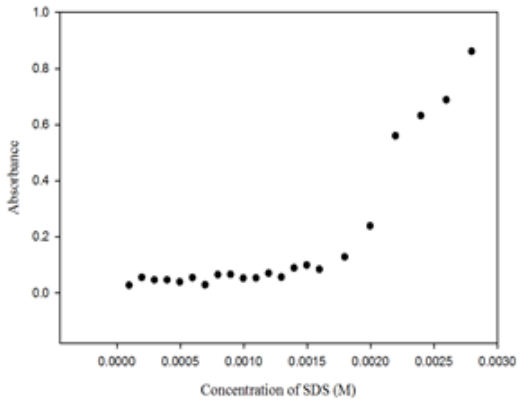


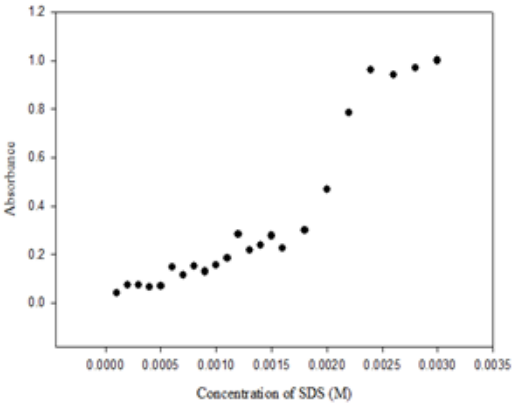
Fig 3. UV-Visible spectrum of SDS-PAN-CaF_2 in aqueous solution.



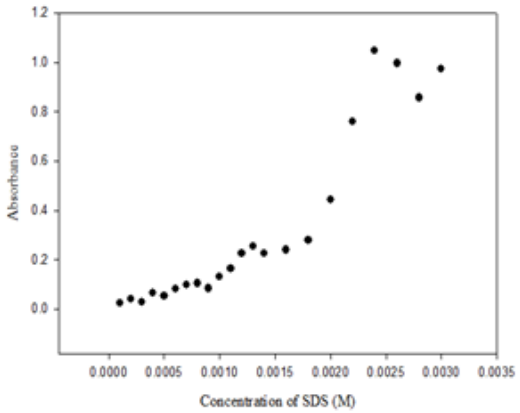
(a) Calcium fluoride



(b) Calcium oxalate monohydrate



(c) Calcium acetate monohydrate.



(d) Calcium chloride.

Fig. 4. Absorbance vs. concentration curve for SDS-PAN-Calcium salts in aqueous solution.

3.3. *Effect of amino acid (glycine, L-alanine, L-valine, L-lysine, L-leucine, L-histidine) on the micellar properties of SDS*

To determine the effect of amino acids on the micellar properties of SDS the UV-Visible spectrum of SDS-PAN-amino acids solution was recorded at 25 °C temperature (Fig. 5).

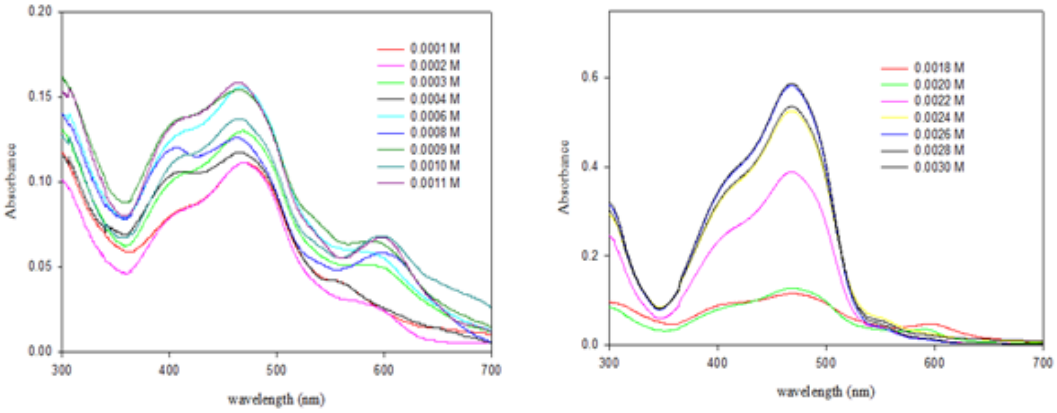
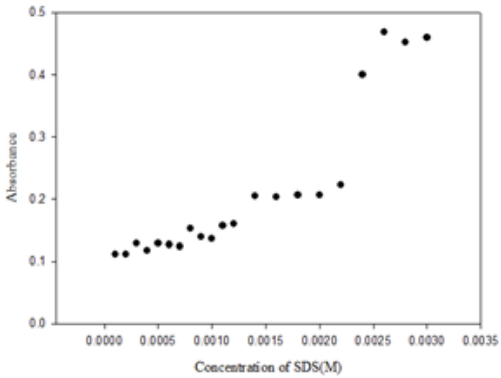
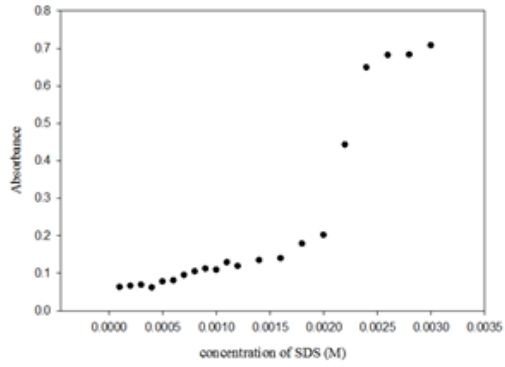


Fig. 5. The UV-Visible spectra of SDS-PAN-glycine in solution.

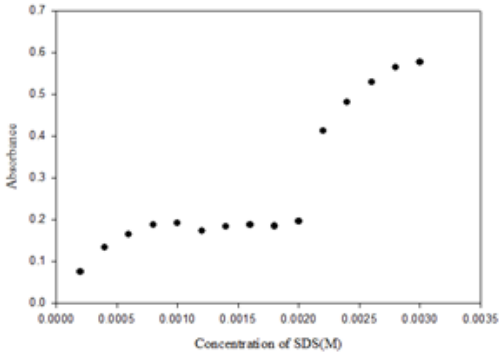
The CMC of SDS in presence of amino acid additives was determined by UV-Visible method by measuring the absorbance of PAN at 470 nm. Absorbance is plotted against the various [SDS] and then CMC of SDS found from the breaking point of the graph (Fig. 6). It was found that in presence of amino acid additives CMC of SDS decreased from 8 mM to 1.6, 1.8, 2.0, 2.0, 2.0, and 2.2 mM for L-leusine, L-valine, L-lysine, L-alanine, L-histidine and glycine, respectively. It is well known that the inorganic electrolytes can increase the surface activity of the solution of ionic surfactant [28] and the CMC and surface tension of its aqueous solution are often decreased in the presence of inorganic electrolytes. In this study, the presence of amino acids corresponds to the addition of inorganic electrolytes to the system. The reason is that, on one hand, the amino acid presents in Zwitter ionic state. So the electrostatic interaction between the ions is the dominant force. The addition of amino acid molecules results in the decreasing of thickness of the solvation layer around ionic head of SDS and the electrostatic repulsive interaction between SD^- ions. So the hydrophilicity of SDS is decreased, i.e., its surface activity is enhanced and its molecules aggregate easily on the surface and in the solution, as a result the values of surface tension and CMC decrease. On the other hand, the water matrix is broken in the presence of amino acid additives [29,30]. The addition of amino acid strengthens the hydrophobicity of SDS and makes the SDS micelles form more easily and decreases the values of CMC. So the effect of amino acids on the system is similar to that of a simple electrolyte. The following types of interactions can occur in the ternary system of amino acid, surfactant, and water: (a) ion–ion interactions between SO_4^{2-} of SDS and the NH_3^+ group of amino acids; (b) between the Na^+ of SDS and the COO^-group of amino acids; (c) ion–peptide group interactions between the ionic head group of the surfactants and the peptide group; (d) hydrophobic–hydrophobic interactions between the alkyl chain of the surfactants and the hydrophobic group of the amino acids. For all the amino acids, it is concluded that ion–ion, and hydrophilic–hydrophilic group interactions



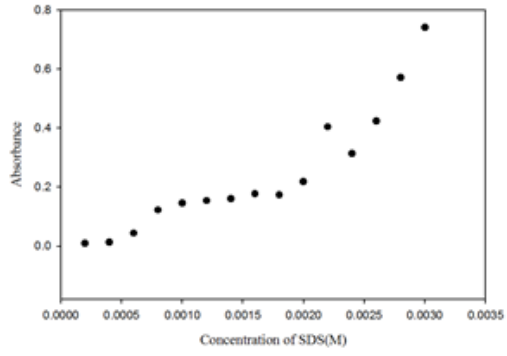
(a) Glycine



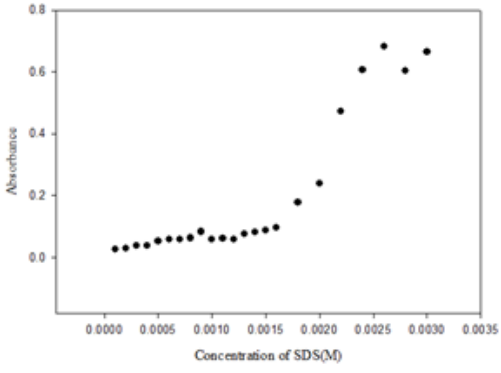
(b) L-alanine



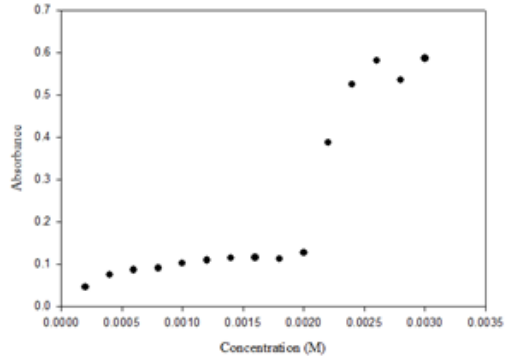
(c) L-histidine



(d) L-valine



(e) L-leucine



(f) L-lysine

Fig. 6. Absorbance vs. concentration curve for SDS-PAN-amino acids in aqueous solution.

are overall predominant over the hydrophobic–hydrophobic and hydrophilic–hydrophobic group interactions in the ternary solutions of SDS-amino acid-PAN and can be attributed to decrease in CMC of SDS in aqueous solution. Li Yu *et al.* [31] studied the effects of amino acids on the CMC of cetyltrimethylammonium bromide (CTAB) in the Tris–HCl buffer solution by surface tension measurement and reported that the CMC of CTAB decreases with the increasing concentration of glycine. We previously have also studied conductometrically [25] the effect of amino acid on the micelle properties of SDS and observed the decrease in CMC in presence of L-alanine, L-valine and glycine additives and the similar results were obtained.

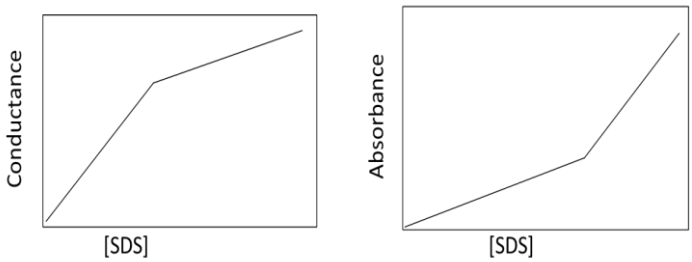
3.4. *Thermodynamic Parameters for SDS micelles in presence of metal complexes, metal salts and amino acid*

The standard free energy change of micellization, $\Delta G^0_{mic,}$ is calculated according to the following equations and the method of least squares (r^2 = 0.982) mentioned in the literature as in table 5 [32]. The free energy of micellization is calculated using the following equation:

$$\Delta G^0_{mic} = (1+f)\ RT\ \ln CMC \qquad (1)$$

Where, *f* is the degree of counter ion binding. The degree of counter ion dissociation α was calculated from the ratio of the slope of the straight lines at pre-micellar regions to post-micellar region of the absorbance vs. concentration curve and found the values are consistent with previously calculated values of *α* by conductometric method (Scheme 1 and Figs. 2, 4 and 6). In conductometric method we calculated α value from the ratio of the slope of the straight line at post micellar region to pre-micellar region of conductance vs. concentration curve [21]. The values of f were calculated by subtracting the values of α from unity. Then the ΔG^0_{mic} was calculated using equation (1) and binding constant (K_b) were derived from the following relation as listed in Table 1.

$$\Delta G^0_{mic} = -\ 2.303RT\ \log K_b \qquad (2)$$



Scheme 1. The variation of conductance (a) and absorbance (b) with respect to SDS concentration. In both cases the intercept point indicate the CMC of SDS.

As shown in Table 1, the apparent Gibbs energies of micellization, ΔG^0_{mic} of SDS in presence of metal complexes, calcium salts and amino acids were found negative which imply that the process of micellization is thermodynamically favorable. Among the series, more negative values are observed for the metal complexes. However, amino acids series as well as metal salts show similar negative values for ΔG^0_{mic} of SDS.

Table 1. Calculated values of degree of ionization (α), degree of counter ion binding (f), the apparent Gibbs energies of micellization (ΔG^0_{mic}), binding constant (K_b) for the micellization of SDS in the presence of metal complexes (0.001 M), amino acids (0.01M), and calcium salts (0.01 M) at 298 K temperature.

Metal complexes	Temperature (K)	Degree of ionizatio, (α)	Degree of counter ion binding, (f)	Apparent Gibbs energies of micellization, ($-\Delta G^0_{mic}$)	Log(k_b)
$[Fe(phendione)_3](ClO_4)_2 \cdot 2H_2O$	298	0.70	0.30	23.40	4.10
$[Co(phendione)_3](ClO_4)_2 \cdot 3H_2O$	298	0.35	0.65	31.79	5.57
$[Cu(phendione)_2](ClO_4)_2 \cdot 2H_2O$	298	0.47	0.53	32.15	5.63
Glycine	298	0.20	0.80	27.30	4.78
L-alanine	298	0.14	0.86	28.65	5.02
L-valine	298	0.21	0.79	28.20	4.91
L-histidine	298	0.15	0.85	28.50	5.00
L-leucine	298	0.10	0.90	30.30	5.31
Calcium Chloride	298	0.30	0.70	26.70	4.67
Calcium Fluoride	298	0.24	0.76	26.60	4.66
Calcium acetate monohydrate	298	0.27	0.73	27.10	4.74
Calcium oxalate monohydrate	298	0.04	0.96	29.80	5.20

4. Conclusion

The study of micellar behavior of SDS in presence of additives such as metal (Fe, Cu, Co, Zn) phendione complexes, calcium salts and amino acids in aqueous solutions were carried out by measuring the absorbance of PAN at 470 nm. The complexes $[Fe(phendione)_3](ClO_4)_2 \cdot 2H_2O$, $[Co(phendione)_3](ClO_4)_2 \cdot 3H_2O$, and $[Cu(phendione)_2](ClO_4)_2 \cdot 2H_2O$, were found to decrease the CMC value of SDS from 8 mM to 0.70 mM, 0.40 mM, and 1.0 mM, respectively. This is due to the attraction among the ionic species (ClO_4^-, metal ion) of complexes with that of surfactant which in turn decreases the electrostatic repulsion among the closely packed ionic head groups and also due to the hydrophobic interaction among the non-polar groups of SDS and bulky hydrophobic phendione ligand of the metal complexes. Both of these factors favor the formation of micelle at lower concentration. In presence of calcium salts ($CaCl_2$, CaF_2, Calcium acetate, Calcium Oxalate$\cdot H_2O$) the CMC of SDS was found to decrease that is consistent

with our previous study carried out by conductometric method. The study of interaction of amino acids with anionic surfactant SDS may provide important information about protein-surfactant and peptide-surfactant interaction in aqueous environment. In the present study glycine, L-alanine, L-valine, L-histidine, L-leucine, L-lysine have been used as additives in SDS aqueous solution which also causes the decrease of CMC of SDS. The thermodynamic parameters for each series were obtained from absorbance versus concentration curves. Among the series more negative values for ΔG^0_{mic} of SDS are observed for the metal complexes. Amino acids series as well as metal salts show similar negative values for ΔG^0_{mic} of SDS. Negative values of ΔG^0_{mic} indicated that the process of micellization is thermodynamically favorable.

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