



Research Article

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Effects of electrolytes on the surface and micellar characteristics of Sodium dodecyl sulphate surfactant solution

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Abstract

The effect of some electrolytes (namely sodium acetate and calcium acetate) on their critical micelle concentration (CMC), have been determined by spectrophotometric, conductometric and surface tension measurement method at 298K, 308K and 318K. From the surface tension data physico-chemical properties such as surface excess concentration (Γ_{\max}) and minimum area per molecule (A_{\min}) at surface have been obtained. From the observed CMC data, free energy of micellization (ΔG_{mic}), entropy change of micellization (ΔS_{mic}), and enthalpy change of micellization (ΔH_{mic}) for the studied surfactant solutions with or without electrolyte have been obtained. The results have been interpreted in light of inter-molecular interaction.

Keywords: Adsorption conductance, Critical micelle concentration, Micellization, Surfactant, Thermodynamic parameters.

INTRODUCTION

Surface science is a fascinating scientific subject that defines the issue of amphiphiles, and more specifically micellar and thermodynamic characteristics of surface active substances called surfactants. Surfactant is coined word from surface active agent that is applied to molecules that migrate to interface between two insoluble physical phases. Surfactants are amphiphilic, which was created by Paul Winsor 50 years ago ^[1] and comes from the Greek words; amphi, mean both and phillos expresses friendship, and the term relates to the fact that all surfactant molecules consists of at least two parts. When the fluid is water one usually talks about the hydrophilic and hydrophobic parts respectively. The hydrophilic part is referred to us the head group and the hydrophobic is the tail.

When the surfactants are dispersed in aqueous solution it adsorbs at interface and self assemble in bulk solution. Adsorption is the concentration of surfactants at interface, while self assembly is the aggregation of surfactants into structure called micelle. Both these processes are driven by the hydrophobic tails being expelled from solution. Surface active agents also aggregate in solution forming micelles ^[2, 3]. The formation of micelles is generally understood in terms of hydrophobic effect which is the main driving force. Besides, the hydrophobicity of surfactant molecules, the hydrophobicity of solvent molecules is also important in understanding micellization process. Addition of small amount of organic solvent has been known to produce marked change in the critical micelles concentration (CMC) of ionic surfactants due to the tendency of the added solvent either to break or make the water structure through solution of hydrophobic part of organic solvent ^[4]. Moreover, formation of micelles has been observed in solvent having high degree of hydrogen bonding.

The driving force for surfactant adsorption is the lowering of free energy of the phase boundary ^[5]. Formation of dimmers, trimers or other polymers in amphiphilic solutions reduces the contact area between the hydrocarbon chain and the aqueous solvent and resulting to decrease in free energy. When the hydrocarbon chain is long enough, hydrophobic driving force results in large scale association structure (micelles). Adsorption of surfactant molecules at interface lowers surface tension (γ) and higher the surfactant adsorption makes the larger reduction of γ , where γ is interfacial tension and given in mJ/m^2 or mN/m . Surfactant self-assembly in aqueous solutions has been investigated both experimentally and theoretically. Experimental measurements of properties such as electrical conductivity, surface tension, dye solubilization capacity, osmotic pressure, or light scattering intensity

as a function of surfactant concentration shows a sharp transition in the value of the measured property over a very narrow range of surfactant concentration. This surfactant concentration is identified as the critical micelle concentration (CMC). At surfactant concentrations below the CMC, mainly singly dispersed molecules and possibly some small aggregates such as dimers and trimers are present in the solution. In contrast, at concentrations above the CMC, micelles containing a large number of surfactant molecules are formed in the solution. At relatively low or moderate surfactant concentrations, these aggregates can assume a variety of shapes such as spherical micelles, slightly asymmetrical globular or ellipsoidal micelles, and large rod like micelles which may be rigid or flexible and spherical bilayer vesicles. At larger concentrations of surfactants in solution, liquid crystalline aggregates can come into existence. Physico-chemical studies of surfactant solutions are important from theoretical as well as applied points of view.

Polymers in aqueous and non-aqueous media and their interaction with various surfactants micelles have widely been studied in the light of aggregation, hydrogen bonding, geometry, correlation time, conformation, hydrodynamic and thermodynamic studies. However, studies on the effect of electrolytes on the surface and micellar characteristics of surface active compounds is only limited. Therefore, in this proposed research work was investigating the effects of some salts on the surface and micellar characteristics of an anionic surfactant such as sodium dodecyl sulphate (SDS). This current study specifically focused to examine the effect of sodium acetate and calcium acetate on the micellar characteristics of SDS on aqueous solution. Furthermore, this research to explore the effect of these studied salts on surface and thermodynamic properties of aqueous SDS solution.

Review of Literature

Surfactant and their Properties

An amphiphilic substances exhibit a double affinity, which can be defined from the physico-chemical point of view as a polar-apolar duality. A typical amphiphilic molecule consists of two parts: i.e., a polar group which contains heteroatoms, means atoms such as O, S, P, or N included in functional groups called alcohol, thiol, ether, ester, acid, sulfate, sulfonate, phosphate, amine, amide etc. On the other hand, an essentially apolar group which is, in general, a hydrocarbon chain of the alkyl or alkyl benzene type, sometimes with halogen atoms and even a few non ionized oxygen atoms. Surfactants are amphiphilic molecules, that dynamically associate in aqueous solution above a certain critical concentration termed as CMC to form large molecular aggregates of colloidal dimensions termed as micelles and above the CMC, there exists a dynamic equilibrium between the monomers and micelles [2, 6, 7]. At surfactant concentrations near CMC, aggregation of surfactant monomers occurs to form roughly spherical or ellipsoidal shaped micelles. Each micelle is composed of a certain number of surfactant molecules that dictate the general size and geometry of the particular micellar system.

As hydrophobic interaction, the solute has either full or partial hydrophobicity on the type of solvent-solute interaction on colloids. When the solutes are amphiphilic in nature, hydrophobic interaction leads to two significant phenomena, viz. adsorption and aggregation [8]. This interaction is not water specific and therefore solvophobic interaction is used as a general term. Thus, self-organization of amphiphiles takes place only in the presence of a solvent and result the solvent properties can be greatly influence the adsorption and aggregation phenomena. Therefore, studies are made on the aggregation

behavior of surfactants by altering the solvent property and such studies provide us information of both fundamental and applied importance. Solvent property can be varied in different ways, for example, (i) by taking pure solvents of different polarity, (ii) by taking mixed solvents containing either mixtures of water and non aqueous solvent or mixtures of two non aqueous solvents, and (iii) by adding electrolytes or non electrolytes to water or any other solvent.

Surfactants

From the commercial point of view surfactants are classified according to their use. The most accepted and scientifically sound classification of surfactants is based on their dissociation in water.

Anionic surfactant

Anionic surfactants dissociated in water to form amphiphilic anion, and a cation, which is in general, an alkaline metal (Na^+ , K^+) or a quaternary ammonium. They are the most commonly used surfactants. They include salts of alkyl benzene sulfonic acid (detergents), fatty acids (soaps), laurylsulfate (foaming agent), di-alkyl sulfosuccinate (wetting agent), lignosulfonates (dispersants) etc. Anionic surfactants accounted 50 % of the world production.

Cationic surfactants

Cationic surfactants are dissociated in water into an amphiphilic cation and an anion, most often of the halogen type. A very large proportion of this class corresponds to nitrogen compounds such as fatty amine salts and quaternary ammoniums, with one or several long chain of the alkyl type, often coming from natural fatty acids. These surfactants are in general more expensive than anionic, because of the high pressure hydrogenation reaction required during their synthesis. As a consequence, they are used only in cases where no cheaper substitute is available, i.e. (1) as bactericide, (2) as positively charged substance which is able to adsorb on negatively charged substrates to produce antistatic and hydrophobant effect, often of greater commercial importance like as corrosion inhibition.

Nonionic surfactants

Nonionic surfactants are about 45% of the overall industrial production. They do not ionize in aqueous solution, because their hydrophilic group is of a non dissociable type, such as alcohol, phenol, ether, ester, or amide. A large proportion of these nonionic surfactants are made hydrophilic by the presence of a polyethylene glycol chain, obtained by the poly condensation of ethylene oxide. They are called poly ethoxylated non ionics. In the past decade glucoside (sugar based) head groups have been introduced in the market, because of their low toxicity. As far as the lipophilic group is concerned, it is often of the alkyl or alkyl benzene type, the former coming from fatty acids of natural origin. The poly condensation of propylene oxide produces a polyether which (in opposition to polyethylene oxide) is slightly hydrophobic. This polyether chain is used as the lipophilic group in the so-called poly ethylene oxide-propylene oxide block copolymers, which are most often included in a different class, e.g. polymeric surfactants.

Amphoteric (ampholytic) surfactants

When a single surfactant molecule exhibits both anionic and cationic charges it is called amphoteric and zwitterionic. This is the case of synthetic products like betaines or sulfobetaines and natural substances such as amino acids and phospholipids. Amphoteric surfactants can be anionic (negatively charged), cationic (positively charged) or non-ionic

(no charged) in a solution, depending on the acidity or pH of the water. In acidic pH solutions, the molecule acquires a positive charge and behaves like a cationic surfactant, whereas in alkaline pH solutions they become negatively charged and behave like an anionic one.

Amphoteric surfactants are compatible with all other classes of surfactants and are soluble and effective in the presence of higher concentrations of electrolytes, acids and alkalis. These surfactants may contain two charged groups of different signs linked by a spacer, which may be rigid or flexible, hydrophilic or hydrophobic, typically 2-8 bridging atoms^[9, 10]. Whereas the positive charge is almost always ammonium, the source of the negative charge may vary (carboxylate, sulphate, and sulphonate). These are mild with high foaming properties, like an example of amphoteric surfactant alkyl betaine^[2].

Effect of Temperature on CMC

The effect of temperature on the CMC of ionic surfactants is not straight forward^[4], for instance, reported that when the temperature is increased, the CMC first decreases, then undergoes through a minimum, and finally increases. Other researcher^[11] has observed a similar pattern with nonionic surfactant solutions.

This ups and down variations always occurs when two opposite effects are competing. On one hand, an increase in temperature can bring a reduction in the hydration of the surfactant hydrophilic group; this is the well-known desolvation effect which is responsible for the cloud point phenomenon of nonionic surfactant solutions. This effect tends to drive the surfactant out of the aqueous solution and thus it favors the formation of micelles, i.e., it decreases the CMC. On the other hand, an increase in temperature results in an increasing disorder in the structure of water phase, in particular the molecules which are located next to the surfactant hydrophobe. The higher in disorder, the less defined the direction of the unfavorable polar/apolar contact, and as a consequence it becomes the weaker. Thus, the hydrophobic effect which drives the surfactant molecule "tail" out of the water phase is also reduced when temperature is increased.

Effect of Co-solute on CMC

The role of co-solute/solvent in the process of formation of micelles in surfactant solution is of considerable interest both from the fundamental and the applied view points since application of surfactants in many physic-chemical and interfacial phenomena largely depend on it^[2]. Solubilizing capacity, surface and micellar characteristics and detergency of amphiphilic compounds are sensitive to the nature of added cosolute/solvent and temperature^[12].

Principles of Determination of CMC

The determination of CMC is generally based on the localization of the position of a breaking point in the concentration dependencies of selected physical or chemical properties of surfactant solutions. Because of the surface activity of these substances, measurements of the surface tension of surfactant solutions represent the principal method of CMCs determination. However, it is rather tedious and time-consuming procedure. In the case of ionic surfactants, the utilization of electrochemical measurements is much more convenient, especially the measurements of the electrical conductivity of their solutions with varying concentration. The conductivity of any solution are directly proportional to the concentration of its ions. The point, where the micelle formation starts, is indicated by the breaking point in concentration dependence of specific conductivity (k). It is easy to find the breaking point, because it marks a significant change of the linear

slope of the dependence $k = f(c)$. The value of CMC is the intercept of two linear plots with mutually different slopes^[13].

Surfactants and Surface Tension

Surface tension is due to asymmetric cohesive force at a surface. The Surface tension of liquids causes the formation of drops and is related to the attractive force between the molecules. These attractive forces are dipole-induce-dipole forces and hydrogen bonding. In the bulk liquid, a molecule senses the equal attractive force in all directions, while for the molecule at the surface of this attraction is lacking in one direction. This asymmetry is the origin of the surface tension. The surface tension is reflection of the cohesive force in liquid, and the surface tension is equivalent to surface free energy. Therefore it can be represented in energy units, erg/cm^2 or mJ/m^2 . In turn, the cohesive energy is a function of the strength of the dispersion force in a liquid. Surface tension is a measure of the free energy of the surface per unit area. It can be thought of as the work required expanding the surface by a unit area. The surface tension of a pure liquid is a constant value at the given liquid.

Effect of cosolute on surface tension

In an aqueous system, added component can affect the surface tension in three different ways. Organic water soluble material such as ethanol normally decreases the surface tension monotonically with increasing concentration. This is due to the preferential adsorption of organic molecules at the liquid air surface. Surfactants on the other hand show a very large reduction in surface tension at very low concentration up to the CMC, where after the surface tension is practically constant. At concentration higher than CMC all additional surfactant will form new micelles thus keeping the surfactant concentration (unimer activities) more or less constant. Electrolytes normally increase the surface tension, due to the reason is that the electrolytes are depleted from the surface i.e., there is a negative adsorption of the ion at the liquid-air surface^[14].

Effect of salt concentration

Addition of salt in surfactant solution is another way of reducing CMC of surfactant. In general, repulsive forces between the head groups of ionic surfactants are fighting against the aggregation. In the presence of salt, the repulsive forces of head group of SDS monomer decreases due to the electrostatic shielding effect resulting in the formation of micelle at lower cmc^[15, 16]. They further explained that electrical double layer was compressed due to the increased electrolyte concentration resulting in the reduced electrostatic attraction between ions and the micelles. The As(V) replaces Cl^- ions in CPC and arsenic solution, the As(V) binds closely with CPC ions and decreases the electrical charge on the surface and reducing CMC^[17]. As a result, non-trapped metals pass through the membrane leading to the lower rejection^[17, 18]. Xu *et al.* reported that the cadmium removal efficiency decreased from 95% to 75% at NaCl concentration of less than 20 mM^[15]. It could be due to the competition between Cd^{2+} and Na^+ ions to get at the micelle surface, and due to the formation of complex of Cl^- and metal. The decrease of chromate (CrO_4^{2-}) removal from 1 to 0.15 mM when NaCl concentration increased from 1 mM to 500 mM. Aoudia *et al.*^[19] reported that Cr^{3+} removal was also reduced with the addition of NaCl. In contrary, the addition of NaCl has negative effect on the reduction of metal removal and the formation of metal chloride. Basar *et al.*^[20] explained that with the increase of NaCl from 2 mM to 100 mM, CTAB rejection increased from 68% to 98%. On the contrary, LABS rejection rate decreased slightly from 38% to 34% at the salt concentration of 2 mM and 100 mM, respectively. Sampler *et al.*^[21] also reported the similar result of

reduction of heavy metals (Cd^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+}) when NaCl was added in the surfactant SDS and alkylbenzenesulfonate.

Thermodynamics of micellization

Thermodynamic free energy of micellization ($\Delta G_{\text{mic}}^{\circ}$) for ionic surfactants with or without cosolute was determined by using the following equation reported earlier [22].

$$\Delta G_{\text{mic}}^{\circ} = (2-\beta) RT \ln X_{\text{cmc}}$$

Where β is counter ion dissociation constant, $R(8.314 \text{ J k}^{-1}\text{mol}^{-1})$ is the gas constant, T the temperature in Kelvin and X_{CMC} stands for the CMC in the mole fraction unit. For nonionic surfactant solution with or without cosolute standard Gibbs free energy of micellization was obtained as: $\Delta G_{\text{mic}}^{\circ} = RT \ln X_{\text{cmc}}$

The standard entropy of micelle formation ($\Delta S_{\text{mic}}^{\circ}$) was calculated from the temperature dependence of standard Gibbs free energy of micellization using the relation:

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

The Standard enthalpy of micelle formation ($\Delta H_{\text{mic}}^{\circ}$) was derived from either Gibb's Helmholtz equation:

$$\Delta G_{\text{mic}}^{\circ} + T \Delta S_{\text{mic}}^{\circ} = \Delta H_{\text{mic}}^{\circ}$$

Surface excess concentration

In the case of surfactants the concentration of solute at the surface is higher than that in the bulk solution. This difference of concentration of solute in the bulk and at the surface is called surface excess concentration (Γ). This surface excess concentration (Γ) at air liquid interface can be calculated using Gibbs adsorption equation:

$$\Gamma = (2.303nRT)^{-1} \frac{dY}{d \log c}$$

where, R is gas constant ($8.314 \text{ JK}^{-1}\text{mol}^{-1}$), $\frac{dY}{d \log c}$ is slope value of the pre micelle plot between Y and $\log[\text{surfactant}]$, T is temperature in K and n is number of particle furnished by each molecule of the surfactant in solution (for SDS acting as bivalent, $n=2$).

MATERIALS AND METHODS

Materials and Apparatus

Materials and apparatus which was used in the study are: Conductivity meter for conductance measurement, conductivity electrode, Double beam UV-visible spectrophotometer equipped with a pair of 10 mm quartz tube, UV lamp, UV light cabinet, Stalagmo meter, Thermostat, magnetic stirrer, etc.

Chemicals

Sodium dodecyl sulphate (BDH chemicals Ltd, England), potassium chloride (99%, Blulux, Laboratory Ltd.), (p-dimethyl amino azo benzene (dye content: 85%, BDH chemicals Ltd, England), Acetone (BDH chemicals Ltd, England), Sodium acetate (BDH chemicals Ltd, England) and Calcium acetate (BDH chemicals Ltd, England), Toluene (HPLC grade, Analytical reagent, CDH(P) LTD, India), ethanol (99% Hayman Ltd, England) and deionized water were used for this study.

Methods

Determination of critical micelle concentration

UV-Visible absorption spectroscopic method

Absorbance of sparingly water soluble dye, p-dimethylaminoazo benzene, mixed with surfactant solutions with or without the salt (electrolyte) was measured using UV-Visible spectrophotometer. Spectral measurements were performed using the blank solution as a reference. The absorption vs. concentration of surfactant was plotted and the CMC is determined from the inflection point of the curve [23].

Conductivity measurement

Conductance of surfactant solution was measured using a digital conductivity meter connected with a dip type conductivity cell. The cell constant was determined by measuring the conductance of standard KCl solution using the relation:

$$\text{Specific conductance (k)} = \text{observed conductance} \times (\ell/a)$$

where ℓ/a = cell constant, ℓ is distance between the two electrodes in the cell and a is surface area of each electrode. The value of cell constant was obtained from observed conductance and the specific conductivity of a standard solution of 0.1M of KCl. CMC value of the surfactants were obtained from the break-point of the plot of specific conductance as a function of surfactant concentration [23].

Equivalent conductance at infinite dilution (Λ_{∞}): The Equivalent Conductance at infinite dilution was determined from the molar conductance (measures the efficiency with which a given electrolyte conducts electricity in solution) of the studied surfactant solution at 298 K, 308 K and 318 K. Equivalent conductance (Λ) of surfactant solutions were calculated from:

$$\Lambda = (1000 \times k) / C$$

where, k is specific conductance (Scm^{-1}) and C is normality of solution in g.equ/dm^3 . Equivalent conductance at infinite dilution (Λ_{∞}) was obtained using Onsager equation:

$$\Lambda = \Lambda_{\infty} - (A \Lambda_{\infty} + B) C^{1/2}$$

Where, A and B are constants.

Surface tension measurement

Surface tension of surfactant solution in water was measured by drop weight method using a stalagmometer. The stalagmometer assembly consists of Pyrex glass bulb of spherical shape with an attached capillary tube and the tip of the end is grounded. The surface tension of the surfactant solutions under study was determined by multiplying the observed weight of one drop with the slope of the standard curve between surface tension of liquid versus weight per drop. A plot of surface tension versus log of surfactant concentration was drawn. From the break point of the plot, the CMC of surfactant was determined.

RESULTS AND DISCUSSIONS

Critical Micelle Concentration

Micellization occurs when surface active compounds form non-covalent clusters in solution; this process is driven by the hydrophobic effect (Rosen, M., 2004) each surface active agent can be characterized

by its critical micelle concentration (CMC). The formation of a micellar aggregates cause significant changes in physical properties, such as conductivity, molecular fluorescence and surface tension of surfactant solutions. Therefore, for the determination of the concentration at which a surfactant forms a micelle, called CMC, it is possible to use electrochemical or spectroscopic techniques and is detected as an inflection point when physicochemical properties like surface tension are plotted as a function of concentration.

For the studied surfactant solutions, critical micelle concentration (CMC) of SDS was determined by conductometric, surface tension and UV-Visible absorbance spectroscopic techniques. Micelle formation is indicated by the inflection point on the concentration dependent specific conductivity (κ) plot and these are presented in figure 1. Absorbance as a function of SDS concentrations for SDS+Dye+H₂O system is described in figure 2. The plot of surface tension versus log [SDS] is presented in figure.3. The CMC values for aqueous surfactant solutions of SDS using different methods were carried out and the data are presented in Table 1.

The break point in the concentration-conductivity curve can be interpreted as sign of aggregation (shown in figure 4). The CMC values for pure SDS solutions at 298 K, 308 K and 318 K are given in table.2 The CMC value of pure SDS aqueous solution obtained from conductance (8.0 mM) and absorbance (7.8mM) methods are in fair agreement. However, as usual CMC of SDS from surface tension measurement (8.3 mM) is higher (figure.5). Average CMC value (8.1 mM) for SDS at 298 K was used in the subsequent calculation reported by Holmber *et al.* [2].

The CMC values were determined from the break point in plots of absorbance as a function of [SDS] for SDS + dye + H₂O solutions containing sodium acetate or calcium acetate are presented in Table.2. CMC of the anionic surfactant (SDS) at 298K decreases with mixing 0.1M electrolytes (sodium acetate or calcium acetate). It may be due to partial neutralization of anionic head group negative charge by electrolyte cations [24]. Furthermore, CMC of SDS is markedly lower in the cases of added sodium acetate and calcium acetate. (Figures 6 & 7). Thus, further decrease in the CMC of SDS on adding Ca (Ac)₂ is attributed to more effective head group charge neutralization by bivalent Ca²⁺ than monovalent Na⁺. Surfactant head group charge neutralization by electrolytes cation facilitates micilization and hence lower CMC.

Surface Physico-Chemical Properties

Surface excess concentration (Γ_{max})

The surface excess is a useful measure of effectiveness of adsorption at the interface. The effectiveness of adsorption is an important factor for determining the properties of surfactants like wetting, contact angle, foaming, etc. The calculated values for Γ_{max} for the studied systems at 298 K are presented in Table 2. As it can be seen, the Γ_{max} for SDS at 298K is lower in the case of Ca(Ac)₂ than for NaAc. This may be because of divalent Ca²⁺ promotes micelle formation by reducing surfactant head group repulsion. The value of minimum area per molecule (A_{min}) of surfactant (SDS) were obtained using,

$$A_{min} = \frac{10}{N} \times 10^{13}$$

where, N is Avogadro's number and A_{min} is minimum area per molecule in nm²

Further, addition of electrolyte causes a decrease in A_{min} . It is more lower in the case of Ca(Ac)₂. It is obvious since Ca²⁺ facilitate micelle formation than Na⁺, so that the surfactant monomers favor to aggregation.

Equivalent Conductance at infinite dilution (Λ_0).

Equivalent Conductance at infinite dilution was obtained using Onsager equation:

$$\Lambda = \Lambda_0 - (A\Lambda_0 + B) C^{1/2}$$

where, A and B are constants.

A plot of Λ versus $C^{1/2}$ is drawn. The intercept of such plot gives Λ_0 value and these values are also recorded and shown in table 2. It is observed that an increase in temperature brings about an increase in the limiting conductance at infinite dilution (Λ_0) for surfactant (SDS), due to enhanced ionic mobility at higher temperature.

Table 1: CMC values of surfactants from the literature

System / methods	CMC (mM) at 298 K
SDS by conductance	8.0
SDS by surface tension	8.3
SDS by absorbance	7.8

Table 2: Critical micelle concentration (CMC), surface excess concentration (Γ_{max}) and minimum area per molecule (A_{min}) for studied surfactant systems with or without electrolytes

System	Temp. (K)	CMC (mM)	$\Lambda_0 \times 10^{-1}$ ($\mu S m^2 mol^{-1}$)	Γ_{max} (1×10^{10}) ($mol cm^{-2}$)	A_{min} (1×10^8) m^2
SDS+H ₂ O	298	8.10	4.40	5.22	3.18
	308	8.17	6.00	-	-
	318	8.25	8.70	-	-
SDS+0.1M NaAc	298	7.65	-	4.23	4.501
SDS+0.1M Ca(Ac) ₂	298	6.01	-	3.32	3.92

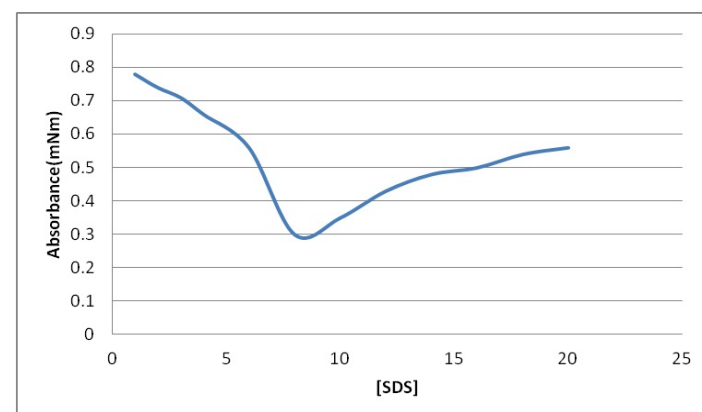


Figure 1: Plot of absorbance (A) as a function of concentrations of [SDS]+water system at 298K [CMC] = 7.9mM

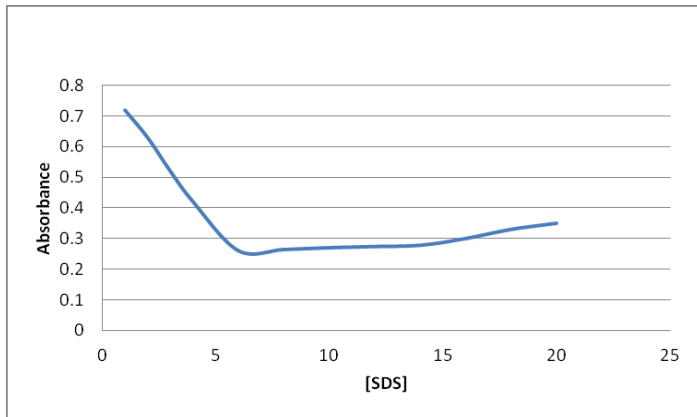


Figure 2: Plot of absorbance (A) as a function of concentrations of [SDS]+0.1M NaAc+ Water system at 298 K

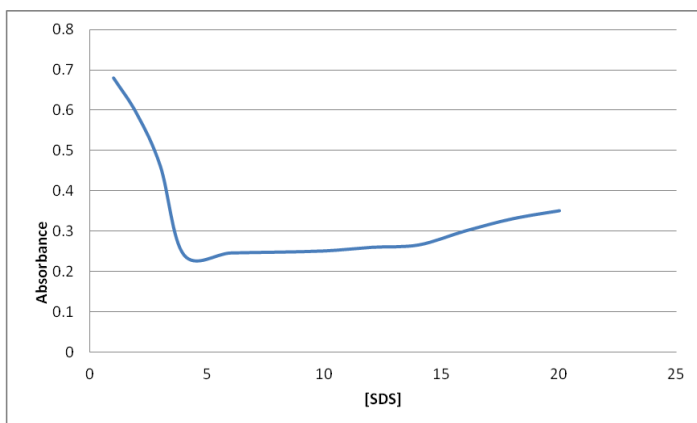


Figure 3: Plot of absorbance (A) as a function of concentrations of [SDS]+0.1M Ca(Ac)₂+water system at 298 K

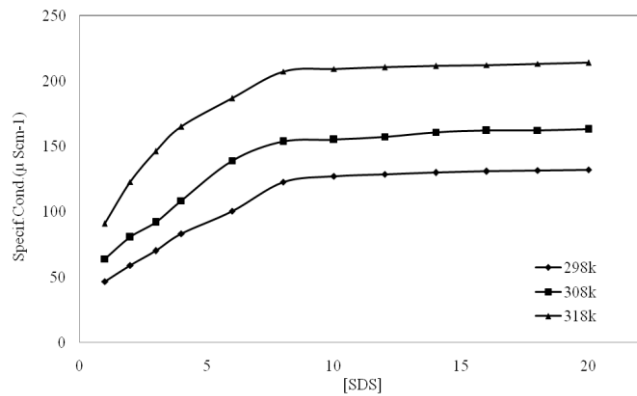


Figure 4: Specific conductance Vs [SDS] at 298K, 308K and 318K. (CMC=8.0mM)

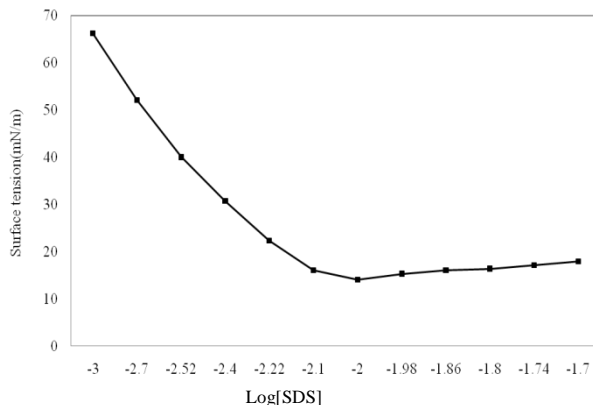


Figure 5: Plot of surface tension Vs log[SDS] at 298K (CMC=8.3mM)

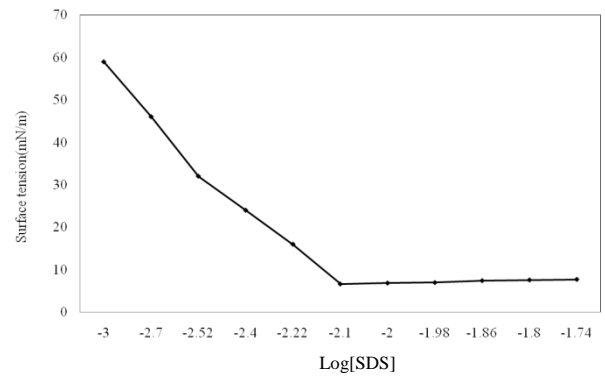


Figure 6: Plot of surface tension Vs log[SDS] for SDS + NaAc + H₂O system at 298K

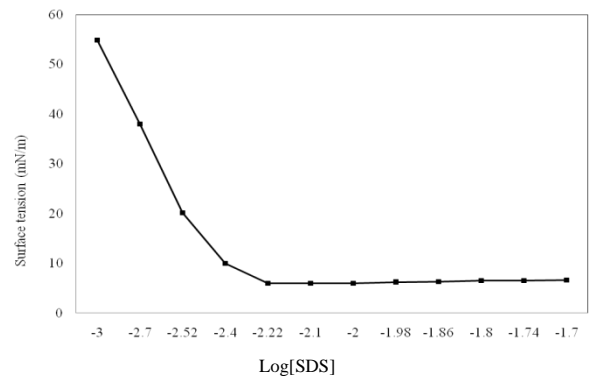


Figure 7: Plot of surface tension Vs log[SDS] for SDS + Ca(Ac)₂ + H₂O system at 298K

Thermodynamic parameters of micellization

The main reason for micelle formation is the attainment of a minimum free energy state. The main driving force for the formation of micelles is the increase of entropy that occurs when the hydrophobic regions of the surfactant are removed from water and the ordered structure of the water molecules around this region of the surfactant molecule is lost.

Any process that leads to free energy decrease will occur spontaneously because it leads to the formation of a more stable system. Micelle formation is, therefore, a spontaneous process. The standard free energy change of micellization (ΔG_{mic}^0) values for studied surfactants with or without electrolyte (sodium acetate and calcium acetate) are all negative ($\Delta G_{mic}^0 < 0$) suggesting the feasibility of the micellization (shown in table.3). The free energy change of micellization becomes more negative on mixing the electrolytes (especially calcium acetate) and also with rise in temperature from 298K to 308K and to 318K. Therefore, addition of electrolytes in a surfactant solution irrespective of the nature of added electrolyte as well as higher temperature both enhances the feasibility of micellization process. Though the micellization process is generally opposed by endothermic enthalpy change, yet the driving force in micellization process is the entropy gain [25, 26]. On mixing of electrolytes, ΔG_{mic}^0 further decreases (become more negative) it shows that ionic salts in aqueous surfactant solution facilitates micellization.

The positive ΔS_{mic}^0 values are attributed to the disruption of water structure around the hydrocarbon part of surfactant molecule as it transfers from the aqueous bulk phase to non aqueous micellar interior, when the electrolytes (0.1M sodium acetate or calcium acetate) were added, the entropy of micellization increases. It is because in the presence of electrolytes in the aqueous solution undergo enhanced water structure due to ion hydration and entropy gain by transfer of surfactant

hydrophobic chain from bulk to micelle involves enhanced water structure disruption [25, 26].

Table 3: Thermodynamic parameters of Micellization for studied surfactant systems at 298k

System	Temp. (K)	$\Delta G_{mic}(\text{kJmol}^{-1}\text{K}^{-1})$	$\Delta S_{mic}(\text{kJmol}^{-1}\text{K}^{-1})$	$\Delta H_{mic}(\text{kJmol}^{-1}\text{K}^{-1})$
SDS+H ₂ O	298	-43.40	0.122	-7.044
SDS+0.1MNaAc	298	-46.69	0.133	-7.01
SDS+0.1M $\text{Ca}(\text{Ac})_2$	298	-49.97	0.140	-7.28

CONCLUSION

Conductometry, UV-visible spectrophotometric and surface tension measurement techniques have been used for studying micelle formation of an ionic surfactant, SDS with or without added electrolytes such as sodium acetate and calcium acetate, and drawn conclusions:

- The CMC decreases with the addition of electrolytes for the studied systems. Such decrease in CMC is more favored on increasing the valence of cation of the electrolyte. Surface excess concentration for the studied systems is in the order of,



- Standard Gibbs free energy change of micellization (ΔG_{mic}^0) is negative for the studied systems indicating the feasibility of micellization process. On addition electrolytes, ΔG_{mic}^0 further decreases showing that the presence of these electrolytes in aqueous solution facilitates the process of micellization.
- Enthalpy of micellization is exothermic in the case of the studied surfactant. The decrease of CMC on mixing electrolytes in surfactant solution suggests that the presence of specially calcium acetate would enhance detergency and solubilizing efficiency of surfactant for organic compounds in aqueous solution.
- In the case of ionic surfactants the presence of electrolytes causes lowering of the CMC but decrease excess surface concentration of surfactants. Hence addition of electrolyte in SDS is more beneficial in treatment of oil spill and detergency, pharmaceutical application and enhanced oil recovery but of disadvantage in concentration of metal ores in the froth floatation process.

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