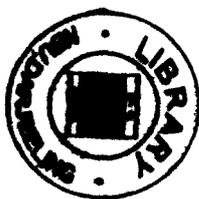


**PHYSICO-CHEMICAL STUDIES ON MICELLAR
PROPERTIES OF SOME SIMPLE AMPHIPHILES
IN AQUEOUS AND NON-AQUEOUS MEDIA**

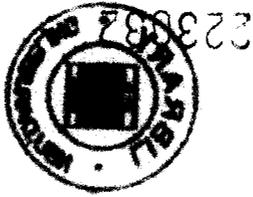
**Thesis Submitted for the Degree of Doctor of Philosophy (Science)
of the University of North Bengal
2009**



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Dedicated to late Prof. D. K. Hagra

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SCOPE AND OBJECT OF THE WORK

Amphiphilic molecules, or amphiphiles, not only are highly interesting from physicochemical view point but also fundamental to life and living bodies. It is not exaggeration to say that all living things are made up of colloids comprising a wide variety of amphiphiles¹. Of these amphiphiles, the surface active substances are also called surfactants, showing strong action on surfaces and interfaces to change their properties profoundly. Surfaces and interfaces are, of course, present everywhere in our daily life and in many kind of industries; so surfactants can be used in application field of every short².

Colloidal and interfacial phenomena play a significant role in many aspect of our modern society. On the one hand colloidal systems are extensively used in the application of detergents, cosmetics, paints and coatings, lubricants, food and pharmaceutical products, foaming agents, wetting agents etc., in solving the day-to-day problems that exist in many field of industrial and domestic processing. On the other hand, these phenomena are also critical to the very fundamental processes of biological membrane formation and functions in living cells³. The nature of colloidal and interfacial science is: (i) to explore the ability of amphiphilic materials to form molecular self-aggregations with the principal goal of advancing knowledge in the field of fundamental studies; (ii) to search for the best surfactants or combination of surfactants for use in new applications in the field of applied research⁴. The study of colloidal and interfacial science is one of a few areas in chemistry that has exhibited this dichotomy of purpose. Since the process of surfactant adsorption at the surface/interface is closely related to the stability of the self-aggregate in the bulk phase⁵, and since by far the largest number of surfactant applications are in aqueous media, the study of self-aggregation in aqueous solution has traditionally been the principal focus of colloidal and interface science⁶.

There has been a renewed interest in behavior of surfactants in solution in the last three decades. One of the main reasons for this renaissance is that a variety of new techniques like neutron scattering, quasielastic light scattering, rheology, luminescence probing, NMR, spin-labeling, etc. which are particularly suitable for studying surfactants in solution has become available on a routine basis in research laboratories⁶. The second

reason is the development of theories to treat the kinetics of micellization which have provided a better understanding of the dynamics of micelle formation, breakdown and organization of the interior of surfactant aggregates⁷⁻¹³. Thirdly, the rejuvenation of the thermodynamic methods through technical improvements and theoretical developments has enabled one to extract better information about surfactant solutions from quantitative analysis of experimental results¹⁴⁻²⁶. The last and the most important reason is the increasing use of surfactants in every industry sector, especially in applications to enhance crude-oil recovery²⁷.

The majority of fundamental studies on solution behavior of anionic surfactants has been made on sodium dodecylsulfate. Surface chemical studies of lithium dodecylsulfate are very limited and hence its surface chemical applications are scarcely found in literature. Its hydrated bulky hydrophilic groups in aqueous solution are expected to play a special role in their solution and interfacial behaviors. How this surfactant behaves individually in solution as well as in binary and ternary mixtures requires a serious attention of research.

Although vast majority of investigations of various single surfactants as well as their mixtures have been made in aqueous medium, relatively few such studies are available in pure nonaqueous solvents²⁸⁻⁵¹. The situation is really worsened in the aqueous mixtures of organic solvents.

The objective of the present work is, therefore, to elucidate different micellar properties of some simple amphiphiles including lithium dodecylsulfate and also their mixtures in aqueous and non-aqueous media from conductometric, volumetric, interferometric, tensiometric and spectrophotometric measurements. The available data have been utilized to examine the different physicochemical properties of these amphiphilic substances in both aqueous and non-aqueous solutions using various existing theories of micellization.

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CHAPTER-I

INTRODUCTION

A common characteristic property of the chemical substances is that they are either soluble in oil or in water. Substances, which are well soluble in water are usually poorly soluble in oil and are known as polar. Substances, which are well soluble in oil are often sparingly soluble in water and are called apolar. An **amphiphile** is a molecule composed of a polar and an apolar part. The polar part is generally referred to as the **head group** (hydrophilic), and the apolar part is known as the **tail** (hydrophobic). The word **amphiphile** is derived from the Greek words *amphi* (= both) and *philios* (= friend). So an amphiphilic molecule likes both oil and water. This combination of water- and oil-loving parts provides this class of substances with a range of interesting features. For example, they have the ability to form aggregates (known as micelles) and other self-assembled structures¹.

Surfactants

The amphiphiles that have the property of getting adsorbed onto the surfaces of a system thus modifying the interface free energies are referred to as surface-active-agents or surfactants. Such molecules have both hydrophilic and hydrophobic regions in their structures as illustrated schematically in Figure 1².

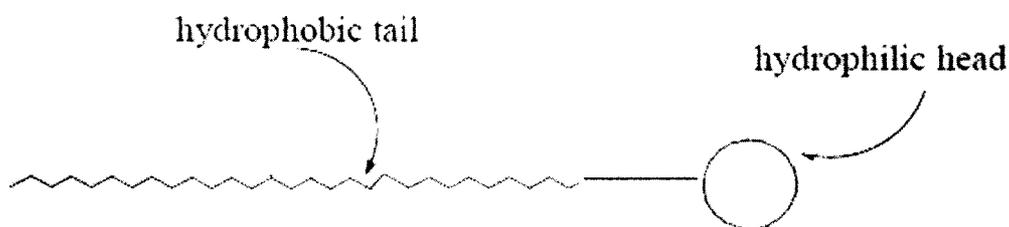


Figure 1. Structure of a surfactant

Most surfactants have a long hydrophobic tail that can be linear or branched which interacts only very weakly with the water molecules in an aqueous environment; hence the chain is called a hydrophobic tail. The hydrophilic head is a relatively small

ionic or polar group that interacts strongly with the water molecules via dipole-dipole or ion-dipole interactions.

Types of Surfactants

Surfactants can be classified according to their physical properties or functionalities. The following is the most common classification based on the nature of the head group.

Ionic surfactant: The head group of an ionic surfactant can be ionized in an aqueous solution. Depending on the outcome of this, there are a number of subcategories. If the charge on the head group is negative, the surfactant is said to be anionic. Among these, we find alkyl sulfates³, alkyl sulphonates⁴, alkyl phosphates^{5, 6} and fatty acid salts^{7, 8} (see Figure 2, for example). If the residual charge is positive, the surfactant is cationic and common examples of this kind are alkyltrimethylammonium^{10, 11} and alkylpyridinium halides¹², an example of which is shown in Figure 2.

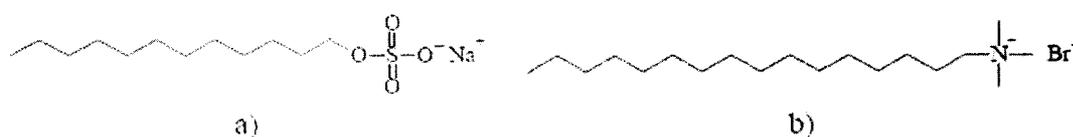


Figure 2. Molecular structure of two common ionic surfactants

a) Sodium dodecylsulfate (SDS)

b) Hexadecyltrimethylammonium bromide (CTAB)

In some surfactant molecules the ionization leads to two separate groups of opposite charges attached to the hydrophobic part^{13, 14}. Such surfactants are called zwitterionic and these are common in biological systems¹⁴. This type of surfactant can also be regarded as nonionic, since their total charge is zero. Catanionic surfactants (Figure 3) consist of oppositely charged surfactant ions, *i.e.*, one surfactant acts as counterion to the other¹⁵⁻¹⁷. Catanionic surfactants can be either symmetric (both alkyl chains are of the equal length) or asymmetric (one chain is shorter than the other).

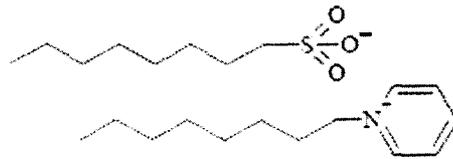


Figure 3. A symmetric catanionic surfactant, octylpyridinium octanesulphonate (OPOS)

Nonionic surfactant: As the name implies, nonionic surfactants lack groups that can easily be ionized. Examples of nonionic surfactants with a polyoxyethylene^{18, 19} and a polyhydroxy^{20, 21} moiety are shown in Figure 4. Compared to ionic surfactants of comparable size, nonionic surfactants form aggregates at lower concentration and the aggregation behaviour is less sensitive to the added salt due to the absence of repelling charges in the head groups.

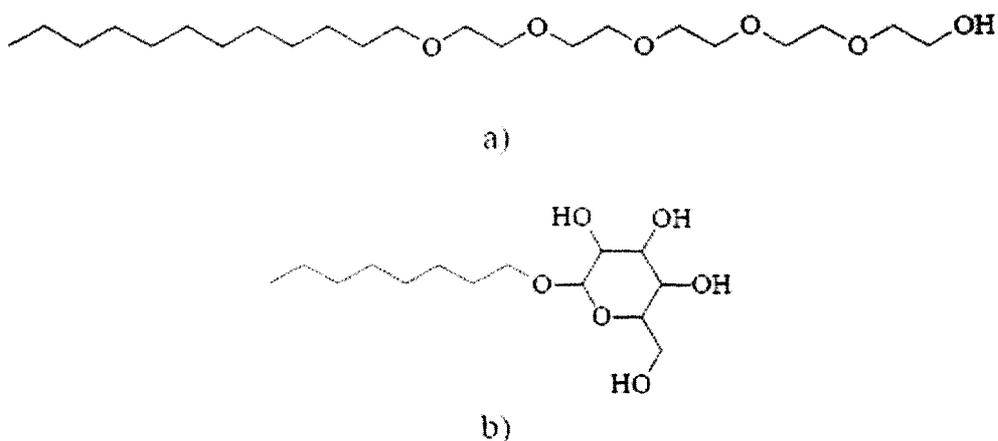


Figure 4. Nonionic surfactants:

- a) Pentaoxyethylene dodecyl ether ($C_{12}E_5$)
- b) n-octyl β -D-glucoside (OG)

Different Types of Aggregates

Micelles: In aqueous solution a micelle is a cluster of surfactants, usually pictured as a spherical particle with a water-free core containing all the tails, and an outer shell

containing the head groups, some water molecules and some of the counterions (Figure 5).

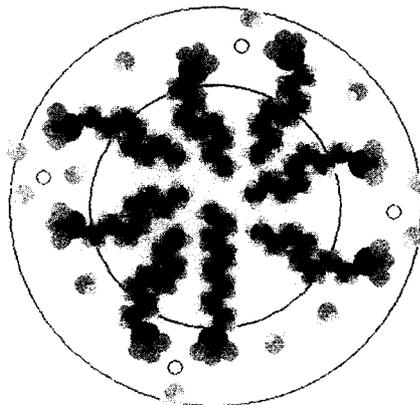


Figure 5. A schematic representation of a micelle showing the hydrocarbon core (inner circle) and head group layer (outer circle) with associated counterions and water molecules.

Micelle formation occurs only beyond a critical concentration of the amphiphiles, referred to as the critical micelle concentration or *cmc*. The formation of micelles, like all self-assembly processes, is governed by thermodynamics, *i.e.*, micelle formation occurs because the system minimizes its Gibbs free energy in the process. Below the *cmc*, surfactants are present as monomers or dimers. Short-chain surfactants can behave like hydrotropes and form less well-defined micellar aggregates. A number of different more complex micellar structures also exist. They can grow lengthwise, forming rod-like²², thread-like or worm-like micelles²³. These micelles, can in turn entangle forming networks^{23, 24}.

Vesicles: Another type of aggregate that can be found in dilute solutions is the vesicle.

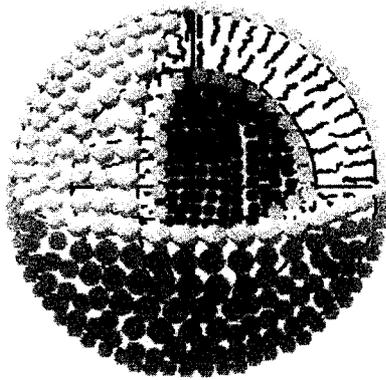


Figure 6. A schematic representation of a vesicle.

A vesicle is a shell^{25, 26}, consisting of a surfactant bilayer, which encapsulates an aqueous interior (Figure 6). These structures can be very large (>100 nm). Vesicles can form inside each other, similar to a Russian doll. Such a particle is called an onion or a multi-lamellar vesicle. Due to the bilayer structure, a vesicle is more related to the lamellar phase than to a micelle. In fact vesicles can be formed by agitating a lamellar phase²⁷. Reverse vesicles have also been found in a phospholipids/triolein/water system²⁸.

Micellar Shape

The structure of a micelle is dictated by the equilibrium between the repulsive forces among hydrophilic head groups and attractive forces among hydrophobic tails. Several structures have been proposed for the micelles. McBain proposed a coexistence of the spherical and lamellar micelles²⁹. Hartley suggested that micelles are spherical entities with charged groups located at the micellar surface³⁰. The Hartley model successfully describes many properties of micellar systems. According to this model, counterions are bound to the charged head groups of the surfactants. Hartley proposed that the inner cores of the micelles have properties of liquid hydrocarbons; thus, micelles are able to solubilize hydrophobic molecules that are otherwise insoluble^{31, 32}. Debye and Anacker proposed rod-shaped micelles rather than spherical or disk-like ones³³. Based on NMR and kinetic studies, Menger reports that micelles are more disorganized with chain looping, nonradial distribution of

chains, and contact of terminal methyl groups with water³⁴. According to the Menger model, micelles have rough surface with water-filled pockets. In general, the spherical form is accepted as the true representation of the micelle (Figure 7).

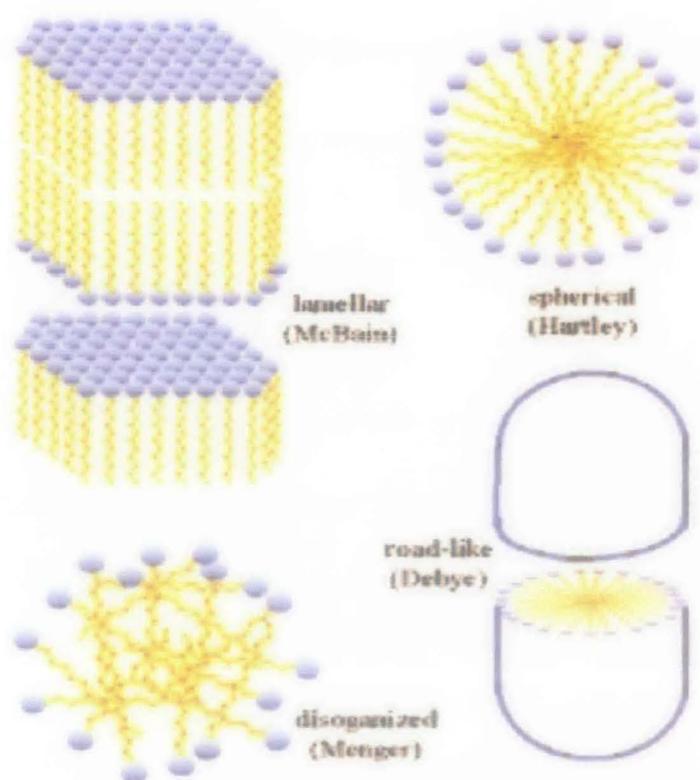


Figure 7. Different proposed structures of a micelle.

With increasing surfactant concentration, the shape of ionic micelles changes in the sequence: spherical - cylindrical - hexagonal - lamellar³¹ (Figure 8). Additional factors that affect the micelle shape are the optimal head group area, the volume, and the chain length of the tail³⁵.

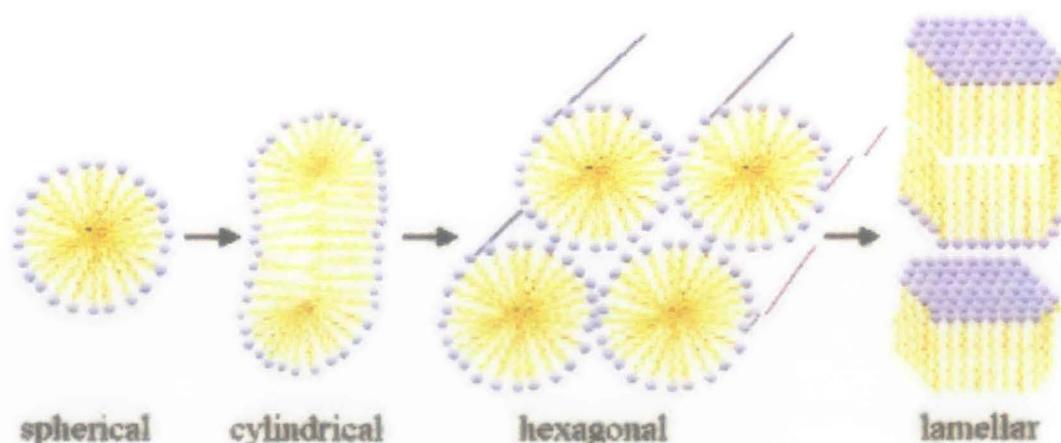


Figure 8. Change in micelle shape with respect to the change in surfactant concentration.

The generalized structure of the cross-section of a typical micelle is assumed to have a liquid core formed by the associated hydrocarbon chains with ionic or polar head groups projected out into the water. In ionic micelles, the Stern layer consists of bound ionic surfactant head groups, counterions, and water molecules. The thickness of the Stern layer is usually only a few angstroms. Figure 9 shows different regions of a spherical micelle. The layer just beyond the Stern layer is a diffuse layer (known as the Guoy-Chapman layer) extending outward to several hundred angstroms. The inner core of the micelle is usually divided into two regions. The hydrophobic tail of the surfactant forms a water free region (inner core). Moving outward from the inner core of the micelle, there is a hydrated region between the inner core and the polar head group of the micelle. This hydrated region is called the palisade layer and is viewed as liquid hydrocarbon. The radius of the inner core and the palisade layer is approximately equal to the length of the fully extended hydrocarbon chain³⁶.

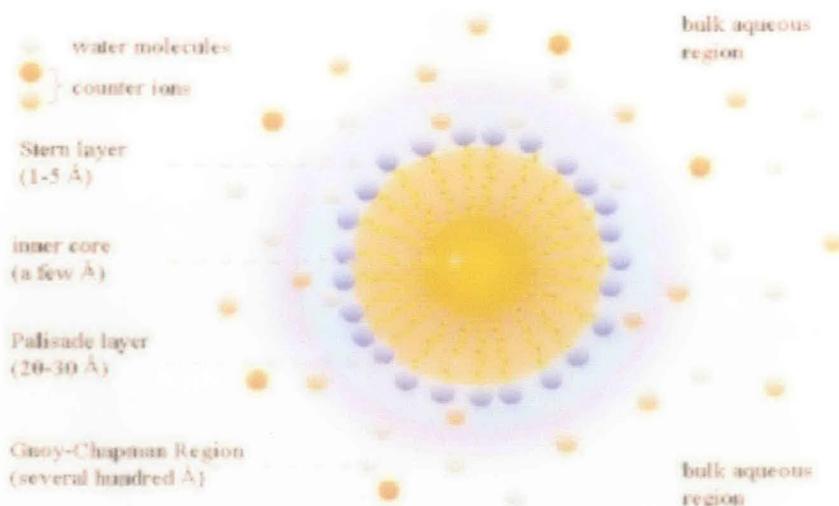


Figure 9. Important micellar regions.

Critical Micelle Concentration (*cmc*) and its Determination

In dilute solutions, surfactant molecules exist as individual species in the media and the solutions have completely ideal chemical and physical properties. As the surfactant concentration increases, chemical and physical properties of the solutions deviate from ideality by varying degrees, and at a certain concentration, aggregation of the surfactant monomers occurs and micelles are formed. This concentration is called the critical micelle concentration (*cmc*)². The critical micelle concentration indicates usually a narrow range of concentrations separating the limits below which most of the surfactant is in the monomeric state and above which virtually all additional surfactant molecules enter the micellar state³⁷.

The *cmc* is a very important solution property of surfactants. Its determination thus requires a special mention. There exist a large number of experimental methods for determining the value of *cmc*. Mukerjee and Misels³⁸ reviewed about 70 methods which have been published for *cmc* determination. The appropriate choice of the method depends upon the availability of the various techniques, the relationship between the technique and the ultimate application, and the personal preferences of the investigator. Many techniques have been used for this purpose including surface tension, osmotic pressure, turbidity, conductivity, capillary electrophoresis, light scattering, spectroscopic techniques including fluorescence^{35, 39-48}. The most

frequently used methods are surface tension, conductivity and fluorescence. The conductivity method is applicable only to ionic surfactants. The critical micelle concentrations of surfactant solutions measured by different methods demonstrate a distinct feature on the change in concentration dependence of the physicochemical properties around the critical micelle concentration as shown in Figure 10.

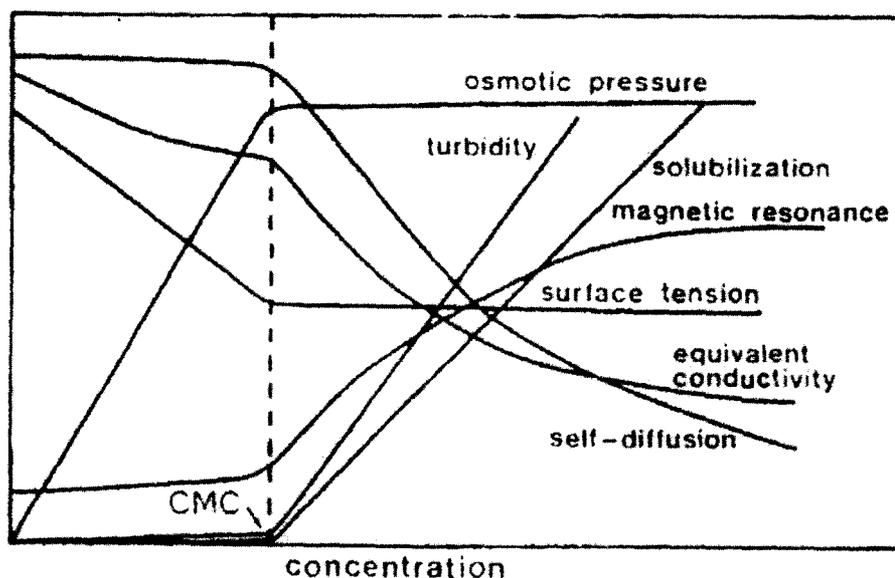


Figure 10. Change in concentration dependence of a wide range of physico-chemical quantities around the critical micelle concentration (After Lindman *et al.*⁴⁹).

The properties show breaks in the plots which are considered as the *cmc* points for the surfactant under investigation. It is to be noted that the *cmc* values determined by different methods fall within a narrow range, *i.e.*, the *cmc* is moderately method dependent. It may be mentioned in this context that the acceptance limit of variation of *cmc* is within $\pm 10\%$.

Factors Affecting Micelle Formation and *cmc*

The hydrophobic chain length: The *cmc* decreases strongly as the length of the hydrophobic part of the surfactant is increased, the decrease being more rapid for nonionic than for ionic surfactants⁵⁰. For a straight chain hydrocarbon surfactant of about 16 carbon atoms or less bound to a single terminal head group, the *cmc* is

usually reduced to approximately half of its previous value with the addition of each methylene group⁴². An even more pronounced decrease in *cmc* with the increase of hydrocarbon chain length has been noted with nonionic surfactants; the addition of one methylene group causes the *cmc* to decrease to one third of its original value⁵¹. The *cmc*s of various homologues of surfactants with a linear alkyl chain follow the equation⁵²,

$$\log cmc = A - Bn \quad (1)$$

where n is the number of carbon atoms in the alkyl chain and A and B are constants specific to the homologous series under a given conditions of constant temperature, pressure etc. Figure 11 shows a linear relationship between $\log cmc$ and the number of carbon atoms in the alkyl chains. For chains containing more than 16 carbon atoms, this relationship no longer holds and further increase in chain length often has no appreciable effect on the *cmc*, possibly due to the coiling of the long chains in solutions⁵³. In case of branched hydrocarbon chains, the effect on the *cmc* is not higher than that for straight chain surfactants. For a given alkyl chain, *cmc* increases in the order: nonionic < zwitterionic < ionic (cationic or anionic)³⁸.

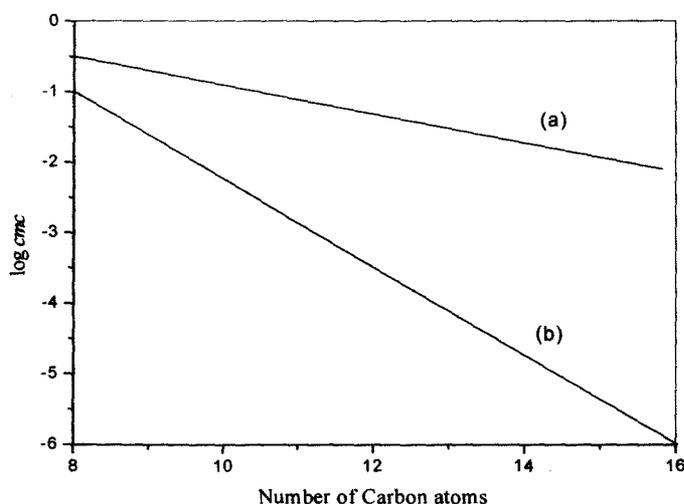


Figure 11. Variation of *cmc* with the hydrocarbon chain length for (a) sodium alkyl sulfate and alkyltrimethylammonium bromide (b) hexaoxyethylene monoalkyl ethers (After Attwood and Florence⁴²).

Temperature: The effect of temperature changes on the *cmc* of surfactants in aqueous solution have been found to be quite complex. For ionic surfactants, the *cmcs* show a parabolic-type variation with temperature passing through a minimum⁵⁴. The minimum in the curve for ionic surfactants occurs typically between 20 and 30 °C. At lower temperatures (generally at 30 °C or below) the *cmc* decreases with increasing temperature, which is probably due to desolvation of parts of monomer which make it hydrophobic, whilst further rise in temperature causes disruption of the water structure around the hydrophobic groups which opposes micellization⁴². A decrease in the micelle size of ionic surfactants with the increase in temperature has also been reported⁵⁵.

Temperature dependence of the *cmcs* for nonionic surfactants is not so predictable, although it has been found that some nonionic surfactants show a *cmc* minimum⁵⁶ around 50 °C. The most drastic effect of temperature on nonionic surfactants is that on solubility. Nonionic surfactants form isotropic solutions below a lower Krafft point and upper cloud point. Heating a clear solution to above the cloud point causes a reversible phase separation: a phase rich in surfactant separates out of solution leaving an aqueous phase containing surfactant monomers.

Effect of additives: A survey of literature shows that additives have a marked effect on the *cmcs* of both ionic and nonionic surfactants⁵⁷⁻⁶⁰. Paradas *et al.*⁵⁹ have shown that there is a large decrease in the *cmcs* of CTAB and SDS in presence of 0.1M NaCl but no significant change was observed in the *cmc* value of polyoxyethylene-*tert*-octylphenylether (Triton X-100 or TX-100). In general, the addition of electrolytes strongly reduces the *cmc* for ionic surfactants, but this has little effect on the *cmcs* of nonionics⁴⁹. Addition of an electrolyte causes a reduction in the thickness of ionic atmosphere surrounding the polar head groups which consequently decreases repulsion between them. These effects are manifested in the reduction in *cmc* and in the increase in the aggregation number. For ionic surfactants, the effect of addition of electrolyte with the same charge as the native counterion on the *cmc* can be empirically quantified with the relationship⁶¹

$$\log_{10} cmc = -a \log_{10} C_c + b \quad (2)$$

where *a* and *b* are constants for a given ionic head group at a particular temperature, and *C_c* is the total concentration of monovalent counterion in molarity.

The critical micelle concentration of nonionic surfactants in aqueous solutions is lowered by the addition of most inorganic salts^{57, 62-64}. The observed changes in the *cmc* of nonionic and zwitterionic materials on the addition of electrolytes cannot be attributed to the same electrostatic effect as that for fully ionic surfactants.

Large amount of small polar organic molecules *e.g.*, ethanol, urea, etc. raises the *cmc*^{65, 66}. The studies on the effect of *n*-alcohols on the aggregation number *n* of ionic surfactants suggest that water-soluble alcohols (methanol to butanol) are predominantly dissolved in the water phase and that the aggregation numbers may increase or decrease depending upon the alcohol concentration⁶⁷. The effect of added alcohols has been reported for nonionic systems, where methanol and ethanol cause an increase in *cmc* and higher alcohols butanol and pentanol cause a decrease in *cmc*^{68, 69}.

Pressure: Studies have been made on the pressure effect on the *cmc* by different techniques⁷⁰⁻⁷⁴. Increases in pressures initially retards the association and after a threshold value (100-200 Mpa), the process is favoured. This is a consequence of water structure disruption by the applied thrust to assist wider distribution of the surfactant molecules in solution to oppose their tendency of association. The release of surfactant monomers from the micelles in the lower range of pressure and their association at higher pressure together with the changed dielectric constant of the solution by the application of pressure also play their specific roles in surfactant organization. This has been supported by the measurement of aggregation number⁷⁵, which shows a minimum for ionic surfactants with respect to pressure.

Counterion effect: A number of studies⁷⁶⁻⁸⁰ indicate that counterions associated with an ionic surfactant have pronounced effect on the micellar properties. Since electrostatic repulsion among the ionic groups would be the greatest for complete ionization, it is not surprising to find that the *cmc* of surfactant in aqueous solution decreases as the degree of counterion binding increases. From regular solution theory (please see later), it is found that the extent of ion pairing in a system will increase as the polarizability and the valence of the counterions increase. Conversely, a larger radius of hydration will result in greater ion separation. It has been found that, for a given hydrophobic tail and anionic head group, the *cmc* decreases in the order, $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+ > \text{N}(\text{CH}_3)_4^+ > \text{N}(\text{CH}_2\text{CH}_3)_4^+ > \text{Ca}^{2+} \approx \text{Mg}^{2+}$. In the case of cationic

surfactants such as dodecyltrimethylammonium halides, the *cmc*s are found to decrease in the order $F^- > Cl^- > Br^- > I^-$ ⁵².

Effect of polar head group: As mentioned earlier, the more the ionization of the surfactants, the higher the *cmc*, due to the increase in electrical work required to form the micelle⁸¹. However, nonionic surfactants have much lower *cmc* than ionic surfactants⁸². The lower *cmc*s of the nonionic surfactants are a consequence of the lack of electrical work necessary in the formation of micelles⁴².

A detailed study on the effect of the nature of the polar group of ionic surfactants on the micellar properties has been reported by Anacker and co-workers⁸³⁻⁸⁵. They concluded that the mean distance of closest approach of a counterion to the charged centre of the surfactant was an important factor determining the micellar size. For example, decylammonium bromide forms much larger micelles than decyltrimethylammonium bromide because Br^- counterions are able to approach more closely to the charged nitrogen atom of decylammonium bromide thus effectively shielding the repulsive electrical forces⁸³. The effect of changing the charge-bearing atom in the polar head group has also been reported⁸⁴. Replacement of nitrogen in decyltrimethylammonium bromide by phosphorus or arsenic causes an increase in the aggregation number with a corresponding decrease in *cmc*.

In polyoxyethylated ether type of nonionic surfactants, increase of polyoxyethylene chain length causes an increase in the *cmc* and decrease in the micellar size⁴². Increase in the polyoxyethylene chain length makes the monomer more hydrophobic giving higher *cmc*.

Thermodynamics of Micelle Formation

Micellization is a spontaneous process and like all other spontaneous physicochemical processes micellization is energetically controlled and guided by the thermodynamic principles. During the process of micellization, 'iceberg' structure of water molecules surrounding the nonpolar hydrocarbon tail of the surfactant is broken with a resultant gain in entropy⁸⁶⁻⁸⁸.

During the past years, significant advances have been made on the ways to calculate the changes in the thermodynamic parameters that accompany micelle formation from experimental data⁸⁹⁻⁹³.

Many workers⁹⁴⁻⁹⁸ paid considerable attention to the thermodynamics of micellization, and in particular to the merits and demerits of various approaches which have been made to this problem.

Two basic approaches that have been made to explain the thermodynamics of micelle formation have gained predominance and these have been generally accepted as useful models^{95, 99-105}. These are (i) the mass action model, and (ii) the phase separation or pseudophase model.

The Mass Action Model: According to the mass action model, micelles and unassociated surfactant ions are assumed to be in association-dissociation equilibrium. The mass action approach was originally applied mainly to ionic surfactants^{103, 104, 106}. Application of this model to nonionic surfactants has been discussed by Corkill *et al.*¹⁰⁷.

(a) Application of mass action model to nonionic surfactants: According to the mass action model, micelles, M , are considered to be formed by a single step reaction from n monomers, S , as,



where, K_M is the equilibrium constant for micelle formation given by

$$K_M = \frac{a_M}{a_S^n} \quad (4)$$

where a terms represent the activities of the relevant species.

Assuming ideality, we may write, as an approximation,

$$K_M = \frac{x_M}{(x_S)^n} \quad (5)$$

where x_M and x_S are the mole fractions of micelle and monomers respectively.

The standard Gibbs free energy of micellization is given by the relation,

$$\Delta G_M^0 = -RT \ln K_M = -RT \ln x_M + nRT \ln x_S \quad (6)$$

The change of free energy per mole of the monomeric unit is then,

$$\Delta G_m^0 = \frac{\Delta G_M^0}{n} = -\frac{RT}{n} \ln x_M + RT \ln x_S \quad (7)$$

At *cmc*, the percentage of monomers undergoing micellization is very small. Therefore, at *cmc* by conceptual approximation,

$$\Delta G_m^0 = RT \ln x_{cmc} \quad (8)$$

(b) *Application of mass action model to ionic surfactants:* The ionic micelle, $M^{\pm(n-m)}$, is considered to be formed by the association of n surfactant ions, S^\pm , and m firmly bound counterions, X^\pm .



Hence,
$$K_M = \frac{a_{M^{\pm(n-m)}}}{a_{S^\pm}^n a_{X^\pm}^m} \approx \frac{x_{M^{\pm(n-m)}}}{x_{S^\pm}^n x_{X^\pm}^m} \quad (10)$$

The standard Gibbs free energy of micellization is given by,

$$\Delta G_M^0 = -RT \ln K_M = -RT \ln x_{M^{\pm(n-m)}} + nRT \ln x_{S^\pm} + mRT \ln x_{X^\pm} \quad (11)$$

Therefore, the free energy per mole of monomeric unit,

$$\Delta G_m^0 = \frac{\Delta G_M^0}{n} = -\frac{1}{n} RT \ln x_{M^{\pm(n-m)}} + RT \ln x_{S^\pm} + \frac{m}{n} RT \ln x_{X^\pm} \quad (12)$$

Again, since the percentage of monomers undergoing micellization is very small and n is usually large, so

$$\Delta G_M^0 = RT \ln x_{S^\pm} + \frac{m}{n} RT \ln x_{X^\pm} \quad (13)$$

If normal electrolyte is used then,

$$x_{S^\pm} = x_{X^\pm} \quad (14)$$

So, at cmc ,
$$x_{S^\pm} = x_{X^\pm} = x_{cmc} \quad (15)$$

Thus,
$$\Delta G_m^0 = \left(1 + \frac{m}{n}\right) RT \ln x_{cmc} = (1 + \beta) RT \ln x_{cmc} \quad (16)$$

where β = fraction of counterions bound.

If $m = 0$ i.e., no counterions bound, as in the case of nonionic surfactants,

$$\Delta G_m^0 = RT \ln x_{cmc} \quad (17)$$

For 100% counterion binding, $\beta=1$ and

$$\Delta G_m^0 = 2RT \ln x_{cmc} \quad (18)$$

The above relations are based on constancy of n and several other valid approximations.

The Pseudophase Model: In the pseudophase model the micelles are considered to form a separate phase at and above the cmc . Thus monomer concentration remains

unchanged at and above cmc , *i.e.*, with increasing surfactant concentration, only micelles are formed.

(a) Application of pseudophase model to nonionic surfactants: To calculate the thermodynamic parameters for the micellization process, we are required to define the standard state. For a surfactant in the micellar state, the micellar state itself is considered to be the standard state.

At constant temperature, if μ_s and μ_m are the chemical potentials of the unassociated surfactant in the aqueous phase and associated surfactant in the micellar phase respectively, and since these two phases are in equilibrium:

$$\mu_s = \mu_m \quad (19)$$

For a nonionic surfactant,

$$\mu_s = \mu_s^0 + RT \ln a_s \quad (20)$$

Assuming the concentration to be low, the activity of surfactant monomer, a_s , may be replaced by the mole fraction of monomer S , x_s ,

$$\mu_s = \mu_s^0 + RT \ln x_s \quad (21)$$

where μ_s^0 is the chemical potential of the surfactant monomer in the standard state.

Since the micellar material is in its standard state, one can write

$$\mu_m = \mu_m^0 \quad (22)$$

The standard Gibbs free energy change for the transfer of one mole of surfactant from solution to micellar phase,

$$\begin{aligned} \mu_m = \mu_m^0 - \mu_s^0 &= \mu_m - \mu_s + RT \ln x_s \\ &= RT \ln x_s \end{aligned} \quad (23)$$

Assuming that the concentration of free surfactant in the presence of micelle is constant and is equal to the cmc value, x_{cmc} , then the free energy per mole of monomer is given by

$$\Delta G_m^0 = RT \ln x_{cmc} \quad (24)$$

(b) Application of pseudophase model to ionic surfactants: In case of an ionic surfactant to calculate ΔG_m^0 , it is necessary to consider not only the transfer of surfactant monomers from the aqueous to micellar phase but also the transfer of m/n

moles of counterions from the standard state to the micelle. Equation (23) is thus written as,

$$\Delta G_m^0 = RT \ln x_s + \frac{m}{n} RT \ln x_x \quad (25)$$

where x_s and x_x are the mole fractions of surfactant ion and counterion respectively. Assuming the concentration of free surfactant and counterion in the presence of micelle to be constant and equal to the *cmc* value, x_{cmc} , then

$$\Delta G_m^0 = \left(1 + \frac{m}{n}\right) RT \ln x_{cmc} = (1 + \beta) RT \ln x_{cmc} \quad (26)$$

where β is the fraction of counterions bound to the micelle.

Thus we get the same equation for ΔG_m^0 for nonionic and ionic micelles as we get in the case of mass action model. The two equations differ slightly because of the differences in the way in which the mole fractions are calculated. In the mass action model, the total number of moles present at the *cmc* is equal to the sum of the moles of water, surfactant ions, micelles, and free counterions whereas total number of moles in the pseudophase model is equal to the sum of moles of water and surfactant. Applying Gibbs-Helmholtz equation and assuming the aggregation number, n , to be large and independent of temperature, the standard enthalpy of micellization (ΔH_m^0) at constant pressure, P , is given by

$$\Delta H_m^0 = -(1 + \beta) RT^2 \left[\frac{\partial \ln x_{cmc}}{\partial T} \right]_P = (1 + \beta) R \left[\frac{\partial \ln x_{cmc}}{\partial (1/T)} \right]_P \quad (27)$$

for ionic micelles, and

$$\Delta H_m^0 = -RT^2 \left[\frac{\partial \ln x_{cmc}}{\partial T} \right]_P = R \left[\frac{\partial \ln x_{cmc}}{\partial (1/T)} \right]_P \quad (28)$$

for nonionic micelles.

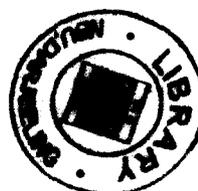
Finally, the standard entropy of micellization per mole of monomer, ΔS_m^0 , may be obtained from

$$\Delta S_m^0 = (\Delta H_m^0 - \Delta G_m^0) / T \quad (29)$$

For the evaluation of ΔH_m^0 and ΔS_m^0 , the *cmc* should be measured at different temperatures and treated according to the Equations (27) to (29). The ΔS_m^0 values are normally positive; negative values are seldom obtained^{108, 109}. Micellization process, therefore, ends up with an increase in entropy; an overall disordered state is

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envisaged. This is due to the release of solvent molecules attached with the nonpolar tails of surfactant monomers by hydrophobic hydration during self organization, the entropy gain by the process exceeds the loss by amphiphilic association, solvation etc., making the overall entropy change positive.

Neither the mass action model nor the pseudophase model for micellization is exactly correct. In both the approaches, at *cmc*, the equilibrium concentration of free monomer is considered equivalent to *cmc*. It is also considered that the aggregation number and counterion binding of micelles are not affected by temperature variation at least within the range of measurements. But despite these limitations, both the mass action and pseudophase models are useful representations of the micellar process and may be used to derive equations relating the *cmc* to the various factors that determine it. There are some other approaches also for the determination of energetics of micellization. Thermodynamics of small-systems have been developed by Hill¹¹⁰. Hall and Pethica⁹⁵ have applied it to non-ionized and non-interacting systems. In this approach the aggregation number is treated as a thermodynamic variable, thereby enabling variations in the thermodynamic functions of micelle formation with the mean aggregation number. A more detailed treatment of multicomponent micelle, describing systems of interacting aggregates, has been developed by Hall^{96, 111-113}.

Another approach to small-system thermodynamics has been formulated by Corkill and co-workers¹¹⁴⁻¹¹⁶ and applied to systems of nonionic surfactants. This multiple-equilibrium model considers equilibria between all micellar species present in solution rather than a single micellar species as was considered by mass action theory.

An interesting model of micelle formation based on geometrical considerations of micelle shape has been proposed by Tanford¹¹⁷ and later extended by Israelachvili *et al*⁹³.

This approach has been further developed by Ruckenstein and Nagarajan⁸⁹. Such an approach is useful for application where the chemical structure of the surfactant is of central importance. The constraints of changing micellar shape and size, variation of counterion association and micellar solvation with temperature and other environmental changes provide challenge to the exactness of the energetic parameters and make the topic worthy of further investigation.

Mixed Micelles

Surface-active compounds used in commercial applications typically consist of a mixture of surfactants because they can be produced at a relatively lower cost than isomerically pure surfactants. In addition, in many surfactant applications, mixtures of dissimilar surfactants often exhibit properties superior to those of the constituent single surfactants due to synergistic interactions between the surfactant molecules¹¹⁸. For example, the critical micelle concentration (*cmc*) of a mixture of anionic and cationic surfactants in aqueous solutions is considerably lower than the *cmc* of each of individual surfactant¹¹⁹. On the other hand, antagonistic interactions in a mixture of hydrocarbon-based and fluorocarbon-based surfactants in aqueous solution result in a mixed system whose *cmcs* are considerably higher than the *cmcs* of the constituent single surfactants^{120, 121}. In general, specific interactions (synergistic or antagonistic) between surfactants result in solutions of surfactant mixtures having micellar and phase behavior properties which can be significantly different from those of the constituent single surfactants. Thus physicochemical studies are required for mixed micelles of ionic-ionic, ionic-nonionic and nonionic-nonionic combinations for formulations, uses and basic understanding.

Theory of Binary Mixed Micelle Formation

By adopting the phase separation model for micellization, a simple theory which treats mixed micelle as an ideal mixture of its components and considers the activity coefficient of free surfactant monomers equal to unity, was proposed by Clint^{122, 123} to predict the *cmc* of the mixture in the form of the following equation,

$$(1/cmc_C) = \sum_{i=1}^n (\alpha_i / cmc_i) \quad (30)$$

Here, α_i denotes the stoichiometric mole fraction of the *i*th component in solution, respectively. The terms cmc_i and cmc_C are the critical micellar concentrations of the *i*th component and the mixture, respectively. According to this model the *cmc* represents the concentration at which the pseudo-phase (mixed micelle) first forms through a process analogous to phase separation. In the ideal-mixing model, the mixture *cmc* was found to be only a function of the *cmcs* of the constituent single surfactants and the composition of the mixture. Ideal-mixing models have been quite successful in predicting the *cmc* of aqueous solutions of binary nonionic¹²⁴⁻¹²⁶ and

binary ionic^{122, 127, 128} surfactants that belong to a homologous series. On the other hand, in solutions which contain two or more non-homologous surfactant species, the measured *cmc*s were often found to be substantially lower than those predicted by the ideal-mixing models^{119, 129, 130}. The observed deviations from ideality were attributed to nonideal mixing effect arising from specific interactions between the different surfactants present in mixed micelle. Later on, various theories for mixed micellization have been put forward¹³¹⁻¹³⁷. We are giving here a brief account of these theories.

Rubingh's theory: According to Rubingh's¹³³ treatment, if two surfactants 1 and 2 form a mixed micelle, the mole fraction X_R of the surfactant 1 in the micelle can be estimated from a knowledge of the critical micelle concentration (*cmc*) of the component surfactants cmc_1 and cmc_2 , the *cmc* of the mixed surfactant, cmc_{mix} , and the mole fraction of the surfactant 1 in the total mixed solute, through the equation

$$\frac{(X_R)^2 \ln[cmc_{mix} \alpha_1 / cmc_1 X_R]}{(1 - X_R)^2 \ln[cmc_{mix} (1 - \alpha_1) / cmc_2 (1 - X_R)]} = 1 \quad (31)$$

From the X_R value its convenient to calculate the interaction parameter, β , and the quantities f_1 and f_2 :

$$\beta = (1 - X_R)^{-2} [\ln(cmc_{mix} \alpha / cmc_1 X_R)] \quad (32)$$

$$f_1 = \exp[\beta(1 - X_R)^2] \quad (33)$$

$$f_2 = \exp[\beta(X_R)^2] \quad (34)$$

where f_1 and f_2 are the activity coefficient of surfactants 1 and 2 respectively in the mixed micelle. The interaction parameter β is a measure of interaction between the components in the micelle (assumed to be constant) which can be obtained from the experimental data.

Motomura's theory: Motomura and co-workers¹³² have shown that the process of mixed micellization can be treated from the view point of thermodynamics. According to this approach, micellization is considered similar to a macroscopic bulk phase, and energetic parameters associated with the process are expressed by excess thermodynamic quantities. The behavior of surfactant molecules in the micelle bears resemblance to that in the adsorbed film.

For a binary mixture of surfactants, Motomura *et al.* considered that surfactant 1 dissociates giving ν_{1a} anions and ν_{1c} cations, while surfactant 2 dissociates giving ν_{2b} cations and ν_{2d} anions and the following relations hold

$$\hat{X}_2 = \nu_2 X_2 / (\nu_1 X_1 + \nu_2 X_2) \quad (35)$$

$$\hat{cmc} = (\nu_1 X_1 + \nu_2 X_2) cmc \quad (36)$$

$$X_M = \frac{\hat{X}_2 - (\hat{X}_1 \hat{X}_2 / \hat{cmc})(\partial \hat{cmc} / \partial \hat{X}_2)_{P,T}}{1 - \delta_d^c \nu_{1c} \nu_{2d} / (\nu_{1c} \nu_2 \hat{X}_1 + \nu_{2d} \nu_1 \hat{X}_2)} \quad (37)$$

where subscripts 1 and 2 refer to surfactants 1 and 2 respectively, X stands for the mole fraction, ν represents the number of ions contributed by a surfactant, the parameters with subscript M represent their state in the micelle, and δ_d^c is the Kroeneker delta defined by $\delta_d^c = 0$ when $d \neq c$ and $\delta_d^c = 1$ when $d = c$. In case of cationic-anionic, anionic-anionic combinations ($\nu_{1a} = \nu_{1c} = \nu_{2b} = \nu_{2d} = 1$), $\hat{X}_2 = X_2$, $\hat{cmc} = 2cmc$ and

$$X_M = \hat{X}_2 - 2(\hat{X}_1 \hat{X}_2 / \hat{cmc})(\partial \hat{cmc} / \partial \hat{X}_2)_{P,T} \quad (38)$$

For nonionic-nonionic pairs ($\nu_{1a} = \nu_{2b} = 1, \nu_{1c} = \nu_{2d} = 0$), $\hat{X}_2 = X_2$, $\hat{cmc} = cmc$ and for cationic-nonionic pair ($\nu_{1a} = \nu_{1c} = 1; \nu_{2b} = 1; \nu_{2d} = 0$), $\hat{X}_2 = 2X_1 / (X_1 + 2X_2)$, $\hat{cmc} = (X_1 + 2X_2)cmc$ and

$$X_M = \hat{X}_2 - (\hat{X}_1 \hat{X}_2 / \hat{cmc})(\partial \hat{cmc} / \partial \hat{X}_2)_{P,T} \quad (39)$$

The determination of $\partial \hat{cmc} / \partial \hat{X}_2$, i.e., the slope of the \hat{cmc} vs. \hat{X}_2 plot then leads to the evaluation of X_M (mole fraction of a component) in the mixed micelle.

Sarmoria and Puvvada's theory: Sarmoria *et al.*¹³⁶ and Puvvada *et al.*¹³⁷⁻¹³⁹ have proposed a molecular thermodynamic model which is applicable to mixed binary solutions of non-ideal surfactant combinations based on the *cmc*s of the component surfactants, the concentrations of the surfactants, the chemical structure of the

hydrophobic and hydrophilic moieties of the individual surfactants, and other solution conditions *e.g.*, temperature, the type and concentration of salts present. Several equations have been derived to calculate the relevant physicochemical quantities¹³⁶. Equation (30) has been modified and the following equations have been proposed

$$(1/cmc_{\text{mix}}) = (\alpha_1 / f_1 cmc_1) + ((1 - \alpha_1) / f_2 cmc_2) \quad (40)$$

$$f_1 = \exp \left[\left\{ \beta_{12} (1 - \alpha^*)^2 \right\} / kT \right] \quad (41)$$

$$f_2 = \exp \left[\left\{ \beta_{12} (\alpha^*)^2 \right\} / kT \right] \quad (42)$$

where f_1 and f_2 are the activity coefficients of component 1 and component 2 in the mixed micelle, β_{12} is the predicted interaction parameter between the surfactant 1 and 2, α^* is the optimal micellar composition where the free energy of micellization attains its minimum value, k is the Boltzmann constant, and T is the temperature in absolute scale. The predictive quantity β_{12} based on fundamental considerations was obtained from the relation,

$$\beta_{12} = g_{\text{core}}^{12} + g_{\text{elec}}^{12} \quad (43)$$

where, g_{core}^{12} and g_{elec}^{12} are the free energy contributions associated with the interactions between the hydrophobic moieties of surfactants 1 and 2 in the micellar core and the electrostatic interactions between the charged hydrophilic moieties of surfactants 1 and 2, respectively. In case of binary mixtures of hydrocarbon-based surfactants $g_{\text{core}}^{12} = 0$, and equation (43) can then be written as

$$\beta_{12} = g_{\text{elec}}^{12} = -K_{\text{elec}} (Z_1 - Z_2)^2 \quad (44)$$

where K_{elec} is a numerical prefactor which can be evaluated from electrostatic theories. For the pairs with similar charges *e.g.*, for nonionic-nonionic, cationic-cationic, and anionic-anionic combinations $\beta_{12} = 0$. For ionic surfactant, g_{elec}^{12} is obtained from the following equation,

$$g_{\text{elec}}^{12} = 2kT \left[\ln(s/2 + (1 + (s/2)^2)^{1/2}) - \{(1 + (s/2)^2)^{1/2} - 1\} / (s/2) \right] - 2kT \left[(4/s\kappa R) \ln((1 + (1 + (s/2)^2)^{1/2}) / 2) \right] \quad (45)$$

where, $s = 4\pi Ze^2/\varepsilon akT\kappa$ and $\kappa^{-1} = (8\pi C_0 e^2 Z^2/\varepsilon kT)^{1/2}$

C_0 is the bulk ionic concentration, a is the available surface area per charge, ε is the dielectric constant of the solvent, Z is the valence of the ionic surfactant, s is a convenient dimensionless parameter, and κ^{-1} is the well known Debye screening length. The factor g_{elec}^{12} can also be given by

$$g_{elec}^{12} = K_{elec} (Z_1 - Z_2)^2 (\alpha^*)^2 + 2((Z_1 - Z_2)Z_2\alpha^* + Z_2) \quad (46)$$

From Equations (45) and (46), K_{elec} is obtained following the recommended procedure of Sarmoria *et al.*, which, in turn, gives the value of β_{12} from Equation (44). Once the value of β_{12} is obtained, several other important parameters could be obtained¹³⁶⁻¹³⁹.

Micelle Formation in Non-aqueous Solvents

Surfactants are widely used both in industry and everyday life. Hence the properties of surfactant aqueous solutions have received considerable attention. The aggregation phenomenon of amphiphiles in non-aqueous media has been the scope of many researchers due to increasing use of these materials in applications which require water-free or water-poor media^{140, 141}. The normal micelles are essentially formed in aqueous medium. In nonpolar solvent media *viz.*, cyclohexane, carbon tetrachloride, hydrocarbons (heptane, octane, decane etc.) normal micelle is not formed. Instead, a reverse orientation of the surfactants takes place in the assembled units, the head groups remain directed towards the interior whereas the tails are projected towards the nonpolar continuum. This is the generalized state of a reverse micelle (Figure 12). Generally, a trace amount of a polar solvent *e.g.*, water is required for easy and stable formation of reverse micelle.

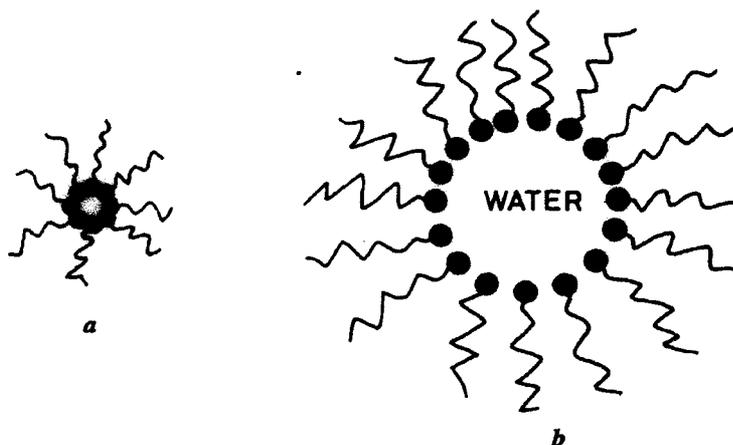


Figure 12. Schematic representation of reverse micelles (a) in absence of water
(b) in presence of water¹⁴².

The reason for micelle formation in organic solvents is somewhat different from that in aqueous solution. The main cause of micellization is the energy change due to dipole-dipole interactions between the polar head groups of the surfactant molecules. In general, aggregation numbers are small in organic media, often not exceeding five monomers per micelle. Instead of a spherical micelle, a lamellar micellar model comprising of a double layer of oriented molecules placed end-to-end and tail-to-tail with sheets of solvent molecules between the surfactant layers was proposed by Kertes and Gutmann¹⁴³. Lamellar aggregation has been reported for metal carboxylates in hydrocarbons¹⁴⁴⁻¹⁴⁷, alkylbenzene and dialkylnaphthalene sulphonates^{148, 149}, sulphosuccinates¹⁴⁸ and lecithin in benzene¹⁴⁹⁻¹⁵¹.

Ruckenstein and Nagarajan¹⁵² from a consideration of the physical factors controlling aggregation, have argued against the existence of a *cmc* in these systems. However, Jean et al.^{153, 154} by positron annihilation technique have confirmed micelle formation for Aerosol OT (sodium 2-ethyhexyl sulfosuccinate) and dodecylammonium propionate in benzene and cyclohexane, and the *cmc* values obtained agreed well with the *cmc* values determined by light-scattering and vapour-pressure depression¹⁵⁵, dye absorption techniques¹⁵⁶, dielectric increment measurements¹⁵⁷ and ¹H nmr^{158, 159}.

Recently, other than these nonpolar solvents, aggregation of several amphiphiles in non-aqueous polar solvents has received considerable attention¹⁶⁰⁻¹⁷¹. Micelle or liquid crystal formation has been reported in solvents such as ethylene

glycol^{168, 169}, glycerol¹⁶⁰, formamide¹⁶¹⁻¹⁶³, and hydrazine^{164, 165}. All these solvents have high cohesive energies and dielectric constants and considerable hydrogen-bonding ability. Evans *et al.*¹⁷² have suggested that the hydrogen-bonding ability of a solvent is a prerequisite for micellization to occur. However, micellization of several amphiphiles has been reported¹⁷³⁻¹⁷⁵ in pure solvents such as acetonitrile, dimethyl sulfoxide and acetone where hydrogen-bonding ability is either nonexistent or very minimal.

In this thesis, we have devoted our attention to the micellization behavior of some anionic and cationic surfactants in aqueous and non-aqueous media with special attention to mixed micellization using different experimental techniques.

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CHAPTER-II

EXPERIMENTAL SECTION

(Materials and Methods)

CHEMICALS

The surfactant lithium dodecylsulfate was from E. Merck, Germany and was used as received.

All the tetraalkylammonium salts were of purum or puriss grade (Fluka, Switzerland). These were purified as described in the literature¹⁻³. Generally these salts were purified by recrystallization. Higher tetraalkyl homologues were recrystallized twice to ensure the highest purity. The recrystallized salts were dried in vacuum and stored in a glass bottle in darkened dessicator over fused CaCl_2 .

Tetramethylammonium bromide (Me_4NBr) was recrystallized from a mixture of methanol and ethanol (1:1) and dried at 363 K for 24 hours.

Tetraethylammonium bromide (Et_4NBr) was recrystallized from methanol and dried at 363 K for 24 hours.

Tetrapropylammonium bromide (Pr_4NBr) was dissolved in a minimum volume of methanol, reprecipitated from dry ether and dried at 363 K for 48 hours.

Tetrabutylammonium bromide (Bu_4NBr) was dissolved in a minimum volume of acetone. Ether was added to the solution till the commencement of precipitation. The solution was then cooled and the resulting crystals were filtered. After a preliminary drying, the salts was finally ground in a mortar and dried at 333 K for 48 hours.

The nonionic amphiphiles polyoxyethylene (23) laurylether (Brij-35 or Bj-35) and polyoxyethylene (10) isoocetyl phenylether (Triton X-100 or TX-100) were from Sigma (USA) and were used without further purification.

The surfactant cetyltrimethylammonium bromide (CTAB) was purchased from Sigma (USA). Tetradecyltrimethylammonium bromide (TTAB) and dodecyltrimethylammonium bromide (DTAB) were of purum grade (Fluka, Switzerland) and were used as received.

SOLVENTS

Pure Solvents

Triply distilled water was used for preparing the experimental solutions. Water was first deionized and then distilled from an all glass distilling set using alkaline KMnO_4 solution. Doubly distilled water was then finally distilled using an all glass distilling set. Precautions were taken to prevent contamination from CO_2 and other impurities. The triply distilled water had a specific conductance of less than $1.5 \times 10^{-6} \text{ Scm}^{-1}$.

Ethylene glycol (EG), G.R.E. Merck, was distilled twice in an all glass distillation set before use. The purified solvent had a density of $1.11000 \text{ g cm}^{-3}$, a coefficient of viscosity of 17.87324 cP and a specific conductance of ca $1.02 \times 10^{-6} \text{ Scm}^{-1}$ at 298.15 K ; these values are found to be in good agreement with the literature values^{4, 5}.

Methanol and acetone used were of A.R grade and great care was taken to ensure that ether was free from peroxide.

Mixed Solvents

The mixed solvents containing 0.10, 0.20, 0.30, 0.40, and 0.50 mass fractions of EG (w_1) were prepared accurately by mixing the requisite amounts of water and EG by weight. The dielectric constants (D), densities (ρ), viscosities (η) and specific conductances (κ) s of EG (1) + water (2) mixtures at 298.15 K are given in Table 1.

Preparation of Experimental Solutions

A stock solution for each surfactant and/or salt in water as well as in different mixed solvents was prepared by weight and the working solutions were obtained by weight dilution. The molar concentrations of the solution were calculated from molality and density values.

METHODS

Density Measurements

The densities were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm³ and an internal diameter of the capillary of about 1 mm. The pycnometer was calibrated at the experimental temperature with doubly distilled water. The precision of the density measurements was $\pm 3 \times 10^{-5}$ g cm⁻³. The measurements were made in an oil bath maintained within ± 0.005 K of the desired temperature by means of a mercury-in-glass thermoregulator and the absolute temperature was determined by a platinum resistance thermometer and Muller bridge⁶.

Viscosity Measurements

The kinematic viscosities were measured by means of a suspended-level Ubbelohde⁷ viscometer with a flow time of about 539 s for distilled water at 298.15 K. The time of efflux was measured with a stop watch capable of recording to ± 0.1 s. The viscometer was always kept in a vertical position in a water thermostat maintained within ± 0.01 K of the desired temperature. The absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge.

Conductance Measurements

Conductance measurements were carried out on a Philips Pye-Unicam PW 9509 conductivity meter with an uncertainty of $\pm 0.1\%$. A 2000 Hz cycle was used. The cell constant (0.731 cm⁻¹) of the dip-type conductance cell was accurately determined using standard KCl solutions by the method of Lind *et. al.*⁸ The

measurements were made in an oil bath maintained within ± 0.005 K as described earlier under density measurements.

Compressibility Measurements

Ultrasonic velocity measurements were carried out in a single crystal variable path ultrasonic interferometer (Mittal Enterprises, New Delhi, India) operating at 5 MHz calibrated with water, methanol and benzene at each temperature. The temperature stability was maintained within ± 0.01 K by circulating thermostated water around the measuring cell by a circulating water bath. The maximum uncertainty of the sound velocity measurements in all cases was ± 0.03 %.

Surface tension Measurements

The surface tensions of the surfactant solutions were measured with a Krüss (Germany) K9 tensiometer by the platinum ring detachment method. The measured tensions were corrected according to the procedure of Harkins and Jordon⁷. The tensiometer was connected to a water-flow cryostat to maintain the temperature equilibration. Prior to each measurement, the ring was heated briefly by holding it above a Bunsen burner until glowing. Duplicate measurements were made to check the reproducibility. The uncertainty of measurements was within ± 1 mNm⁻¹.

Spectral Measurements

A UV-visible (240) Shimadzu (Japan) spectrophotometer operating in dual beam mode was employed for spectral measurements using matched pair of quartz cuvettes of pathlength 1 cm under thermostated condition (298.15 K). Spectral measurements were performed on the basis that TX-100 absorbs maximum at 276.5 nm and the absorbance (A) gets perturbed at the micellar point⁹. Here 3 mL of water was taken in a pair of cuvettes. Surfactant solution was then progressively added in the sample cell as required. Optical density at each stage of surfactant addition was measured after thorough mixing at the absorption maximum (276.5 nm) of TX-100.

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Table 1. Solvent Properties of EG (1) + Water (2) Mixtures at 298.15 K

$100w_1$	D	$\rho/\text{g cm}^{-3}$	η/cP	$\kappa/\text{S cm}^{-1}$
0	78.30	0.99707	0.89030	1.50×10^{-6}
10	75.65	1.00949	1.15197	6.32×10^{-6}
20	72.68	1.02245	1.46935	5.34×10^{-6}
30	69.77	1.03570	1.90253	5.11×10^{-6}
40	67.00	1.04943	2.56252	2.00×10^{-6}
50	63.93	1.06216	3.33176	1.42×10^{-6}
100	37.07	1.11000	17.87324	1.02×10^{-6}

CHAPTER-III

Study of Micellization Properties of Lithium Dodecyl Sulfate in Aqueous Solutions from Conductivity, Density, and Adiabatic Compressibility Measurements

INTRODUCTION

Self-association of hydrophobic molecules generally is of great importance for many physiological molecules, food constituents and drugs. More recently, surfactants have been the subject of intense investigation due to their wide industrial and technological applications. The micellization of surfactants above a critical concentration (called the critical micelle concentration, *cmc*) is an important solution property which needs evaluation to know the existence of micelle in solution and to obtain the thermodynamic parameters associated with the process which are essential for characterization and comparison in the light of spontaneity and stability^{1, 2}. Though, many investigations have been done on sodium dodecylsulfate (SDS)³⁻¹⁰, but much is not known about micellar behavior of lithium dodecylsulfate (LDS) at different temperatures.

The results on conductometric, densitometric, and interferometric measurements on aqueous solutions of lithium dodecylsulfate at different temperatures are reported here. Among these measurements, densitometric and interferometric measurements were never considered in the past for the evaluation of micellar properties of LDS. From the experimental data, the ionization degree of micelle, α , free energy of micellization, ΔG_m° , standard enthalpy of micellization, ΔH_m° , standard entropy of micellization ΔS_m° , apparent molar volume, and apparent molar adiabatic compressibility were calculated. These parameters provide useful information regarding the solution behavior of lithium dodecylsulfate in aqueous solutions.

Chanchal Das and Dilip K. Hazra

Indian J. Chem. 44A (2005) 1793-1799

EXPERIMENTAL

Materials and Methods

Lithium dodecylsulfate (E. Merck, Germany) was used as received. Doubly distilled water (specific conductance, 2-3 $\mu\text{S cm}^{-1}$) was used in all preparations. Measurements were made at each temperature in a thermostated water-bath maintained within ± 0.01 K.

The conductometric measurements were carried out on a Pye-Unicam PW9509 conductivity meter at a frequency of 2000 Hz using a dip-type cell of cell constant 1.14 cm^{-1} and having an accuracy of 0.1%. Solutions were prepared by mass for the conductance runs, the molalities being converted to molarities by the use of densities. Corrections were made for the specific conductance of water at all temperatures.

Densities were measured with an Ostwald-Sprengel type pycnometer of about 25 mL capacity and an internal diameter of the capillary of about 1 mm. Uncertainties in the solute concentration and weighing can produce errors in the density values of *ca.* $5 \times 10^{-5} \text{ g cm}^{-3}$.

Sound velocities were measured using a single-crystal variable-path ultrasonic interferometer (Mittal Enterprises, New Delhi) working at 5 MHz. The temperature stability was maintained within ± 0.01 K by circulating thermostated water around the cell by a circulating pump. The details of these procedures have been described in Chapter II.

RESULTS AND DISCUSSION

Conductivity results:

The variations of the specific conductivity of LDS solutions with the molality of LDS at various temperatures are shown in Fig. 1. An approximate value of the ionization degree of micelles, $\alpha = S_2/S_1$, was determined from the ratio of the mean gradients of the specific conductivity (κ) vs. concentration plots above (S_2) and below (S_1) the *cmc*¹¹⁻¹⁵.

According to the charged phase separation model of micellization, the activity of the monomer remains constant above *cmc*, and the standard free energy of

micellization per mole of monomer, ΔG_m^0 , can be calculated from the following relation¹⁶:

$$\Delta G_m^0 = (2 - \alpha) RT \ln X_{cmc} \quad (1)$$

where X_{cmc} is the value of cmc expressed in mole fraction. The standard enthalpy, ΔH_m^0 , and entropy, ΔS_m^0 , of micellization were obtained, on the assumption that α is practically constant (Table 1). Insertion of Eq. 1 into the Gibbs-Helmholtz equation gives the following relations^{17, 18}:

$$\Delta H_m^0 = -(2 - \alpha) RT^2 \left(\frac{\partial \ln X_{cmc}}{\partial T} \right)_p \quad (2)$$

$$\Delta S_m^0 = (\Delta H_m^0 - \Delta G_m^0) / T \quad (3)$$

The value of $(\partial \ln X_{cmc} / \partial T)_p$ was determined by fitting the $\ln X_{cmc}$ vs. T data with the polynomial function

$$\ln X_{cmc} = a + bT + cT^2 \quad (4)$$

The values of the fitting constants were $a = 4.33464$, $b = -.08681$, and $c = 1.44288 \times 10^{-4}$. The temperature dependent values of cmc obtained from different measurements, α and the thermodynamic parameters at different temperatures are presented in Table 1.

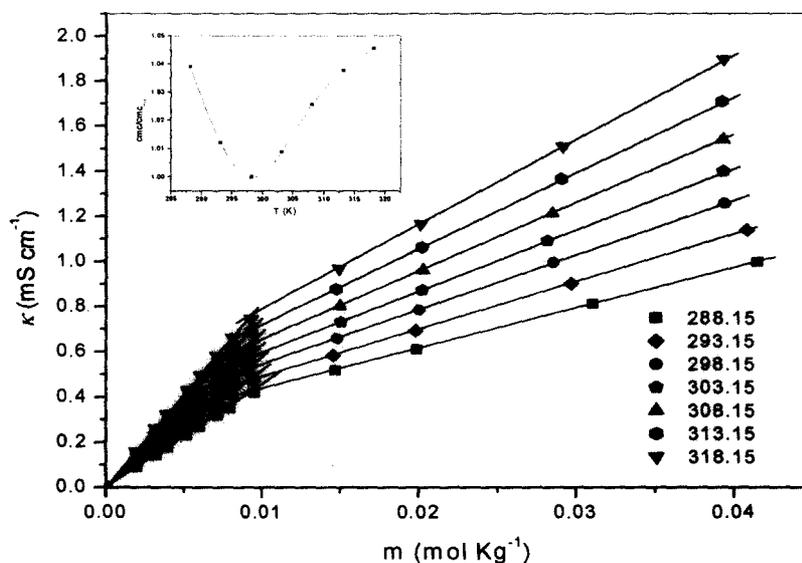


Figure 1. Dependence of specific conductivity of LDS on molality at various temperatures (The plot of dependence of cmc on temperature is displayed in the inset).

The *cmc* value of aqueous LDS at 298.15 K determined conductometrically is in good agreement with that reported earlier⁴. The temperature dependence of *cmc* for LDS is illustrated in the inset of Fig. 1, where a shallow minimum at around 298.42 K is observed.

The values of the degree of ionization, α , of micelles of LDS increases with temperature as found earlier for cationic surfactants^{12, 19}. The higher values of the degree of ionization of LDS can be explained qualitatively in terms of larger size of the hydrated Li^+ ion which cannot approach the highly charged surface of micelle. However, the value obtained at 298.15 K is much higher than those reported earlier^{4, 20}. The mean value of $\Delta\alpha/\Delta T$ estimated in the temperature range 288.15 to 318.15 K amounts to 0.0014 K^{-1} for LDS. This value is low compared with those found earlier for other cationic surfactants: dodecyltrimethylammonium chloride (0.0030)²¹, tetradecyltrimethylammonium bromide (0.0030)²² and tetradecyldimethylphenylammonium bromide (0.0029)²³.

Analysis of the thermodynamic parameters of micellization indicates that the aggregation of LDS is driven mainly by the positive ΔS° . Similar changes from entropic to enthalpic micellization with the rise of temperature have been noted with many different surfactants^{18, 24-26}. The standard free energies of micellization for LDS decrease linearly with temperature. The slow rate of decrease of ΔG_m° with the rise of temperature is typical for aqueous solutions of surfactants and this results from an entropy-enthalpy compensation effect²⁷⁻³¹. Positive values of ΔH_m° , such as those noted at the lowest temperatures, are generally attributed to the release of structural water from the hydration layers around the hydrophobic parts of the micelle³². Such hydrophobic interactions become increasingly insignificant with the partial breakdown of the structure of water as the temperature is increased. The negative ΔH_m° values at the higher temperatures suggest the importance of the London-dispersion interactions as an attractive force contribution for micellization³³. However, it may be seen from Table 1 that at a certain temperature the enthalpy of micellization vanishes and the process is driven solely entropically. This is a direct consequence of Eq. 2 only when the temperature dependence of α is neglected.

Density studies:

Density (ρ) measurements of aqueous solutions of LDS are presented in Fig. 2 in the form of plots of $(\rho - \rho_0)$ vs. the molality of LDS, ρ_0 being the density of water at the appropriate temperature. It is seen that in both pre- and postmicellar regions studied, the densities increase linearly with the increase of molality.

The apparent molar volumes, V_ϕ of LDS as a function of molality at the temperatures studied were obtained using the following Eq. 5³¹ :

$$V_\phi = \frac{M}{\rho} - \frac{10^3(\rho - \rho_0)}{m\rho\rho_0} \quad (5)$$

where M and m are the molecular mass and the molality of the solute, respectively. The variation of V_ϕ with reciprocal molality is illustrated in Fig. 3. It can be seen that the apparent molar volumes remain almost constant in the lower concentration region followed by a sharp increase beyond cmc .

For an ionic surfactant system below cmc , the dependence of density on concentration can be expressed as²¹

$$(\rho - \rho_0)10^3 = [(M_f + M_c) - (V_f + V_c)\rho_0]m \quad (6)$$

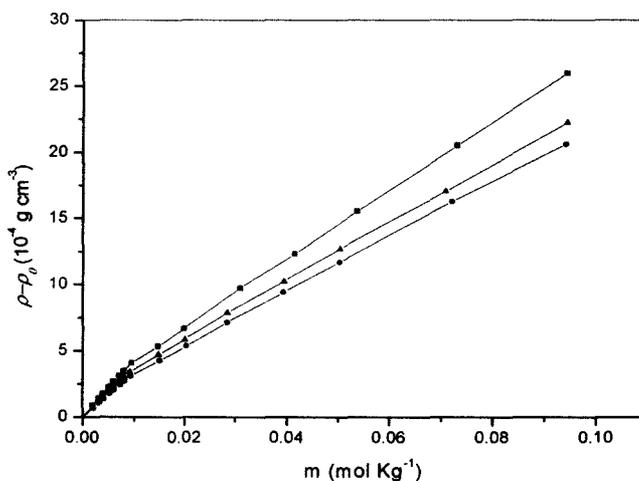


Figure 2. Density vs. molality plot for LDS at 288.15(■), 298.15(▲), and 308.15 (●) K.

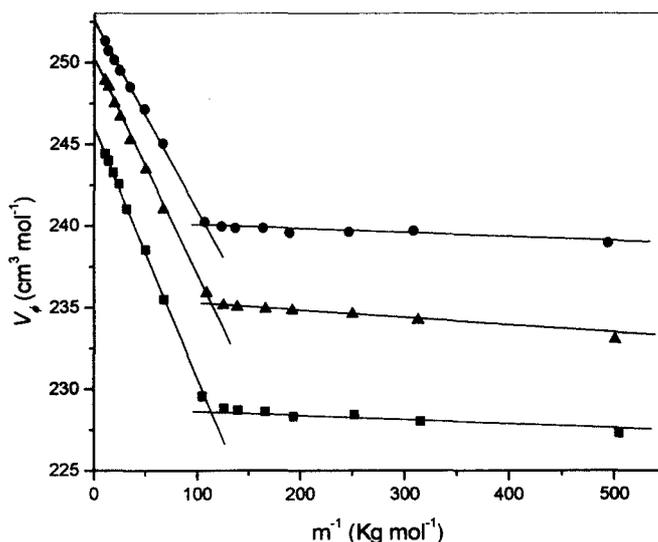


Figure 3. Variation of V_ϕ with reciprocal molality for LDS at various temperatures (Symbols as in Figure 1).

where M_f , V_f and M_c , V_c are the molecular masses and the apparent molar volumes of the surfactant ions and counter ions, respectively. If these apparent molar volumes were negligibly concentration-dependent, then Eq. 6 predicts a linear relationship between density and concentration. Indeed, such a behavior is seen in Fig. 2. The values for $(V_f + V_c)$ thus estimated amount to 229.23 ± 0.26 , 235.60 ± 0.24 and $240.44 \pm 0.34 \text{ cm}^3 \text{ mol}^{-1}$ at 288.15, 298.15 and 308.15 K, respectively. These values can be taken as zero-order approximation of the accurate values as it is well known that the apparent molar volumes are, in general, concentration-dependent. The observed increase in $(V_f + V_c)$ term with temperature is related to the relaxation of structured water engaged in the solvation of the hydrocarbon chain, the head group, and the counter ion. A similar behavior has also been reported for decylbenzylidimethyl chloride³⁴ and dodecylbenzylidimethyl chloride solutions²¹.

Since it is generally accepted that the solutions of surfactants in the premicellar region behave as singly dispersed system, the V_ϕ values may be described by³⁵

$$V_\phi = V_\phi^0 + A_v m^{1/2} + B_v m \quad (7)$$

where V_ϕ^0 is the value of apparent molar volume at infinite dilution, A_v is the Debye Hückel limiting slope and B_v is an adjustable parameter, which measures the

deviations from the limiting law. For 1:1 electrolytes at 288.15, 298.15 and 308.15 K, the values of A_v are 1.696, 1.865 and 2.04 $\text{cm}^3\text{kg}^{1/2}\text{mol}^{-3/2}$, respectively. Experimental values of V_ϕ in the premicellar region were fitted to Eq. 7 and the values of V_ϕ° obtained are listed in Table 2. The V_ϕ° values for LDS increase almost linearly with temperature in conformity with the observations for other surfactant systems^{21 36}

Assuming the rule of additivity for the apparent molar volumes of the ions in the system to be valid, we can write

$$n_{\text{LDS}} V_\phi = n_f V_f + n_c V_c + n_m V_m \quad (8)$$

where V_m is the apparent molar volume of the micelles in the system and n_{LDS} the total number of moles of the surfactant, whereas n_f , n_c and n_m are the number of moles of free monomers, free counterions, and micelles, respectively. Since LDS is a 1:1 electrolyte, then, according to the pseudo-phase separation model below cmc :

$$m_f = m_c = m \quad (9a)$$

and above cmc ²⁴ :

$$m_f = cmc$$

$$m_c = cmc + \alpha(m - cmc) \quad (9b)$$

$$m_m = \frac{m - cmc}{N_{\text{agg}}}$$

where N_{agg} is the aggregation number of the micelle. Dividing Eq. 8 by the mass of the solvent (in kg) and taking into account the relations in Eq. 9, we obtain the following set of equations²¹

$$V_\phi = (V_f + V_c) \quad m \leq cmc \quad (10a)$$

$$V_\phi = (V_m/N_{\text{agg}} + \alpha V_c) - [V_m/N_{\text{agg}} + (\alpha - 1) V_c - V_f] cmc/m \quad m \geq cmc \quad (10b)$$

If we assume that the molar volumes of the ionic species are not concentration-dependent, then, from the last equation a linear decrease of V_ϕ versus $1/m$ plot can be expected in the concentration range above cmc . According to Eq. 10a, the value of V_ϕ should be constant in the concentration range below cmc . Such a plot is shown in Fig.3. It can be seen that the system conforms approximately to the expected behavior. Thus, Eq. 10 may be considered as an acceptable approximation of the behavior of the system. We can assign the intersection of the lines above and below cmc as the corresponding cmc . The values obtained at 288.15, 298.15, and 308.15 K from conductometry and interferometry, agree very well (*cf.* Table 1).

Linear fitting of the points in the $cmc/m \leq 1$ region allows us to obtain the value of the apparent molar volume, V_ϕ^{cmc} , (intercept + slope) of the surfactant at cmc , and the change in the apparent molar volume upon micellization, ΔV_ϕ^{cmc} (slope). The results are shown in Table 2. The deviation of about 0.25 to $0.35 \text{ cm}^3 \text{ mol}^{-1}$ between the values of V_ϕ^{cmc} obtained by applying Eq. 10b (for data above cmc) with corresponding values of $(V_f + V_c)$ obtained via Eq. 6 (for data below cmc) can be taken as a measure of the error in the results. The values of V_ϕ^{cmc} for LDS are found to be positive. A similar observation was also reported earlier for other surfactant system.^{34,37} It is generally accepted that this effect is mainly due to the release of structured water in the hydration shell of the monomers when the micelles are formed.

According to Eq. 10b, the slope of V_ϕ vs. cmc/m plot, ΔV_ϕ^{cmc} , shows a positive dependence on the degree of ionization. The last magnitude, as pointed out above, grows with temperature. Thus, an increase in ΔV_ϕ^{cmc} values should be expected when the temperature is raised. This effect might be interpreted as being due to growth in the electrostatic repulsion between the ionic head groups at the surface of the micelles. Results in Table 2 show, however, a reverse behavior, *i.e.*, ΔV_ϕ^{cmc} decreases with temperature. Again, the structured water surrounding the hydrocarbon chain of the monomers might be the origin of this phenomenon. At higher temperatures, the water sheath is less structured, and thus its contribution to ΔV_ϕ^{cmc} due to the release of water molecules is much lower. This effect is mainly responsible to compensate the growth in ΔV_ϕ^{cmc} due to the increase of the electrostatic repulsion that occurs when the degree of ionization rises.²¹

Adiabatic compressibility studies:

The concentration dependence of the ultrasound velocity in aqueous solutions of LDS at temperatures 288.15, 298.15 and 308.15 K is shown in Fig. 4. Each plot can be divided into two linear segments, which correspond to the monomeric and micellar forms of the surfactant in aqueous solution.

The change in adiabatic compressibility, β_s of the aqueous solutions of LDS with the surfactant concentration at different temperatures has been depicted in Fig. 5. The β_s values can be calculated from the relation $u^2 = 1/(\rho\beta_s)$, where u is the ultrasound velocity, expressed in m s^{-1} , and ρ is the density, expressed in kg m^{-3} of the aqueous surfactant solution. Again each plot can be divided into two line segments

corresponding to monomeric and micellar forms of the surfactant. The signs of the slopes of the plots for the monomeric forms are always negative, while the sign of the slopes above *cmc* depends on the temperature and it increases with increased temperature. A similar behaviour was also observed by Zielinski *et al*³⁷ for aqueous solutions of dodecyltrimethylammonium bromide.

For surfactant system of sufficiently low concentration, the dependence of the adiabatic compressibility, β_s , on molality, (below and above *cmc*), can be expressed by two approximation equations²⁴ of the exact equations used by Zielinski *et al*³⁷:

$$\frac{1000(\beta_s - \beta_{s_0})}{\rho_0} = (\bar{\beta}_{s_1} - \beta_{s_0}) V_{\phi_1} m \quad m < cmc \quad (11a)$$

$$\frac{1000(\beta_s - \beta_{s_0})}{\rho_0} = (\bar{\beta}_{s_m} - \beta_{s_0}) V_{\phi_m} (m - cmc) \quad m > cmc \quad (11b)$$

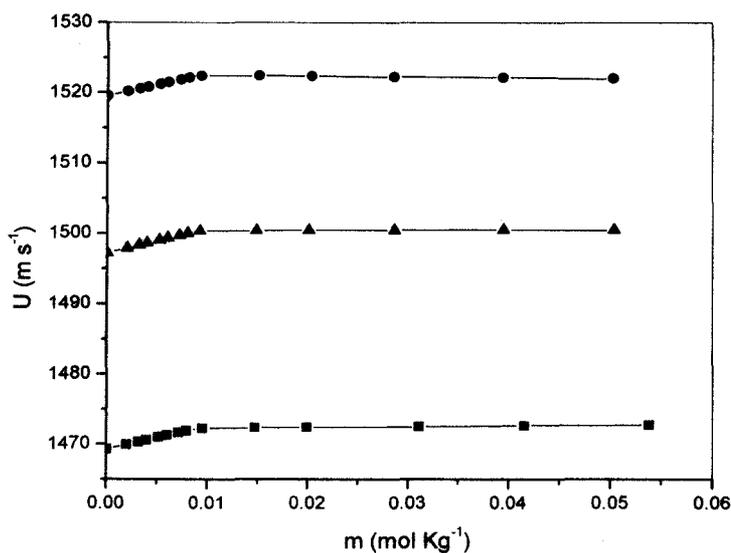


Figure 4. Effect of LDS molality on ultrasound velocity, u , in aqueous solutions at three different temperatures (Symbols as in figure 1).

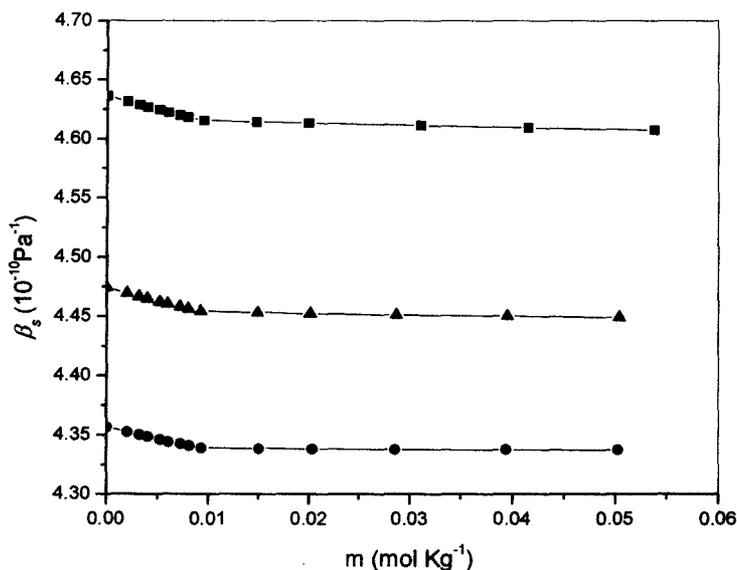


Figure 5. Dependence of adiabatic compressibility, β_s , of LDS on molality in aqueous solutions at 288.15(■), 298.15(▲), and 308.15 (●) K.

where V_{ϕ_1} and V_{ϕ_m} are the apparent molar volumes of the system below and above the *cmc*, respectively, ρ_0 is the density of pure water (in g cm⁻³), β_{s_0} , β_{s_1} and $\bar{\beta}_{s_m}$ are the adiabatic compressibility of pure water and apparent adiabatic compressibilities of surfactant in the monomeric and micellar states, defined respectively by

$$\beta_{s_0} = -1/V_0 (\partial V_0 / \partial P)_s, \quad \bar{\beta}_{s_1} = -1/V_{\phi_1} (\partial V_{\phi_1} / \partial P)_s, \quad \bar{\beta}_{s_m} = -1/V_{\phi_m} (\partial V_{\phi_m} / \partial P)_s$$

Figure 5 shows that the dependence of β_s on molality is well represented by two straight lines of different slopes in the pre- and postmicellar regions. From the value of the slope above *cmc*, the value of $\bar{\beta}_{s_m}$ can be estimated by applying Eq 11b. The results obtained are shown in Fig. 6. The value of $\bar{\beta}_{s_m}$ increases asymptotically at all experimental temperatures to a limiting value, which compares well with the behavior for other surfactant systems^{1, 37-39}. The limiting values obtained for $\bar{\beta}_{s_m}$ are 3.87×10^{-10} , 3.99×10^{-10} , and 4.20×10^{-10} Pa⁻¹ at 288.15, 298.15, and 308.15K respectively.

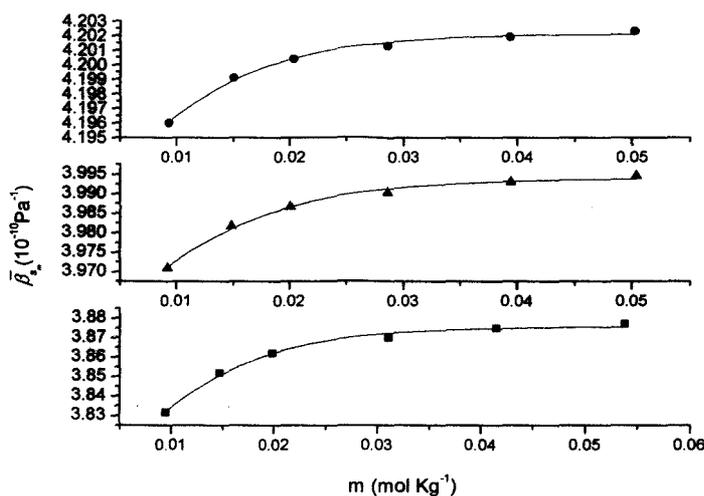


Figure 6. Molality dependence of the apparent adiabatic compressibility of LDS at 288.15(■), 298.15(▲) and 308.15 (●) K.

CONCLUSIONS

This investigation shows that the *cmc* of lithium dodecylsulfate in aqueous medium is temperature dependent and exhibit a shallow minimum at around 298.42K. Moreover, different experimental techniques exhibit almost the same *cmc* values for the surfactant. The high degree of ionization for the surfactant system is due to larger size of hydrated Li⁺ ion. The weak temperature dependence of the standard Gibbs energy of micellization reflects an enthalpy-entropy compensation effect. The apparent molar volume change upon micellization, ΔV_{ϕ}^m may be attributed to several processes, an important contribution coming probably from the dehydration of the counter-ions bound to the micelle.

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TABLE-1

cmc, α , and Thermodynamic Parameters of LDS at Various Temperatures^a

Temp/K	α	<i>cmc</i> /mM			$\Delta G_m^0/\text{kJ mol}^{-1}$	$\Delta H_m^0/\text{kJ mol}^{-1}$	$\Delta S_m^0/\text{J K}^{-1} \text{mol}^{-1}$
		cond	dens	comp			
288.15	0.405	9.33	9.11	9.08	-33.21	4.03	129.24
293.15	0.415	9.09			-33.68	2.51	123.45
298.15	0.426	8.98	8.96	8.93	-34.06	0.89	117.22
303.15	0.437	9.06			-34.36	-0.80	110.70
308.15	0.446	9.21	9.28	9.18	-34.66	-2.59	104.07
313.15	0.457	9.32			-34.92	-4.47	97.23
318.15	0.465	9.39			-35.26	-6.46	90.52

^aThe uncertainties of α , *cmc*, ΔG_m^0 , ΔH_m^0 and ΔS_m^0 are ± 5 , ± 4 , ± 3 , ± 4 and ± 4 % respectively.

TABLE-2

Apparent Molar Volumes at Infinite Dilution, V_{ϕ}° , those at cmc , V_{ϕ}^{cmc} , and their Changes upon Micellization, ΔV_{ϕ}^{cmc} for LDS at 288.15, 298.15 and 308.15 K

$T(K)$	$V_{\phi}^{\circ}(\text{cm}^3 \text{ mol}^{-1})$	$V_{\phi}^{cmc} (\text{cm}^3 \text{ mol}^{-1})$	$\Delta V_{\phi}^{cmc} (\text{cm}^3 \text{ mol}^{-1})$
288.15	227.16 \pm 0.24	229.04 \pm 0.28	17.17 \pm 0.19
298.15	232.99 \pm 0.38	235.28 \pm 0.34	14.88 \pm 0.23
308.15	238.92 \pm 0.21	240.06 \pm 0.26	12.37 \pm 0.18

CHAPTER-IV

Effect of Tetraalkylammonium Salts on the Micellar Behavior of Lithium Dodecyl Sulfate: A Conductometric and Tensiometric Study

INTRODUCTION

The function and properties of surfactant systems depend on their structural type, concentration and composition in addition to other factors, *viz.*, temperature, pressure, *pH*, solvent and additives. Surfactants and their mixtures with additives in aqueous solutions are of interest for their chemical, pharmaceutical, mineral processing, and petroleum engineering applications^{1,2}. Micelles with charged surfaces bind counterions selectively, and their solution properties are sensitive to the type and concentration of counterions³⁻¹³. Recently, studies on the counterion effect of R_4N^+ ions are gaining recognition in micellar systems^{4, 14-16}. Due to their hydrophobic nature, quaternary ammonium ions (R_4N^+) differ remarkably from the alkali metal cations. Yu and Xu reported an interesting micellar growth behavior of tetrabutylammonium bromide and an anionic surfactant^{17, 18}. Since R_4N^+ cations modify the structure of water around them in a similar way as some simple hydrocarbons do, it could be of considerable interest to explore how this kind of interaction would affect the micellar properties of an anionic surfactant.

In the present study, the effect of some quaternary ammonium bromides, R_4NBr ($R= H, CH_3, C_2H_5, C_3H_7, \text{ and } C_4H_9$) on the micellar properties of lithium dodecylsulfate (LDS) has been studied by the method of conductometry and tensiometry. To derive energetic information of the self-aggregation of the amphiphile, *cmc*s of LDS with solutions of strength 0.001 M of different symmetrical quaternary ammonium salts were determined in the 288.15-318.15 K-temperature range at 10 K intervals conductometrically. Cloud point (CP) phenomenon of this surfactant with tetrabutylammonium bromide (Bu_4NBr) has also been investigated.

EXPERIMENTAL

Materials and Methods

The surfactant lithium dodecylsulfate (E. Merck, Germany) has been used as received. The tetraalkylammonium bromides were of purum or puriss grade (Fluka, Switzerland) and were purified as described in the literature^{19, 20}. These salts were purified by recrystallization and the higher homologues were recrystallized twice to ensure maximum purity. The recrystallized salts were dried in vacuo at elevated temperatures for 12 h. Doubly distilled water (specific conductance, $2-3 \mu\text{S cm}^{-1}$) was used in the preparations. Measurements were made at each temperature in a thermostated water-bath maintained within $\pm 0.01 \text{ K}$.

In the conductance method, a concentrated surfactant solution, prepared in different aqueous tetraalkylammonium salt solutions, was added in installments with the help of microsyringe to the respective aqueous solutions of tetraalkylammonium salt, placed in a wide-mouth test tube fitted with a dip-type conductivity cell of cell constant 1.14 cm^{-1} . After each addition, conductance of the solution was measured (after thorough mixing and temperature equilibration) with a Pye-Unicam PW9509 conductivity meter at a frequency of 2000Hz. The measurements were duplicated. The conductance values were uncertain within the limit of $\pm 1\%$.

The surface tension of the surfactant solutions were measured with a Krüss (Germany) K9 tensiometer by the platinum ring detachment method. The measured tensions were corrected according to the procedure of Harkins and Jordon²¹. Here also, the addition of the concentrated surfactant solutions in installments using a Hamilton microsyringe was done and measurements were taken after mixing and temperature equilibration. Duplicate measurements were performed to check the reproducibility. The uncertainty of the measurements was within $\pm 0.1 \text{ mNm}^{-1}$.

Freshly prepared stock solutions of LDS were used to obtain different sample solutions for CP measurements. The solutions were taken in Pyrex glass tubes, which were then immersed in a thermostat and heated with a uniform rate of $0.1^\circ \text{C}/\text{min}$. The first appearance of turbidity was taken as the CP.

RESULTS AND DISCUSSION

Critical micellar concentration

The *cmc*s of LDS in presence of different symmetrical quaternary ammonium salts were determined by conductometry and tensiometry. Some selected experimental results are presented in Figs. 1 and 2a-e. Conductometric plots exhibit typical behavior with two linear segments whose intersection is usually treated as corresponding to the *cmc*. In the tensiometric determination of the *cmc*s, we chose the bulk concentration as the *cmc* at which the surface tension reaches the constant equilibrium value in the γ -log c curves. The *cmc* values realized by the two methods (conductometry and tensiometry) are presented in Table 1. The *cmc* obtained from surface tension measurements were always found to be lower than those obtained from conductance measurements. Similar method dependent *cmc* values are common in the literature^{22, 23}.

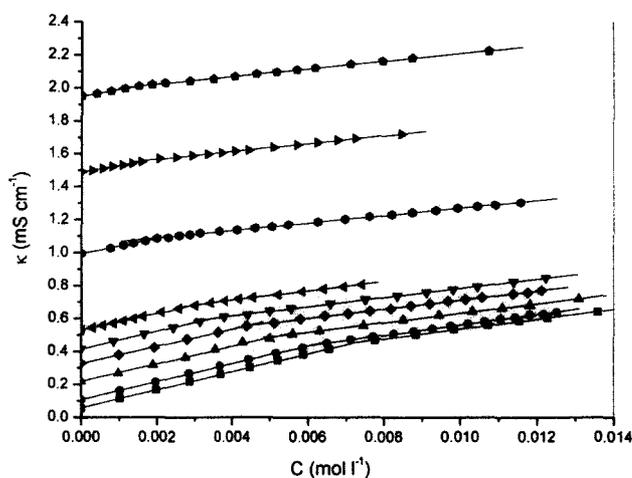


Figure 1. Dependence of specific conductivity of LDS on molarity in presence of 0.0005 (■), 0.001 (●), 0.002 (▲), 0.003 (◆), 0.004 (▼), 0.005 (◄), 0.010 (●), 0.015 (►) and 0.020 (◆) M of Et₄NBr.

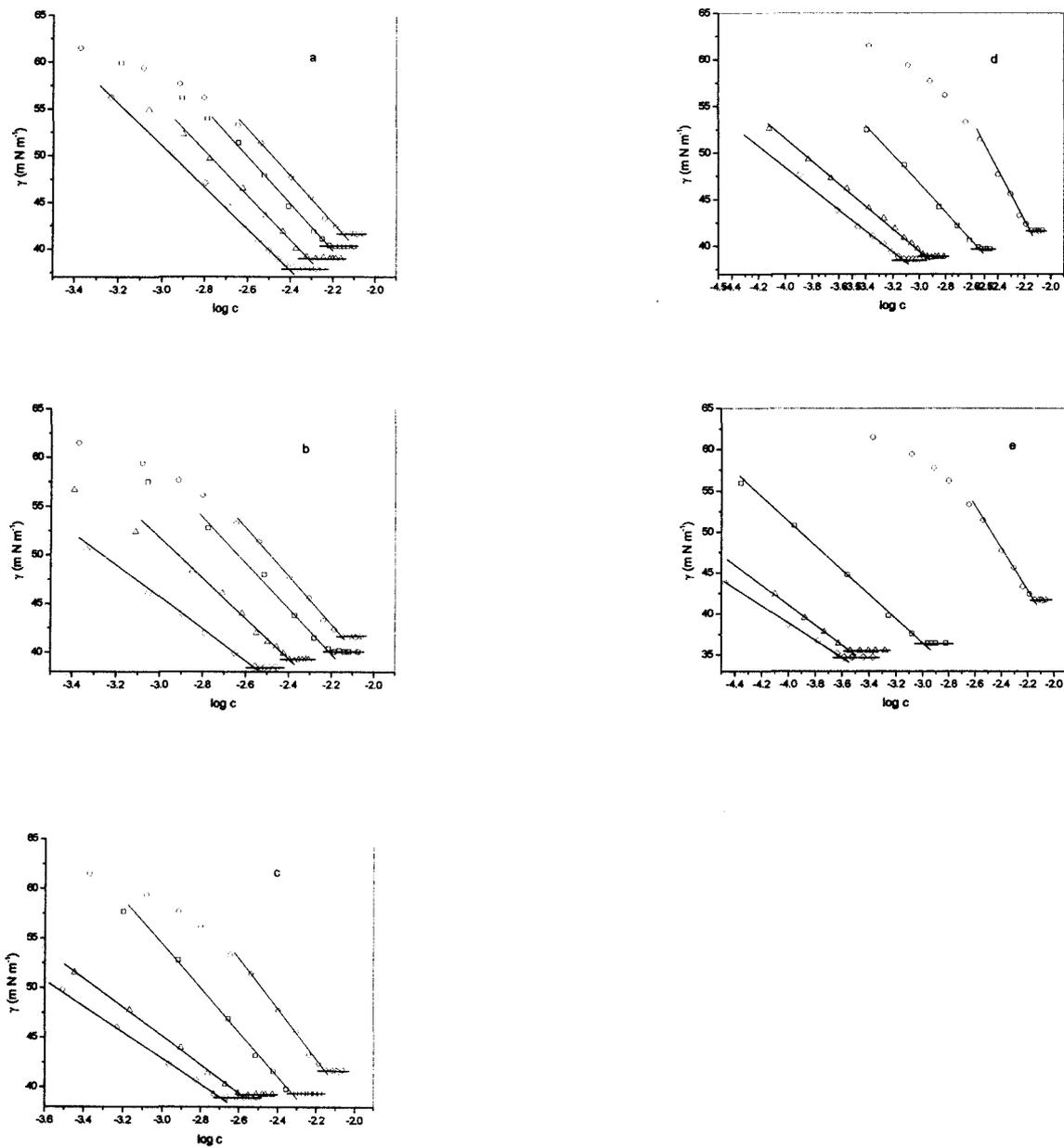


Figure 2a-e. Variation of γ with $\log c$ for LDS in presence of 0.000 (\circ), 0.001 (\square), 0.005 (Δ), and 0.010 (\diamond) M of different tetraalkylammonium salts. (a) NH_4Br ; (b) Me_4NBr ; (c) Et_4NBr ; (d) Pr_4NBr ; and (e) Bu_4NBr .

The *cmc* of the surfactant has been found to decrease in presence of R_4NBr , the decreases being dependent upon the concentration of R_4NBr . Due to the neutralization of the effective head group charge of the ionic surfactant in presence of simple salts, the electrical atmosphere in the aqueous surfactant solution is altered; this results in a reduced electrostatic repulsion between the polar head groups and hence the micelles are formed at much lower concentration as compared to the situation in pure water. The marked reduction in the *cmcs* with the size of the alkyl group in the quaternaries may be attributed to the hydrophobic interaction of the hydrocarbon part of the quaternary ammonium ions with the hydrocarbon core of the micelle overriding the electrostatic contribution.

Counterion binding of micelle

It is clear, on one hand, that ionic micelles are charged and have counterions and on the other, not all counterions are free in the sense of having the same activity or mobility as those of a simple electrolyte. Yet there is at present no unambiguous method of measuring this degree of freedom or of binding of the counterions. The principal experimental measurements used in these interpretations are conductance slopes, light scattering, and *cmc* determination as a function of counterion concentration. The conductance slope method for the determination of counterion binding was not used here because of its insensitivity in presence of moderate salt concentration. We have employed the method of *cmc* determination as a function of counterion concentration for determining the counterion binding using the Corrin-Harkins equation^{24, 25}

$$\log cmc = \text{CONSTANT} - \beta \log [\text{counterion}] \quad (1)$$

The plots of $\log cmc$ vs. $\log [\text{counterion}]$ show a linear dependence of $\log cmc$ on $\log [\text{counterion}]$ in the range $[\text{counterion}] > 0.001$ M for Bu_4NBr and > 0.003 M for other salts. However, a deviation from linearity occurs in the lower concentration region. Considering only the linear part of the plots shown in Fig. 3, counterion binding has been calculated and presented in Table 2. The result shows that counterion binding, β , increases with the increasing size of alkyl chain length of tetraalkylammonium salts.

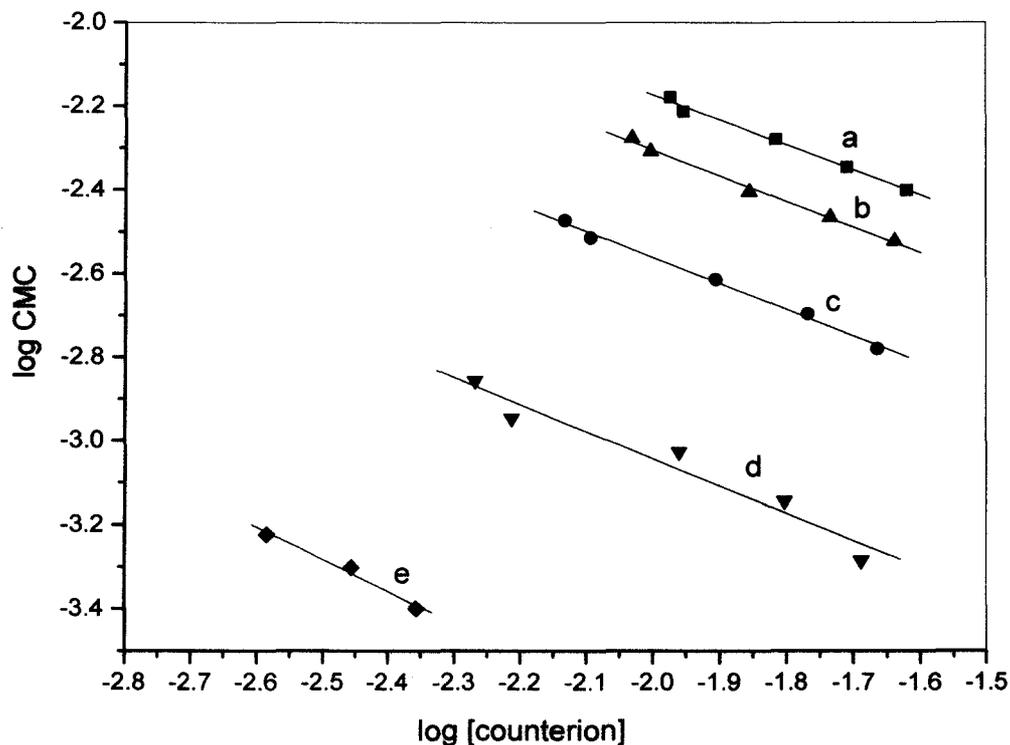


Figure 3. Plot of log [counterion] vs. log *cmc* of different tetraalkylammonium salts (a) NH_4Br ; (b) Me_4NBr ; (c) Et_4NBr ; (d) Pr_4NBr ; and (e) Bu_4NBr .

Again the hydrophobic interaction of the tetraalkylammonium ions with the hydrocarbon core of the micelle may be the origin of the above observation. It may be mentioned that in the Corrin-Harkins^{24, 25} relation the counterion binding has been considered to be independent of salt concentration. The effect of changed aggregation number in the salt environment on the counterion condensation has also been ignored.

Thermodynamics of micellization

According to the charge phase separation model of micellization, the activity of the monomer remains constant above *cmcs* and the standard free energy of micellization per mole of monomer, ΔG_m^0 can be calculated from the following relation²⁶:

$$\Delta G_m^0 = (1 + \beta)RT \ln X_{cmc} \quad (2)$$

where X_{cmc} is the value of cmc expressed in mole fraction. The standard enthalpy of micellization, ΔH_m^0 , was calculated from the following equation^{27, 28}:

$$\Delta H_m^0 = (1 + \beta)RT^2 (\partial \ln X_{cmc} / \partial T)_p \quad (3)$$

obtained by inserting Eq. (2) into Gibbs-Helmholtz equation based upon the assumption that β is practically temperature-independent.

The values of $\partial \ln X_{cmc} / \partial T$ was determined by fitting $\ln X_{cmc} - T$ with the polynomial function

$$\partial \ln X_{cmc} = a + bT + cT^2 \quad (4)$$

where a , b and c are temperature-independent constants. Then,

$$\ln X_{cmc} / \partial T = b + 2cT \quad (5)$$

The change in the standard entropy of micellization can then be obtained from

$$\Delta G_m^0 = \Delta H_m^0 - T\Delta S_m^0 \quad (6)$$

The temperature dependence of the relative cmc values for LDS in presence of 0.001 M of various tetraalkylammonium salts is illustrated in Fig. 4. The minima in these curves occur typically between 300 to 305 K for all the additives. An initial decrease in the relative cmc values with temperature may be ascribed to the dehydration of the monomers, while further temperature increase causes disruption of the structured water around the hydrophobic groups which opposes micellization. The $cmcs$ and the different thermodynamic parameters in presence of 0.001 M of various tetraalkylammonium salts are presented in Table 2. Analysis of the thermodynamic parameters of micellization indicates that the aggregation of LDS is driven mainly by the positive ΔS_m^0 . Similar changes from entropic to enthalpic micellization with temperature increase have also been observed with some other surfactants²⁹⁻³¹. The standard free energies of micellization for LDS in presence of various quaternary ammonium salts, decreases linearly with temperature. The slow decrease of ΔG_m^0 with the growth of temperature is typical for aqueous solutions of surfactants and this results from entropy-enthalpy compensation effect³²⁻³⁴. Decreasing values of ΔG_m^0 with increasing chain length of the alkyl substituent of the added salts indicate that the micellization of LDS becomes more favorable as the hydrophobicity of quaternaries increases. Positive values of ΔH_m^0 such as those noted at the lowest temperatures are generally attributed to the release of structural waters molecules from the hydration

layers around hydrophobic parts of the micelle. The high positive value of ΔH_m^0 in the presence of Bu_4NBr indicates an increased hydrophobicity of the micelle due to the penetration of the alkyl chains of Bu_4NBr with a large hydrophobic volume into the micellar core. Geometric restriction makes it infeasible for all four chains to penetrate. Hence, two chains are located at the micellar surface layer in contact with water thus forming an iceberg structure around the chains³⁵. Such hydrophobic interactions become increasingly insignificant with the partial breakdown of the structure of water as temperature is increased, the negative ΔH_m^0 values suggesting the importance of the London-dispersion interactions as an alternative force contribution for micellization.³

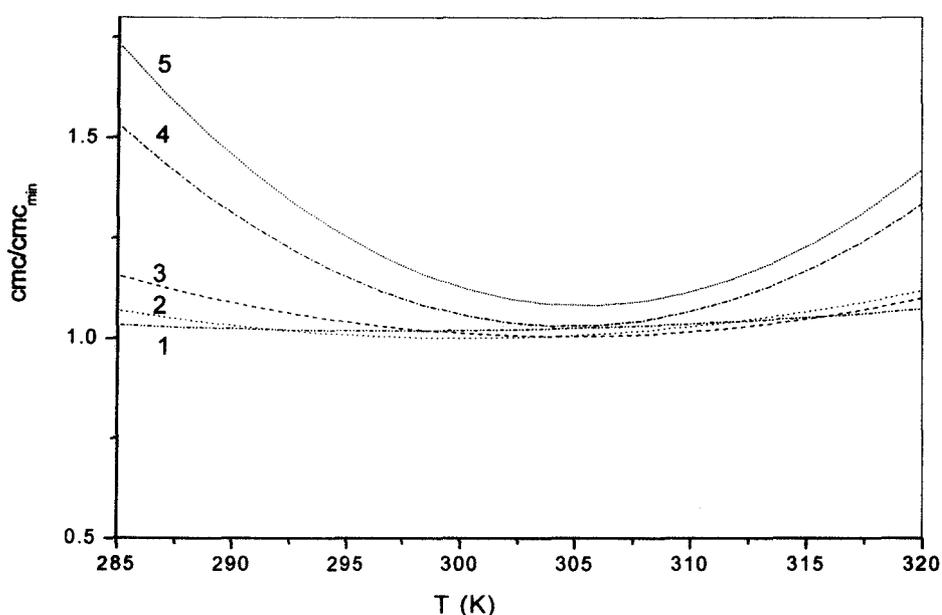


Figure 4. Temperature dependence of relative cmc values for LDS in presence of 0.001 M of different tetraalkylammonium salts (1) NH_4Br ; (2) Me_4NBr ; (3) Et_4NBr ; (4) Pr_4NBr ; and (5) Bu_4NBr .

Interfacial adsorption

The variation of surface tension as a function concentration of aqueous solution of LDS in the absence and presence of various quaternary ammonium salts is

shown in Fig. 2 The *cmcs* have been determined from bulk property corresponding to the surfactant concentration at which surface tension reaches the constant equilibrium value.

The maximum interfacial adsorption, Γ_{\max} , of LDS in presence of different tetraalkyl salts has been evaluated according to a suitable form of the Gibbs adsorption equation^{26, 28}.

$$\Gamma_{\max} = -\frac{1}{4.606RT} \left(\frac{d\gamma}{d \log c} \right) \quad (7)$$

The slope of the linear portion of the γ vs. $\log c$ curve below the *cmc* was determined by the method of least squares.

The minimum surface area per surfactant head group at the aqueous solution-air interface, A_{\min} , nm² / molecule, is then calculated from the equation³⁷

$$A_{\min} = 10^{18} / N_A \Gamma_{\max} \quad (8)$$

where N_A is the Avogadro's number.

Interfacial properties of LDS in presence of various tetraalkylammonium salts are presented in Table 1. The *cmc* of LDS in water is found to be 8.98 mM at 298.15 K in agreement with those reported in the literature^{12, 38}. The γ_{cmc} in the γ vs. $\log c$ profile of LDS decreases with increasing concentration of R₄NBr salts as well as with increasing chain length of the alkyl groups of the additives. The factor 4.606 in the denominator of Eq. 7 depends on the charge of the adsorbed amphiphile at the air/liquid interface. In presence of excess salts, the amphiphile ions behave like neutral species and the factor reaches its limiting value of 2.303. In presence of added R₄NBr at a concentration of 0.005 to 0.01 mol dm⁻³, the factor 2.303 is realistic. The values of Γ_{\max} and A_{\min} obtained on such a basis are listed in Table 1. The results, in general, indicate lower interfacial adsorption at *cmc* (Γ_{\max}) in presence of the salts as additives in solution. The variation of A_{\min} with the concentration of a given additive follows an opposite trend to that of the Γ_{\max} values. The observed trends in the measured parameters in the studied salt environments are considered to be inherently controlled by interfacial charge neutralization in presence of R₄NBr. For quantification of the observations on a firm basis, further study in this direction is worthwhile.

CP Phenomenon

It is well known that Bu_4NBr is one of the most effective additives in producing CP phenomenon in anionic surfactants^{35, 39}. In this study, we have also measured the CP of 0.025, 0.05 and 0.1 M LDS in the presence of different amounts of Bu_4NBr . From the data in Table 4, it is clear that CP decreases with increasing salt concentration, while an increase is observed with an increase in the surfactant concentration. Clouding behavior has been attributed to the dehydration of the hydrophobic group of the surfactant with the increase in temperature³⁹. Large amount of added salt screens the electrostatic repulsion and this is believed to be responsible for the ionic micellar system exhibiting CPs. The butyl chain of Bu_4NBr may penetrate into the micellar interior due to hydrophobic interaction^{35, 39}. Van der Waals attraction and the penetration effect will help attract two micelles together, while the electrical repulsion will prevent the micellar contact. Dehydration of the ionic heads of the surfactant monomers takes place on increasing the temperature, which increases the interaction between the anionic heads and Bu_4N^+ . At the CP the micelles would collapse and this results in the formation of two phases. An increase in the concentration of Bu_4NBr will produce more structured water and the phase separation is expected to appear at a lower temperature since the LDS concentration is constant. This is clearly reflected in Table 3.

CONCLUSIONS

The above measurements show that the *cmc* of lithium dodecylsulfate is dependent upon the concentration and the alkyl chain length of the added tetraalkylammonium bromide salts. The marked reduction in *cmc* with the increase in the size of the alkyl chain of the quaternaries may be attributed to the hydrophobic bonding of these salts with the hydrophobic core of the micelles. The weak temperature dependence of the standard Gibbs energy of micellization reflects an enthalpy-entropy compensation effect. The decreasing values of ΔG_m^0 with increasing chain length of the alkyl substituents of the added salts indicates that micellization of LDS becomes more favorable as the hydrophobicity of the quaternaries increases. The occurrence of the cloud point phenomenon for this anionic surfactant in presence of Bu_4NBr is accounted for in terms of the penetration of the butyl chains of the Bu_4N^+ ions into the hydrophobic cores of two neighboring micelles due to the hydrophobic effect.

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TABLE-1

Critical Micellar Concentration and Interfacial Properties of LDS in Presence of Different Quaternary Ammonium Salts at 298.15 K

[salt] (mol dm ⁻³)	cmc / mM		γ_0 (mN / m)	γ_{cmc} (mN / m)	$10^6 \Gamma_{max}$ (mol m ⁻²)	$10^2 A_{min}$ (n m ²)
	Cond	s.t.				
			NH₄Br			
0.0000	8.98	7.12	72.2	41.8	2.01	82.52
0.0005	8.63	-				
0.001	8.24	5.86	72.1	40.3	2.06	80.64
0.002	7.72	-				
0.003	6.97	-				
0.004	6.63	-				
0.005	6.13	4.80	72.0	38.9	1.89 (3.78)	87.66 (175.32)
0.01	5.27	3.82	71.9	37.9	1.87 (3.74)	88.54 (177.08)
0.015	4.51	-				
0.02	3.97	-				
			Me₄NBr			
0.0005	8.31	-				
0.001	7.62	6.33	71.8	40.1	1.81	91.68
0.002	6.90	-				
0.003	5.90	-				
0.004	5.30	-				
0.005	4.93	4.02	71.7	39.3	1.55 (3.10)	107.05 (214.10)
0.01	3.94	2.80	71.6	38.5	1.33 (2.66)	124.74 (249.48)
0.015	3.43	-				
0.02	3.00	-				
			Et₄NBr			
0.0005	7.12	-				
0.001	6.25	4.69	71.7	39.4	1.86	
0.002	5.17	-				
0.003	4.47	-				
0.004	3.37	-				
0.005	3.06	2.51	71.6	39.3	1.25 (2.50)	133.25 (266.50)
0.01	2.43	1.94	71.4	39.0	1.15 (2.30)	145.00 (290.00)
0.015	2.00	-				
0.02	1.66	-				
			Pr₄NBr			
0.0005	4.00	-				
0.001	3.34	2.86	71.6	39.7	1.33	125.31
0.002	2.41	-				
0.003	1.96	-				
0.004	1.39	-				
0.005	1.13	1.15	71.3	38.9	1.02 (2.04)	162.93 (325.86)
0.01	0.94	0.73	70.8	38.6	1.01 (2.02)	163.41 (326.82)
0.015	0.72	-				
0.02	0.52	-				
			Bu₄NBr			
0.0005	1.55	-				
0.001	1.24	0.98	69.1	36.4	1.26	131.66
0.002	0.63	-				
0.003	0.47	-				
0.004	0.37	-				
0.005	-	0.29	67.0	35.5	1.06 (2.12)	157.22 (314.44)
0.01	-	0.26	65.9	34.7	0.90 (1.80)	184.48 (368.96)

The uncertainty limit of *cmc* is $\pm 3\%$

TABLE-2

Critical Micellar Concentrations and Thermodynamic Parameters of LDS in Presence of 0.001 M of Various Quaternary Ammonium Salts at Different Temperatures

Temp/ K	cmc/mM	β	$\Delta G_m^0/ \text{kJ mol}^{-1}$	$\Delta H_m^0/ \text{kJ mol}^{-1}$	$T\Delta S_m^0/ \text{kJ mol}^{-1}$
NH₄Br					
288.15	8.41		-33.71	0.29	34.00
298.15	8.24		-34.75	-1.35	33.40
308.15	8.55	0.60	-35.98	-3.21	32.77
318.15	8.61		-37.12	-5.34	31.78
Me₄NBr					
288.15	7.96		-34.14	-1.20	32.94
298.15	7.62		-35.44	-8.42	27.02
308.15	7.78	0.61	-36.05	-16.61	19.94
318.15	8.35		-37.43	-25.83	11.60
Et₄NBr					
288.15	6.99		-35.06	-1.40	33.66
298.15	6.25		-36.74	-13.55	23.19
308.15	6.44	0.63	-37.85	-27.35	10.50
318.15	6.96		-38.73	-42.88	-4.15
Pr₄NBr					
288.15	4.71		-37.06	28.86	65.92
298.15	3.33		-39.77	4.00	43.77
308.15	3.77	0.65	-40.57	-24.46	16.11
318.15	4.11		-41.52	-56.70	-15.18
Bu₄NBr					
288.15	1.99		-43.16	71.27	114.42
298.15	1.24		-46.73	45.07	91.80
308.15	1.56	0.76	-47.23	14.78	62.01
318.15	1.59		-48.70	-19.79	28.91

The uncertainties of the ΔG_m^0 , ΔH_m^0 and ΔS_m^0 are ± 4 , ± 3 and ± 4 % respectively.

TABLE-3

Cloud Point Data on LDS + Tetrabutylammonium Bromide System

[Bu ₄ NBr] (mol dm ⁻³)	CP ^a (°C)		
	[LDS] = 0.025 M M	[LDS] = 0.050 M	[LDS] = 0.100
0.30	22.4	22.8	24.4
0.25	23.4	24.2	25.9
0.20	24.6	25.5	28.4
0.15	26.1	27.7	31.6
0.10	28.1	31.6	40.7
0.05	34.8	46.5	>100
0.04	37.8	59.2	>100
0.03	43.6	>100	>100
0.02	60.3	>100	>100
0.01	>100	>100	>100

^aReproducibility: ± 0.1 °C

CHAPTER-V

Mixed Micellization of Anionic-Nonionic Surfactants in Aqueous Media: A Physicochemical Study with Theoretical Consideration

INTRODUCTION

A significant amount of research work has been devoted for investigating the physicochemical properties of a mixed micelle containing two or more surfactants of variable structures in solution. The extensive use of these multiple-surfactant systems has currently been promoted owing to their much favorable practical applications than single component systems. In this respect, industrial, pharmaceutical, technological, and biochemical fields are of great importance. In the pharmaceutical field, for example, mixed micelle has been found to enhance the absorption of various drugs in human body¹⁻³. A number of mixtures of cationic and anionic surfactant mixtures has been used in cleaning products to facilitate the dissolution and improved tolerance of water hardness⁴. Due to their synergistic behavior at *cmc*, cosmetic industries use the mixed micelles in low concentrations to avoid potential skin irritation⁵⁻⁷. This synergistic phenomenon can also be highly beneficial for the environment as it allows the amount of surfactant released, and hence their impact, to be substantially reduced⁸.

In view of the tremendous application potentials and economical consideration of a mixed micelle, it is necessary to search for the most suited surfactant combinations with desired requirements (such as, surface activity, solubility, catalytic property, etc.). In mixed micellar systems of ionic, nonionic and zwitterionic surfactants, three types of interactions may operate, *viz.*, favorable (ionic-nonionic, ionic-zwitterionic and cationic-anionic), unfavorable and ideal mixing (nonionic mixtures). In aqueous medium, pure and mixed surfactants can form micelles after a threshold concentration, called the critical micellar concentration (*cmc*), which can be assessed by various methods to understand the self-organizing behavior of surfactants.

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From a theoretical point of view, mixed surfactant systems have been the object of great investigations and attract much interest in recent years to provide appropriate thermodynamic models capable not only of describing the behavior of mixed systems, but also for predicting their properties⁹⁻¹⁶.

In this work, we have used lithium dodecylsulfate (LDS), polyoxyethylene(23)laurylether (Bj-35), and polyoxyethylene-*tert*-octylphenylether (Triton -100 or TX-100) in binary and ternary mixtures in aqueous medium. These surfactants differ in size and structure; LDS and Bj-35 have 12 carbon atoms in the linear chain whereas TX-100 consists of 8 carbon atoms attached with phenyl ring. There are 23 ethylene oxide residues in Bj-35 and 9-10 ethylene oxide residues in TX-100. Here, micellization and other physicochemical properties (*e.g.*, extent of counterion binding, interfacial adsorption, thermodynamics of micellization, mutual interaction parameter and micellar compositions, etc.) of the pure components and their binary and ternary mixtures have been studied. Theories of Clint^{17,18}, Rosen^{9,19}, Rubingh²⁰, Motomura^{21,22}, Georgiev²³, Maeda^{24,25}, and Blankschtein^{26,27}, have been used to unravel the nature of interactions among the micellar components.

EXPERIMENTAL

Materials and Methods

The anionic surfactant lithium dodecylsulfate was a product of Merck (Germany) and the nonionic amphiphiles polyoxyethylene(23)laurylether, and polyoxyethylene-*tert*-octylphenylether were purchased from Sigma (USA). All the products were used without further purification. All solutions were prepared in doubly distilled water and the experiments were performed at 298.15 ± 0.1 K.

The tensiometric experiments are performed using a platinum ring by the ring detachment method in a calibrated K9 Tensiometer (Krüss, Germany). Detailed procedure has been described in Chapter II. Each experiment was repeated several times to achieve good reproducibility. The measured surface tension (γ) values were corrected according to the procedure of Harkins and Jordon. The γ values were accurate within ± 0.1 mN m⁻¹.

The conductance measurements were performed with a Pye-Unicam PW-9509 conductivity meter at a frequency of 2000 Hz using a conductivity cell of cell constant 1.0 cm⁻¹. The same procedure of addition of surfactant as in tensiometry was

followed. The uncertainty of the measurements was within $\pm 1\%$. The details of the measurements have been given in Chapter II.

A UV-visible (240) Shimadzu (Japan) spectrophotometer operating in dual beam mode was employed for spectral measurements using matched pair of quartz cuvettes of pathlength 1 cm under thermostated condition (298.15 K). Spectral measurements were made on the basis that TX-100 absorbs maximum at 276.5 nm and the absorbance (A) gets perturbed at the micellar point¹⁴. Here 3 mL of water are taken in a pair of cuvettes. Surfactant solution is then progressively added to the sample cell as required. Optical density at each stage of surfactant addition is measured after thorough mixing at the absorption maximum (276.5 nm) of TX-100. Then the absorbance was plotted against the logarithm of surfactant concentration and the breakpoint of the profile was considered as the *cmc*.

RESULTS AND DISCUSSION

Critical micellar concentration (cmc)

The *cmc*s of the pure surfactants (LDS, TX-100 and Bj-35), and the mixed micellar systems of binaries (LDS/TX-100, LDS/Bj-35 and TX-100/Bj-35) and ternaries (LDS/TX-100/Bj-35) were determined from the point of intersection of two straight lines obtained by tensiometry (γ vs. $\log[\text{surf}]$), conductometry (κ vs. $[\text{surf}]$), and spectrophotometry (A - $\log[\text{surf}]$), as illustrated in the representative Figs. 1a, b and c. The values, thus obtained, are presented in Tables 1 and 2. In case of LDS/TX-100 and LDS/Bj-35, tensiometric and conductometric methods were used to determine the *cmc*s, whereas for TX-100/Bj-35, spectrophotometric method replaced conductometry. It is seen from Table 1 that the *cmc* values of different mixed surfactant combinations fall within the *cmc* ranges of the components and for ionic/nonionic mixtures, *cmc* values shift towards the nonionic side rather than the ionics. It is observed that the *cmc* values of various binary compositions increase with increasing mole fraction of LDS (α_{LDS}) for the mixtures of LDS/TX-100 and LDS/Bj-35 and of TX-100 ($\alpha_{\text{TX-100}}$) for TX-100/Bj-35 mixtures. The tensiometric *cmc* values are higher than their conductometric counterparts in ionic/nonionic mixtures, but for most of the nonionic/nonionic combinations, spectrophotometric *cmc* values are larger than those obtained from tensiometric method. Since the *cmc* values are method-dependent, we have taken the average *cmc* values for theoretical calculations. From

Table 1, it is apparent that the theoretical *cmc*s for TX-100/Bj-35 are lower than the experimental values whereas the reverse is true for other two combinations. In all binaries, the experimental *cmc* values deviate from the Clint *cmc*s (please see later) indicating nonideal behavior of these mixtures. The variation in *cmc* (experimental *cmc*, Clint *cmc*, and SPB *cmc*) (please see later) with the composition in case of three binary mixtures are graphically represented in Fig. 2. In this work, we obtain the same trend in the *cmc* values of binary mixtures (anionic/nonionic and nonionic/nonionic) comparable to some earlier works¹⁰⁻¹⁶. In Table 2, the *cmc* values of the ternaries increase systematically with increasing proportion of LDS in the mixture. This observation is comparable with the previous studies^{10, 14-16}.

Adsorption at the air/water interface

Surfactants, due to their amphiphilic nature in aqueous medium, adsorb at air/solution interface. This results in lowering of cohesive force among the water molecules at the interface and thus, surface tension of water decreases on progressive addition of a surfactant. This process continues up to complete saturation of the interface by the amphiphiles. Beyond this limit, surfactants get aggregated in bulk solution to form micelles without hampering the interface, without showing any change in the surface tension values on surfactant addition. The point of discontinuity in a γ vs. $\log C$ profile indicates the tensiometric *cmc*. The Gibbs surface excess (Γ_{\max}) has been calculated¹⁰⁻¹⁶ from the least-square slope of Π vs. $\log C$ plot using Equation (1),

$$\Gamma_{\max} = \frac{1}{2.303nRT} \text{Lt}_{C \rightarrow \text{cmc}} \frac{d\Pi}{d\log C} \quad (1)$$

where Π is the surface pressure ($\gamma_{\text{H}_2\text{O}} - \gamma_{\text{surfactant}}$), R is the universal gas constant, T is the absolute temperature, n is the average number of species present in solution per surfactant monomer. Here, n is taken as unity for pure surfactants, their binary and ternary mixture, *i.e.*, the contribution of counterions of cationic surfactants has been neglected. C is the total molar amphiphile concentration in molarity scale. Here, for dilute solution, activity is replaced by concentration.

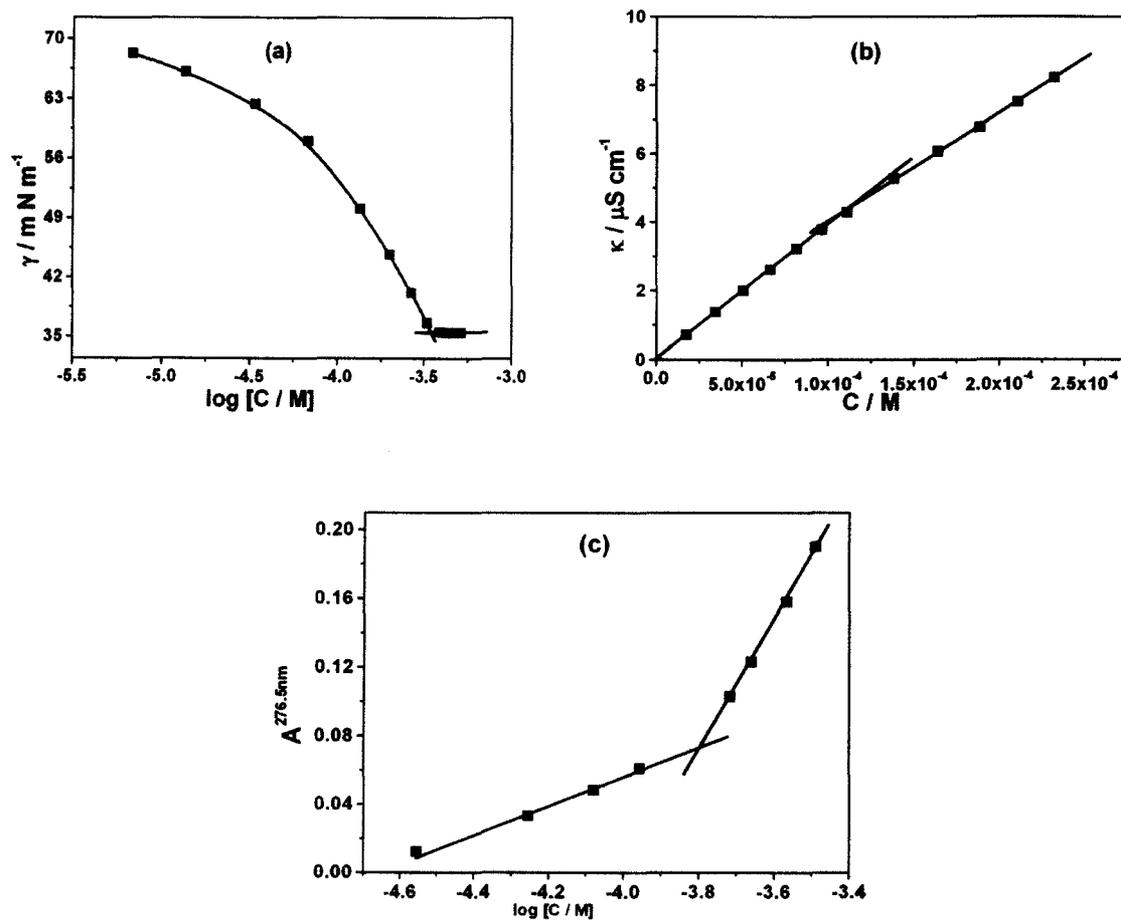


Figure 1. Representative tensiometric (a), conductometric (b), and spectrophotometric(c) profiles for dilution of concentrated surfactant mixtures in water.

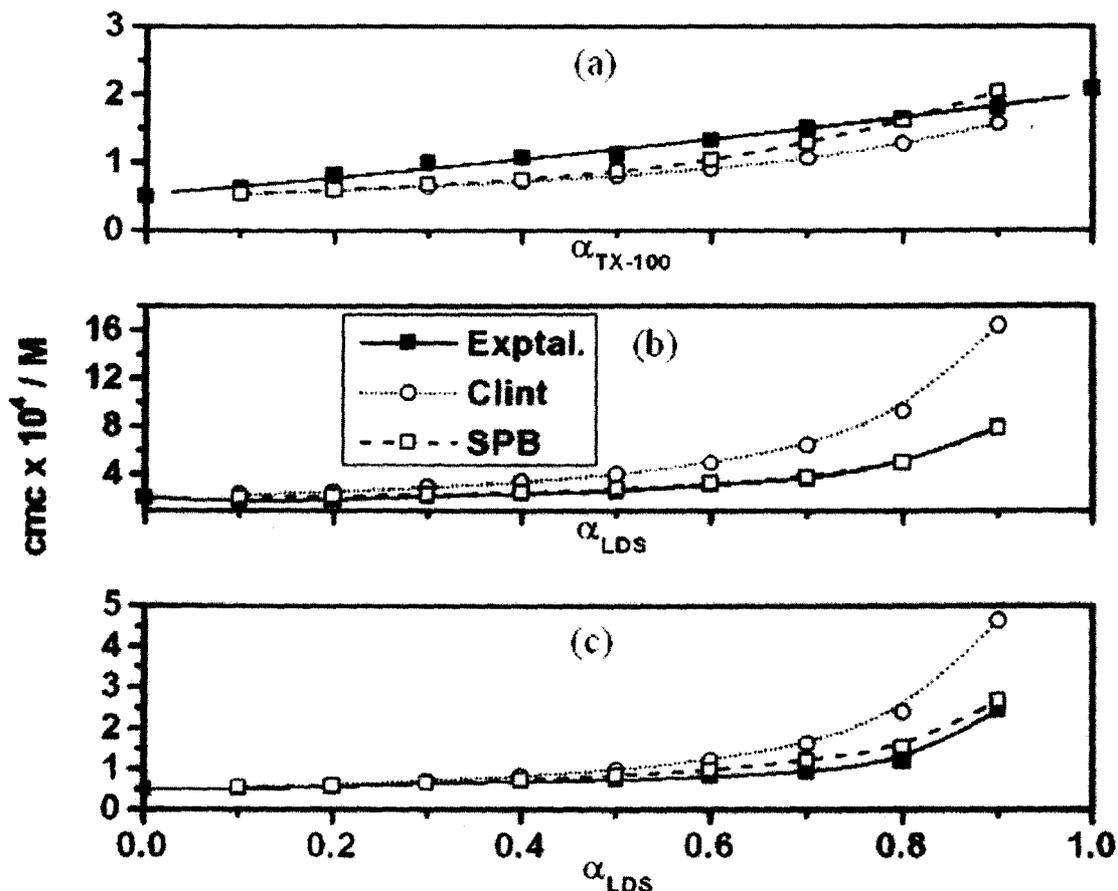


Figure 2. Variation of cmc as a function of composition in mixed systems; (a) TX-100/Bj-35, (b) LDS/TX-100, and (c) LDS/Bj-35.

The area of exclusion (A_{min}) per surfactant head group at complete air/solution interfacial saturation near cmc region can be calculated using the relation¹⁰⁻¹⁶,

$$A_{min} = \frac{10^{18}}{N_A \Gamma_{max}} \quad (2)$$

where N_A is the Avogadro's number.

Γ_{max} and A_{min} are expressed in mol m^{-2} and $\text{nm}^2 \text{molecule}^{-1}$ units, respectively. The values of Π_{cmc} (surface pressure at the cmc of the solution), Γ_{max} and A_{min} of binary and ternary mixtures are reported in Tables 3 and 4, respectively. It is observed from Table 3 that Π_{cmc} and Γ_{max} values decrease with increasing mole fraction of LDS in the ionic/nonionic mixed systems, indicating gradual lowering of

surface activity of those binaries, whereas in case of nonionic/nonionic binary combinations, the surface activity increases with increasing stoichiometric mole fraction of TX-100. The same trend is also followed in case of the ternary mixtures (Table 4), *i.e.*, in these mixtures the greater the mole fraction of TX-100, the greater is the surface activity. Due to the repulsion between the same charges on LDS molecules, they have larger A_{\min} values (Table 3). In Table 3, the trend in A_{\min} values of binaries is just the reverse to that of Γ_{\max} as expected from the reciprocal interdependence.

The more surface active an amphiphile is, the more efficient it is in lowering the surface tension of water and the smaller is the amount of surfactant required to lower the surface tension of the solvent by a given amount. If C_{20} be the concentration of a given surfactant to lower the surface tension of the medium by 20 mN m⁻¹, pC_{20} ($=-\log C_{20}$) therefore is a measure of propensity of the amphiphile towards interfacial adsorption. The ease of a particular component toward micellization compared to interfacial adsorption is, therefore, given by cmc/C_{20} . Table 3 shows that among pure surfactants, surface activity (*cf.* pC_{20} values) is in the order of LDS < TX-100 < Bj-35. It may be due to the greater degree of solvation at LDS head group aided by ion-dipole interaction compared to dipole-induced dipole interaction for the nonionics. Since, the former force is more efficient than the later, LDS has a greater tendency to stay in the bulk phase compared to TX-100 and Bj-35 and hence, exhibits lower surface activity than the nonionics. Among the nonionics, greater numbers of polyoxyethylene linkages in Bj-35 facilitate its bulk solubilization whereas the comparatively smaller chain in TX-100 increases its solubility in bulk solution. Under these competing situations, it is the smaller hydrophobicity of the surfactant chain which plays the decisive role over the former. For all the binary mixtures, pC_{20} values decrease significantly with increasing stoichiometric mole fraction of TX-100 (TX-100/Bj-35) and of LDS (LDS/TX-100 and LDS/Bj-35) indicating more and more surface adsorption. On the other hand, cmc/C_{20} value for ionic/nonionic mixtures increases up to $\alpha_{\text{LDS}} = 0.5$ and then decreases, suggesting that for extreme compositions of LDS, interfacial adsorption is preferred, but for moderate compositions, micellization prevails over Langmuirian adsorption. But for TX-100/Bj-35 mixtures, no such regularity is observed.

Energetics of micellization and interfacial adsorption

The standard free energy of micellization per mole of monomer unit (ΔG_m^0) for the nonionic binary mixture (TX-100/Bj-35) is calculated by using,

$$\Delta G_m^0 = RT \ln(cmc) \quad (3)$$

For binary ionic/nonionic mixtures (LDS/TX-100 and LDS/Bj-35) as well as for ternary combinations (LDS/TX-100/Bj-35), equation 3 is modified as,

$$\Delta G_m^0 = (1 + g) RT \ln(cmc) \quad (4)$$

where g is the fraction of counter ions bound to the micelle obtained conductometrically and accounts for the free energy contribution arising out of counterions condensation onto the micellar interface. The ratio of slopes of post and pre-micellar regions of specific conductance (κ) vs. concentration of surfactant (C) plot gives the value of fraction of counterion dissociation (f). The degree of counterion condensation is, therefore, $g = 1 - f$. Although other methods for the evaluation of g are available, this simplest method is often employed in the literature and is used in limited mixed micellar systems.

The standard free energy of interfacial adsorption (ΔG_{ad}^0) at the air/water interface is obtained from the relation¹⁰⁻¹⁶,

$$\Delta G_{ad}^0 = \Delta G_m^0 - (\Pi_{cmc} / \Gamma_{max}) \quad (5)$$

where Π_{cmc} is the surface pressure at cmc .

The values of Π_{cmc} , g , ΔG_m^0 , and ΔG_{ad}^0 for binary and ternary mixtures are presented in Tables 3 and 4, respectively. The g values for the binary mixtures of LDS with TX-100 and Bj-35 are low and increase with α_{LDS} due to the increase in the surface charge density of the mixed micelles in the presence of higher proportion of the ionic amphiphile. For ternary mixtures, g values are low and are independent of micellar composition. The ΔG_m^0 values for TX-100/Bj-35 system (Figure 3) which increase (in magnitude) regularly with increasing α_{TX-100} , indicating more spontaneous micellization. The values of ΔG_m^0 for LDS/TX-100 combination decrease upto $\alpha_{LDS} = 0.5$ and increase thereafter, but the free energy values for LDS/Bj-35 do not follow any regular trend. This parallelism in the relative magnitudes of ΔG_m^0 and ΔG_{ad}^0 with the cmc/C_{20} ratio supported our earlier

proposition regarding physical significance of cmc/C_{20} . For ternaries, ΔG_m^0 values are found to be composition dependent (Table 4) and these are higher for $\alpha_{LDS}=0.125$ but lower for $\alpha_{LDS}=0.625$. The variation in ΔG_{ad}^0 with the mole fraction of surfactant 1 (α_1) is represented in Figure 4, which shows that for both TX-100/Bj-35 and LDS/Bj-35 mixtures ΔG_{ad}^0 are virtually invariant with α_1 . The values of ΔG_{ad}^0 of the former mixture are comparatively higher in magnitude than the later mixture. ΔG_{ad}^0 of LDS/TX-100 system increases up to $\alpha_{LDS}=0.7$ followed by a decrease. The values of ΔG_{ad}^0 of ternary systems are comparatively higher than those of binary systems where third combination in Table 4 shows the maximum in magnitude.

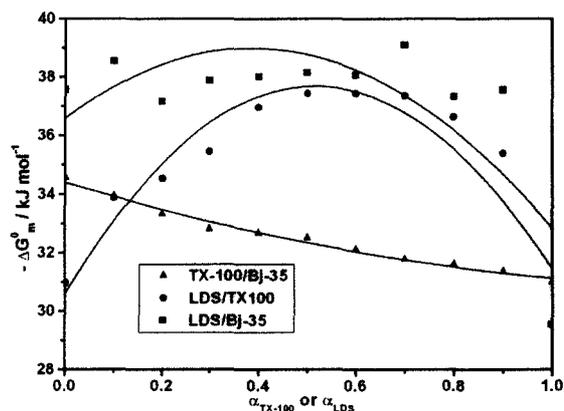


Figure 3. Variation of ΔG_m^0 as a function of composition in mixed system.

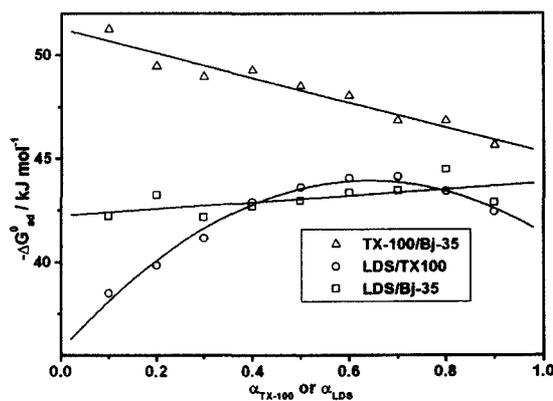


Figure 4. Variation of ΔG_{ad}^0 as a function of composition in mixed system.

In the following “Theoretical section,” we considered experimental *cmc* of the mixed systems averaged over the conductometric and tensiometric values; the spectrophotometric values are not considered due to large divergence over the entire proportion regime.

THEORETICAL SECTION

Clint model

This model^{17, 18} predicts the *cmc* of mixed surfactant systems (cmc_C) with known composition from a knowledge of individual *cmcs* of the mixing components according to the equation,

$$(1/cmc_C) = \sum_{i=1}^n (\alpha_i / cmc_i) \quad (6)$$

Here, α_i denotes the stoichiometric mole fraction of the *i*th component in solution, respectively. The terms cmc_i and cmc_C are the critical micellar concentrations of the *i*th component and the mixture, respectively. Any negative deviation in the experimental value of *cmc* from that of cmc_C reflects an overall

synergistic (attractive) interaction whereas overall antagonistic (repulsive) interaction is inferred from a positive deviation.

Table 1 reflects synergistic behavior in TX-100/Bj-35 system upto $\alpha_{\text{TX-100}} = 0.6$, and antagonistic behavior thereafter. For the ionic/nonionic systems, however, synergism is evident over the entire range of composition, which may arise out of the interaction between the dodecylsulfate ion and the ether-oxygen atoms of the nonionic surfactants (TX-100 and Bj-35) through the counterion Li^+ of the anionic surfactant as proposed by Matsubara *et al.*²⁸.

Rosen model

This model¹⁹ focuses on the adsorbed Langmuirian mixed surfactant film at the air/solution interface and is basically an optimization algorithm. A closer resemblance with the experimental area of exclusion (A_{min}) is obtained from the A_{min} values of the respective pure components using computational iteration, which leads to the mole fraction of the component (X_1^σ) and interaction parameter at the interface among the components (β^σ) as the optimization parameters. The two equations involved in the iteration procedure are,

$$\frac{(X^\sigma)^2 \ln[\text{cmc}_{\text{mix}} \alpha_1 / C_1^0 X^\sigma]}{(1 - X^\sigma)^2 \ln[\text{cmc}_{\text{mix}} (1 - \alpha_1) / C_2^0 (1 - X^\sigma)]} = 1 \quad (7)$$

and

$$\beta^\sigma = \left(\frac{\ln[\text{cmc}_{\text{mix}} \alpha_1 / C_1^0 X^\sigma]}{(1 - X^\sigma)^2} \right) \quad (8)$$

where cmc_{mix} , C_1^0 and C_2^0 are the molar concentrations of the mixture, surfactant 1 and surfactant 2 respectively at a fixed γ value corresponding to tensiometric cmc of the pure component 1 and α_1 is the stoichiometric mole fraction of surfactant 1 in solution.

The β^σ and X_1^σ values of the binary mixtures are presented in Table 5. The negative β^σ values for the ionic/nonionic combinations indicate synergistic interaction. In TX-100/Bj-35 mixtures, Table 5 shows that the mole fractions of TX-100 in the mixed interfacially adsorbed monolayer are always greater than the corresponding stoichiometric proportion reflecting greater tendency of TX-100 to be adsorbed at the air/solution interface as compared to Bj-35. Moreover, the interaction parameters suggest antagonism among the surfactant monomers in the adsorbed film the extent of

which increases with increasing stoichiometric proportion of TX-100 in the mixture. In LDS/TX-100 and LDS/Bj-35 mixtures, smaller proportion of LDS in the mixed adsorbed film compared to its analytical bulk proportion suggests that LDS is relatively reluctant toward interfacial adsorption which is probably due to the greater degree of solvation of the head group of ionic surfactants through ion-dipole interaction compared to dipole-induced dipole interaction of water dipoles with polarizable ether head groups of nonionic surfactants under study. The interaction parameter in either case evidenced synergism which may arise from the ion-dipole interaction between the head groups of ionic/nonionic surfactant pair, or as a result of dispersion interaction between the hydrophobic tail or through participation of the Li^+ in coordination which acts as a bridge between the two kinds of surfactants.

Rubingh model

This is another iterative algorithm²⁰ similar to the Rosen model, but the focus here is on the micellar phase formed in bulk solution. The micellar mole fraction (X_R) of a surfactant in the mixed aggregated state and the molecular interaction parameter (β^R) can be calculated by solving the coupled equations,

$$\frac{(X_R)^2 \ln[\text{cmc}_{\text{mix}} \alpha_1 / \text{cmc}_1 X_R]}{(1 - X_R)^2 \ln[\text{cmc}_{\text{mix}} (1 - \alpha_1) / \text{cmc}_2 (1 - X_R)]} = 1 \quad (9)$$

and

$$\beta^R = \left(\frac{\ln[\text{cmc}_{\text{mix}} \alpha_1 / \text{cmc}_1 X_R]}{(1 - X_R)^2} \right) \quad (10)$$

where cmc_1 , cmc_2 , and cmc_{mix} are the critical micellar concentrations of surfactant 1, surfactant 2, and their mixture under the same physicochemical conditions, respectively, at a stoichiometric mole fraction of α_1 .

The activity coefficients of surfactants 1 and 2 in the mixed micelle (f_1 and f_2) can be evaluated from the equations,

$$f_1 = \exp[\beta^R (1 - X_R)^2] \quad (11)$$

and

$$f_2 = \exp[\beta^R (X_R)^2] \quad (12)$$

The values of X_R , β^R , f_1 , and f_2 for the binary mixtures are tabulated in Table 5. For TX-100/Bj-35 mixtures, the Rubingh model is insolvable up to $\alpha_{\text{TX-100}} = 0.6$ due to divergence in series. For compositions with $\alpha_{\text{TX-100}} > 0.6$, the relative proportion of

TX-100 in micellar phase is lower compared to its stoichiometric proportion and the interaction parameter reflects antagonistic behavior with the extent of antagonism increasing with increasing $\alpha_{\text{TX-100}}$. The antagonism predicted by the Clint model is therefore also reflected in the Rubingh model.

For ionic/nonionic combinations, the proportion of LDS in the micellar phase is less compared to its stoichiometric proportion with the exception of $\alpha_{\text{LDS}} = 0.1$ for LDS/TX-100 system. The lower *cmc* of the nonionics as compared to LDS manifests relatively lower affinity of LDS towards self-aggregation compared to the nonionics, which is reflected in the above computation. The interaction parameters over the entire composition regime are negative, implying synergistic behavior as also obtained from the Clint model.

Motomura model

This model^{21, 22} considered mixed micelles as a macroscopic bulk phase from thermodynamic point of view. In this model, excess thermodynamic quantities are used to evaluate various energetic parameters. The fundamental equation is,

$$X_{\text{Mo}} = \hat{X}_2 - \left(\hat{X}_1 \hat{X}_2 / \hat{cmc} \right) \left(\partial \hat{cmc} / \partial \hat{X}_2 \right)_{\text{T,P}} \quad (13)$$

where $\hat{X}_2 = v_2 \alpha_2 / (v_1 \alpha_1 + v_2 \alpha_2)$ and $\hat{cmc} = (v_1 \alpha_1 + v_2 \alpha_2) cmc$. Subscripts 1 and 2 denote surfactants 1 and 2, respectively, α and v represent stoichiometric mole fraction and the number of dissociated ions by a surfactant molecule in solution. The micellar mole fractions (X_{Mo}) of a surfactant in the binary mixtures evaluated by Motomura equation are shown in Table 5.

The mean activity coefficient of surfactant 1 in micelle (f_1) according to this model²⁹ is presented by the equation,

$$\hat{X}_1 \hat{cmc} / cmc_1^0 = f_1 X_{1(\text{Mo})} \quad (14)$$

and the f_1 values of all binary mixtures are shown in Table 5. For TX-100/Bj-35 system, the mole fractions of TX-100 were found to be less than the corresponding stoichiometric proportions signifying greater propensity of Bj-35 toward micelle formation compared to TX-100 as expected from the lower *cmc* of Bj-35 compared to

TX-100. For LDS/TX-100 system, LDS prefers micellar phase for lower stoichiometric proportions ($\alpha_{\text{LDS}}=0.1$ and 0.2) and thereafter TX-100 dominates the micellar phase over LDS when the stoichiometry and micellar mole fraction are considered. Moreover, there exists a minima at $\alpha_{\text{LDS}} = 0.6$ in the X_{Mo} vs. α_{LDS} profile. For LDS/Bj-35 system, again, the micellar proportion of LDS outweighs its stoichiometric proportion for $\alpha_{\text{LDS}} = 0.1$ and 0.2 and thereafter it is Bj-35, which wins the competition toward micellization forming minima in the X_{Mo} vs. α_{LDS} profile at $\alpha_{\text{LDS}} = 0.4$. Large deviation of f_{Mo} from unity for ionic/nonionic mixtures indicates participation of counterions in the micellar phase²⁹.

Georgiev model

Based on the Markov's chain model for polymerization process of mixed micelles²³, this theory relates the micellar composition (X_{G}) with α_1 and other two parameters, G_1 and G_2 as follows,

$$(X_1^{\text{G}}/X_2^{\text{G}}) = (\alpha_1/\alpha_2) [(G_1\alpha_1 + \alpha_2)/(G_2\alpha_2 + \alpha_1)] \quad (15)$$

where G_i represents the ratio between the equilibrium constants for the formation of micelles constructed by the same type of surfactants (K_{ii}) and different types of surfactants (K_{ij}). For the binary mixtures, X_{G} values are presented in Table 5.

For all the binary mixtures, X_{G} increases with increasing α_1 excepting $\alpha_{\text{LDS}} = 0.4$ for LDS/TX-100 system. For nonionic/nonionic mixed micelles, X_{G} values are much lower compared to α_1 , whereas those for ionic/nonionic systems are greater at lower mole fractions and smaller at higher mole fraction of LDS.

Maeda model

This model is based on the short range electrostatic interactions present in the ionic/nonionic mixed micellar systems. The concept of this model is that the presence of nonionic species in the micellar phase can reduce the head group repulsion in the ionic/nonionic mixed micelle. The standard free energy change due to the micellization process could be represented as a polynomial function of the mole fraction of component 2 in the micellar phase according to the equation,

$$\Delta G_{\text{Ma}}^0 = RT(B_0 + B_1\alpha_2 + B_2\alpha_2^2) \quad (16)$$

where

$$B_0 = \ln X_{C_1} \quad (17)$$

X_{C_1} is the *cmc* of the surfactant 1 in mole fraction unit. If the component 1 self-assembles, the micellar free energy change can be expressed as a dimensionless quantity, B_0 ($= \ln X_{C_1} = \Delta G_m^0/RT$). The parameter B_1 is related to the standard free energy change associated with the introduction of one ionic species into a nonionic micelle coupled with the release of one nonionic species from the micelle, *i.e.*, B_1 plays an important role for the change in the *cmc* values of nonionic micelles when an ionic species enters the micelle²⁴. B_2 is the interaction parameter in the micellar phase. R and T denote the universal gas constant and the absolute temperature, respectively. Again,

$$B_1 + B_2 = \ln(X_{C_2}/X_{C_1}) \quad (18)$$

(X_{C_2} is the *cmc* of surfactant 2 in mole fraction unit),

$$B_2 = -\beta_R \quad (19)$$

(β_R being the interaction parameter in the micellar phase obtained from Equation 10).

The values of ΔG_{Ma}^0 , B_0 , B_1 , and B_2 are presented in Table 6. B_0 is a constant for a binary mixture. B_1 and B_2 values do not follow any pattern with respect to α_{ionics} . ΔG_{Ma}^0 values decrease regularly with increasing α_{LDS} in both binary mixtures and they deviate more than do the free energy (ΔG_m^0) values obtained from Gibbs Helmholtz equation, reflecting the importance of counterion binding in the formation of ionic/nonionic mixed micelles.

Very recently, Maeda²⁵ introduced another theoretical model which used the Gibbs Duhem relation to predict the excess free energy (g^{ex}) of the ionic/nonionic mixed micelle. The relevant equation is,

$$g^{ex} = X_{Ma} \ln f_1 + (1 - X_{Ma}) \ln f_2 \quad (20)$$

where X_{Ma} is the micellar mole fraction according to this model, f_1 and f_2 hold the same rationale as before. X_{Ma} can be calculated by plotting $\ln(\text{cmc})$ vs. α_1 using the relation,

$$X_{Ma} = \frac{\alpha_1 \left[1 - (1 - \alpha_1) \left(\frac{\partial(\ln cmc)}{\partial \alpha_1} \right) \right]}{\left[1 + \nu(1 - \alpha_1) \left\{ \alpha_1 \left(\frac{\partial(\ln cmc)}{\partial \alpha_1} \right) + 1 \right\} \right]} \quad (21)$$

The degree of counter ion binding (ν) is negligible in our case in the aqueous medium and the equation then becomes

$$X_{Ma,(\nu=0)} = \alpha_1 \left[1 - (1 - \alpha_1) \left(\frac{\partial(\ln cmc_{mix})}{\partial \alpha_1} \right) \right] \quad (22)$$

The activities of the components 1 and 2 are given by,

$$a_1 = X_{Ma} f_1 = \alpha_1 (cmc_{mix} / C_1)$$

and

$$a_2 = (1 - X_{Ma}) f_2 = (1 - \alpha_1) (cmc_{mix} / C_2)$$

β^{Ma} can be calculated from,

$$\beta^{Ma} = g^{ex} / [X_{Ma} (1 - X_{Ma})] \quad (23)$$

Table 6 shows the X_{Ma} , f_1 , f_2 , g^{ex} , and β^{Ma} values obtained from the present analysis.

It is observed that X_{Ma} does not follow any trend with α_1 up to $\alpha_{LDS} = 0.6$ but beyond this composition, it increases with α_1 . The value of f_1 increases up to $\alpha_{LDS} = 0.6$ and then it decreases, but f_2 follows a reverse trend. The value of g^{ex} initially decreases and then increases at higher mole fraction of LDS. β^{Ma} is composition independent. Similar trend is observed in case of the thermodynamic parameters (g^{ex} and β^{Ma}). In all cases, however, X_{Ma} is much lower than α_1 .

SPB model

Another thermodynamic theory developed by Blankschtein *et al.*^{26, 27} (referred to as the SPB model) also predicts quantitatively the cmc , micellar composition, shape, and phase behavior on the basis of hydrophobic, structural, and electrical interactions between the binary components. Thus, Clint equation is written in the form,

$$(1/cmc_{mix}) = (\alpha_1 / f_1 cmc_1) + ((1 - \alpha_1) / f_2 cmc_2) \quad (24)$$

In the above equation, the f terms represent the activity coefficients of the surfactants in the mixed micelle and are expressed by the relations given below,

$$f_1 = \exp \left\{ \left[\beta_{12} (1 - \alpha^*)^2 \right] / kT \right\} \quad (25)$$

and

$$f_2 = \exp\left\{\beta_{12} (\alpha^*)^2 / kT\right\} \quad (26)$$

where β_{12} is the predicted interaction parameter between surfactants 1 and 2, α^* is the optimal micellar composition (denoted by X_{SPB} , where the free energy of mixed micellization reaches its minimum value). The following equation,

$$\frac{\beta_{12}(1-2\alpha^*)}{kT} + \ln\left(\frac{\alpha^*}{1-\alpha^*}\right) = \ln\left(\frac{\alpha_1 \text{cmc}_2}{(1-\alpha_1)\text{cmc}_1}\right) \quad (27)$$

is solved iteratively to obtain α^* and β_{12} and by using these values, f terms can be calculated according to equations 25 and 26. It is observed from Table 7 that X_{SPB} increases with increasing α_1 for all the binaries and that the X_{SPB} values are much lower than α_1 values. In most of the compositions of all mixtures, X_{SPB} is lower than X_{R} , X_{Mo} or X_{G} . In the LDS/TX-100 and LDS/Bj-35 combinations, $\beta_{\text{SPB}} < \beta_{\text{R}}$ (in most cases) and the negative values of β_{SPB} indicate an attractive interaction. In the case of TX-100/Bj-35 system, positive β_{SPB} values manifest repulsive interaction between the surfactants. The activity coefficients of the surfactants in nonionic systems are unity while these values of LDS are very low compared to those of TX-100 and Bj-35 for other two combinations. In case of ionic/nonionic systems, the activity coefficients of nonionic surfactants are nearly unity according to Rubingh, Maeda and SPB methods. The cmc values of TX-100/Bj-35 mixtures obtained from the SPB model are lower than those obtained experimentally excepting for $\alpha_{\text{TX-100}} = 0.9$ and higher than those obtained by the Clint approach. Again, in case of ionic/nonionic combinations, the cmc values follow the reverse order ($\text{obs} < \text{SPB} < \text{Clint}$). There are more deviations of the cmc values found in case of LDS/TX-100 mixtures particularly at higher mole fractions of LDS denoting the presence of non-ideality for mutual interaction of amphiphiles in the micelle. This deviation of cmc is the limitation of SPB theory.

CONCLUSIONS

The experimental *cmc* values of TX-100/Bj-35 mixtures are higher than those predicted from Clint equation, while the reverse trend is observed for LDS/TX-100 and LDS/Bj-35 combinations indicating the presence of non-ideality in these micelles. This is also true for the ternary combinations. Here, the behavior of mixed micelle is also interpreted theoretically. The mole fraction of a particular component in the micelle is generally lower than the stoichiometric mole fraction of that component indicating that the extent of transfer of that component (surfactant) from solution into micelle is very low. The binary systems LDS/TX-100 and LDS/Bj-35 demonstrate synergistic interaction due to the indirect interaction between dodecylsulphate ions of LDS and ether oxygen atoms of TX-100 or Bj-35 through the Li^+ counter ions.

Clint model is an idealization which neglects the interactions among different surfactants in the aggregated state. Rubingh model treats mixed micelle as regular solution which is questionable when the counterion condensation at micellar interface is considered in presence of ionic surfactants. Motomura model considers mixed micelle as a macroscopic phase and the micellar mole fraction and activity coefficients are defined in terms of excess thermodynamic quantities with reference to the spherical dividing surface which makes the excess number of water molecules outside the dividing surface equal to zero. With the advent of newer physicochemistry and their continuous modification, the theoretical hierarchy turned more realistic. The variation in the molecular interaction parameters following different theories arises either from oversimplification of some assumption necessary for the development of the theory or from a continuous source of discrepancy arising out of different scaling in different theories.

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TABLE-1

Critical Micellar Concentration^a (*cmc*) of Pure, Binary and Ternary Mixtures of Surfactants at 298.15 K.

α_{TX-100} (I) or α_{LDS} (II)	S.T	Cond.	Spectro.	Av. <i>cmc</i>	Clint <i>cmc</i>
TX-100 / Bj-35 (10^4 <i>cmc</i> / mol dm ⁻³) (I)					
0.0	0.49	-	0.49	-	-
0.1	0.63	-	1.45	0.53	0.53
0.2	0.81	-	1.57	0.58	0.58
0.3	0.99	-	1.62	0.64	0.64
0.4	1.05	-	1.67	0.71	0.71
0.5	1.12	-	1.73	0.79	0.79
0.6	1.32	-	1.77	0.90	0.90
0.7	1.51	-	1.82	1.05	1.05
0.8	1.62	-	1.86	1.26	1.26
0.9	1.79	-	1.96	1.57	1.57
1.0	2.07	-	2.07	-	-
LDS / TX-100 (10^4 <i>cmc</i> / mol dm ⁻³) (II)					
0.0	2.07	-	-	2.07	-
0.1	1.86	1.70	-	1.78	2.29
0.2	1.95	1.78	-	1.86	2.57
0.3	2.20	2.22	-	2.21	2.92
0.4	2.35	2.48	-	2.41	3.38
0.5	2.57	2.59	-	2.58	4.02
0.6	3.21	3.08	-	3.15	4.96
0.7	3.82	3.27	-	3.55	6.46
0.8	4.96	4.89	-	4.93	9.28
0.9	8.40	7.58	-	7.99	16.4
1.0	71.61	71.61	-	71.61	-
LDS / Bj-35 (10^4 <i>cmc</i> / mol dm ⁻³) (II)					
0.0	0.49	-	-	0.49	-
0.1	0.51	0.51	-	0.51	0.54
0.2	0.52	0.55	-	0.54	0.61
0.3	0.66	0.63	-	0.64	0.70
0.4	0.70	0.65	-	0.68	0.81
0.5	0.72	0.69	-	0.71	0.97
0.6	0.86	0.73	-	0.80	1.21
0.7	1.03	0.80	-	0.92	1.61
0.8	1.18	1.15	-	1.16	2.38
0.9	2.43	2.40	-	2.42	4.62
1.0	71.61	71.61	-	71.61	-

^aThe average uncertainty in *cmc* is ± 3 %.

TABLE-2

Critical Micellar Concentration^a (*cmc*) of Ternary Mixtures of Surfactants at 298.15

K.

$\alpha_{LDS} / \alpha_{TX-100} / \alpha_{Bj-35}$	S.T.	Cond.	Spectro.	Av. <i>cmc</i> (Clint <i>cmc</i>)
		$10^4 \text{ cmc} / \text{mol dm}^{-3}$		
0.125 / 0.250 / 0.625	0.99	1.00	1.11	1.00 (0.72)
0.125 / 0.625 / 0.250	1.16	0.96	1.46	1.06 (1.23)
0.250 / 0.125 / 0.625	0.98	0.98	1.20	0.98 (0.75)
0.250 / 0.625 / 0.125	1.59	1.34	1.52	1.46 (1.79)
0.333 / 0.333 / 0.333	1.24	0.97	1.60	1.10 (1.19)
0.625 / 0.125 / 0.250	1.60	1.58	1.79	1.59 (1.73)
0.625 / 0.250 / 0.125	2.05	1.98	1.94	2.02 (2.61)

^aThe average uncertainty in *cmc* is ± 3 %.

TABLE-3

Interfacial Parameters and Counterion Binding of Pure and Binary Surfactant Combinations at 298.15 K.

α_{TX-100} (I) or α_{LDS} (II)	10^3 $\Pi_{cmc} /$ $J m^{-2}$	10^6 $\Gamma_{max} /$ $mol m^{-2}$	$A_{min} /$ $nm^2/molecule^{-1}$	g	$-\Delta G_m^0 /$ $kJ mol^{-1}$	$-\Delta G_{ad}^0 /$ $kJ mol^{-1}$	pC_{20}	(cmc/C_{20})
TX-100 / Bj-35 (I)								
0.0	29.2	2.15	0.77	-	34.56	48.14	5.04	5.43
0.1	30.9	1.79	0.93	-	33.93	51.22	5.20	16.48
0.2	32.0	1.99	0.84	-	33.31	49.43	5.14	16.43
0.3	33.0	2.05	0.81	-	32.81	48.91	5.10	15.23
0.4	34.1	2.06	0.81	-	32.67	49.24	5.08	15.03
0.5	34.9	2.18	0.76	-	32.51	48.49	5.02	14.56
0.6	36.2	2.28	0.73	-	32.10	48.01	5.03	15.64
0.7	37.1	2.47	0.67	-	31.77	46.81	4.98	16.43
0.8	37.6	2.47	0.67	-	31.59	46.81	4.96	15.41
0.9	38.6	2.70	0.61	-	31.35	45.62	4.87	13.57
1.0	39.5	2.95	0.59	-	30.98	44.37	4.84	14.26
LDS / TX-100 (II)								
0.0	39.5	2.95	0.56	-	30.98	44.37	4.84	14.26
0.1	38.8	8.39	0.20	0.08	33.87	38.49	4.11	2.30
0.2	38.6	7.27	0.23	0.11	34.52	39.83	4.15	2.81
0.3	38.1	6.69	0.25	0.15	35.45	41.14	4.12	2.95
0.4	37.5	6.33	0.26	0.20	36.96	42.89	4.14	3.10
0.5	37.0	6.00	0.28	0.23	37.44	43.60	4.14	3.54
0.6	37.0	5.58	0.30	0.25	37.43	44.06	4.03	3.38
0.7	36.8	5.42	0.31	0.26	37.36	44.14	3.95	3.19
0.8	36.2	5.32	0.31	0.27	36.62	43.43	3.80	3.08
0.9	35.8	5.08	0.33	0.28	35.38	42.42	3.58	3.04
1.0	28.0	3.22	0.52	0.33	29.53	38.21	2.69	4.42
LDS / Bj-35 (II)								
0.0	29.2	2.15	0.77	-	37.56	48.14	5.04	5.43
0.1	29.2	6.27	0.26	0.09	38.54	42.22	4.55	1.79
0.2	28.9	6.16	0.27	0.12	37.16	43.23	4.57	1.91
0.3	30.0	6.01	0.28	0.10	37.88	42.15	4.41	1.71
0.4	28.3	5.88	0.28	0.12	38.01	42.69	4.41	1.71
0.5	28.0	5.68	0.29	0.13	38.14	42.94	4.42	1.85
0.6	28.3	5.43	0.31	0.15	38.06	43.35	4.30	1.74
0.7	28.3	5.25	0.32	0.16	39.09	43.45	4.16	1.45
0.8	27.4	5.09	0.33	0.20	37.32	44.47	4.17	1.61
0.9	27.6	4.98	0.33	0.22	37.56	42.86	3.87	1.81
1.0	28.0	3.22	0.52	0.33	29.53	38.21	2.69	4.42

TABLE-4

Interfacial and Thermodynamic^a Parameters of Ternary Combinations of LDS, TX-100 and Brij-35 at 298.15 K.

$\alpha_{LDS} / \alpha_{TX-100} / \alpha_{Brij-35}$	$10^3 \Pi_{cmc} / \text{J m}^{-2}$	$10^7 \Gamma_{max} / \text{mol m}^{-2}$	$A_{min} / \text{nm}^2 \text{ molecule}^{-1}$	g	$-\Delta G_m^0 / \text{kJ mol}^{-1}$	$-\Delta G_{ad}^0 / \text{kJ mol}^{-1}$	pC_{20}	cmc/C_{20}
0.125 / 0.250 / 0.625	32.90	2.24	0.74	0.15	37.72	52.42	5.00	10.28
0.125 / 0.625 / 0.250	36.10	2.72	0.61	0.20	39.17	52.46	4.96	10.85
0.250 / 0.125 / 0.625	32.30	1.96	0.85	0.06	34.81	51.32	5.10	13.25
0.250 / 0.625 / 0.125	37.15	2.62	0.63	0.13	35.98	50.16	4.92	12.45
0.333 / 0.333 / 0.333	33.90	2.31	0.72	0.10	35.80	50.47	4.94	11.14
0.625 / 0.125 / 0.250	32.10	2.19	0.76	0.12	35.44	50.08	4.76	9.57
0.625 / 0.250 / 0.125	34.20	2.40	0.69	0.13	35.09	49.34	4.71	10.14

^aThe average uncertainty in each of ΔG_m^0 , and ΔG_{ad}^0 are $\pm 3\%$.

TABLE-5

Molecular Interaction Parameters of Binary Mixtures in Aqueous Medium and 298.15

K

$\alpha_{\text{TX-100}} \text{ (I) or}$ $\alpha_{\text{LDS}} \text{ (II)}$	Rosen Model		Rubingh Model			Motomura Model		Georgiev Model
	X_1^σ	β^σ	X_R	β^R	f_1 / f_2	X_{Mo}	f_i	X_G
			TX-100 / Bj-35 (I)					
0.1	0.32	0.78	-	-	0.11/0.90	0.01	0.46	0.08
0.2	0.34	0.93	-	-	0.31/0.96	0.07	0.49	0.12
0.3	0.30	2.35	-	-	0.64/0.99	0.12	0.46	0.17
0.4	0.29	3.26	-	-	7.30/1.00	0.21	0.46	0.24
0.5	0.63	3.33	-	-	2.43/1.01	0.32	0.50	0.32
0.6	0.72	5.35	-	-	2.69/1.02	0.44	0.50	0.41
0.7	0.78	10.53	0.09	2.08	5.05/1.02	0.58	0.59	0.54
0.8	0.88	18.90	0.47	1.01	1.31/1.22	0.71	0.56	0.69
0.9	0.95	26.33	0.75	0.65	1.06/2.21	0.85	0.59	0.86
			LDS / TX-100 (II)					
0.1	0.05	-3.62	0.14	-5.44	0.02/0.90	0.17	1.08	0.21
0.2	0.15	-5.30	0.15	-4.58	0.04/0.90	0.24	1.01	0.36
0.3	0.14	-4.36	0.16	-4.12	0.05/0.90	0.25	1.02	0.43
0.4	0.20	-5.27	0.21	-4.53	0.06/0.82	0.16	0.77	0.59
0.5	0.23	-5.46	0.23	-4.23	0.08/0.80	0.10	0.69	0.49
0.6	0.20	-3.91	0.24	-3.83	0.11/0.80	0.01	0.61	0.49
0.7	0.24	-4.00	0.28	-4.10	0.12/0.73	0.17	0.62	0.52
0.8	0.25	-3.13	0.31	-3.70	0.17/0.70	0.43	0.84	0.54
0.9	0.31	-2.83	0.38	-3.39	0.27/0.61	0.80	1.90	0.64
			LDS / Bj-35 (II)					
0.1	0.14	-7.03	0.05	-4.76	0.01/0.99	0.27	1.29	0.26
0.2	0.20	-7.68	0.09	-4.84	0.02/0.96	0.31	1.23	0.30
0.3	0.11	-4.35	0.07	-3.75	0.04/0.98	0.06	1.02	0.39
0.4	0.17	-5.35	0.12	-4.38	0.03/0.94	0.02	0.83	0.43
0.5	0.18	-4.76	0.17	-5.06	0.03/0.86	0.11	0.81	0.46
0.6	0.20	-4.85	0.20	-5.26	0.03/0.81	0.32	1.03	0.47
0.7	0.19	-3.74	0.24	-5.57	0.04/0.73	0.51	1.23	0.50
0.8	0.29	-5.58	0.27	-5.76	0.05/0.66	0.68	1.41	0.52
0.9	0.32	-4.59	0.29	-4.43	0.11/0.69	0.90	1.01	0.57

TABLE-6

Free Energy and Interaction Parameters of Ionic / Nonionic Binary Mixtures Obtained from Maeda Models in Aqueous Medium at 298.15 K^a

α_{LDS}	Maeda Model ²⁴				Maeda Model ²⁵				
	$-B_0$	B_1	$-B_2$	$-\Delta G_{\text{Ma}}^0$	X_{Ma}	f_1	f_2	$-g^{\text{ex}}$	β^{Ma}
LDS / TX-100									
0.1		9.21	5.44	28.84	0.11	0.02	0.86	0.55	-5.82
0.2		8.35	4.58	27.30	0.14	0.03	0.83	0.64	-5.39
0.3		7.89	4.12	26.03	0.13	0.06	0.86	0.50	-4.48
0.4		8.30	4.53	24.55	0.10	0.11	0.78	0.45	-5.02
0.5	12.50	8.00	4.23	23.69	0.08	0.18	0.68	0.50	-6.74
0.6		7.60	3.83	23.10	0.09	0.24	0.67	0.50	-6.11
0.7		7.87	4.10	22.31	0.17	0.17	0.62	0.70	-5.04
0.8		7.47	3.70	22.04	0.33	0.13	0.71	0.89	-4.04
0.9		7.16	3.39	21.82	0.59	0.13	0.95	1.21	-5.03
LDS / Bj-35									
0.1		9.97	4.76	32.20	0.15	0.004	1.10	0.73	-5.87
0.2		10.05	4.84	30.05	0.20	0.006	1.10	0.94	-5.90
0.3		8.96	3.75	28.73	0.19	0.011	1.13	0.77	-4.94
0.4		9.59	4.38	26.78	0.15	0.020	0.98	0.61	-4.74
0.5	13.94	10.27	5.06	24.96	0.11	0.036	0.81	0.55	-5.60
0.6		10.47	5.26	23.68	0.11	0.050	0.73	0.60	-6.29
0.7		10.78	5.57	22.61	0.16	0.045	0.67	0.83	-6.21
0.8		10.97	5.76	21.94	0.30	0.034	0.68	1.30	-6.13
0.9		9.64	4.43	21.94	0.57	0.042	1.16	1.75	-7.17

^a ΔG_{Ma}^0 in kJ mole⁻¹ unit.

TABLE-7

Micellar Compositions (X_{SPB}), Interaction Parameter [$\beta_{SPB}(kT)$], Activity Coefficient (f), and cmc s of Binary Mixtures at 298.15 K at Different Stoichiometric Compositions (X).

α_{TX-100} (I) or α_{LDS} (II)	X_{SPB}	β_{SPB} (kT)	f_1	f_2	$10^4 cmc/(mol dm^{-3})$ Obs/SPB/Clint
TX-100 / Bj-35 (I)					
0.1	0.03	0.21	1.22	1.00	0.63/0.53/0.53
0.2	0.06	0.38	1.40	1.00	0.81/0.59/0.58
0.3	0.09	0.54	1.56	1.00	0.99/0.66/0.64
0.4	0.14	0.54	1.49	1.01	1.05/0.74/0.71
0.5	0.19	0.53	1.41	1.02	1.12/0.85/0.79
0.6	0.26	0.70	1.46	1.05	1.32/1.02/0.90
0.7	0.36	0.87	1.43	1.12	1.51/1.28/1.05
0.8	0.49	0.96	1.29	1.25	1.62/1.60/1.26
0.9	0.68	1.32	1.14	1.84	1.79/2.04/1.57
LDS / TX-100 (II)					
0.1	0.07	-3.99	0.03	1.00	1.78/2.09/2.29
0.2	0.11	-4.10	0.04	1.00	1.98/2.16/2.57
0.3	0.14	-4.02	0.05	1.00	2.21/2.32/2.92
0.4	0.17	-4.16	0.07	1.00	2.23/2.47/3.38
0.5	0.20	-4.12	0.08	1.00	2.58/2.76/4.02
0.6	0.23	-4.02	0.11	1.00	3.15/3.21/4.96
0.7	0.26	-4.13	0.15	1.00	3.55/3.76/6.46
0.8	0.30	-4.00	0.20	1.00	4.93/4.97/9.28
0.9	0.37	-3.85	0.37	1.00	7.99/7.82/16.4
LDS / Bj-35 (II)					
0.1	0.03	-4.03	0.02	1.00	0.51/0.53/0.54
0.2	0.05	-4.08	0.02	1.00	0.54/0.58/0.61
0.3	0.07	-3.93	0.03	1.00	0.64/0.64/0.70
0.4	0.09	-4.09	0.03	1.00	0.68/0.71/0.81
0.5	0.11	-4.18	0.04	1.00	0.71/0.82/0.97
0.6	0.13	-4.16	0.04	1.00	0.80/0.97/1.21
0.7	0.16	-4.28	0.06	1.00	0.92/1.19/1.61
0.8	0.20	-4.65	0.06	1.00	1.16/1.50/2.38
0.9	0.26	-4.25	0.13	1.00	2.42/2.67/4.62

CHAPTER-VI

Physicochemistry of Mixed Micellization: Binary and Ternary Mixtures of Cationic Surfactants in Aqueous Medium

INTRODUCTION

Mixed aqueous surfactant systems often exhibit better performance over the individual components^{1,2} in terms of lowering of surface tension of aqueous solution. These systems are, thus, capable of exhibiting enhanced detergency and solubilizing capacity for insoluble substances in aqueous solution, and are widely used in the areas of suspension, wetting, emulsification, and different technological, biochemical, pharmaceutical applications³. The molecular structures of amphiphiles, their concentration, and composition along with the environmental conditions, such as temperature, *pH*, pressure, presence of additives³ significantly influence the activity of the surfactant mixtures.

Owing to their amphiphilic nature, surfactants prefer to get adsorbed interfacially in the low concentration region; whereas above a certain critical concentration, they self-aggregate to form assembled structure. The size, shape and composition of these aggregated structures depend on the amphiphile concentration and other physicochemical parameters like temperature, presence of salt, etc. The critical amphiphile concentration required for the onset of formation of such aggregates (known as micelles) is referred to as the critical micellar concentration (*cmc*). Because micelles can be treated to form a separate phase within a surfactant solution, various physicochemical properties could, therefore, change dramatically depending upon whether the micelles are formed or not. Measurement of such properties with varying surfactant concentration leads to a discontinuity in the profile which allows the determination of *cmc* of the surfactant. The properties generally exploited in *cmc* determination include surface tension⁴⁻⁹, conductance⁴⁻⁹,

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fluorescence intensity¹⁰, heat capacity^{11, 12}, light scattering¹³. The changes in these properties occur over a narrow range of surfactant concentration. Moreover, the concentration dependent changes in these properties in the pre- and postmicellar regions can be described by two separate straight lines and their point of intersection may be taken as the *cmc* of the surfactant.

Investigations on the interactions between the surfactants in a mixture could provide valuable information regarding the self-aggregation and association thermodynamics in such systems¹⁴⁻³¹. In this chapter, studies on the binary and ternary combinations of three cationic surfactants namely, dodecylpyridinium chloride (DPC), cetylpyridinium chloride (CPC), and tetradecyltrimethylammonium bromide (TTAB) have been reported. The first two (DPC and CPC) have the same pyridinium head groups and different tail lengths (12 and 16 C) whereas TTAB has a methyl substituted quaternary ammonium head group linked with a 14 C tail. Three binary combinations, CPC/TTAB, DPC/TTAB and CPC/DPC and the ternary mixture of CPC/DPC/TTAB have been studied using tensiometry and conductometry. Various parameters such as *cmc*, Gibbs surface excess (Γ_{\max}), minimum area of exclusion per surfactant monomer at the air/solution interface (A_{\min}), pC_{20} (where C_{20} is the surfactant concentration required to decrease the surface tension of the solvent by 20 units), degree of counterion binding (g) on micellar interface along with such thermodynamic parameters as Gibbs adsorption energy (ΔG_{ad}^0), Gibbs micellization energy (ΔG_{m}^0), can be obtained by using these two methods. Existing theories of Clint³², Rosen^{33, 34}, Rubingh³⁵, Motomura³⁶⁻³⁷, Blankshtein³⁸⁻⁴⁰, Rubingh and Holland⁴¹ are applied to evaluate the theoretical *cmc*, micellar and interfacial mole fractions and interaction parameters among the surfactants in micellar and interfacial monolayer, surface free energy, activity coefficient, etc.

EXPERIMENTAL

Materials and Methods

The cationic surfactants dodecylpyridinium chloride (DPC), cetylpyridinium chloride (CPC), and tetradecyltrimethylammonium bromide (TTAB) were purchased from Sigma (USA). All the products were used without further purification. The solutions were prepared in doubly distilled water and the experiments were performed at 298.15K.

The tensiometric experiments are performed using a platinum ring by the ring detachment method in a calibrated K9 Tensiometer (Krüss, Germany) details of which have been reported in Chapter II. Each experiment was repeated several times to achieve good reproducibility. The measured surface tension (γ) values were corrected according to the procedure of Harkins and Jordon. The uncertainties in the γ values were always within $\pm 0.1 \text{ mN m}^{-1}$.

The conductance measurements were done with a Pye-Unicam PW-9509 conductivity meter at a frequency of 2000 Hz using a conductivity cell of cell constant 1.0 cm^{-1} . The uncertainty of the measurements was within $\pm 0.1\%$. The measurement details can be found in Chapter II.

RESULTS AND DISCUSSION

Critical micellar concentration (cmc) determination

The *cmc* obtained tensiometrically corresponds to the surfactant concentration at which there is a distinct break in the air/solution interfacial tension vs. $\log[\text{surfactant}]$ isotherms (Fig. 1). Phenomenologically, this *cmc* corresponds to the saturation of interfacial adsorption. Beyond this concentration, the added surfactant molecules can hardly affect the topology of the interfacially adsorbed surfactant monolayer rather they prefer to self-associate in the bulk solution to form micelles whereby the hydrophobic tails of individual surfactant monomers are buried within hydrophilic encapsulation provided by their polar head groups^{5, 23}. On initiation of the self-association, the counterions of ionic surfactants with significantly large mobility start to adsorb onto the micelle-solution interface. This leads to a dramatic change in the electrical transport property of the solution as a result of a decrease in the number of effective charge carriers in solution and is reflected in a sharp break in the specific conductance (κ) vs. surfactant concentration isotherm (Fig. 2). The conductometric *cmc*, therefore, corresponds to the initiation of self-association of ionic surfactants in bulk solution. If the interfacial saturation and bulk association processes are coherent, the *cmc* values obtained by either method should agree with each other.

For all the pure surfactants, *cmc* determined by either method are found to be in close agreement with each other (*cf.* Tables 1 and 2). The *cmc* values were found to

increase as the tail length of the surfactants decreases. Although, CPC and DPC have the same pyridinium head groups, their *cmc* differs by a factor of ~ 19 reflecting that the hydrophobic interaction predominates over the electrostatic interaction in the micellization process.

For CPC/TTAB and DPC/TTAB binary systems, the *cmc* values obtained from conductometry and tensiometry are in reasonable agreement whereas for CPC/DPC mixed system, the tensiometric *cmc* is found to be much lower than that determined by conductometry signifying a concentration delay (lag) between interfacial saturation and self-aggregation processes. In all the mixtures, the *cmc* values are close to the component with higher tail length (lower *cmc*) and these increase with increasing stoichiometric mole fraction of the shorter-tail-component in the mixture. A detailed discussion on this aspect has been made in the theoretical section (see later).

Interfacial adsorption

The process of interfacial adsorption is mainly entropy-driven whereby there is an expulsion of water molecules solvating the monomer in bulk solution through hydrophobic hydration on micellization. In some cases, exothermic enthalpy change associated with the micellization process adds to the entropic effect to make the process thermodynamically spontaneous. The onset of interfacial saturation can be envisaged from a sharp break in the tensiometric isotherm beyond which the interfacial tension remains almost invariant with surfactant concentration. The interfacial tension at the point of *cmc* (γ_{cmc}) is a measure of efficacy of the surfactant to reduce the interfacial tension of the solution in the form of a monolayer. The same for a surfactant or a mixture of surfactants toward interfacial adsorption is quantified by the Gibbs surface excess (Γ_{max}) at the air/water interface and can be calculated using the least-squares slope of Π vs. $\log C$ plot^{4-10, 42} using Eq. (1)

$$\Gamma_{max} = -\frac{1}{2.303nRT} \text{Lt}_{C \rightarrow cmc} \frac{d\Pi}{d \log C} \quad (1)$$

where Π is the surface pressure ($\gamma_{H_2O} - \gamma_{surfactant}$), R is the universal gas constant, T is the absolute temperature, and n is the average number of ions present in solution per

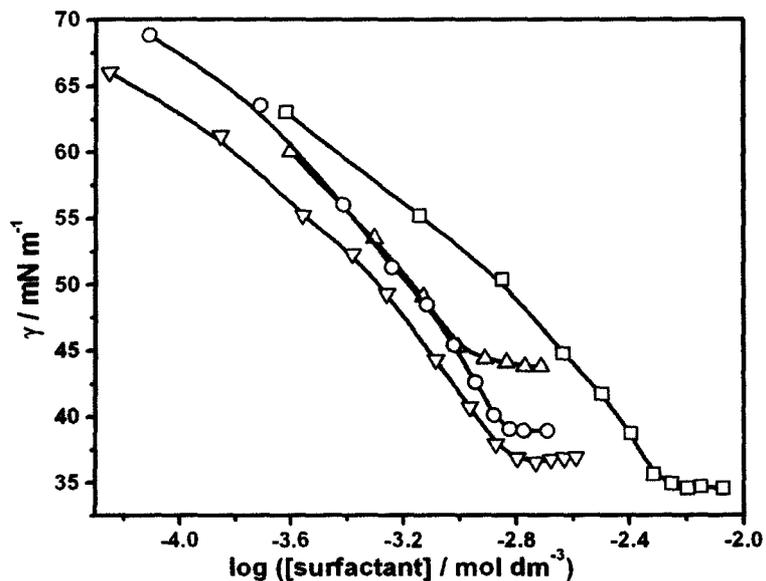


Figure 1. Tensiometric plot of binary mixtures (∇) CPC/TTAB, $\alpha_{\text{CPC}} = 0.25$; (\square) DPC/TTAB, $\alpha_{\text{DPC}} = 0.4$; (Δ) CPC/DPC, $\alpha_{\text{CPC}} = 0.9$; and ternary mixtures (\circ) DPC/CPC/TTAB (0.333/0.333/0.333) at 298.15K.

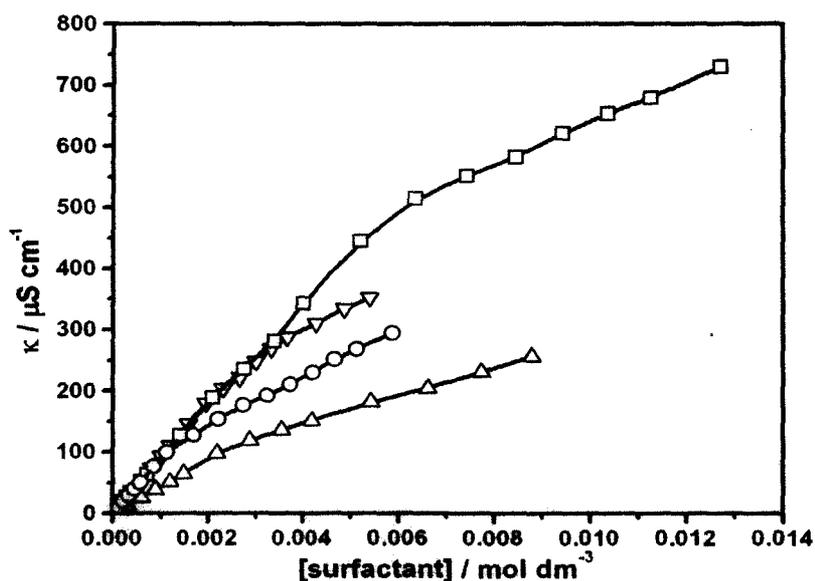


Figure 2. Conductometric plot of binary mixtures (∇) CPC/TTAB, $\alpha_{\text{CPC}} = 0.1$; (\square) DPC/TTAB, $\alpha_{\text{DPC}} = 0.4$; (Δ) CPC/DPC, $\alpha_{\text{CPC}} = 0.75$; and ternary mixtures (\circ) DPC/CPC/TTAB (0.125/0.625/0.250) at 298.15K.

surfactant monomer. Here, n is taken as unity for pure surfactants, their binary and ternary mixture, *i.e.*, the contribution of counterions of cationic surfactants has been neglected. Its estimation from the knowledge of counterion condensation at the micellar interface seems to be a crude approximation due to the large discrepancy in radius of curvature, which significantly affect the counterion condensation between the micellar interface and the air/solution interface. C is the total molar surfactant concentration⁶.

The area of exclusion (A_{\min}) per surfactant monomer at complete saturation of air/water interface near *cmc* can be calculated using the equation,

$$A_{\min} = \frac{10^{18}}{N_A \Gamma_{\max}} \quad (2)$$

where the factor 10^{18} arises out of conversion from m to nm and N_A is the Avogadro's number. Γ_{\max} and A_{\min} are expressed in $\text{mol } m^{-2}$ and $nm^2 \text{ molecule}^{-1}$ units, respectively.

C_{20} is the surfactant concentration³⁶ required to reduce the surface tension of water by $20 \text{ mN } m^{-1}$ and negative logarithm of C_{20} is called pC_{20} . The higher the surface activity of a surfactant, the smaller is the C_{20} value. The cmc/C_{20} ratio dictates the preference of a surfactant blend toward micellization compared to interfacial adsorption^{35, 43}.

The values of Π_{cmc} , Γ_{\max} , pC_{20} and cmc/C_{20} of the pure surfactants as well as their binary and ternary mixtures are shown in Tables 3 and 4. Among the pure surfactants TTAB has the lowest γ_{cmc} value ($34.1 \text{ mN } m^{-1}$) followed by DPC ($39.4 \text{ mN } m^{-1}$) and CPC ($44.3 \text{ mN } m^{-1}$). The Γ_{\max} value increases with increasing tail length and eventually A_{\min} decreases with increasing tail length. The pC_{20} values also follow the same trend as Γ_{\max} as expected if the tensiometric isotherms are linear in the pre-micellar region. The increasing Γ_{\max} and pC_{20} values with increasing tail length is a consequence of increasing surface activity arising out of increasing hydrophobicity of the longer tail surfactant. The lowering in A_{\min} signifies greater compactness of the surfactant-saturated monolayer arising from an increased van der Waals attraction among the surfactant tails. The cmc/C_{20} value increases with decreasing chain length dictating the preference of the shorter-tailed surfactant toward micellization over interfacial adsorption. The ratio of the slopes of pre- to

postmicellar regions of the specific conductance (κ) vs. the surfactant concentration (c) plot gives an estimate of the fraction of counterions condensed (g)^{4,7-10, 23}. The g values for the single amphiphiles decrease in the order: TTAB<CPC<DPC. The lowering of g with decreasing tail length within a homologous series may originate from a change in micellar size.

For the CPC/TTAB mixtures, Π_{cmc} and A_{min} decrease with increasing amount of CPC; Γ_{max} , however, follows a reverse trend. There is a significant lowering in g for pure TTAB micelle even in the presence of a very small amount of CPC and g reaches a minimum at $\alpha_{CPC} = 0.5$; pC_{20} , on the other hand, reaches a maximum at $\alpha_{CPC} = 0.5$. For the DPC/TTAB blend, Π_{cmc} and Γ_{max} values pass through a maximum at around $\alpha_{DPC} = 0.4$. The pC_{20} values, however, follow no regular trend. The variation of g is found to be regular and it decreases with increasing stoichiometric proportion of DPC in the mixtures.

Π_{cmc} in CPC/DPC system slowly decreases while Γ_{max} increases with increasing α_{CPC} . The most important observation is that the g value of pure DPC is decreased drastically upon addition of CPC upto $\alpha_{CPC} = 0.5$. This indicates a decrease in surface charge density probably through stacking interaction among the π electron clouds which is operative only when there exists a disparity in the chain length of the surfactant. This lowers the extent of counterion condensation which destabilizes the micellar structure and can account for the concentration lag between interfacial saturation and bulk micellization in this system.

Energetics of micellization and interfacial adsorption

The standard free energy of micellization per mole of monomer unit (ΔG_m^0) for pure surfactants and their mixtures can be obtained from

$$\Delta G_m^0 = (1 + g) RT \ln X_{cmc} \quad (3)$$

where X_{cmc} is the cmc in mole fraction scale and the factor $(1 + g)$ accounts for the free energy contribution arising from the counterion condensation on micellar surface.

The standard free energy of interfacial adsorption (ΔG_{ad}^0) at the air/water interface can be obtained from the relation

$$\Delta G_{ad}^0 = \Delta G_m^0 - \left(\frac{\Pi_{cmc}}{\Gamma_{max}} \right) \quad (4)$$

where Π_{cmc} is the surface pressure at *cmc*.

The free energy changes associated with micellization (ΔG_m^0) and interfacial adsorption (ΔG_{ad}^0) for binary and ternary mixtures are given in Tables 3 and 4, respectively. The *g* values for binary mixtures of CPC/TTAB and DPC/TTAB are higher compared to those of CPC/DPC system. For ternary mixtures, *g* values are maximum for higher α_{CPC} and minimum for higher α_{DPC} . ΔG_m^0 values for CPC/TTAB and CPC/DPC systems increase with increasing α_{CPC} (Fig. 3), indicating that the micellization process becomes more and more spontaneous with CPC, but the reverse trend is observed in case of DPC/TTAB system. The values of ΔG_m^0 for the ternaries demonstrate that micellization becomes more favourable for mixtures richer in CPC. ΔG_{ad}^0 values follow the same trend as do the ΔG_m^0 values for CPC/TTAB, DPC/TTAB and for ternaries, but for CPC/DPC no such regularity is observed.

THEORETICAL SECTION

Clint Model

This model^{14, 32} predicts the *cmc* of mixed surfactant systems (cmc^C) with known composition from a knowledge of individual *cmcs* of the components according to the equation

$$\left(1/cmc^C\right) = \sum_{i=1}^n (\alpha_i / cmc_i) \quad (5)$$

Here, α_i denotes the stoichiometric mole fraction of the *i*th component in the solution. The terms cmc_i and cmc^C are the critical micellar concentrations of the *i*th component and the mixture, respectively. Any negative deviation of the experimental *cmc* from the calculated value (cmc^C) reflects an overall synergistic (attractive) interaction whereas overall antagonistic (repulsive) interaction is inferred from a positive deviation.

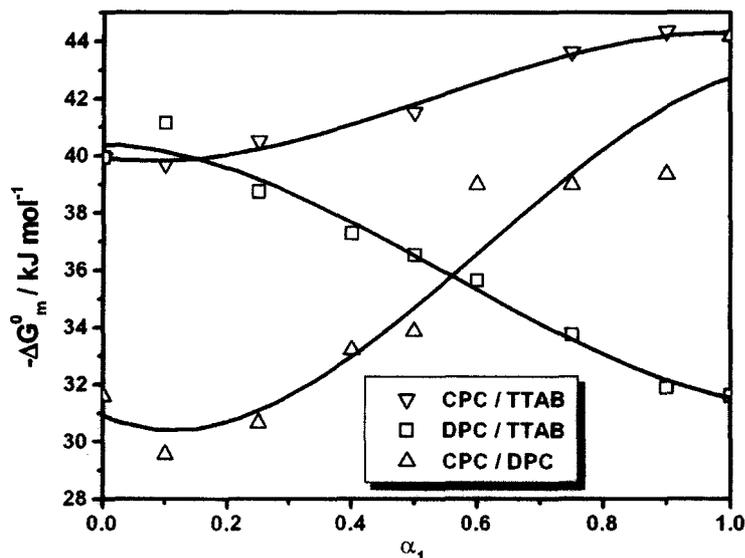


Figure 3. Variation of ΔG_m^0 as a function of composition in mixed binary systems at 298.15K.

It is observed from Table 1 that for DPC/TTAB and CPC/DPC binary systems, the Clint cmc s are lower than the average experimental cmc s whereas those for CPC/TTAB system are greater than the experimental ones indicating nonideality of these mixtures due to mutual interaction between the surfactants in the micelle. In the case of ternaries (Table 2), Clint cmc s do not follow any regular trend with the surfactant composition.

Rosen model

This model focuses on the adsorbed Langmuirian mixed surfactant film at the air/solution interface^{33, 34} and is basically an optimization algorithm. A closer resemblance with the experimental area of exclusion (A_{min}) is obtained from the A_{min} values of the respective pure components using computational iteration which leads to the mole fraction of the component (X_1^σ) and interaction parameter at the interface among the components (β^σ) as the optimization parameters. The two equations involved in the iteration procedure are,

$$\frac{(X^\sigma)^2 \ln[cmc_{\text{mix}} \alpha_1 / C_1^0 X^\sigma]}{(1 - X^\sigma)^2 \ln[cmc_{\text{mix}} (1 - \alpha_1) / C_2^0 (1 - X^\sigma)]} = 1 \quad (6)$$

and

$$\beta^\sigma = \frac{\ln[cmc_{\text{mix}} \alpha_1 / C_1^0 X^\sigma]}{(1 - X^\sigma)^2} \quad (7)$$

where cmc_{mix} , C_1^0 and C_2^0 are the molar concentrations of the mixture, pure surfactants 1 and 2 respectively at a fixed γ value corresponding to the tensiometric cmc of pure component 1 and α_1 is the stoichiometric mole fraction of surfactant 1 in solution.

The β^σ and X^σ values of the binary mixtures are presented in Table 5. The negative β^σ values for the three binaries investigated indicate synergistic interaction in these systems. The interaction parameter decreases regularly with increasing α_1 for CPC/TTAB and DPC/TTAB mixtures, but for CPC/DPC mixture, the values are highly irregular. Higher X^σ values compared to α_1 for all cationic/cationic system indicate that surfactant 1 would tend to be adsorbed preferentially at the air/water interface compared to surfactant 2. The X^σ values for CPC/DPC system are very much higher than the other two binaries (CPC/TTAB and DPC/TTAB) reflecting more surface activity of the former system.

Rubingh Model

Following this approach³⁵, the micellar mole fraction (X_R) of a surfactant in a mixed aggregated state and the molecular interaction parameter (β^R) can be obtained by solving Eqs. (8) and (9) iteratively:

$$\frac{(X_R)^2 \ln[cmc_{\text{mix}} \alpha_1 / cmc_1 X_R]}{(1 - X_R)^2 \ln[cmc_{\text{mix}} (1 - \alpha_1) / cmc_2 (1 - X_R)]} = 1 \quad (8)$$

and

$$\beta^R = \frac{\ln[cmc_{\text{mix}} \alpha_1 / cmc_1 X_R]}{(1 - X_R)^2} \quad (9)$$

where cmc_1 , cmc_2 , and cmc_{mix} are respectively the critical micellar concentrations of surfactants 1, 2, and their mixture at a mole fraction of α_1 .

The activity coefficients of surfactants 1 and 2 in the mixed micelle (f_1 and f_2) can be evaluated from the Eqs.

$$f_1 = \exp[\beta^R (1 - X_R)^2] \quad (10)$$

and

$$f_2 = \exp[\beta^R (X_R)^2] \quad (11)$$

The values of X_R , β_R , f_1 , and f_2 for the binary mixtures are listed in Table 5. It can be seen from this Table that for CPC/TTAB and CPC/DTAB mixtures, the micellar mole fraction (X_R) increases with increasing mole fraction of surfactant 1, while no such systematic variation of X_R is observed for CPC/DPC mixtures. For CPC/TTAB and CPC/DPC systems, the values of X_R are higher than those of α_{CPC} , but for DPC/TTAB mixtures, X_R values are always lower than the α_{CPC} values. For any given mole fraction of surfactant 1 in the three binary mixtures, X_R values increase in the order: DPC/TTAB < CPC/TTAB < CPC/DPC. A comparison of the X^σ and X_R values (Table 5) shows that DPC/TTAB mixtures have much greater X^σ values than X_R values thus indicating greater surface activity of the component DPC in the mixed state. On the other hand, for CPC/TTAB mixed micelles, X^σ values are slightly lower compared to X_R values (except at $\alpha_{CPC} = 0.1$) indicating equal or to some extent higher priority in surface saturation and micelle forming properties.

β_R values for all mixtures are negative (except at $\alpha_{CPC} = 0.25$ and 0.40 for CPC/DPC system) demonstrating synergistic interaction in these systems. This conclusion can also be drawn from the lower experimental *cmc* in most of the cases of these mixtures than the Clint *cmc*. For CPC/DPC binary mixtures, β_R values indicate antagonistic interaction among themselves. A comparison of the Clint *cmc* values for this system with those obtained experimentally also pointed to the same behavior.

Motomura Model

This model^{36, 37} considers mixed micelles as a macroscopic bulk phase from a thermodynamic point of view. Here, excess thermodynamic quantities are used to evaluate various energetic parameters. The fundamental equation is

$$X_{Mo} = \hat{X}_2 - \left(\hat{X}_1 \hat{X}_2 / \hat{cmc} \right) \left(\partial \hat{cmc} / \partial \hat{X}_2 \right)_{T,P} \quad (12)$$

where $\hat{X}_2 = \frac{v_2 \alpha_2}{v_1 \alpha_1 + v_2 \alpha_2}$ and $\hat{cmc} = (v_1 \alpha_1 + v_2 \alpha_2) cmc$

Subscripts 1 and 2 refer to surfactants 1 and 2, respectively, and α and ν represent the stoichiometric mole fraction and the number into which a surfactant molecule dissociates in solution. The micellar mole fractions (X_{Mo}) of a surfactant in the binary mixtures evaluated by Motomura equation are shown in Table 5.

According to this model³⁸, the mean activity coefficient of surfactant 1 in the micelle (f_1) is obtained from

$$\hat{X}_1 \hat{cmc} / cmc_1^0 = f_1 X_{1(Mo)} \quad (13)$$

and the f_1 values for all binary mixtures are shown in Table 5. For CPC/TTAB and CPC/DPC, X_{Mo} values are higher than the stoichiometric mole fraction of CPC. This signifies that for these two mixed surfactant systems, CPC prefers the micellar phase. On the other hand, for DPC/TTAB, the X_{Mo} values are always found to be lower than the α_{DPC} values. This indicates a greater affinity of TTAB toward micelle formation compared to DPC as expected from a lower cmc of TTAB than that of DPC. Motomura model is independent of the nature of surfactant and their counterions and predicts the micellar composition only.

SPB Model

Another thermodynamic theory developed by Blankschtein (SPB) *et al.*³⁸⁻⁴⁰ also predicts quantitatively the cmc , micellar composition, shape, and phase behavior on the basis of hydrophobic, structural, and electrical interactions between the binary components. Clint equation is written in the form,

$$\frac{1}{cmc_{mix}} = \frac{\alpha_1}{f_1 cmc_1} + \frac{1 - \alpha_1}{f_2 cmc_2} \quad (14)$$

where the f terms represent the activity coefficient of the surfactant in the mixed micelle and can be expressed by the following relations

$$f_1 = \exp \left[\frac{\beta_{12} (1 - \alpha^*)^2}{kT} \right] \quad (15)$$

and

$$f_2 = \exp \left[\frac{\beta_{12} (\alpha^*)^2}{kT} \right] \quad (16)$$

where β_{12} is the predicted interaction parameter between surfactants 1 and 2, α^* is the optimal micellar composition (denoted by X_{SPB} , where the free energy of mixed micellization reaches its minimum value). The following equation

$$\frac{\beta_{12}(1-2\alpha^*)}{kT} + \ln\left(\frac{\alpha^*}{1-\alpha^*}\right) = \ln\left(\frac{\alpha_1 \text{ cmc}_2}{(1-\alpha_1) \text{ cmc}_1}\right) \quad (17)$$

is solved iteratively to obtain α^* and β_{12} and by using these values, the activity coefficients can be calculated according to equations 15 and 16. It is observed from Table 6 that X_{SPB} increases with increasing α_1 for all the binaries and the X_{SPB} values are much lower than α_1 in DPC/TTAB, but much higher than α_1 in case of CPC/TTAB and CPC/DPC systems. In most of the compositions of all these mixtures, X_{SPB} is lower than X_{R} , X_{M_0} or X_{G} . In the CPC/TTAB mixtures, $\beta_{\text{SPB}} < \beta_{\text{R}}$ (in most cases) and negative values of β_{SPB} indicate attractive interaction. In the case of DPC/TTAB (excepting $\alpha_{\text{DPC}} = 0.9$) and CPC/DPC systems, positive β_{SPB} values denote repulsive interaction between the surfactants. In case of all binary systems, the activity coefficients of component 1 are found to be nearly unity following Rubingh, and SPB models. The *cmc* values of CPC/TTAB (excepting $\alpha_{\text{CPC}} = 0.1$) and DPC/TTAB mixtures obtained by the SPB method are lower than those obtained experimentally and more or less comparable with those obtained by the Clint theory. Again, in case of CPC/DPC combination, the *cmc* values follow the reverse trend (SPB > obs > Clint). Higher deviations in the *cmc* values found in case of CPC/DPC mixture particularly at lower mole fraction of CPC indicate nonideality for mutual interaction of amphiphiles in the micelle. This is a limitation of SPB theory.

Rubingh-Holland model

Theoretical treatment of surfactant mixtures with more than two components is very limited⁴¹. The theory of Rubingh and Holland⁴¹ (RH) has been properly tested to determine the micellar composition, activity coefficient and *cmc* of ternary systems. The activity coefficients of surfactants in a binary mixed micelle can be estimated from the relations 10 and 11. In a multicomponent mixture, the activity coefficients f_i, f_j, f_k, \dots of the mixed micelle-forming amphiphilic species i, j, k, \dots can be expressed by the RH equation⁴¹.

$$\ln f_i = \sum_{\substack{j=1 \\ (j \neq i)}}^n \beta_{ij} x_j^2 + \sum_{\substack{j=1 \\ (i \neq j \neq k)}}^n \sum_{k=1}^{j-1} (\beta_{ij} + \beta_{ik} - \beta_{jk}) x_j x_k \quad (18)$$

where β_{ij} denotes the net (pairwise) interaction between components i and j , and x_j is the mole fraction of the j th component in the micelles; β_{ik} , β_{jk} , and x_k have similar significance. Equation 19 is valid at the *cmc*.

$$x_i = \alpha_i C_j f_j x_j / (C_i \alpha_j f_i) \quad (19)$$

where the terms C_i and C_j represent *cmcs* of the i th and j th components, respectively, and α_i and α_j are the mole fractions of the i th and j th components in the micelle.

The average interaction parameter (β_{av}^R) values for the binary mixtures CPC/TTAB, DPC/TTAB, and CPC/DPC obtained from the equation of Rubingh (Eq. 9), were used in equation 18 to evaluate the activity coefficients f_1 , f_2 , and f_3 for the ternary system DPC/CPC/TTAB using the computer controlled "successive substitution" method. By putting the f value in equation 19, the *cmc* of the mixed micelle was found out. The mole fractions of the individual components (X^{RH}), the activity coefficients (f^{RH}), and the cmc^{RH} values thus obtained have been presented in Table 7. It is found that X_{DPC}^{RH} values are much higher than the stoichiometric mole fraction α_{DPC} (exception in 6th combination) and X_{CPC}^{RH} values are fairly lower than α_{CPC} values, whereas most of the X_{TTAB}^{RH} values are lower than α_{TTAB} values (exception lies in 4th, 6th, and 7th sets of combinations) demonstrating that the mixed micelles mainly consists of DPC. RH theory has already been applied to various combinations of surfactants, namely, ionic/nonionic/nonionic^{7, 8, 44, 45}, ionic/ionic/nonionic^{4, 46}, ionic/ionic/ionic^{47, 48}. The activity coefficient of CPC (f_{CPC}^{RH}) is close to unity, whereas f_{DPC}^{RH} is moderately high compared to f_{TTAB}^{RH} indicating that CPC and DPC control the activity of the third component. The *cmc* values obtained by RH method are higher than those obtained experimentally (except the 2nd combination). But in all cases, the Clint *cmcs* are higher than the experimental *cmcs* and those obtained from the Rubingh-Holland model indicating synergistic interactions in these ternary systems. The deviation of Rubingh-Holland *cmcs* from the experimental values points to the limitation of this theory for the present ternary system.

CONCLUSIONS

This chapter reports the mixed micellization behavior of three cationic surfactants cetylpyridinium chloride (CPC), tetradecyltrimethylammonium bromide (TTAB), and dodecylpyridinium bromide (DPC) with different tail lengths using tensiometry and conductometry from a thermodynamic viewpoint. Increasing *cmc* with decreasing tail length signifies the dominant effect of hydrophobic interaction in dictating the self-aggregation behavior. The coherence of *cmc* values obtained by tensiometry and conductometry for pure and CPC/TTAB and DPC/TTAB binary combinations suggests concurrence of interfacial saturation by surfactant monomer and their self-aggregation in bulk solution. A finite and significant lag in *cmc* determined by those two methods for CPC/DPC binaries and the ternary systems DPC/CPC/TTAB indicates a decrease in charge density at the micellar interface arising out of π - π interaction among the pyridinium head groups of surfactants with dissimilar tail lengths. Negative deviation in the experimental *cmc* for the binary combinations again infers the van der Waals attractive interaction among the similarly charged surfactant head groups.

The Rosen model predicts the interfacially adsorbed layer and interaction parameters. Rubingh, Motomura and SPB models, on the other hand, deal with the micellar phase. For CPC/TTAB system, these three models predict more or less similar composition of the micellar phase. The interaction parameters in the micellar phase predicted by Rubingh model are all negative signifying synergistic interaction. With increasing stoichiometric amount of CPC, its proportion in monolayer and micellar phase increases. This increase in the amount of CPC in the interfacial layer is, however, less prominent than that in micellar phase. In DPC/TTAB system, the Rubingh, Motomura, and SPB models predict similar composition in the micellar phase. The variation of micellar composition with the stoichiometric composition is again more pronounced in micellar phase compared to that in the monolayer. For CPC/DPC system, however, there is a discrepancy in micellar composition as predicted by Rubingh, Motomura, and SPB models. The deviation of the experimental *cmcs* from those obtained using the RH model for the DPC/CPC/TTAB ternary system may be ascribed to the incompatibility of the three amphiphiles due to the dissimilarity in their nonpolar tail and ionic head groups.

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TABLE-1

Critical Micellar Concentrations^a (*cmc*) of Pure CPC, TTAB and DPC, and their Binary Mixtures at 298.15K

α_{CPC} (I) or α_{DPC} (II)	S.T.	Cond.	Av. <i>cmc</i>	<i>cmc</i> ^c
CPC/TTAB ($10^3 \text{ cmc} / \text{mol dm}^{-3}$) (I)				
0.00	3.715	3.524	3.620	-
0.10	2.564	2.716	2.640	2.846
0.25	1.556	2.255	1.906	2.154
0.50	1.247	1.562	1.404	1.534
0.75	0.998	1.250	1.124	1.191
0.90	0.920	1.313	1.026	1.050
1.00	0.910	1.036	0.973	-
DPC/TTAB ($10^3 \text{ cmc} / \text{mol dm}^{-3}$) (II)				
0.00	3.715	3.524	3.620	-
0.10	3.908	3.992	3.950	3.931
0.25	4.645	4.731	4.688	4.513
0.40	5.297	5.781	5.539	5.297
0.50	5.929	6.435	6.182	5.991
0.60	7.211	7.131	7.171	6.895
0.75	9.453	9.387	9.420	8.910
0.90	11.695	12.414	12.054	12.588
1.00	17.132	17.608	17.370	-
CPC/DPC ($10^3 \text{ cmc} / \text{mol dm}^{-3}$) (I)				
0.00	17.132	17.608	17.370	-
0.10	4.291	8.631	6.461	6.468
0.25	3.254	7.764	5.509	3.332
0.40	2.218	5.190	3.704	2.244
0.50	1.527	3.950	2.739	1.843
0.60	1.465	2.775	2.120	1.563
0.75	1.445	2.469	1.957	1.273
0.90	1.096	2.296	1.696	1.074
1.00	0.910	1.036	0.973	-

^aThe average uncertainty in *cmc* is $\pm 2\%$

TABLE-2

Critical Micellar Concentrations^a (*cmc*) of the Ternary Mixtures of CPC, TTAB and DPC at 298.15K

$\alpha_{DPC} / \alpha_{CPC} / \alpha_{TTAB}$	S.T.	Cond.	Av. <i>cmc</i> (Clint <i>cmc</i>)
	$10^3 \text{ cmc} / \text{mol dm}^{-3}$		
0.125 / 0.250 / 0.625	1.517	1.862	1.690 (2.289)
0.125 / 0.625 / 0.250	1.153	1.367	1.260 (1.392)
0.250 / 0.125 / 0.625	2.138	2.322	2.230 (3.169)
0.250 / 0.625 / 0.125	1.183	1.388	1.286 (1.447)
0.333 / 0.333 / 0.333	1.462	1.628	1.545 (2.206)
0.625 / 0.125 / 0.250	2.667	3.981	3.324 (4.282)
0.625 / 0.250 / 0.125	1.941	2.213	2.077 (3.054)

^aThe average uncertainty in *cmc* is $\pm 3\%$.

TABLE-3

Interfacial and Counterion Binding Parameters of Pure CPC, TTAB and DPC, and their Binary Mixtures at 298.15K

α_{CPC} (I) or α_{DPC} (II)	$10^3 \Pi_{cmc} /$ $J m^{-2}$	$10^6 \Gamma_{max} /$ $mol m^{-2}$	$A_{min} /$ $nm^2/molecule$	g	$-\Delta G_m^0 /$ $kJ mol^{-1}$	$-\Delta G_{ad}^0 /$ $kJ mol^{-1}$	pC_{20}	cmc/C_{20}
CPC/TTAB (I)								
0.00	37.9	4.52	0.37	0.645	39.94	48.33	3.09	4.41
0.10	36.1	4.63	0.36	0.583	39.70	47.50	3.19	4.09
0.25	35.7	4.89	0.34	0.564	40.50	47.81	3.36	4.38
0.50	34.0	4.97	0.33	0.557	41.52	48.36	3.38	3.38
0.75	31.5	5.19	0.32	0.602	43.62	49.69	3.36	2.59
0.90	29.2	5.50	0.30	0.615	44.34	49.65	3.34	2.23
1.00	27.7	5.99	0.28	0.601	44.17	48.79	3.28	1.84
DPC/TTAB (II)								
0.00	37.9	4.52	0.37	0.645	39.94	48.33	3.09	4.45
0.10	37.4	4.29	0.39	0.710	41.14	49.86	3.07	4.62
0.25	37.6	4.48	0.37	0.639	38.73	47.11	3.01	4.85
0.40	37.2	5.13	0.32	0.606	37.27	44.52	2.86	3.97
0.50	36.6	4.25	0.39	0.592	36.51	45.12	2.91	5.07
0.60	35.7	3.47	0.48	0.579	35.62	45.92	2.93	6.14
0.75	34.6	3.30	0.51	0.542	33.73	44.21	2.80	5.94
0.90	33.7	3.12	0.53	0.500	31.88	42.67	2.67	5.66
1.00	32.6	2.6	0.64	0.554	31.59	44.14	2.48	5.29
CPC/DPC (I)								
0.00	32.6	2.60	0.64	0.554	31.59	44.14	2.48	5.29
0.10	31.6	2.27	0.73	0.338	29.56	43.48	3.20	10.24
0.25	30.7	2.51	0.66	0.371	30.65	42.88	3.24	9.57
0.40	29.8	2.75	0.60	0.370	33.19	44.03	3.28	7.13
0.50	29.6	3.74	0.44	0.355	33.85	41.76	3.24	4.73
0.60	28.7	3.96	0.42	0.521	38.98	46.23	3.23	3.61
0.75	28.1	4.14	0.40	0.509	38.98	45.77	3.25	3.47
0.90	27.6	4.51	0.37	0.503	39.36	45.48	3.24	2.97
1.00	27.7	5.99	0.28	0.601	44.17	48.79	3.28	1.84

TABLE-4

Interfacial and Thermodynamic^a Parameters of the Ternary Combinations of DPC, CPC and TTAB at 298.15K

$\alpha_{DPC} / \alpha_{CPC} / \alpha_{TTAB}$	$10^3 \Pi_{cmc}$ / J m ⁻²	$10^6 \Gamma_{max}$ / mol m ⁻²	A_{min} / nm^2 molecule ⁻¹	g	$-\Delta G_m^0 /$ kJ mol ⁻¹	$-\Delta G_{ad}^0 /$ kJ mol ⁻¹	pC_{20}	cmc/C_{20}
0.125 / 0.250 / 0.625	34.6	5.76	0.29	0.391	-36.44	42.45	3.31	3.43
0.125 / 0.625 / 0.250	32.2	5.21	0.32	0.566	-42.19	48.37	3.33	2.68
0.250 / 0.125 / 0.625	35.4	4.45	0.37	0.338	-34.12	42.08	3.24	3.92
0.250 / 0.625 / 0.125	30.4	4.96	0.33	0.529	-41.11	47.24	3.27	2.41
0.333 / 0.333 / 0.333	33.2	5.90	0.28	0.416	-37.42	43.05	3.24	2.67
0.625 / 0.125 / 0.250	33.5	4.90	0.34	0.321	-32.36	39.20	3.06	3.81
0.625 / 0.250 / 0.125	32.1	5.34	0.31	0.328	-34.1	40.12	3.13	2.81

^aThe average uncertainty in each of ΔG_m^0 , and ΔG_{ad}^0 are $\pm 3\%$.

TABLE-5

Molecular Interaction Parameters of Binary Mixtures in Aqueous Medium and 298.15K

α_{CPC} (I) or α_{DPC} (II)	Rosen Model		Rubingh Model			Motomura Model	
	X^σ	β^σ	X_R	β^R	f_1 / f_2	X_{Mo}	f_1
CPC/TTAB (I)							
0.10	0.43	-3.49	0.34	-0.46	0.82 / 0.95	0.30	0.91
0.25	0.52	-3.48	0.55	-1.21	0.78 / 0.69	0.60	0.81
0.50	0.62	-2.71	0.73	-0.88	0.94 / 0.62	0.73	0.99
0.75	0.74	-2.16	0.84	-1.16	0.97 / 0.43	0.88	0.98
0.90	0.84	-1.94	0.92	-1.40	0.99 / 0.31	-	0.94
DPC/TTAB (II)							
0.10	0.37	-7.82	0.05	-0.89	0.45 / 1.00	0.07	0.29
0.25	0.40	-6.17	0.06	-0.09	1.08 / 1.00	0.08	0.82
0.40	0.43	-4.93	0.14	-0.18	0.87 / 1.00	0.07	1.75
0.50	0.45	-4.38	0.20	-0.19	0.88 / 0.99	0.10	1.75
0.60	0.47	-3.54	0.23	-0.16	1.10 / 1.01	0.20	1.26
0.90	0.65	-1.58	0.64	-0.32	0.96 / 0.88	0.76	0.82
CPC/DPC (I)							
0.10	0.73	-2.18	0.60	-1.56	0.78 / 0.57	0.12	7.31
0.25	0.76	-2.96	0.89	+0.33	1.00 / 1.30	0.64	3.13
0.40	0.81	-3.16	0.97	+1.16	1.00 / 3.02	-	-
0.50	0.80	-4.04	0.86	-1.51	0.97 / 0.33	-	-
0.60	0.89	-1.83	0.97	-0.01	1.00 / 1.01	0.78	1.67
0.75	0.97	-	-	-	-	0.77	1.96
0.90	0.99	-	-	-	-	0.91	1.73

TABLE-6

Micellar Compositions (X_{SPB}), Interaction Parameters [$\beta_{SPB}(kT)$], Activity Coefficients (f), and cmc s of Binary Mixtures at 298.15K at Different Stoichiometric Compositions

α_{CPC} (I) or α_{DPC} (II)	X_{SPB}	$\beta_{SPB} (kT)$	f_1	f_2	$10^3 cmc/(mol dm^{-3})$ Obs/SPB/Clint
CPC/TTAB (I)					
0.10	0.292	-0.146	0.93	0.99	2.640 / 2.760 / 2.846
0.25	0.553	-0.608	0.89	0.83	1.906 / 1.853 / 2.154
0.50	0.788	-1.962	0.92	0.30	1.404 / 0.972 / 1.534
0.75	0.918	-8.605	0.94	-	1.124 / 0.010 / 1.191
0.90	0.971	-27.221	0.98	-	0.973 / - / 1.050
DPC/TTAB (II)					
0.10	0.022	0.035	1.034	1.000	3.950 / 3.934 / 3.931
0.25	0.064	0.060	1.054	1.000	4.688 / 4.529 / 4.513
0.40	0.122	0.058	1.046	1.001	5.539 / 5.330 / 5.297
0.50	0.172	0.050	1.035	1.001	6.182 / 6.033 / 5.991
0.60	0.238	0.069	1.041	1.004	7.171 / 6.980 / 6.895
0.90	0.652	-0.358	0.958	0.859	12.054 / 11.59 / 12.588
CPC/DPC (I)					
0.10	0.665	2.567	1.334	3.112	6.461 / 10.67 / 6.468
0.25	0.856	-	2.330	-	5.509 / 9.070 / 3.332
0.40	0.923	-	1.650	-	3.704 / 4.013 / 2.244
0.50	0.947	-	1.486	-	2.739 / 2.892 / 1.843
0.60	0.964	-	1.356	-	2.120 / 2.199 / 1.563
0.75	0.982	-	1.536	-	1.957 / - / 1.273
0.90	0.994	-	1.578	-	1.696 / - / 1.074

TABLE-7

Micellar Composition (X^{RH}), Activity Coefficient (f^{RH}), and cmc_{RH} in Ternary Mixtures of DPC/CPC/TTAB by RH Model at 298.15K and at Different Stoichiometric Compositions (α)

$\alpha_{\text{DPC}} / \alpha_{\text{CPC}} / \alpha_{\text{TTAB}}$	$X_{\text{DPC}}^{\text{RH}} / X_{\text{CPC}}^{\text{RH}} / X_{\text{TTAB}}^{\text{RH}}$	$f_{\text{DPC}}^{\text{RH}} / f_{\text{CPC}}^{\text{RH}} / f_{\text{TTAB}}^{\text{RH}}$	$10^3 cmc / (\text{mol dm}^{-3})$ RH/obsd/Clint
0.125 / 0.250 / 0.625	0.574 / 0.117 / 0.414	0.835 / 1.093 / 0.707	1.791 / 1.690 / 2.289
0.125 / 0.625 / 0.250	0.830 / 0.008 / 0.162	0.972 / 1.010 / 0.489	1.236 / 1.260 / 1.392
0.250 / 0.125 / 0.625	0.450 / 0.033 / 0.517	0.749 / 1.082 / 0.798	2.492 / 2.230 / 3.169
0.250 / 0.625 / 0.125	0.713 / 0.013 / 0.274	0.923 / 1.063 / 0.587	1.301 / 1.286 / 1.447
0.333 / 0.333 / 0.333	0.700 / 0.032 / 0.267	0.921 / 1.61 / 0.590	1.833 / 1.545 / 2.206
0.625 / 0.125 / 0.250	0.547 / 0.116 / 0.336	0.857 / 1.072 / 0.682	3.453 / 3.324 / 4.282
0.625 / 0.250 / 0.125	0.741 / 0.093 / 0.166	0.958 / 1.017 / 0.524	2.707 / 2.077 / 3.054

CHAPTER-VII

Thermodynamic and Interfacial Adsorption Studies on the Micellar Solutions of Alkyltrimethylammonium Bromides in Ethylene Glycol (1) + Water (2) Mixed Solvent Media

INTRODUCTION

Surfactants are widely used both in industry and everyday life, and their properties in aqueous solutions have received considerable attention. Recently, the aggregation phenomenon of amphiphiles in nonaqueous media has been the subject of many researchers due to the increasing use of these materials in such areas as lubrication and cleaning operations, which require water-free or water-poor media.^{1,2} The solvents used in these studies are strongly polar with water-like properties; some common examples include ethylene glycol, formamide, and glycerol.³⁻¹² Most of these investigations focused mainly on two aspects: the requirement from a solvent for amphiphilic assembly and the structural properties of the aggregates formed in these media. To address these issues, a frequently used approach is the gradual replacement of water by other polar solvents, as this allows one to explore wide range of polarities. Several studies have been carried out following this approach.¹³⁻²¹ For the amphiphilic aggregation to occur, the solvent media should have high cohesive energies, dielectric constants and considerable hydrogen bonding ability.^{22,23}

In the present work, the micellization behavior of three alkyltrimethylammonium bromides, *viz.*, hexadecyltrimethylammonium bromide (CTAB), tetradecyltrimethylammonium bromide (TTAB) and dodecyltrimethylammonium bromide (DTAB) in EG (1) + water (2) mixed solvent media has been studied. Previously, very few studies on these systems have been reported. Backlund *et al.*²⁴ investigated the aggregation and phase behaviour of TTAB in water, EG and their

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mixtures at 30 °C. Ruiz¹¹ reported the thermodynamic studies of TTAB in EG (1) + water (2) mixtures. Gharibi *et. al.*²⁵ have also carried out electrochemical studies associated with micellization of TTAB, among other cationic surfactants, in the same solvent mixtures at 25 °C. In this investigation, we have carried out conductivity and surface tension measurements on the systems mentioned above to study their micellization behavior. The influence of temperature on the micellization and adsorption behaviours of these amphiphiles will also be investigated. The ability of EG (1) + water (2) mixtures to bring about self-association will be characterized by the Gordon parameter.²⁶

EXPERIMENTAL

Materials and Methods

The surfactant CTAB was purchased from Sigma; TTAB and DTAB were of Fluka (Switzerland) purum grade and these were used as received. Ethylene glycol (99 %+, spectroscopic grade) was from Aldrich. Doubly distilled water (specific conductance, 2 to 3 $\mu\text{S cm}^{-1}$) was used to prepare the solutions. All experiments were carried out with freshly prepared solutions.

The conductometric measurements were carried out on a Pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz using a dip-type cell of cell constant 1.14 cm^{-1} . The cell was calibrated by the method of Lind *et al.*²⁷ using aqueous potassium chloride solutions. Solutions were prepared by mass for conductance runs, the molalities being converted to molarities by the use of densities measured with an Ostwald-Sprengel type pycnometer of about 25 cm^3 capacity. Corrections were made for the specific conductance of solvents at all temperatures. The measurements were made in a water bath maintained within ± 0.01 K of the desired temperature.

The surface tensions of the surfactant solutions were measured with a Krüss (Germany) K9 tensiometer by the platinum ring detachment method. The tensiometer was connected to a water-flow cryostat to maintain the temperature equilibration. Prior to each measurement, the ring was heated briefly by holding it above a Bunsen burner until glowing. Several independent solutions were prepared by mass and duplicate measurements were performed to check the reproducibility. The uncertainty of the measurements was within $\pm 1 \times 10^{-3} \text{ N}\cdot\text{m}^{-1}$.

RESULTS AND DISCUSSION

The critical micellar concentrations (*cmc*) were determined from the inflections in the plots of conductivity as a function of the surfactant concentration (*C*). The data points above and below the inflection are fitted to two linear equations and the *cmc* was obtained from the intersection. This method is found to be reliable and convenient for the present system because of the significant variations of conductivity with surfactant concentration in the pre- and postmicellar regions. The ratio of the slopes of the plots of κ versus *C* above and below the *cmc* gives an estimate of the micellar degree of counter ion dissociation (α). A representative plot (Fig. 1) shows the concentration dependence of the conductivity of TTAB in EG (1) + water (2) mixtures with varying amounts of EG. Fig. 2, on the other hand, shows the concentration dependence of the conductivity of CTAB in a given EG (1) + water (2) mixture with $w_1 = 0.30$ at different temperatures. Table 1 lists the values of *cmc* and the micellar degree of counterion dissociation (α) of the surfactants in different EG (1) + water (2) media at 298.15 K. Table 2 reports the *cmc* and α values in the mixture with $w_1 = 0.30$ in the temperature range 303.15 to 323.15 K. The *cmc* values of these surfactants in water were found to be in good agreement with those previously reported in the literature.²⁸ The micellar degrees of counterion dissociation for a given surfactant are found to increase as the mixed solvent media get richer in EG (*cf.* Table 1). An increase in *cmc* originates mainly from the small magnitude of the tail transfer free energy from EG compared to that from water. This effect can be quantified in the EG (1) + water (2) micellar solutions investigated through the estimation of free energy for the transfer of one methylene CH₂ group from bulk phase to the micellar pseudophase ($\Delta G_{\text{CH}_2}^0$) by using eq. 1:^{6,28}

$$(2 - \alpha) \ln cmc = \text{const} + m \left[\frac{\Delta G_{\text{CH}_2}^0}{RT} \right] \quad (1)$$

According to this equation, $\Delta G_{\text{CH}_2}^0$ can be estimated from the slope of the linear plot of $(2 - \alpha) \ln cmc$ against the number of carbon atoms (*m*) in the surfactant chain for a homologous series of surfactants. Good straight lines were obtained for pure water and for the five EG (1) + water (2) mixtures studied. Table 3 summarizes the $\Delta G_{\text{CH}_2}^0$ values thus obtained. The values reported here in water are found to be in good agreement with those reported in the literature.^{6,28}

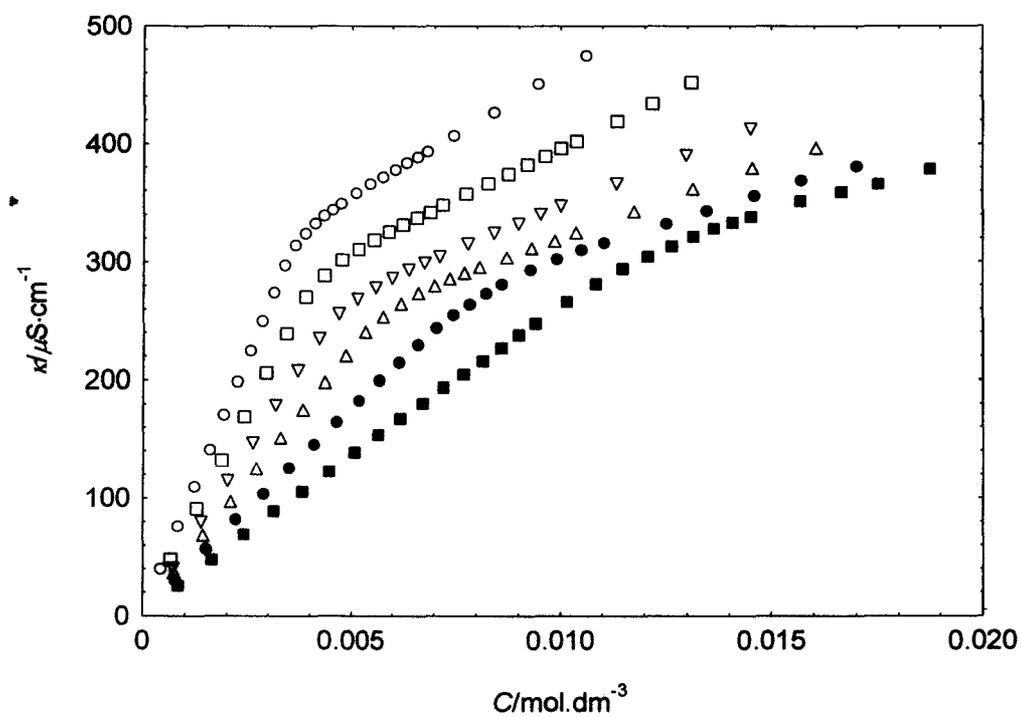


Figure 1. Conductivity (κ) versus concentration of tetradecyltrimethylammonium bromide (C) in EG (1) + water (2) mixtures at 298.15 K: ○, water; □, $w_1 = 0.10$; ▽, $w_1 = 0.20$; △, $w_1 = 0.30$; ●, $w_1 = 0.40$; ■, $w_1 = 0.50$.

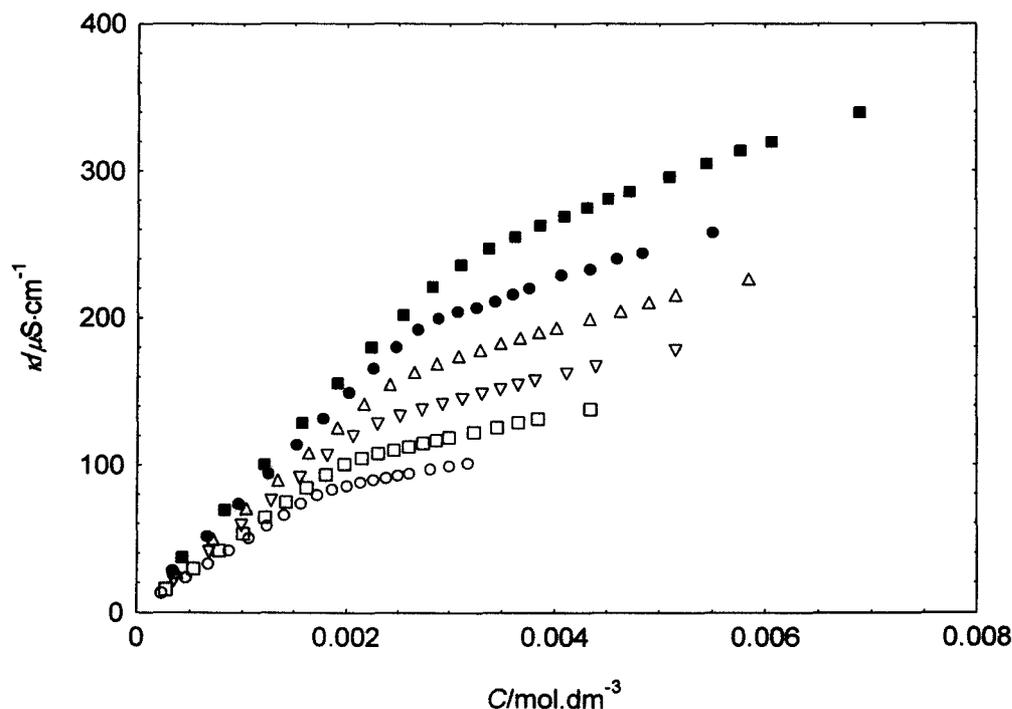


Figure 2. Conductivity (κ) versus concentration of hexadecyltrimethyl ammonium bromide (C) in EG (1) + water (2) mixture at different temperature: \circ , 298.15 K; \square , 303.15 K; ∇ , 308.15 K; \triangle , 313.15 K; \bullet , 318.15 K; \blacksquare , 323.15 K.

From Tables 1 and 2, it is apparent that the degrees of counterion dissociation for the surfactants increase regularly with both EG addition and temperature increase. This observed increase in α may be attributed to a decrease in the charge density on the micellar surface caused by the decrease in the aggregation number of the micelle.

The ability of EG (1) + water (2) mixtures to bring about the self-association of the amphiphiles can be related to the cohesive energy density,²⁹ which can be conveniently characterized by the Gordon parameter, $G = \gamma / \bar{V}^{1/3}$, where γ and \bar{V} are respectively the solvent surface tension and molar volume. Table 4 shows the Gordon parameter values for the different mixtures used as bulk phase in the micellar solutions studied. The G parameter points out that an increase in the amount of EG in

EG (1) + water (2) mixtures results in a decrease in the solvent cohesiveness, thereby improving the solvation of the hydrocarbon tails in the bulk phase and decreasing the solvophobic effect. The increase in the solubility of the hydrocarbon tails in EG (1) + water (2) mixtures gives rise to an increase in the *cmc* as noted in Table 1.

In order to analyze the variation of *cmc* with temperatures, we have considered the mass-action model for micellization. According to this model, the process of micellization of cationic surfactants may be described by



where D^+ represents the surfactant ions, X^- the corresponding counterions, and M^{p+} the aggregate of n monomers with an effective charge of p . The Gibbs energy of micelle formation per mole of surfactant, ΔG_m^0 , is given by,

$$\Delta G_m^0 = RT \left[-\frac{1}{n} \ln a_{M^{p+}} + \ln a_{D^+} + \left(\frac{p}{n} \right) \ln a_{X^-} \right] \quad (3)$$

in which a represents the activity of the species indicated. If the aggregation number (n) is large, the first term in the parenthesis is negligibly small and both a_{D^+} and a_{X^-} can be replaced by the corresponding activities at the *cmc*. In addition, taking into account that *cmcs* occur in dilute solutions, the activity can again be replaced by the concentration of surfactant (expressed in mole fractions) at the *cmc*. Introduction of these approximations in eq. 3 yields³⁰

$$\Delta G_m^0 = (2 - \alpha)RT \ln x_{cmc} \quad (4)$$

where $\alpha = p/n$ is the degree of counterion dissociation and x_{cmc} is the *cmc* of a surfactant in mole fraction unit. The corresponding enthalpy change (ΔH_m^0) is given by

$$\Delta H_m^0 = -RT^2 \left[(2 - \alpha) \left(\frac{\partial \ln x_{cmc}}{\partial T} \right)_p - \ln x_{cmc} \left(\frac{\partial (1 - \alpha)}{\partial T} \right)_p \right] \quad (5)$$

If the change in α with temperature is small over the temperature range investigated, this equation can be expressed as

$$\Delta H_m^0 = -(2 - \alpha)RT^2 \left(\frac{\partial \ln x_{cmc}}{\partial T} \right)_p \quad (6)$$

Therefore, the enthalpy of micellization may be obtained if the dependence of the *cmc* on temperature is known. In the present study the contribution of the second term

(within the parentheses) in eq. 5 is negligible, so we used eq. 6 to estimate ΔH_m^0 values. With this purpose, $\ln x_{cmc}$ values for the three surfactants in EG (1) + water (2) mixture with $w_1 = 0.30$ were plotted against T and the slope was taken as equal to $\left(\frac{\partial \ln x_{cmc}}{\partial T}\right)_p$. These plots are shown in Fig. 3. A linear plot was observed for each of the surfactant system investigated. A similar kind of linearity has also been observed by Ruiz¹¹ for TTAB in EG (1) + water (2) mixture with higher EG content. Finally, once ΔG_m^0 and ΔH_m^0 have been calculated, the entropic contribution, $T\Delta S_m^0$, may be determined from

$$T\Delta S_m^0 = \Delta H_m^0 - \Delta G_m^0 \quad (7)$$

In addition, the effect of a cosolvent or additive on the micellization process can be studied by means of the Gibbs energy of transfer (ΔG_{trans}^0) defined by³¹

$$\Delta G_{trans}^0 = (\Delta G_m^0)_{H_2O+EG} - (\Delta G_m^0)_{H_2O} \quad (8)$$

The standard Gibbs energies of micellization (ΔG_m^0) and the Gibbs energies of transfer (ΔG_{trans}^0) for the three surfactants studied in EG (1) + water (2) mixtures at 298.15 K are given in Table 1. From this table, it can be seen that the micellization becomes less spontaneous upon addition of an increasing amount of EG to water.

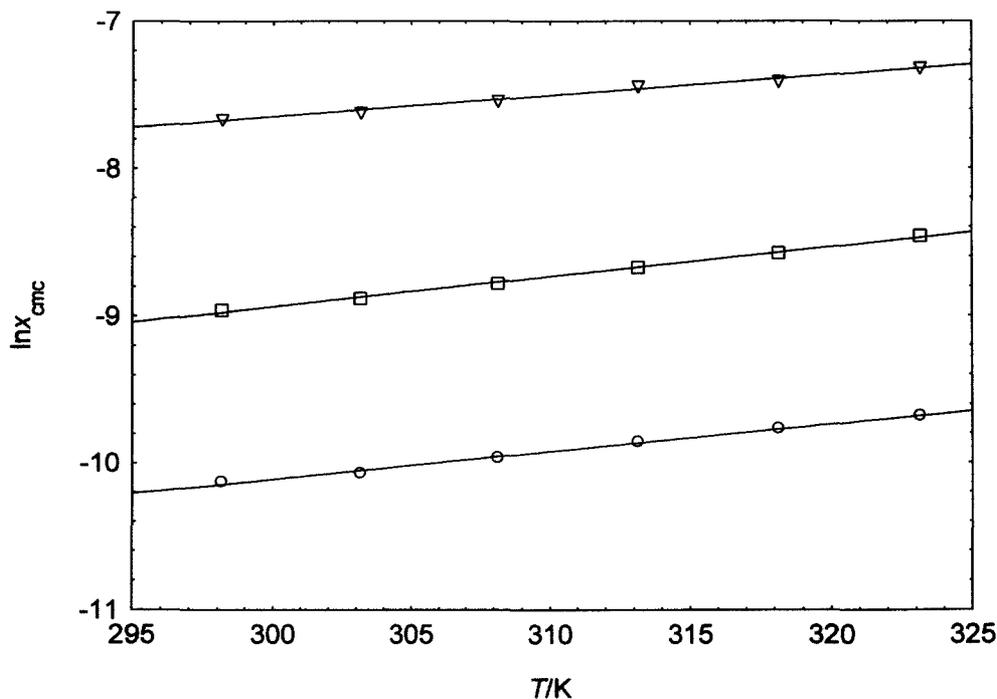


Figure 3. Plots of $\ln x_{cmc}$ versus temperature for different alkyltrimethylammonium bromides in EG (1) + water (2) mixture with $w_1 = 0.30$: ○, CTAB; □, TTAB; ▽, DTAB.

The different thermodynamic parameters of these surfactants in a given EG (1) + water (2) mixture with $w_1 = 0.30$ are given in Table 2. Our results show that the degree of counterion dissociation (α) of micelle for all these three surfactants increases with temperature as found earlier for other cationic surfactants^{32,33} in aqueous solutions. The Gibbs energies of micellization are, in all cases, negative and become more negative for CTAB as the temperature increases, whereas a reverse trend is observed for TTAB and DTAB. This observation suggests that aggregation becomes more favorable with the increasing alkyl chain length of the alkyltrimethylammonium bromide surfactants in EG (1) + water (2) mixture with $w_1 = 0.30$. The enthalpy of micellization is negative and becomes more negative with increasing temperature. On the other hand, the $T\Delta S_m^0$ values are, in general, positive and becomes less positive as temperature increases. These results could suggest that

the micellization of the alkyltrimethylammonium bromides in EG (1) + water (2) mixture with $w_1 = 0.30$ is still governed by entropy-enthalpy compensation effect, and the presence of EG has a minor effect on the solute-solvent interactions. Similar behavior has also been observed previously³⁴ for sodium dodecylsulfate in different binary aqueous mixtures.

The values of $\Delta G_{\text{trans}}^0$ estimated using eq. 8 are listed in Table 1. For all surfactant systems investigated, the values of $\Delta G_{\text{trans}}^0$ were found to be positive. The positive values of $\Delta G_{\text{trans}}^0$ can be attributed to the reduction in the solvophobic interactions caused by the improved solvation, which leads to an increase in the solubility of the hydrocarbon tails in the presence of EG and consequently there will be an increase in *cmc*.

The excess surface concentration (Γ_{max}) and the minimum area per surfactant molecules (A_{min}) at the air/solvent interface were obtained using the surface tension measurements from the following equations:³⁵

$$\Gamma_{\text{max}} = -\frac{1}{2RT} \left(\frac{\partial \gamma}{\partial \ln C} \right)_{T,p} \quad (9)$$

$$A_{\text{min}} = \frac{1}{N_A \Gamma_{\text{max}}} \quad (10)$$

here R is the gas constant, N_A the Avogadro's number, γ the surface tension, and C the concentration of surfactant in solution. The value of the surface pressure at the *cmc* (Π_{cmc}) were obtained by using the following equation:

$$\Pi_{\text{cmc}} = \gamma_0 - \gamma_{\text{cmc}} \quad (11)$$

where γ_0 is the surface tension of the solvent and γ_{cmc} is that of the surfactant solution at the *cmc*.

Finally, the Gibbs energy of adsorption (ΔG_{ads}^0) was determined from:

$$\Delta G_{\text{ads}}^0 = \Delta G_{\text{m}}^0 - \frac{\Pi_{\text{cmc}}}{\Gamma_{\text{max}}} \quad (12)$$

where the standard state in the surface phase is defined as the surface covered with a monolayer of surfactant at a surface pressure equal to zero. The dependence of surface tension with the logarithm of the molar concentration of CTAB is shown in the Fig. 4. The values of *cmc*, Γ_{max} , A_{min} and ΔG_{ads}^0 are listed in Table 5. The *cmc* values

obtained by surface tension measurements are in good agreement with those obtained from conductometric measurements. One can see that the values of Γ_{\max} increase and those of A_{\min} decrease, when the length of hydrocarbon chain increases. It shows that the more hydrophobic the surfactant molecules are, the stronger is the tendency of those molecules to escape from the solvent to the air/solvent interface (there is less affinity between solvent and surfactant molecules), resulting in a more packed surface. An increase in the amount of EG in the EG (1) + water (2) mixtures results in a decrease in Γ_{\max} , and an increase in A_{\min} . This indicates an increased solubilization of EG into the micelles leading to an increase in the surface area per surfactant molecule as the solvent medium becomes richer in EG. All of the ΔG_{ads}^0 values listed in Table 5 are negative, indicating that the adsorption of surfactant at air/mixture interface takes place spontaneously. This process is also found to be more spontaneous as the hydrocarbon chain of the surfactant gets longer and as the medium becomes richer in water. Besides, ΔG_{ads}^0 values are more negative than the corresponding ΔG_{m}^0 values. This indicates that when a micelle is formed, work needs to be done to transfer the surfactant molecules in the monomeric form at the surface to the micellar state in the mixed solvent media.³⁶

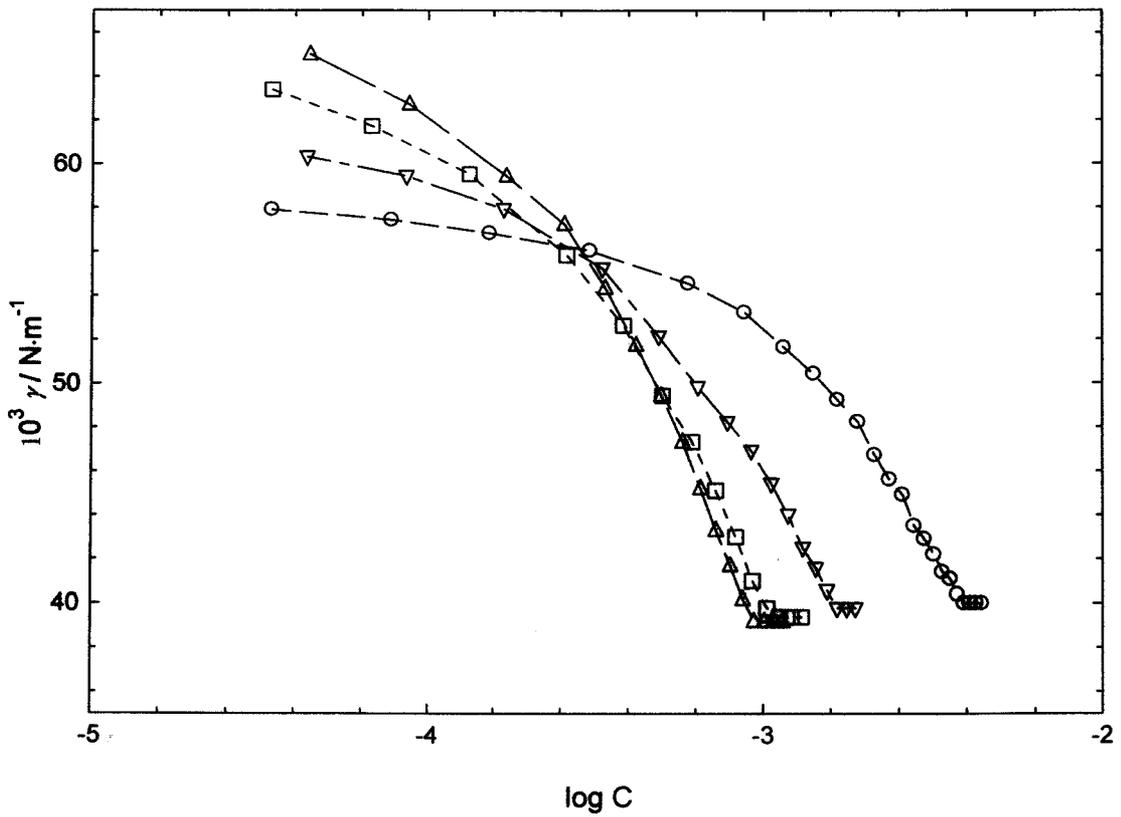


Figure 4. Variation of γ with $\log C$ for CTAB in different EG (1) + water (2) mixtures at 298.15 K : Δ , water; \square , $w_2 = 0.10$; ∇ , $w_2 = 0.30$ and \circ , $w_2 = 0.50$.

CONCLUSIONS

The critical micelle concentration and the micellar ionization degree of dissociation of the investigated alkyltrimethylammonium bromides *viz.*, hexadecyl-, tetradecyl-, and dodecyltrimethylammonium bromide in water-ethylene glycol mixed solvent media are always found to be greater than the corresponding values in aqueous media. From the study of the temperature dependence of the *cmc* of these surfactants in water-30 wt % of EG mixture, it has been demonstrated that the micellization is mainly governed by enthalpy-entropy compensation effect and the presence of EG only has a minor effect on the solute-solvent interaction. Data on the thermodynamics of adsorption indicate that the surface activity of these surfactants is found to decrease with the addition of EG to water at a given temperature and that the adsorption of surfactant at air/mixture interface takes place spontaneously.

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TABLE-1

Critical Micellar Concentration (cmc), Degree of Counterion Dissociation (α), Gibbs Energy of Micellization (ΔG_m^0), and Gibbs Energy of Transfer (ΔG_{trans}^0) Values for Alkyltrimethylammonium Bromides in EG (1) + Water (2) Mixtures at 298.15 K^a

$100w_1$	$10^3 cmc / \text{mol}\cdot\text{dm}^{-3}$	α	$-\Delta G_m^0 / \text{kJ}\cdot\text{mol}^{-1}$	$\Delta G_{trans}^0 / \text{kJ}\cdot\text{mol}^{-1}$
CTAB				
0	0.93	0.269	47.19	
10	1.14	0.276	45.85	1.34
20	1.33	0.279	44.81	2.38
30	1.79	0.284	43.10	4.09
40	2.57	0.315	40.46	6.73
50	4.22	0.340	37.43	9.76
100	91.45 ^b	0.716	22.11	-
TTAB				
0	3.74	0.250	41.67	
10	4.13	0.255	40.84	0.83
20	4.80	0.268	39.59	2.08
30	5.77	0.285	38.10	3.57
40	8.14	0.327	35.39	6.28
50	11.94	0.378	32.39	9.28
100	147.84	0.658	19.71	21.96
DTAB				
0	14.47	0.261	35.58	
10	16.82	0.271	34.44	1.14
20	18.72	0.288	33.36	2.22
30	21.11	0.312	32.07	3.51
40	26.96	0.374	29.57	6.01
50	35.40	0.430	27.13	8.45
100	191.77	0.715	18.06	17.52

^a The uncertainty limits of cmc , α , and ΔG_m^0 are ± 3 , ± 4 , and $\pm 4\%$ respectively.

^b Measured at 323.15 K.

TABLE-2

Thermodynamic Parameters for Micellization of Alkyltrimethylammonium Bromides in EG (1) + Water (2) Mixture with $w_1 = 0.30$ at Different Temperatures^a

T/ K	$10^3 cmc/mol \cdot dm^{-3}$	α	$-\Delta G_m^0/kJ \cdot mol^{-1}$	$-\Delta H_m^0/kJ \cdot mol^{-1}$	$T\Delta S_m^0/kJ \cdot mol^{-1}$
CTAB					
298.15	1.79	0.284	43.10	23.59	19.51
303.15	1.89	0.294	43.33	24.25	19.08
308.15	2.10	0.303	43.35	24.92	18.43
313.15	2.34	0.311	43.37	25.61	17.76
318.15	2.56	0.320	43.43	26.30	17.13
323.15	2.80	0.325	43.58	27.05	16.53
TTAB					
298.15	5.77	0.285	38.10	25.57	12.53
303.15	6.22	0.299	38.09	26.21	11.88
308.15	6.88	0.308	38.08	26.94	11.14
313.15	7.68	0.315	38.06	27.71	10.35
318.15	8.46	0.326	38.00	28.41	9.59
323.15	9.51	0.333	37.89	29.19	8.70
DTAB					
298.15	21.11	0.312	32.07	17.76	14.31
303.15	22.07	0.340	31.88	18.06	13.82
308.15	23.90	0.367	31.55	18.36	13.19
313.15	26.43	0.394	31.12	18.65	12.47
318.15	27.36	0.417	31.00	18.97	12.03
323.15	29.94	0.432	30.82	19.39	11.43

^a The uncertainty limits of cmc , α , ΔG_m^0 , ΔH_m^0 , and ΔS_m^0 are ± 3 , ± 4 , ± 4 , ± 3 and $\pm 5\%$ respectively.

TABLE-3

Values of the Free Energy ($\Delta G_{\text{CH}_2}^0$) for the Transfer of One Methylene (CH_2) Group from the Bulk Phase to the Micellar Pseudophase for Alkyltrimethylammonium Bromide Micellar Solutions in EG (1) + Water (2) Mixtures at 298.15 K

100w ₁	0	10	20	30	40	50
$\Delta G_{\text{CH}_2}^0 /$ kJ·mol ⁻¹	2.92	2.87	2.84	2.69	2.59	2.37

TABLE-4

Surface Tension (γ), Molar Volume (\bar{V}), and Gordon Parameter (G) for EG (1) + Water (2) Mixtures at 298.15 K

100w ₁	10 ³ $\gamma /$ N·m ⁻¹	$\bar{V}^a /$ dm ³ ·mol ⁻¹	$G /$ J·m ⁻³
0	71.9	18.07	2.74
10	66.9	21.85	2.39
20	64.2	25.64	2.18
30	61.7	29.42	1.99
40	59.9	33.21	1.86
50	58.0	36.99	1.74
100	48.6	55.92	1.27

^a Estimated considering $\bar{V} = \bar{V}_1 x_1 + \bar{V}_2 (1 - x_1)$, where x_1 is the mole fraction of EG in the mixture and \bar{V}_1 and \bar{V}_2 are the molar volumes of EG and water, respectively.

TABLE-5

Critical Micellar Concentration (cmc), Excess Surface Concentration (Γ_{max}), Minimum Area Per Molecule (A_{min}), Surface Pressure at the cmc (Π_{cmc}) and Gibbs Energy of Adsorption (ΔG_{ads}^0) for Alkyltrimethylammonium Bromides in EG (1) + Water (2) Mixtures at 298.15 K

$100w_1$	$10^3 cmc / \text{mol}\cdot\text{dm}^{-3}$	$10^6 \Gamma_{max} / \text{mol}\cdot\text{m}^{-2}$	$10^{20} A_{min} / \text{m}^2$	$10^3 \Pi_{cmc} / \text{N}\cdot\text{m}^{-1}$	$-\Delta G_{ads}^0 / \text{kJ}\cdot\text{mol}^{-1}$
CTAB					
0	0.94	0.705	236	32.80	93.71
10	1.11	0.595	278	27.54	92.14
30	1.66	0.500	332	21.88	86.86
50	3.86	0.470	354	17.98	75.68
TTAB					
0	3.80	0.525	316	38.41	114.83
10	4.14	0.395	420	32.55	123.24
30	5.33	0.285	582	27.94	136.13
50	10.69	0.200	830	20.79	136.34
DTAB					
0	11.44	0.495	334	40.20	116.79
10	13.07	0.360	462	34.88	131.33
30	16.97	0.255	650	27.85	141.29
50	28.35	0.180	898	19.36	134.69

CHAPTER-VIII

Summary of the Works Done

The present dissertation has been divided into eight chapters.

Chapter I forms the background of the present work. After presenting a brief introduction of surfactants, some important aspects of micellar shape and size have been discussed. The importance and utility of various methods in the determination of critical micelle concentration (*cmc*) and the different factors affecting the micelle formation and the *cmc* have been described. The different models of thermodynamics of micelle formation¹⁻²² and their applications to both ionic and nonionic surfactants have been presented. The importance of mixed micelles and the theories of binary mixed micelle formation are highlighted. A brief account of the studies on micelle formations in nonaqueous solvents has been given stressing the importance of such work.

In chapter II the methods of purifications of different chemicals used in the study and the various experimental techniques for obtaining the results presented in the dissertation have been described.

Chapter III describes the micellization behavior of lithium dodecylsulfate in aqueous solution by using conductivity, density and adiabatic compressibility measurements. The critical micelle concentrations for the surfactant system have been determined by all these methods. The ionization degree of micelles, $\alpha = S_2/S_1$, at different temperatures were determined from the ratio of the mean gradients of the specific conductivity (κ) against concentration plots above (S_2) and below (S_1) the *cmc*²³⁻²⁶. The standard free energy change of micellization per mole of monomer, ΔG_m° , has been calculated considering the charge phase separation model²⁷ of micellization. The variation in standard enthalpy change upon aggregation has been determined by using Gibbs-Helmholtz equation. The changes of the apparent molar volume upon micellization of the surfactant have been calculated from density

measurements. Using density and ultrasound velocity measurements the apparent adiabatic compressibilities of the surfactant solutions have also been obtained.

In chapter IV the effect of some quaternary ammonium bromides R_4NBr ($R=H, CH_3, C_2H_5, C_3H_7$ and C_4H_9) on the micellar properties of lithium dodecylsulfate (LDS) micelles has been studied by conductometric and tensiometric techniques. The degree of the counterion binding, β , is found to increase with the increasing size of the alkyl chain length of the tetraalkylammonium ions. The thermodynamics of micelle formation of ionic surfactant LDS in the presence of 0.001M of different quaternary salts have been thoroughly assessed by the critical micelle concentration (*cmc*) measurement in the 288.15–318.15 K-temperature range at 10 K intervals conductometrically. Results show a shallow minimum of the *cmc* values typically between 300 to 305 K for LDS micelles in presence of various salts. The standard free energy of micellization has been found to decrease upon growth of temperature. The standard enthalpy change on aggregation was calculated by using the Gibbs–Helmholtz equation. Tensiometric results show a significant reduction in the solution surface tension with increasing electrolyte concentration. The surface excess of LDS and its minimum area at the air–water interface in the presence of different R_4NBr environment has been determined. The micellar solution of LDS has been found to exhibit a cloud point phenomenon in the presence of Bu_4NBr . The occurrence of cloud point phenomenon is accounted for in terms of the penetration of butyl chains at the surface layer of one micelle into another due to the hydrophobic effect^{28, 29}.

Chapter V describes the physicochemical studies on mixed micellization of the anionic surfactant, LDS and nonionic surfactants polyoxyethylene(23)laurylether (Brij-35) and polyoxyethylene(10)isooctyl phenylether (Titron-100) in aqueous media. Several parameters viz. *cmc*, degree of counterion binding, free energies of micellization and interfacial adsorption have been evaluated from conductometric, tensiometric and spectrophotometric methods. Established theories of Clint³⁰, Rosen³¹, Rubingh³², Motomura³³, Georgiev³⁴, Macda³⁵ and Blankschein^{36, 37} has been applied to evaluate the mole fractions of different components in the self-aggregated phase, the interaction parameter, free energy contributions and expected *cmc*.

In chapter VI Mixed micellization behavior of aqueous binary and ternary mixtures systems of cetylpyridinium chloride (CPC), tetradecyltrimethylammonium bromide (TTAB), and dodecylpyridinium bromide (DPC) has been studied at 298.15 K. Parameters like *cmc*, degree of counterion binding, free energies of micellization and interfacial adsorption have been evaluated from conductometric and tensiometric methods. Various existing theories^{30-37, 38} have been used and the results were compared with the experimental observations to obtain information on the interactions prevailing in the mixed surfactant systems.

In chapter VII micellization behavior of three alkyltrimethylammonium bromides *viz.*, hexadecyl-, tetradecyl-, and dodecyltrimethylammonium bromide (CTAB, TTAB, and DTAB, respectively) in ethylene glycol (EG) (1) + water (2) mixed solvent media with varying mass fractions of EG (w_1) has been studied by means of electrical conductivity and surface tension measurements. Temperature dependence of the critical micelle concentrations was also investigated in order to understand the micellar thermodynamics of these systems. The mass action model^{39, 40} of micelle formation was applied to obtain the thermodynamic parameters of micellization. Only small differences have been observed in the standard molar Gibbs energies of micellization over the temperature range investigated. The enthalpy of micellization was found to be negative in all cases whereas the entropic contributions were always positive, indicating that an enthalpy-entropy compensation effect is the governing factor for micellization. Surface tension measurements also provide information about the effects of the addition of ethylene glycol to water on the excess surface concentration, minimum area per surfactant molecule, the surface pressure at the critical micelle concentrations, and standard Gibbs energy of adsorption. The Gordon parameters⁴¹ for the EG (1) + water (2) mixtures were also estimated by means of surface tension measurements to assess the ability of EG (1) + water (2) mixtures to bring about the self-association of the surfactants investigated.

A summary of the works done has been given in chapter VIII.

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CHAPTER-IX

CONCLUDING REMARKS

Amphiphilic molecules or amphiphiles show numerous interesting properties that are now being actively investigated in many laboratories. Most of the present day knowledge of micellar solutions has come from studies on various surfactants by means of variety of techniques like neutron scattering, quasielastic light scattering, luminescence probing, NMR, spin labeling, chemical relaxation etc. Various thermodynamic properties e.g., apparent molar volume, adiabatic compressibilities, heat capacities, surface tension etc. as well as transport properties e.g., conductance, rheology etc. give important information about micellar solutions. We have, therefore, determined some thermodynamic and transport properties of a number of selected simple amphiphiles in aqueous and non-aqueous media from the measurements of their conductance, surface tension, apparent molar volumes and adiabatic compressibilities. Attempt have also been made to determine the mixed micellar properties of some simple ionic-ionic, ionic-nonionic and nonionic-nonionic surfactant mixtures by means of conductance, surface tension and spectroscopy as these mixtures of surfactants often exhibit properties superior to those of the constituent single surfactants due to synergistic interactions between the surfactant molecules.

Thermodynamics of micellization provide a lot of information on the strength and nature of surfactant-solvent and solvent-solvent interactions. These properties can be derived from the study of surfactant aggregation as a function of temperature. Since the micellization process is most often revealed by the surfactant concentration value at which aggregation takes place *i.e.*, at the so-called critical micelle concentration (*cmc*), it is important to have appropriate procedure to obtain reliable *cmc* values in different solvent media. Different methods have been used to obtain the critical micelle concentration (*cmc*). Proper evaluation of the *cmc*, the degree of counterion dissociation (β), maximum interfacial adsorption (Γ_{\max}), minimum area per surfactant molecule (A_{\min}) and surface pressure at *cmc* (Π_{cmc}) would of great help in determining the surfactant-solvent and solvent-solvent interactions. However, the

cmc values are method dependent and though conductance slopes, light scattering and *cmc* determination as a function of counterion concentration are used as principal experimental techniques for measuring the degree of counterion dissociation, yet there is no unambiguous method of measuring this degree of freedom or of binding of counterions. Efforts should be made to find out a suitable method for the determination of *cmc* as well as the degree of counterion dissociation.

The determination of apparent molar volumes and apparent molar adiabatic compressibilities of surfactant solutions is useful as a guide to the structural properties of these solutions, particularly in the study of surfactant-solvent interactions. The concentration dependence of these properties in aqueous medium can be used to study (i) the electrostatic repulsion between the head groups of the surfactant (ii) the liberation of water molecules from around the hydrocarbon tails of the surfactant molecules (iii) the release of the water molecules from the counterions upon binding to the micelles. The relative magnitude of the limiting apparent molar volumes and the limiting apparent molar adiabatic compressibilities would enable us to provide important information about the solution behaviour of surfactants in aqueous solution.

In general, specific interactions (synergistic or antagonistic) between surfactants result in solution of surfactant mixture having micellar and phase behaviour properties which can be significantly different from those of the constituent single surfactants. Consequently, understanding specific interactions between the various surfactant species present in solution is of central importance to the surfactant technologist. In spite of their considerable practical importance, as well as the challenging theoretical issues associated with the description of these complex fluids, solutions of surfactant mixtures have not received full attention that they deserve. These aspects need consideration and further study.

However, it is necessary to remember that surfactant-solvent interactions are very complex in nature. There are strong electrical forces between the surfactant ions and between the surfactant and solvents. Nevertheless, if careful judgment is used, valid conclusion can be drawn in many cases from conductivity, surface tension, apparent molar volume and apparent molar adiabatic compressibility measurements relating to degree of structure and order of the system.

More extensive studies of the different thermodynamic and transport properties of surfactants will be of immense help in understanding the nature of surfactant-solvent interactions and role of the solvents in different micellar properties.

