Effect of Electrolyte Concentration and Temperature on CMC of Surfactants

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Summary: The relation for the free energy of micellization in case of ionic as well as nonionic surfactants has been updated by including the effect of ionic strength and the size of the ions used. For the verification of the final relation and to compare the results one gets through different techniques like viscometry, light absorption/transmission, surface tension and conductance have been employed to determine critical micelles concentration (CMC) of sodium dodecyl sulphate and sodium tetradecyl sulphate surfactants. It is found that when the electrolyte concentration is very low the viscometry does not give reliable results where as light absorption/transmission does. The surface tension measurement and conductance measurement give reliable and reproducible results at any electrolyte concentration and temperature. A new way of interpretation of conductivity data has also been proposed, through which one can get better results even in the presence of high ionic strength. The results so obtained show the decrease in CMC with the increase in electrolyte concentration and approaches to a constant value. This decrease is in the order of $Na^+ > K^+ > Li^+$. This trend is explained in terms of change in shape of the micelles, specific absorption of electrolytes, variation in double layer thickness and hence variation in the free energy of the system and hydrodynamic radius of the ions used. It is also found that the CMC decreases with the increase in temperature of the system, which is explained in terms of solubility of the surfactants, change in shape of the micelles and free energy of the system with the temperature. Further these variations are in accordance with the equation derived by us.

Introduction

Quite a good number of surfactants are available in the market, which have got wide spread applications in different industries like dyesfuffs, cosmetics, detergents, paints, plastic fibers, pesticides, pharmaceutical, lubricants etc, They also play a vital role in the oil industry of enhanced tertiary oil recovery and in environmental protection e.g. in oil slick dispersents etc. Recognizing the importance of surfactants a residential school was held at Bristol University during 1983, to develop a science of such compounds. On the other hand their properties very much depend upon their concentration in solution, ionic strength of the media and the temperature. For example a specific property of a surfactant will be different if its amount dissolved is less or greater than critical micelles concentration (CMC). Further the CMC depends upon different parameters. Keeping in view these facts, different investigators/research workers showed their interest in this field and a number of research articles are published [1-21]. These investigations are mostly about the mechanism of formation of micelles, change in shape of micelles, the flow properties of surfactants etc. However very little work has been carried out to determine CMC, and to study the effect of different parameters upon it.

Further the values obtained by different authors are different for the same system [22,23]. Moreover the theories available in the literature [24] for the change in free energy of the system, during micelles formation is not very clear and does not clearly indicate the influence of different parameters like ionic strength, ionic size, temperature etc. upon the micelles formation.

Therefore, we have planned to investigate different surfactants with reference to their CMC and effect of ionic strength and temperature upon it. For the purposes number of techniques are used and their reliability is verified and then the case is studied by varying the ionic strength, ionic size and temperature of the system. In addition the theory available for the free energy regarding micellization and effect of above mentioned different parameters is updated and the results are discussed in the light of these relations and other phenomenon involved during the process.

Theory

The most general equation involving the total free energy difference which favours micellization and retains it as such [25] is

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$\Delta G = \Delta G_1$ (Van der Waals/hydrophobic effects) $+ \Delta G_2$ (shortrange)$+ \Delta G_2$ (electrostatic) $+ \Delta G_2$ (steric) $+ \Delta G_2$ (other effects).

Here ΔG is the difference or change in free energy of the system, ΔG_1 means the forces which contribute to the attraction between the molecules/particles and ΔG_2 means the forces which contribute to the repulsion of the molecules/particles. ΔG_3 may be attractive or repulsive. In practice it is not necessary to consider all these contributions simultaneously except in certain special cases. We shall here deal only with ΔG_1 (Van der waals/hydrophobic effect) and long range, short range repulsive potentials due to electrostatic or steric contribution i.e. ΔG_2 (electrostatic).

To consider the hydrophobic or attractive portion of free energy for nonionic surfactants, let us consider the association of N single molecules S of surface active agent to form a micelle M and represented by the following equation.

$$NS = M \qquad (2)$$

by the law of mass action, we can write

$$K = [M]/[S]^N \qquad (3)$$
$$K = C_m/C_\infty^N$$

Where $C_m = [M]$, $C_\infty = [S]$ and K being the equilibrium Constant. Thus the free energy of micellizationis is given as;

$$-\Delta G_1 = , RT \ln K$$

$$-\Delta G_1 = RT \ln C_m, -N RT \ln C_\infty$$

If N is of the order of 100 we can write

$$\Delta G_1 = RT \ln C_\infty$$

If above CMC all the additional surface active agents, added, form new micelles then the C_m remains constant and we can .write [24,26].

$$\Delta G_1 = RT \ln[CMC] \qquad (4)$$

For ionic surface active agents, we have to consider the charge created due to itself and the presence of other ions in the system. For the purpose let us first calculate the work done in bringing two

charges q_1, q_2 together from infinite separation to a distance d in a medium of permitivity ε which is given as:

$$\Delta W = - \int_\infty^d F dh = q_1 q_2 (4 \pi \varepsilon d) \qquad (5)$$

Where $F = q_1 q_2 /(4 \pi \varepsilon d^2)$ and ε_0 is the permitivity of the free space. On the other hand the work done can be taken equal to ΔG. According to Boltzman, distribution Law

$$n = n^\circ \exp(-\Delta G /kT) \qquad (6)$$

n and n° being the average concentration and considered relative to that of n° at reference level taken as the zero energy. For electrostatic case

$$n(+) = n^\circ \exp(-z^+ \varepsilon \Psi/kT) \qquad (7)$$

$$n(-) -n^\circ \exp(+z^- \varepsilon \Psi/ kT) \qquad (8)$$

or

$$n_i = n^\circ \exp(-z_i z^- \varepsilon \Psi/ kT) \qquad (9)$$

n (+) and n (-) are the concentration of positive and negative ions. Z is the valency of the charges. Ψ and κ are electrical potential and Boltzman constant respectively. The volume charge density in the neighbourhood of the surface is given by

$$p = \Sigma_i, n_i Z_i, e \qquad (10)$$

For the purpose of finding potential distribution around a sphere or spherical particle, let us consideer the Gouy Chapman model whcich was originally for the flat plate model [27] and in Cartisian coordinate, the poisson's equation for an electrostatic purpose can be written as:

$$\nabla^2 \psi = - \rho/\varepsilon \qquad (11)$$

Substituting equations (9) and (10) in (11) we get complete Poisson - Boltzman equaion.

$$\nabla^2 \psi = d^2\psi/dx^2 = - 4\pi/\varepsilon \Sigma_i n^\circ_i Z_i \varepsilon \exp(-Z_i \varepsilon \psi/kT) \qquad (12)$$

Using Laplace operator for a radially symmetric potential we get

$\nabla \Psi = 1/r^2 \, d/dr \, (r^2 \, d \, \Psi/dr) = -4\pi/e\Sigma_i n_i Z_i \, e \, Exp \, (-Z_i \, e \, \Psi/kT)$

This equation can not be solved analytically and we have to use Debye-Huckel approximation [28] valid for small values of the potential. Expanding exponential to linear terms we get.

$$1/r^2 \, d \, \Psi \, /dr(r^2 d/dr)=k^2 \qquad (13)$$

This equation can be solved through substitution method and gives.

$$\Psi = \Psi_o \, a/r \, Exp \, (-K(r-a)) \qquad (14)$$

Where a and r are the radius of the particles / micelles and distance from the centre to the point where potential is to be measured respectively, Ψo is the potential at the surface of the particle. κ is called the Debye length or double layer thickness and is given as

$$K = (e^2 \, \Sigma \, n_i \, Z_i^2/\epsilon kT)^{\frac{1}{2}} \qquad (15)$$

Knowing the potential variation with r in a Spherical particle/micelles, we can estimate the free energy of it by the following equation [29]

$$\Delta G= \int_o^{\Psi_o} Qd\Psi \qquad (16)$$

Where,Q is the charge of particles and given as:

$$Q = a\epsilon \, (1 + Ka)\Psi_o \qquad (17)$$

When there is no other charge present except, surfacts own, then

$$K = O \text{ and } Q = a\epsilon \, \Psi_o$$

Putting the value of Q in equation (16) and taking $d\Psi = d\Psi_o$ and solving for G then for κ = O we get

$$\Delta G = \int_o^{\Psi_o} a\epsilon \, \Psi o \, \Psi^o$$

or

$$\Delta G = -1/2 \, a\epsilon \, \Psi^2 \qquad (18)$$

When κ has got some definite value then

$$\Delta G = \int_o^{\Psi_o} a\epsilon \, (1 + ka) \, \Psi_o \, d \, \Psi$$

$$\Delta G = 1/2 \, a\epsilon \, (1 + Ka) \, \Psi o^2 \qquad (19)$$

Upto now we have neglected the size of the ions present in the system and if we take that into account and suppose that its size is a_1 then the value of Q will be given as:

$$Q= a\epsilon \, (I+.Ka +Ka_1) \, \Psi o \qquad (20)$$

and the value of ΔG will be given as

$$\Delta G = - \int_o^{\Psi_o} a\epsilon \, (1 + Ka + Ka_1) \, \Psi_o \, d \, \Psi \qquad (21)$$

The ΔG one gets from equation (18) (19) and (21) will be ΔG_2 and the net energy involved will be.

$$\Delta G = \Delta G_1 + \Delta G_2 \qquad (22)$$

If the net effect is decrease in free energy then it will stabilize the system and vise versa

Results and Discussion

The use of surfactants is extremely wide spread both in industry and for domestic purpose. However their activity as a surfactant begins after micellization. The mechanism of micelles formation is shown in figure 1 i.e. when the concentration of a surfactant increases above a certain limit, called critical micelles concentration (CMC), the non polar chains come close to each other in such a way that the polar ends point towards aqueous media. These aggregates of molecules are called micelles. Due to this aggregation, almost all the physical properties change. To make use of this phenomena, we measured the viscosity, transmittance and absorbance of light, conductance and surface tension of the system for CMC determination.

The results obtained through viscosity measurement were almost constant, irrespect of concentration of the surfactants. The measurements were repeated several times for both the surfactants
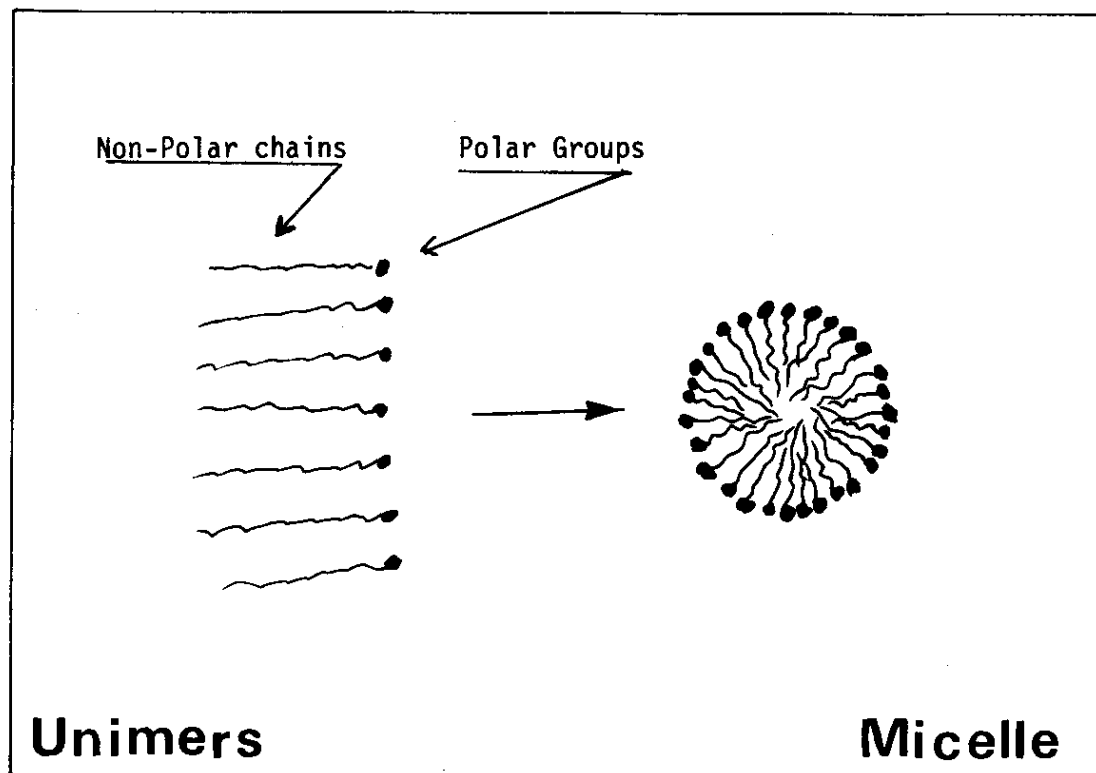
Fig. 1:   A schematic representation of micelles formation by a surfactant in aqueous media

but we were unable to get a reliable value of CMC through this technique, which is contrary to the schematic representation shown in [22,23]. This is probably due to: (i) the viscosity depends upon both size and number of molecules/particles. Whereas during micellization, the number decreases and the size increases (ii) it is also possible that during viscosity measurement the micelles can change to unimers or can disaggregate under high shear rate and hence it becomes difficult to find CMC through this technique. Therefore this technique was not used for the purpose.

The other techniques applied were light absorbance and transmitttance measurement. The data obtained by both the techniques showed a. clear change of CMC and hence it was possible to find out CMC through these techniques (see figure 2). This figure shows that transmittance provided more clear change in data as compared to absorbanee at CMC. However, some errors were found due to some insoluble material, which may be present in the sample. These errors became more pronounce when the salts were added. This may be due to

insoluble/dust particles present in the salts, as dust scatters a lot of light and hence was not possible to measure the absorbed/transmitted light, properly. These errors were so high that it was not possible to get reproduceable results for CMC.as a result we did not provide and discuss the results obtained through these techniques. The surface tension was measured and found that it gave reproducible results in the absence as well as presence of salts (see figure 3). The results obtained for STS and SDS in pure water and obtained through these techniques are comparable to each other and also to data available in the literature [22,23].

Another technique which also found to be useful and gave reproducible results was the conductance measurement. This technique was simple to apply for the measurement of CMC i.e. it was just plotting the conductance versus concentration of the surfactants (see figure 4). However, it was found to be better if ratio of conductance to concentration to be plotted versus square root of concentration of surfactants. In this
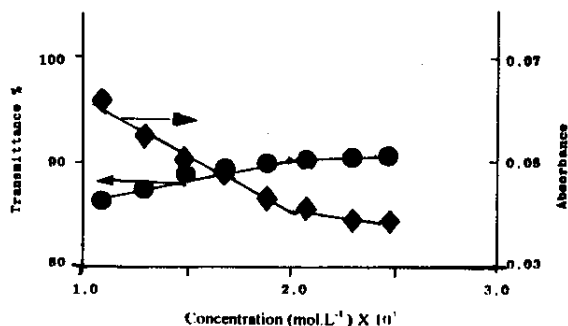
Fig. 2:   Light transmitted and absrbance by STS dissolved in pure water.
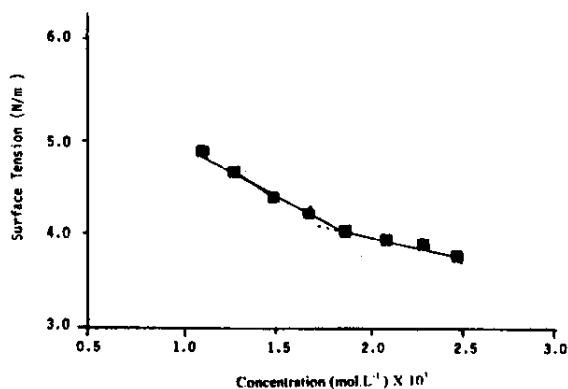

Fig. 3:   Surface tension of STS dissolved in pure water as a function of its concentration.

way it provided enhanced change at CMC and was possible to get better and reliable results. Further when the ionic strength was very high than it was not possible to get CMC just by plotting simple conductance versus concentration of the surfactant (see figure 5). therefore it was necessary to plot the ratio of conductance to concentration versus square root of concentration. However, in this way we got totally another different trend of conductance variation with concentration (compare figure 4 and 6). To overcome this problem and to get reliable and accurate results, even in the presence of high ionic strength, we substructed the conductance of the solvent from that of solutions and then the results were divided by concentration of surfactants and plotted versus square root of concentration of surfactants. In this way it was possible to obtain the same trend in the data as quoted by others [22,23] and provided reliable results. Further through this technique it was possible to get accurate results at any ionic strength and at any temperature. The surface tension and conductance measurements, were performed for the measurement of CMC after addition of electrolytes. It was observed that by the increase in electrolytes concentration the error in the results were also increased. The reasons being: (i) the impurities present in the salts will increase and hence the error; (ii) with the increase in electrolyte
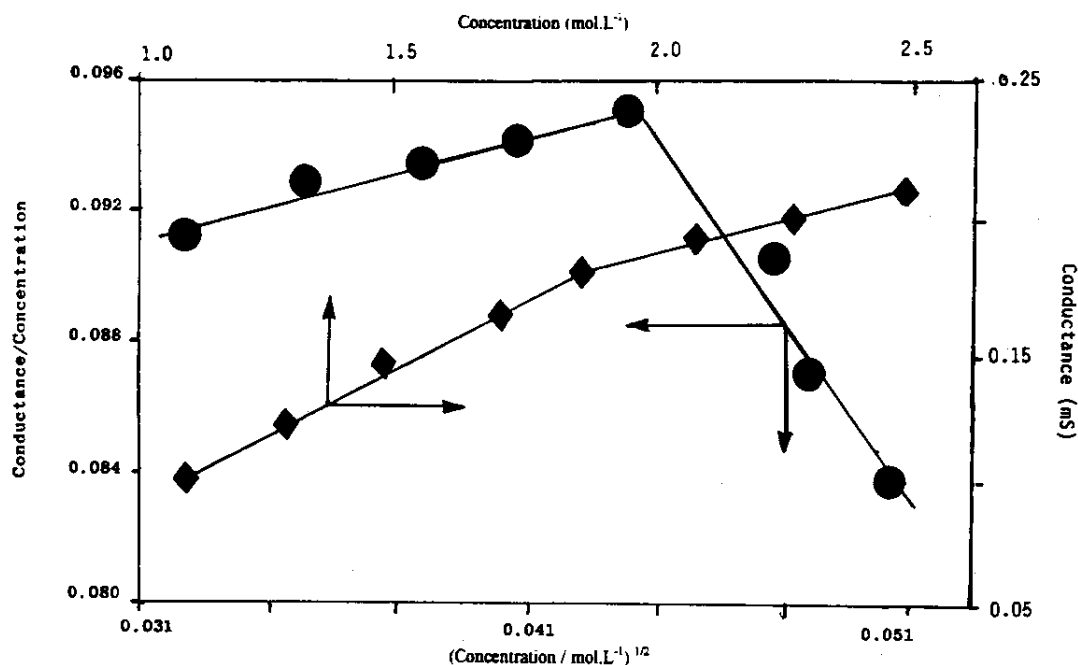

Fig. 4:   Conductance of STS as a function of concentration (■) and (●) ratio of conductance/to concentration of it as a function of square root of concentration, dissolved in aqueous solution of 0.05M LiCl.
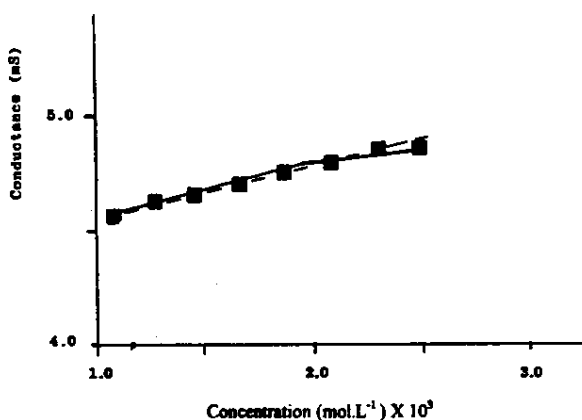
Fig. 5:   Conductance of STS as a function of its concentration dissolved in 0.05M LiCl solution. The dotted line represents the actual data, whereas the solid line is forced one .to get CMC

It was observed that the CMC obtained by different techniques were almost the same (see table-1). The small differences were due to the theories used for the purpose for different techniques through which we get the results is a Havent. For .example, the light scattering phenomenon is very sensitive to bigger micelles/particles/molecules present in the system, where as the conductivity to smaller charged

Table-1: Critical micelles concentration of SDS and STS surfactants in pure water as determined by different techniques.

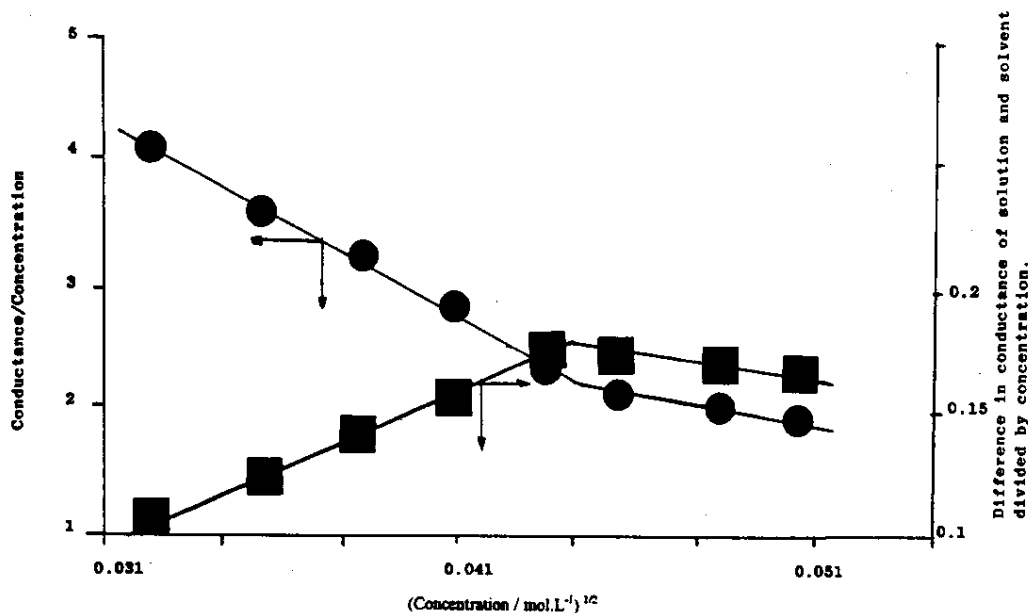| Techniques Used	Critical Micelles Concentration X 10^3 (mol.L^{-1})	
	SDS	STS
Light transmittance	7.80	1.82
Light absorbance	7.75	1.87
Conductance	8.00	2.01
Surface tension	8.20	2.10

Fig. 6:   Conductance to concentration ratio of STS as a. function of square root of concentration and difference in conductance of solution and solvent divided by concentration of STS as a function of.STS.concentration dissolved in aqueous solution of 0.05M LiCl.

concentration the shape of the micelles can change from spherical to cylindrical [11,17,30]. As we know the change in shape plays an important role, especially in viscosity measurement and hence the conductivity may change [15,18,19,30]. Inspite of all this, the results were found to be reproducible and reliable

particles etc. Therefore we believe the results are reliable. Further such difference is also noted by others [22-24], and the result are in the same order as quoted in [24] and different than in [22].

As can be seen from table-1, the CMC of SDS is $8.0 \pm 0.3 \times 10^{-3}$ and that of STS $2.0 \pm 0.2 \times 10^{-3}$

Table-2: Critical Micelles concentration of SDS and STS in the presence of different electrolytes as determined by surface tension and conductance measurement.

Electrolytes used and their concentration (mol.L⁻¹)	:CMC X 10³ of SDS CMC X 10³ of STS			
	Surface Tension	Conductance	Surface Tension	Conductance
LiCl				
0.05	5.72	5.68	1.82	1,80
0.10	5.57	5.52	1.77	1.72
0.20	5.60	5.62	1.81	1.71
0.30	5.80	5.71	1.75	1.65
NaCl				
0.05	7.40	7.35	1.94	1.93
0.10 -	7.15	7.05	1.90	1.85
0.20	7.01		1.95	1:92
0.30	7.05	7.00	1.95	1.93
KCl				-
0.05	6.52	6.45	1.90	1.85
0.10	6.50	6.42	1.85	1:81
0.20	6.48	6.43	1-86	1,84
0.30	6.42	6.40	1.83	1.80

moles/liter, The difference in the CMC of two surfactants is due to the difference in the number of carbon atoms in the chains of the surfactant. With the increase in chain length the free energy increases and hence the CMC decreases. The free energy and the CMC for nonionic surfactants is approximately related to carbon atoms in the chain as [24,31].

$$\Delta G = A-Bn. \quad (23)$$

Where A and B are constants and depend upon different parameters, n is the number of carbon atoms in the chain of the surfactants. For ionic surfactants we have to take into account the charge due to surfactants and the ionic strength [see equations (19) and (20)].

The results obtained through surface tension and conductance measurements are listed in table-2 and plotted in figure 7. This figure gives the variations in CMC of STS and SDS with the increase in concentration of Li^+ Na^+ and K^+. To discuss the effect of electrolyte concentration, we have to consider that the total free energy of micellization of ionic surfactant is related to CMC of the system through the equations (1-22). These equations show that ΔG_1 (attractive) remains almost constant whereas ΔG_2 (repulsive) increases with the increase in ionic strength of the salt added. Therefore, as a result the CMC decreases with the increase in ionic strength. If we look into the figure 7, we see that the CMC firstly decreases very rapidly and then levels off. This is due
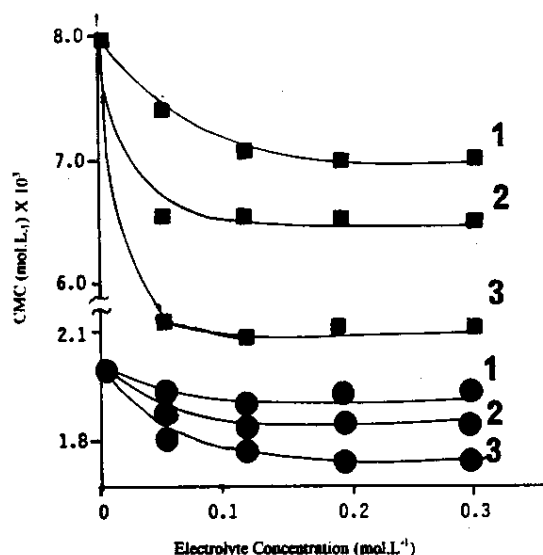

Fig. 7:   Effect of electrolyte concentration on CMC of (■) SDS and (●)STS. The . number on the graphs means (1) LiCl (2) KCl (3) NaCl.

to the fact that by the increase in ionic strength, the Ψ or Q drops with the increase in ionic strength in the same way [27] i.e. almost in the exponential form as per equation (14) and hence the CMC. Further this decrease in CMC with the increase in electrolyte concentration is in accord with the literature [10,22,23,24,31]. This means, that though the equation (19) and the equation (22) are derived on the theories, originally based on the colloid particles concept but work very well and can explain the

phenomena of micelliztion. It is also to be noted that the earlier micelles formation may change the shape as stated by [11,20.21,32]. further, if we,compare the dispersion in the results we find that this is in the order of KCl> LiCl> NaCl. it means that the change in shape of the micelles happens at earliest stage for KCl and latest for NaCl. moreover there can also be a specific absorption, which can play a greater role in controlling the size [33].

If we compare the decrease in CMC With the addition of electrolytes, we find that in all cases the CMC decreases with the addition of electrolyte and then becomes constant as observed by different authors [22,24,31] and discussed earlier. However the extent of decrease in CMC is different for different electrolytes and is in the order of $Na^+ > K^+ > Li^+$ which is opposite to the hydrodynamic radius of ions i.e. $Li^+ > K^+ > Na^+$ [21,34]. This order is the same for both surfactants and it can be explained in terms of free energy, which is affected by size of the ions [27] and related to it through equation (21). This equation tells that bigger the size of ions, more the energy will be and hence lower the CMC value. This is what we get (see figure 7). Further the extent of decrease in CMC of SDS and STS by the addition of electrolyte is in the same ratio and as that in CMC. This proves that the electrical double layer and ionic size play primary role in controlling the CMC of the micelles and hence equation (21) is obeyed by the system.

To see the effect of temperature, the conductance measurements were made at four different temperatures 10-40°C. As it was not possible to measure the surface tension at different temperatures, so we were compelled to get the results only through conductance measurements. The results so obtained are plotted in figure 8. These results show that the CMC decreases with the temperature for both the surfactants. however this decrease is higher in case of SDS and lower in case of STS. It almost approaches to a constant value as early as 25°C for STS and decreases even upto 40 °C for SDS. This decrease in CMC may be due to the reason .that with the increase in temperature the free energy of the system is effected in two ways i.e. the G_i through equation (4) and G2 through equation (15) and (19). Due to this over all change in free energy, the CMC decrease and it is according to our theory
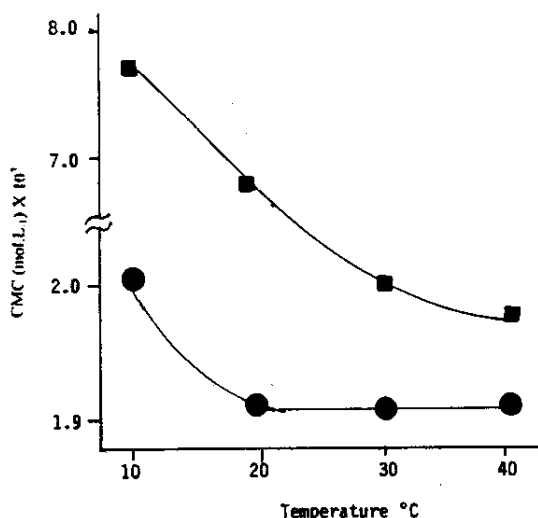

Fig. 8:   Effect of temperature on CMC of (■) SDS and (●) STS dissolved in pure water.

and expectations. Further the change in shape of the micelles from spherical to cylindrical/rod like with the decrease in temperature of the system [30,35,36] can also be one of the reason for such decrease. It is also pointed out that these observations are in accordance to [6,25] and contrary to [1] observations.

Experimental

Chemicals

The surfactants used during this investigation were sodium dodecyl sulphate (SDS) and sodium tetradecyl sulphate (STS). These were obtained from Switzerland. These were of analytic grade and used without further purification. Ions free water was used as a solvent. Different salts used in this study were NaCl, KCl and LiCl these salts were obtained from E.Merck, Germany and used without further purification.

Preparation of Solutions

A stock solution of STS and SDS were prepared by dissolving a known amount of these surfactants, either in the pure (ion free) water or in the solution of NaCl, KCl or LiCl of known concentration. The rest of the solutions were prepared by dilution method. Solutions so prepared were subjected to different studies like light absorption / light transmittance, conductance measurement, viscosity and surface tension measurement.

Procedure

Light Absorption/Transmittance Measurement

The measurements were made at a wave length of 498 nm. The concentration of surfactants was varied over a wide range to be able to measure critical micelles concentration. The instrument used for the purpose was spectronie-21 of Bausch and Lamb, Japan. The instrument was firstly calibrated and then the measurements were made.

Viscosity Measurement

The viscosity of all the surfactant solutions and the solvent was determined at a fixed temperature using Ostward type viscometer, the viscosity bath used for the purpose was supplied by a German firm which provided a required constant temperataure with in ± 0.02 °C variatiens. The viscometer was carefully washed, rinsed and dried before use:

For the flow time measurement a fixed volume of solution and solvent were used. The viscometer was so selected that the solvent flow time was more than 100 seconds, so that the contribution of kinematic energy was to be minimum.

Surface Tension Measurement

The surface tension of the solvent and the solutions was measured by using stalagmometer at constant temperature. For the purpose the number of drops of a fixed volume was counted and the surface tension was calculated.

Conductance Measurement

The conductance of the solvent and the solutions was determined by using Hunna conductometrer made in Italy. The measurements were made for different concentrations and temperature, after carefully washing the electrodes and the container.

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