Study of Thermodynamic Parameters on the Micellar Behaviour of Sodium Decyl Sulfate and Potassium Decyl Sulfate (Anionic Surfactants) in Alcohol+ Water Systems

Mayank*

*Associate Professor, Department of Chemistry, Multanimal Modi College, Modinagar

Abstract

In order to understand the colloidal behaviour of anionic surfactants in mixed solvents, a systematic study on the conductance in aqueous and mixed solvents have been made to determine the CMC, investigate the validity of various equations in these systems and to evaluate the various thermodynamic parameters for their association process. The CMC is defined as a concentration above which any added surface active agent molecules appear with high probability as micellar aggregates. Micelle formation (micellization) is regarded as a phase separation starting at CMC, which represents the saturation concentration of the phase containing single molecules of surface active agents. Although, this approach explains some features of the micelle formation, the available experimental evidences seem to be in agreement with the former one. The thermodynamic principles underlying micelle formation are conceptually simple. The hydrophobic effect provides the driving force for aggregation, whereas repulsion between head groups limits the size that a micelle can attain. The conductance behaviour of Sodium decyl sulfate and Potassium decyl sulfate surfactants in alcoholic and water systems have been studied .The standard Gibbs energy change(ΔG^o) ,enthalpy change (ΔH^o) standard entropy change (ΔS^o) for micellization process have been derived .

Key Words: Sodium decyl sulfate, Potassium decyl sulfate, CMC, Micelles, conductivity, anionic surfactants, alcohol-water system, entropy, Gibb`s free energy, enthalpy.

Introduction

The usefulness of CMC values in various qualitative and quantitative investigations involving surface active agents can be gauged from the fact that the surface and interfacial activity of the amphipathic (polar and non-polar) monomers is closely reflected in CMC values. Above all CMC parameters vary according to whether the solute is monomer or aggregation. Since above the CMC, the activity of monomers rises very slowly, so it is also a measure of the concentration at which the thermodynamic activity of the monomers and therefore, its net surface activity and absorbability to various substrates, level off to a nearly constant value.

Mukherji and Mysels (1) have discussed the CMC concept as well as plot procedure while collecting CMC of surface active agents in various systems of aqueous media and performed seventy one different types of experiments to determine the CMC. Some of the important experiments listed by them are conductivity, surface tension, interfacial tension, viscosity, potentiometry, spectrometry, solubility, light scattering etc.

In all these above mentioned methods, CMC is usually determined by plotting some property as a function of concentration which leads to an intersection point corresponding to CMC. It is evident that the value obtained depends on the type of representations as well as on the physicochemical parameters used. For surface active agents with low CMC, micelle formation begins abruptly and the uncertainties involved are rather small while this is not the case for surface active agents with high CMC. The micelle formation in an aqueous solution is known to be affected by organic additives and there have been many investigations concerning the effects of organic additives on the CMC of anionic surfactants (2-3).Mesa (4) observed the dependence of CMC on temperature and reported the existence of minimum CMC value at a temperature which is peculiar to the system. Furthermore, the CMC values may not be available experimentally due to an insignificant change in physical parameters which follow the aggregation process. Such a situation is met with all aggregation processes where only small number of monomeric surfactant molecules is involved. The problem involved in the determination of CMC values in such cases has been solved by using higher degree of precision using regression analysis to observe the micelle formation. This fact has been confirmed by a large number of investigators (5-8).

Micelle formation (micellization) has been treated either as a stepwise phenomenon or as a phase transition in aqueous solutions of non-linear block polymer (9). In the first approach the micelles aggregate and the monomers of surface active agents are assumed to be in association- dissociation equilibrium and the law of mass action is applied. From time to time several views have been proposed to explain micelle formation in aqueous (10-12) and non-aqueous solutions (13-15). The studies on surfactant behaviour in solvents of medium and high dielectric constant have also been carried out by several workers (16-18). Several workers (19-20) have observed the influence of polar head groups on the CMC and micellar aggregation number of surface active agents.

Materials and Methods

The surface active agents were procured from various organizations. Anionic surfactants used were of high degree of purity (checked by observing no minima in γ vs. log C plots). The CMC of these surfactants in water were found closer to the literature value (**1**).Most of the chemicals used in the study were A.R grade, except a few which were laboratory chemicals of high grade purity. These were used after proper purification. The purity of organic liquids was checked by measuring physical constants like boiling point, density, refractive index and viscosity. Triple distilled water and pyrex glass assembly were used throughout the experiment. Fresh solutions of surfactants were employed for all measurements.

A digital conductivity meter model CM-180 (Elico private limited) and a dipping type conductivity cell with plantinized electrodes were used for measuring the conductance of the surfactant solutions. The experiments were carried out in a thermostat at constant temperature $\pm 0.05^0$C.The cell constant (1.01) for the cell was determined by using standard solutions of KCl of A.R grade. All data were obtained by concentration runs i.e. solutions were diluted by adding the solvent into the clean dry cell and the conductance was measured. Several measurements were made to ascertain the reproducibility of results and the conductivity data were reproducible to 0.5%.

The conductance behaviour of all these surfactants in solutions has been studied by applying the general equation for their conductance behaviour in solution:

$\log \Lambda_M = A + B \log_{10} C$

Where A and B are constants and C is the concentration of the surfactants in mole litre^{-1} and Λ_M is the molar conductivity in ohm^{-1}mole^{-1}cm^2. The value of log Λ_M for zero values of log C (i.e. C=1) have been calculated by extrapolation of log Λ_M vs. log C curves which signify for the constant A as log $\Lambda_{(C=1)}$. The conductance behaviour of all these surfactants in solutions has been studied (2) by applying the general equation (**i**) for their conductance behaviour in solution:

$\log \Lambda_M = A + B \log_{10} C$ ……(**i**)

where A and B are constants and C is the concentration of the surfactants in mole litre^{-1} and Λ_M is the molar conductivity in ohm^{-1}mole^{-1}cm^2. The value of log Λ_M for zero values of logC (i.e. C=1) have been calculated by extrapolation of log Λ_M vs. log C curves which signify for the constant A as log $\Lambda_{(C=1)}$.

The variation of molar conductivity with temperature has been dealt in terms of equation (**ii**):

$$\Lambda_M = A.\, e^{-\Delta E / RT}$$

or $$\ln \Lambda_M = \ln A - \frac{\Delta E}{RT}$$

or $$\log_{10} \Lambda_M = \log_{10}A - \frac{\Delta E}{2.303\ RT} \qquad \text{.......(ii)}$$

Validity of this equation has been tested and the energy of activation of molar conductivity has been derived from the linear plots of log Λ_M vs. 1/T for all the systems. For the aggregation process, when counter ions are bound to the micelle, the standard Gibbs energy change for micellization (per mole of monomer), ΔG^o for the phase separation model is given by the expression (iii):

$$\Delta G^o = 2RT \ln CMC_x \qquad \text{......(iii)}$$

where CMC_x is expressed as a mole fraction of surfactant at CMC. The total number of mole present at the CMC is equal to the sum of moles of the solvents and the surfactant.

The enthalpy change for micellization process (ΔH^o) has been evaluated from the slope of log CMC_x vs. $\frac{1}{T}$ respectively using the familiar equation (**iv, v**):

$$\frac{d}{dT} \ln CMC_x = \frac{\Delta H^o}{RT^2}$$

where CMC_x represent the CMC in term of mole fraction of surfactant at CMC. Integration of above equation leads to:

$$\ln CMC_x = - \frac{\Delta H^o}{RT} + C$$

or $$\log_{10} CMC_x = - \frac{\Delta H^o}{2.303RT} + C \qquad \text{......(iv)}$$

The standard entropy change for micellization processes (ΔS^o) is evaluated using the expression:

$$\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T} \qquad \text{......(v)}$$

Results and Discussion

The conductivity values for all the alkanol+water systems increase with increase in NaDeS and KDeS surfactants concentration and the temperature as well. The variation of conductivity values with increasing molar concentration of alkanol for a given NaDeS concentration at 30^{0}C is observed. For a given NaDeS concentration an increase in conductivity values with increasing concentration of methanol and propanol-1 has been observed whereas a decrease in conductivity has been noticed with increasing concentration of butanol in water. In methanol+water and propanol-1+water systems the increase in conductivity values has been explained in term of release of counter ions and partly due to liberation of surfactants ions whereas in case of butanol-1 and t-butanol a decrease has been assigned due to relative solubility of butanol in water.

Furthermore, for propanol-1+water system CMC at first decreases and after passing through a minimum it increases on increasing propanol-1 concentration. The driving force of micellization is the hydrophobic effect and opposing micelle formation is the electrostatic repulsion between similar charged polar head groups of the surfactants The decrease in CMC is thus due to incorporation of the alkanol into the micelle whereas an increase may be assigned due to the fact that alkanol disrupts the water structure. Initial decrease in CMC on addition of propanol-1 may result from the penetration of propanol-1 molecules in to the micelle. At the minimum CMC, micelles become saturated with propanol-1, additional propanol-1 molecule moves in to solvent resulting it to be more hydrophobic. This causes an increase in CMC on further addition of propanol-1.

The CMC values however increase with increasing temperature of each system studied and can be satisfactorily explained in terms of the dominating behaviour of increased kinetic energy of monomer over the

aggregation of the hydrocarbon chain. The Similar trend has also been observed in KDeS for all the system as well as at different temperatures. This might be due to same number of carbon atoms in hydrocarbon chain (C=10) of both the surfactants i.e. NaDeS and KDeS. However CMC values for NaDeS are relatively lower than KDeS under similar conditions. The values of log Λ_M and log C for NaDeS and KDeS in all the alkanol+water systems and at different temperatures confirm the validity of equation (i).

Theoretical important values of limiting molar conductivity A (i.e. log $\Lambda_{C=1}$) and constant B for NaDeS in 0.5M alkanol+water systems at different temperature (Table-1) have been obtained by plots of log Λ_M vs. log C. The similar trends in A and B values for KDeS were noticed. This might be due to similar hydrophobic nature of both the surfactants.

The values of the activation energy for NaDeS and KDeS at molar conductivity are obtained by linear plots of log Λ_M vs. 1/T by using equation (ii).Activation energy for NaDeS and KDeS are found to be constant but different below CMC as well as above CMC for all the systems studies (Table-2). Furthermore, higher ΔE values below CMC region confirm that after micellization, the energy of activation decreases since the micelle formation is exothermic. As a result of aggregation of hydrocarbon chain of the monomer is sufficient energy is released which predominates the electrical repulsion between ionic head groups and to balance the decrease in entropy accompanying aggregation.

The standard Gibbs energy (ΔG^0) values have been derived using equation (iii) for NaDeS in different alkanol+water systems at 30^0C (Table-3) and KDeS in 0.5M alkanol+water systems (Table-4). Fig.1 represents the plots of ΔG^0 vs. molar concentration of NaDeS in alkanol+water systems 30^0C.

The linear plots of log CMC_x vs. 1/T are made to calculate standard enthalpy change of micellization per mole of monomer of NaDeS and KDeS by using equation (iv).
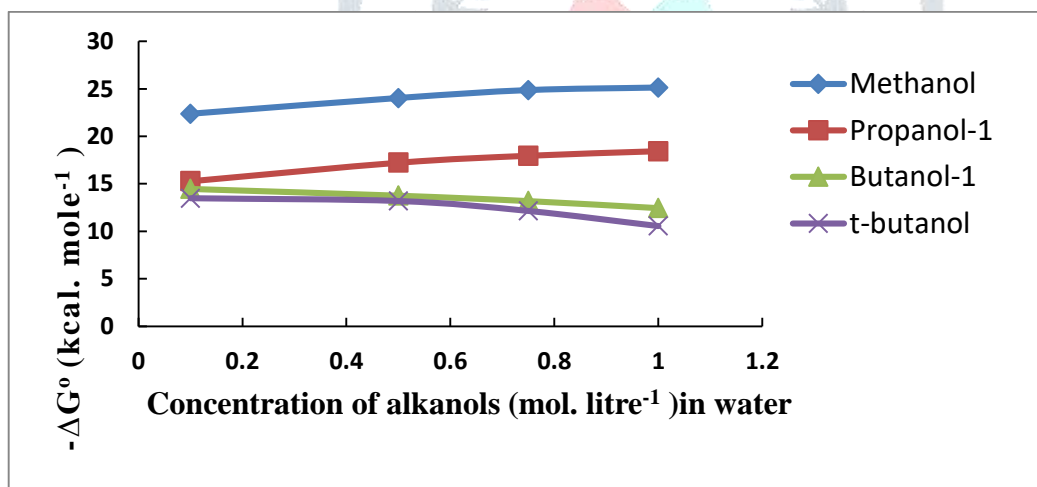

Fig.1: Plots of (-ΔG^0) vs. molar concentration of alkanol+water systems for NaDeS at 30^0C.

Micellar interactions of anionic surfactants in alcoholic and water systems by conductivity and thermodynamic analysis provided valuable information regarding structural changes in the constituent's molecules of system and surfactants which are characterized by hydrophobic interactions as well as hydrophobic hydration. The calculated thermodynamic parameter entropy was found greater than enthalpy suggesting micellization is former driven. Moreover negative value of enthalpy and Gibbs free energy values indicated that the systems are feasible and is of exothermic in nature while positive value of entropy explain that the driving force for micellization is entropic i.e. the tendency of hydrophobic group of surfactants transfer from solvent system to the interior of micelle.

TABLE-1

Values of constant A (log $\Lambda_{C=1}$) for sodium decylsulfate (NaDeS) in 0.5M alkanol+water systems at different temperature.

Temperature	MeOH		PrOH-1		BuOH-1		t-BuOH	
	A	B	A	B	A	B	A	B
30^{0}C	0.300	0.330	0.284	0.310	0.261	0.340	0.253	0.350
35^{0}C	0.310	0.331	0.295	0.310	0.282	0.344	0.275	0.350
40^{0}C	0.350	0.332	0.310	0.320	0.302	0.348	0.294	0.350
45^{0}C	0.380	0.332	0.321	0.322	0.314	0.348	0.326	0.360

TABLE-2

Values of ΔE below and above the CMC obtained from $\log\Lambda_M$ vs. 1/T plots in kcal in 0.5M alkanol+water systems.

Alkanol+water	ΔE (kcal)			
	MeOH	PrOH-1	BuOH-1	t-BuOH
Below CMC	2.301	1.840	2.761	2.300
Above CMC	1.610	1.380	1.839	1.840

TABLE-3

Values of ΔG^o (kcal mol^{-1}) for sodium decylsulfate (NaDeS) in different alkanol+water systems at 30^{0}C.

Concentration of alkanol in water	MeOH	PrOH-1	BuOH-1	t-BuOH
0.10M	22.36	15.28	14.46	13.47
0.50M	24.02	17.22	13.75	13.18
0.75M	24.85	17.95	13.18	12.14
1.00M	25.12	18.43	12.44	10.56

TABLE-4

Values of ΔG^o (kcal mol^{-1}) for potassium decylsulfate (KDeS) in 0.5M alkanol+water systems at different temperature.

Temperature	MeOH	PrOH-1	BuOH-1	t-BuOH
30^{0}C	26.04	27.74	28.72	29.58
35^{0}C	18.72	20.65	21.54	22.83
40^{0}C	17.81	18.04	15.26	14.15
45^{0}C	16.72	17.14	14.25	10.95

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