



# Study of Micelles Aggregation of Cationic Surfactants, tetradecyltrimethylammonium bromide (TTAB) and hexadecyltrimethylammonium bromide (HTAB) in Aqueous Solution of Alcohols

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## Abstract

The solution properties of the tetradecylmethylammonium bromide (TTAB) and hexatetradecylmethylammonium bromide (HTAB) surfactants in different systems have been studied. Micelle formation in different alkanol+water systems at 40°C has been obtained by  $\kappa$  vs. C plots. The conductivity ( $\kappa$ ) values for both the surfactant in alkanol+water systems decrease with the increase of carbon atoms. The molar conductivity ( $\Lambda_M$ ) of these surfactants (obtained in the usual manner from the conductivity data) decreases as the concentration of the solution increase. The thermodynamic functions for the micellization were calculated at various conditions. The standard Gibbs energy  $\Delta G^0$  values have been derived using equation. The linear plots of  $\log CMC_x$  vs.  $1/T$  are made to calculate standard enthalpy. Standard Gibbs energy and entropy for micellization process has also been evaluated.

**Key Words:** Aggregation number, Counter ion, CMC, Micelles, conductivity, Cationic surfactants, Alcohol-water system, Thermodynamic parameters.

## Introduction

Surfactants are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic groups (their tails) and hydrophilic groups (their heads). Therefore, a surfactant contains both a water-insoluble (or oil-soluble) component and a water-soluble component. Surfactants will diffuse in water and adsorb at interfaces between air and water or at the interface between oil and water, in the case where water is mixed with oil. The water-insoluble hydrophobic group may extend out of the bulk water phase, into the air or into the oil phase, while the water-soluble head group remains in the water phase. The aggregation of monomers of surface active agents in some solvents forms particles of colloidal dimensions, called micelles. The concentration at which the micelle formation takes place is called critical micelle concentration (CMC). In order to understand the colloidal behaviour of anionic surfactants in mixed solvents, a systematic study on the conductance of sodium decyl sulfate in aqueous and alkanols have been made with a view to determine whether or not the micellar aggregates are formed for such systems. CMC are determined, if any by the graphs and investigate the validity of various equations in these systems.

Micelle formation of cationic surfactants in aqueous (1) and non-aqueous media i.e. solvents of low dielectric constants e.g. benzene, xylene, toluene etc. (2) has been reviewed. Adderson and Taylor (3) observed that the CMC of cationic surfactants in water decreases with increase in chain length of alkyl groups and also observed that three factors contribute to the enthalpy changes of micellization, namely those associated with head group aggregation, those with breakdown of hydrocarbon stabilized water structure and changes due to the transfer of the hydrocarbon to micelles. Surface mixed films of cationic surfactants at aqueous solution/air interface has been studied by Paluch and Korchowicz (4). Eastoe and coworkers (5) reported the properties of solution of asymmetric chain cationic surfactants.

Several authors (6, 7) explained the micelle formation of cationic surfactants in organic solvents (chloroform, dimethyl formide, dimethyl sulphoxide, formamide, N-methyl acetamide) on the basis of factors like dielectric constant of the medium and hydrogen bonding capability. Akisada and coworkers (8) studied the unusual behaviour of CMC for binary mixture of alkyltrimethylammonium bromide due to the chain length difference. Micelle formation of cationic surfactants in alkanols and alkanol+water systems has been reported by many workers (9, 10, 11). Bahadur and Chand (12) have studied the effect of additives on dodecylammonium chloride. Conductometric and Fluometric investigation on the mixed micellar systems of cationic surfactants in aqueous media were studied by Moore and coworkers (13). The CMC of TTAB and HTAB in aqueous buffered and unbuffered systems have been reported by Fuguet and coworkers (14). Szymczyk and coworkers (15) measured the surface tension and conductivity of a system containing mixture of CTAB and CPyB. Hato and Shinoda (16) have determined CMC, Krafft point, solubilization etc, of bivalent metal alkyl sulfates. The associative interactions and surface tension in ionic surfactant solution at concentrations is much lower than the CMC was reported by Nikolov and coworkers (17). Moroi and coworkers (18) have also reported CMC of binary mixtures of mono and bivalent metal alkyl sulfates in aqueous solutions. Despite these findings on micellar aggregation of bivalent metal alkyl sulfates in aqueous media, not much is known about their solution properties in polar organic solvents. Some investigation comments on the absence of surfactants micelles in alkanol and suggest that surfactants behave like electrolytes in alkanol.

Moroi and coworkers (13) have determined the CMC of sodium dodecylsulfate-bivalent metal dodecyl sulfate in aqueous solution and explained their results by modifying the charge density at the micellar surface and the effective coefficient of an electrostatic contribution to the micelle formation. Furthermore, conductivity of mixed sodium decylsulfate and sodium dodecylsulfate was reported by Mysels and Otter (21). Thermometric titration study on the micelle formation of sodium decylsulfate in water at 15-45°C was reported by Kiraly and Dekany (22). Kinetic study (23) and thermodynamic study (24) of sodium decylsulfate has been reported by several workers.

## Materials and Methods

The surface active agents were procured from various organizations. Cationic surfactants used were of high degree of purity (checked by observing no minima in  $\gamma$  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  $\pm 0.05^\circ\text{C}$ . 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:

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

Where A and B are constants and C is the concentration of the surfactants in mole litre<sup>-1</sup> and  $\Lambda_M$  is the molar conductivity in ohm<sup>-1</sup>mole<sup>-1</sup>cm<sup>2</sup>. The value of  $\log \Lambda_M$  for zero values of  $\log C$  (i.e. C=1) have been calculated by extrapolation of  $\log \Lambda_M$  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):

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

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

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

Validity of this equation has been tested and the energy of activation of molar conductivity has been derived from the linear plots of  $\log \Lambda_M$  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),  $\Delta G^\circ$  for the phase separation model is given by the expression (iii):

$$\Delta G^\circ = 2RT \ln CMC_x \quad \dots\dots (iii)$$

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 ( $\Delta H^\circ$ ) has been evaluated from the slope of  $\log CMC_x$  vs.  $\frac{1}{T}$  respectively using the familiar equation (iv, v):

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

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

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

$$\text{or} \quad \log_{10} CMC_x = - \frac{\Delta H^\circ}{2.303RT} + C \quad \dots\dots(iv)$$

The standard entropy change for micellization processes ( $\Delta S^\circ$ ) is evaluated using the expression:

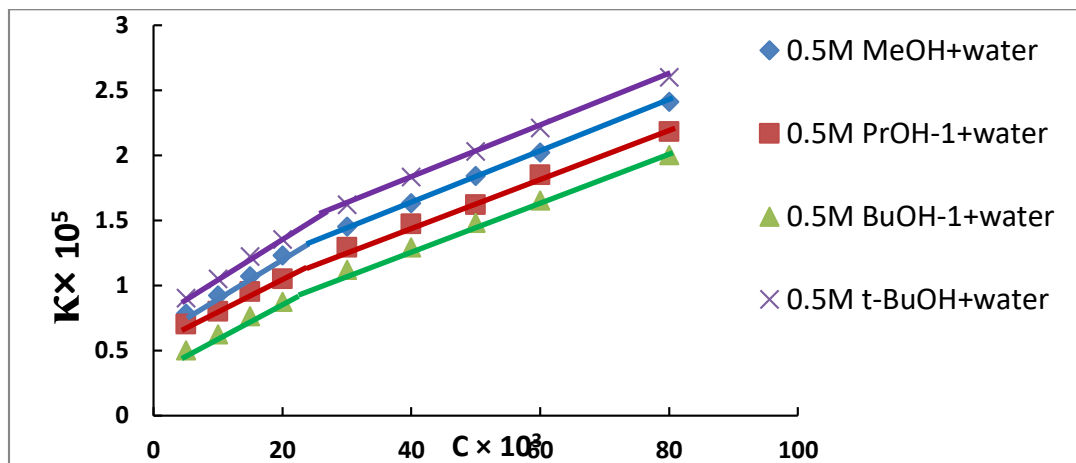
$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \quad \dots\dots (v)$$

## Results and Discussion

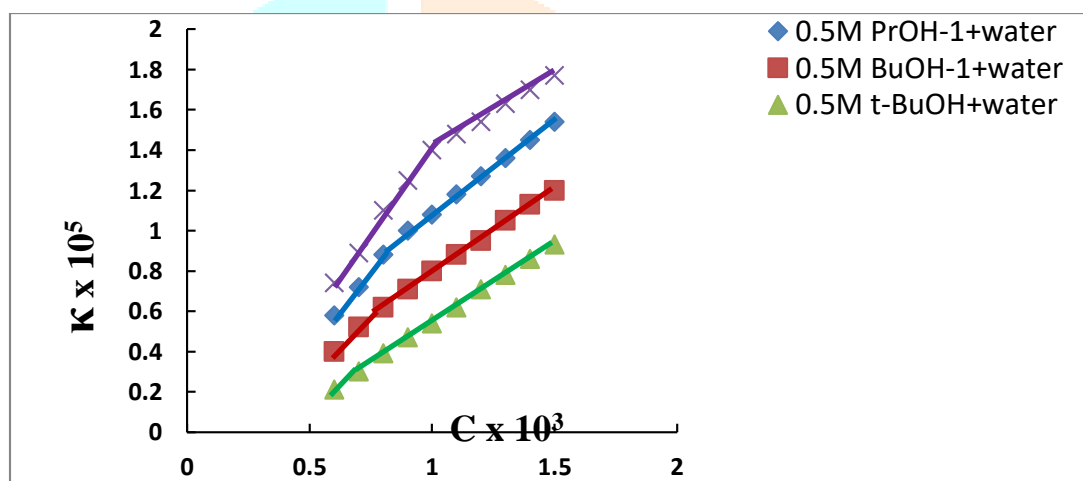
The conductivity ( $\kappa$ ) of tetradecyltrimethyl ammonium bromide (TTAB) and hexadecyl trimethyl ammonium bromide (HTAB) surfactants have been measured in alkanol (methanol, propanol-1, butanol-1 and t-butanol)+water systems within the temperature range (35-50°C). The conductivity ( $\kappa$ ) values for both the surfactant in alkanol+water systems decrease with the increase of carbon atoms in hydrophobic chain of the surfactant as well as in the alkanol used as solvent and exhibit the order: TTAB > HTAB

Micelle formation of tetradecyltrimethylammonium bromide (TTAB) and hexadecyltrimethylammonium bromide (HTAB) in different alkanol+water systems at 40°C has been obtained by  $\kappa$  vs. C plots. All these plots ( $\kappa$  vs. C) are not smooth and show a break at a point indicating the probable formation of micelle (a representative set of figures has been shown in **Fig.1 & 2**); the values of CMC so obtained are recorded in **Table-1**. The values of CMC decrease with increase of carbon atoms in hydrophobic chain of surfactants as

well as for all 0.5M alkanol+water system (**Table-1**). CMC values of TTAB and HTAB in 0.5M methanol+water system increase with increasing temperature and reported in **Table-2**.



**Fig.1:** Plots of conductivity ( $\kappa$ ) vs. molar concentration ( $C$ ) for TTAB in 0.5M alkanol+water systems at 40°C.



**Fig.2:** Plots of conductivity ( $\kappa$ ) vs. molar concentration ( $C$ ) for HTAB in 0.5M alkanol+water systems at 40°C.

The molar conductivity ( $\Lambda_M$ ) of these surfactants (obtained in the usual manner from the conductivity data) decreases as the concentration of the solution increase. The nature of decrease seems to be due to the tendency of the surfactants to form aggregates at higher concentration. The general equation:  $\log \Lambda_M = A + B \log C$  has been applied and the plots of  $\log \Lambda_M$  vs.  $\log C$  are found linear for both surfactants in all alkanol+water systems. The value of surfactants A and B are reported in **Table-1** and **2**. The increasing trend of B values for these surfactants in 0.5M methanol+water systems with temperature also confirm the temperature dependence of CMC.

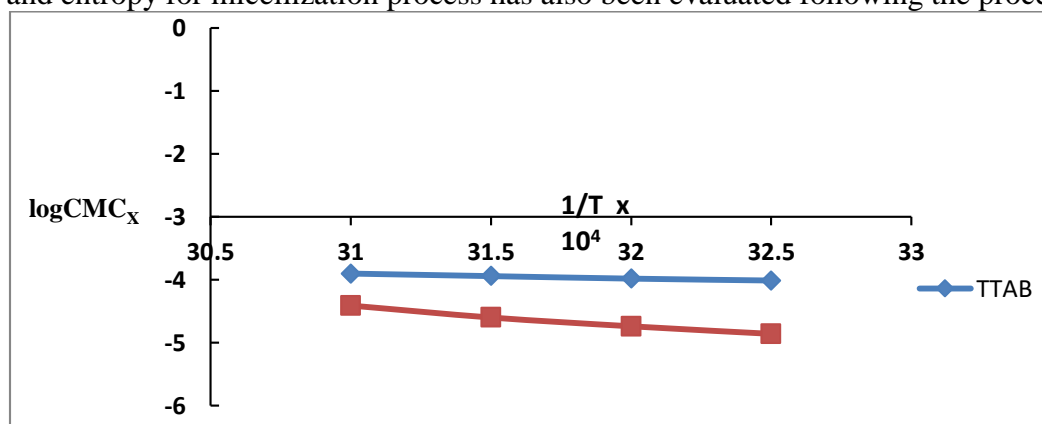
The values of the activation energy (**Table-1**) for TTAB and HTAB in 0.5M alkanol+water systems are obtained by linear plots of  $\log \Lambda_M$  vs.  $1/T$  by using equation (ii). Activation energy for TTAB and HTAB are found to be constant but different below CMC as well as above CMC for 0.5M alkanol+water systems studied (**Table-3**).

Furthermore, higher  $\Delta E$  values below CMC region confirm that after micellization the energy of activation decrease since the micelle formation is assumed when the energy released as a result of aggregation of hydrocarbon chain of the monomer is sufficient to overcome the electrical repulsion between ionic head groups and to balance the decrease in entropy accompanying aggregation. The standard Gibbs

energy  $\Delta G^0$  values have been derived using equation (iii) for TTAB and HTAB in 0.5M alkanol +water systems and reported in **Table-1**.  $\Delta G^0$  values for both the cationic surfactants in 0.5M methanol+water systems at different temperature (35<sup>0</sup>C-50<sup>0</sup>C) are reported in **Table-2**.

The linear plots of  $\log CMC_x$  vs.  $1/T$  (**Fig.3**) are made to calculate standard enthalpy change of micellization per mole of monomer of TTAB and HTAB by using equation (iv) and the values are 3.658 and 8.468 kcal. Mol<sup>-1</sup> for TTAB and the entropy change for micellization process of TTAB and HTAB in 0.5M methanol+water systems at different temperatures are calculated from the equation (v) and summarized in **Table-2**.

The enthalpy change for micellization process ( $\Delta H^0$ ) derived from the linear plots of  $\log CMC_x$  vs.  $1/T$  is found to be **5.028** kcal. mole<sup>-1</sup> in 10% toluene + methanol systems. Standard Gibbs energy and entropy for micellization process has also been evaluated following the procedure reported .



**Fig.3:** Plots of  $\log CMC_x$  vs.  $1/T$  for TTAB and HTAB in 0.5M methanol+water systems. HTAB in 0.5M methanol+water systems respectively.

TABLE-1

Values of CMC and other parameters for cationic surfactants in 0.5M alkanol+water systems at 40<sup>0</sup>C.

Surfactant	Alkanol + water	CMC×10 <sup>3</sup> (mol.litre <sup>-1</sup> )	A	B	-ΔE (kcal mol <sup>-1</sup> )	-ΔG <sup>o</sup> (kcal mol <sup>-1</sup> )
TTAB	MeOH	33.6	1.724	0.114	4.02	11.36
	PrOH-1	31.2	0.562	0.274	4.12	10.60
	BuOH-1	31.0	0.009	0.368	4.36	10.55
	t-BuOH	28.0	0.008	0.374	4.58	10.52
HTAB	MeOH	0.98	2.050	0.109	4.54	12.86
	PrOH-1	0.89	0.941	0.182	4.49	12.20
	BuOH-1	0.76	0.462	0.292	4.39	12.10
	t-BuOH	0.68	0.228	0.278	4.28	12.06

TABLE-2

Values of CMC and other parameters for cationic surfactants in 0.5M methanol+water at different temperatures.

Surfactant	Temp.	CMC×10 <sup>3</sup> (mol.litre <sup>-1</sup> )	A	B	-ΔG° (kcal mol <sup>-1</sup> )	-ΔS°×10 <sup>3</sup> (kcal mol <sup>-1</sup> )
TTAB	35°C	30.9	1.719	0.110	11.28	48.47
	40°C	33.6	1.724	0.114	11.36	47.98
	45°C	36.4	1.729	0.119	11.40	47.40
	50°C	39.4	1.734	0.124	11.48	46.91
HTAB	35°C	0.78	2.02	0.103	12.90	69.32
	40°C	0.98	2.05	0.109	12.86	68.19
	45°C	1.24	2.07	0.114	12.76	66.85
	50°C	1.50	2.09	0.120	12.74	65.70

TABLE-3

Values of ΔE below and above the CMC obtained from logΛ<sub>M</sub> vs. 1/T plots in kcal in 0.5M alkanol+water systems.

Surfactant	Alkanol + water	ΔE ( kcal.)			
		MeOH	PrOH-1	BuOH-1	t-BuOH
TTAB	Below CMC	4.10	4.22	4.48	4.65
	Above CMC	3.42	3.68	3.92	4.10
HTAB	Below CMC	3.84	3.95	4.06	4.23
	Above CMC	3.02	3.10	3.24	3.86

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