
BIBECHANA

A Multidisciplinary Journal of Science, Technology and Mathematics

ISSN 2091-0762 (online)

Journal homepage: <http://nepjol.info/index.php/BIBECHANA>

Surface Tension Studies on the Micellization of Cetyltrimethylammonium Bromide in Presence and Absence of KCl and NaCl in Aqueous Media at Room Temperature

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Article history: Received 30 August, 2013; Accepted 5 October, 2013

Abstract

Precise measurements on Surface tension of cetyltrimethylammonium bromide in presence and in absence of KCl and NaCl in aqueous media are reported. The results showed a sharp decrease in surface tension with increase in concentration of cetyltrimethylammonium bromide and then almost constant value of surface tension was observed. Also, the surface tension decreases with addition of salts. The surface tension of cetyltrimethylammonium bromide is found more in presence of KCl than NaCl in aqueous media. In presence of monovalent salts, the critical micelle concentration (cmc) value decreases which is explained on the basis of the orientation of the surfactant and reduction of the free energy of the surface, thus decreasing surface tension. The graphs of surface tension versus concentration are used in determining the critical micelle concentration (cmc).

Keywords: Cetyltrimethylammonium bromide, Surface tension, Critical micelle concentration, Aqueous media.

1. Introduction

The Cetyltrimethylammonium Bromide (CTAB) is a long chain carbon molecule with a polar head group, which is hydrophilic and a hydrophobic carbon tail. The molecular weight of CTAB is 364.5 and specific gravity is 0.9. CTAB forms spherical micelles above CMC (Critical Micellar Concentration), which is 0.0008 in D₂O and is 0.00001 in H₂O [1]. The surface of the micelle is charged and is therefore classified as cationic micelle.

It is well known that salts (ionic compounds) and non-electrolytes (alcohols, diols, urea, thiourea) can alter the delicate balance of the hydrophobic-hydrophilic interaction of the micelle-forming surfactant in different ways [2-5]. It is, therefore, important to understand the key role of forces that govern the micellization behavior in the presence of various additives. Surface tension is a measure of the free energy of the surface per unit area. Surfactants are substances which alter the surface properties of liquids, even when present in small quantities. Composed of two fractions, a lyophilic group and a lyophobic group, surfactants migrate to the surface, resulting in the lyophilic portion lying within the solution and the lyophobic group orienting itself away from the solution. This orientation of the surfactant reduces the free energy of the surface, thus decreasing surface tension and increasing

surface viscosity. Surfactants reduce the amount of work necessary to create unit surface area i.e. surface tension of a solution is lowered when surfactants are present [6]. The following are a few generalizations regarding surface tension and surfactants, followed by a discussion of surfactants and dynamic surface tension.

Higher concentrations of surfactants lower the surface tension in comparison to the pure solvent state. The limiting value of surfactant concentration that produces a surface tension decrease is the critical micelle concentration [7]. Furthermore; the steeper decrease in surface tension is evident only at high surfactant concentrations.

As the temperature increase, the molecular interaction between the liquids molecules are weaker, since hydrogen bond is the main factor for association between two molecules which are very weak bond, so it can be break easily when the temperature increase leading to decrease in surface tension. We found in the literature [8] that surface tension decreases with increasing temperatures. This decrease can be attributed to the higher surface activity at the higher bulk temperatures and adsorption of contaminates in the system was postulated for this anomaly.

In this paper, we report a study of the aggregation process of CTAB at room temperature in absence and in presence of KCl and NaCl by surface tension method in aqueous media.

2. Experimental

Surface tension measurements were carried out on a stalagmometer. The surface tension of CTAB in absence and presence of salts was measured by drop count method using a stalagmometer.

The experimental set up used for determining surface tension by drop count method was of the standard type (stalagmometer) which is an instrument used to determine the surface tension of a liquid. It was designed by Troube and consists of a pipette with a capillary outflow to be the end of which is flattened out. This is done to give a larger dropping surface. The surface is carefully ground flat and polished. There are two marks, one just above the bulb A, while the other is just below it.

Before using the stalagmometer was first carefully washed with a solution of chromic acid and then with distilled water. Finally, it was washed with acetone and water and dried. It must be kept in mind that the tip of the lower end should not come in contact with hand, desk or some other thing, as it will be contaminated with trace of grease. Slight traces of grease will alter the size of the drops, hence their number. The stalagmometer was held vertical and was not shaken because otherwise the drop will fall out even before attaining its maximum size.

In this process, first the stalagmometer was filled with distilled water as above without changing the pressure. Then the drop count was started. By following the same process all the liquids or solutions of varied strength of CTAB in presence and absence of salt (NaCl and KCl) was measured.

The calculation of the surface tension was done through the following expression:

$$\gamma_{soln} = \left(\frac{n_{solv}}{n_{soln}} \right) \left(\frac{d_{soln}}{d_{solv}} \right) \gamma_{solv} \quad (1)$$

where,

γ_{soln} = surface tension of solution

γ_{solv} = surface tension of solvent

n_{soln} = number of drops of solution

n_{solv} = number of drops of solvent

d_{soln} = density of solution

d_{solv} = density of solvent

If the surface tension of one of the liquids i.e. known then that of the other can be easily calculated from equation (1).

Cetyltrimethylammonium bromide (CTAB), KCl and NaCl were used as purchased from Loba Chemical, India. The water used in the experiments was doubly distilled. The solutions prepared at

room temperature (301.15 K). All the measurements were carried out at the same temperature i.e. room temperature.

3. Results and Discussion

A linear decrease in surface tension was observed with increase in surfactant (CTAB) concentration up to CMC. The CMC of the surfactant decreased in the presence of NaCl and KCl, the decrease being depended upon the concentration of added salt. When an increasing amount of the surfactant is added then the concentration of surfactant on water interface increases. This is manifested as beginning until the concentration at which the cooperative interaction between the surfactant and salt first occurs indicating the onset of the micelle formation. The surface concentration of the surfactant does not increase because all added surfactant associates with salt. This results in a flat part in the surface-tension log [surfactant] curve. This invariance of surface tension with log [surfactant] thus terminates at a surfactant concentration at which the salt becomes saturated by the surfactant and the surface tension starts to decrease again. A concentration of surfactant is finally reached beyond which addition of the surfactant can hardly affect the surface tension of the solution.

This inflection marks the surfactant concentration where all the added surfactant starts to form the surfactant micelles.

When surfactant and salt are mixed in solution, salting-out phenomenon often happens [9-12]. According to hydration theory [13] salting-out is the result of preferential movement of water molecules, which immobilize and quench their role as solvents, from coordination shells of surfactant molecules to those of salts. The effects of halide salts on the growth of micelles in ionic surfactant solutions have been systematically studied [14,15]. With the addition of inorganic salts, the reduced electrostatic repulsion among the surfactant head groups is a key factor to influence the morphology of aggregates in ionic surfactant solutions. For conventional single-chain cationic surfactants, micelles may change from global to rod like or wormlike with the addition of inorganic salts [16,17]. The surface tension and cmc of CTAB in presence of KCl is more than in presence of NaCl because the valence and structure of salts play an important role in the aggregation behavior of cationic surfactants. Inorganic salts affect surfactant aggregation mainly through reducing the electrostatic interaction among the surfactant head groups, and K^+ is more efficient to promote the aggregation of the surfactant than Na^+ . Thus, the cmc of surfactant in KCl is less than in NaCl.

In tensiometry, the *cmc*'s were the threshold surfactant concentrations required to saturate the air/solution interface and were obtained from the sharp breaks in the surface tension (γ) versus log [surfactant] profiles respectively. It is observed that in a given salt-water mixture, the *cmc* of pure CTAB decreases. Two factors must be considered to explain this significant influence of salts on the *cmc* value of CTAB: (a) the presence of salt increases the cohesive energy density, or the solubility parameter, of water, thus decreases the solubility of the monomeric form of the surfactant and hence the *cmc*, and (b) the cosolvent causes an increment in the relative permittivity of the aqueous phase, favouring the mutual attraction of the ionic heads in the micelle, thus supporting micellisation and decreasing the *cmc*.

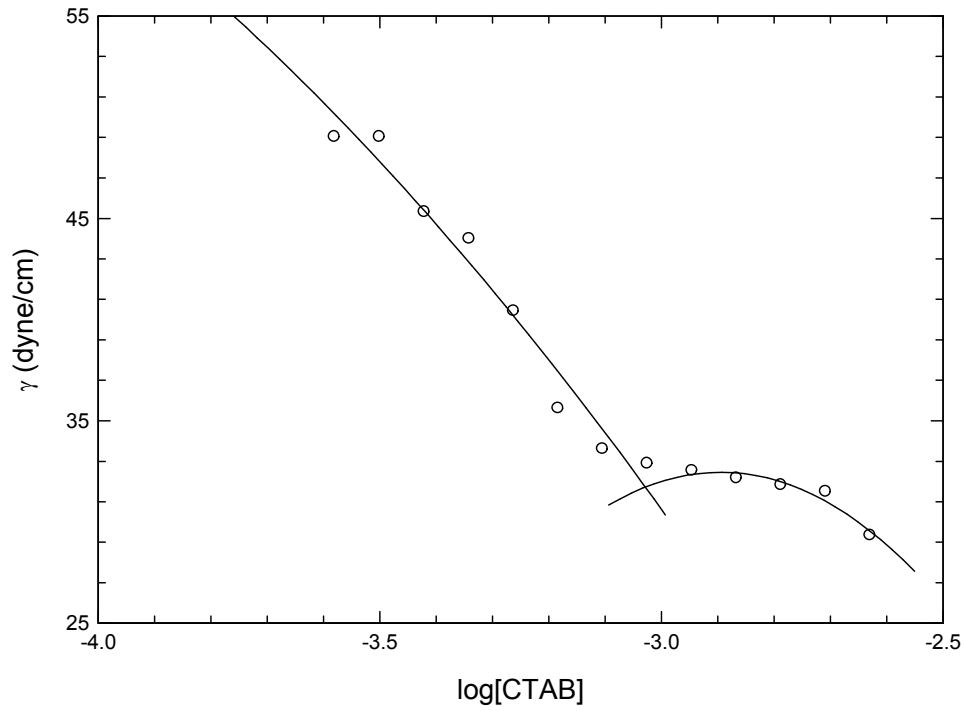


Fig.1: variation of γ with $\text{Log}[\text{CTAB}]$ for CTAB in distilled water at room temperature

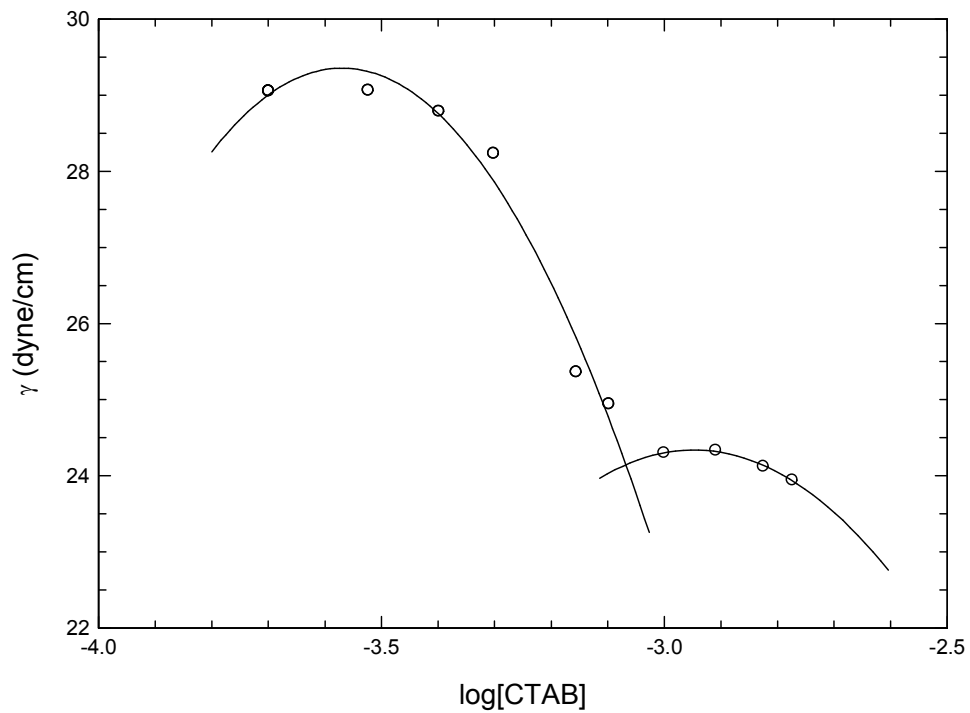


Fig. 2: variation of γ with $\text{Log}[\text{CTAB}]$ for CTAB in NaCl at room temperature

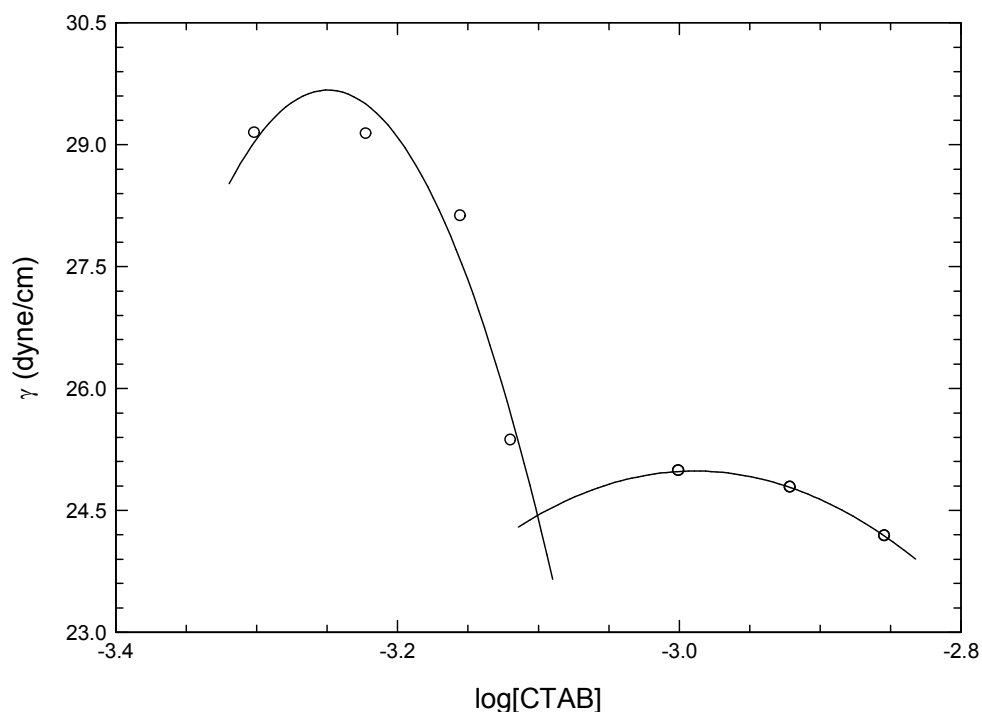


Fig.3: variation of γ with Log[CTAB]for CTAB in KCl at room temperature

Table 1. The Critical Micellar Concentration (cmc) obtained from Surface Tension of Cetyltrimethylammonium bromide in Aqueous Media at 301.15 K

T (K)	Water <i>cmc</i> (mM)	0.01 mol.L ⁻¹ NaCl <i>cmc</i> (mM)	0.01 mol.L ⁻¹ KCl <i>cmc</i> (mM)
301.15 K	0.95	0.87	0.76

4. Conclusions

The following conclusions have been drawn from above results and discussion. The results showed an decrease in surface tension of cetyltrimethylammonium bromide with concentration and addition of salts. The surface tension of cetyltrimethylammonium bromide is found more in presence of KCl than NaCl in aqueous media. Also, in the presence of KCl, the cmc of cetyltrimethylammonium bromide decreases more in comparison with presence of NaCl.

Acknowledgements

One of the authors (Kabita Jha) is thankful to the University Grant Commission (UGC), Nepal, for providing grants for M. Sc. thesis work and we are grateful to Associate Professor G.S. Shrivastav, Head of the department of Chemistry, Mahendra Morang Adarsh Multiple Campus, Tribhuvan University, Biratnagar for providing the research facilities to conduct this research work.

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