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Micellization Behavior of Cetyltrimethylammonium bromide in Presence and Absence of Na_2SO_4 and $MgSO_4$ in Aqueous media

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Abstract

Viscosity and surface tension measurements of cetyltrimethylammonium bromide (CTAB) in presence and absence of Na_2SO_4 and $MgSO_4$ in aqueous media are reported. The results showed an increase in viscosity with increase in concentration of cetyltrimethylammonium bromide in presence and absence of salts where as the decrease in surface tension with increase in concentration of cetyltrimethylammonium bromide in presence and absence of salts. The viscosity of CTAB was observed lowest in pure water and increases in presence of $MgSO_4$ and then more increases in presence of Na_2SO_4 where as the surface tension of CTAB was observed highest in pure water and decreases in presence of Na_2SO_4 and then more decreases in presence of $MgSO_4$.The critical micelle concentration (cmc) of CTAB decreases in presence of salts in both viscosity and surface tension measurements. The decreasing cmc of CTAB are found to be more in the presence of Na_2SO_4 in comparison with the presence of $MgSO_4$ for both measurements. The graphs of viscosity versus log[C] and the surface tension versus log[C] are used in determining the critical micelle concentration (cmc).

Keywords: Critical micelle concentration; Cetyltrimethylammonium bromide; Viscosity; Surface tension.

1. Introduction

Cationic surfactants do show antibacterial properties and are used as cationic softeners, lubricants, retarding agents and antistatic agents and in some cases consumer use also. Hence, cationic surfactants offer some additional advantages over other class of surfactants [1-4]. Like all other surfactants CTAB also shows a rapid change in viscosity when the physical and chemical compositions of the solution are changed [5]. In viscometric determination of CMC of pure surfactant in presence and absence of Na_2SO_4, $MgSO_4$, the viscosities (η) are plotted as a function of the logarithm of the surfactant. The surface tension of a solution is lowered when surfactants are present [6]. The limiting value of surfactant concentration that produces a surface tension decrease is the critical micelle concentration [7]. In tensiometric determination of the cmc of pure surfactants, the surface tensions (γ) are plotted as a function of logarithm of the surfactant concentration. The two fitted lines meet in the curve at the particular point. That point of intersection is known as cmc of the solution.The effective factors, such as the addition of electrolytes, buffer pH, temperature, addition of organic modifiers, ionic strength of the aqueous solution, and presence of additives can change the cmc value from that determined in pure water[8-10]. Addition of electrolyte in the surfactant solution decreases the cmc value [11].

In this paper, we report a study of the aggregation process of CTAB at room temperature in the absence and in the presence of Na_2SO_4 and $MgSO_4$ in aqueous media at room temperature by viscometric and surface tension method.

2. Experimental

Cetyltrimethylammonium bromide (CTAB), Na_2SO_4 and $MgSO_4$ were used as purchased from Loba Chemical, India. The water used in the solutions prepared at room temperature experiments was doubly distilled. The viscometric measurements were performed at room temperature using an Ostwald viscometer. Several independent solutions were prepared, and runs were performed to ensure the reproducibility of the results. To check whether the reduced viscosities depend on the shear rate in the concentration range investigated. This did not lead to different values of the reduced viscosity. Solvent medium from those of the surfactant solutions in presence and absence of salt was taken. The viscometer was always suspended vertically at room temperature. The viscometer was cleaned and dried every time before each measurement. The flow time for constant volume of solution through the capillary was measured with a calibrated stop watch.

The coefficient of viscosity of a given liquid can be calculated according to the following equation:

$$\eta_1 = \left(\frac{d_1}{d_2}\right)\left(\frac{t_1}{t_2}\right)\eta_2 \tag{1}$$

η_1 = coefficient of viscosity of the solution
η_2 = coefficient of viscosity of the solvent
t_1 = time flow of the solution
t_2 = time flow of the solvent
d_1 = density of the solution
d_2 = density of the solvent

The density of any one solution must be known which is calculated by using the expression:

$$d_1 = \left(\frac{w_1}{w_2}\right)d_2 \tag{2}$$

d_1 = density of liquid
d_2 = density of water
w_1= weight of liquid
w_2= weight of water

Before using the stalagmometer was first carefully washed with a solution of chromic acid and then with doubled distilled water. Finally it was washed with acetone and water and dried.

The surface tension of CTAB in absence and presence of Na_2SO_4 and $MgSO_4$ was measured by drop count method using a stalagmometer. 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 solutions of varied strength of CTAB in presence and absence of salts (Na_2SO_4 and $MgSO_4$) was measured.

The following equation is used to calculate the surface tension of required solution:

$$\gamma_{soln} = \left(\frac{n_{solv}}{n_{soln}}\right)\left(\frac{d_{soln}}{d_{solv}}\right)\gamma_{solv} \tag{3}$$

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 is known then that of the other can be easily calculated from the equation (3).

3. Results and Discussion

The specific viscosity decreases with decrease of concentration of CTAB and there is a pronounced break and then remains constant. The breaking point is known as critical micelle concentration, cmc (Fig. 1-3). Our results indicate that there is increase in viscosity with increase in concentration of salt added. The viscosity of CTAB in presence of Na_2SO_4 is more than in presence of $MgSO_4$ (Table1), this is because while $MgSO_4$ is absorbed on the surface of the micelle, Na_2SO_4 remains in the bulk of the solution. Addition of salt is known to decrease cmc of the solution [12]. Increasing the salt concentration reduces the electrostatic Debye screening length around the surfactant, which encourages the formation of longer micelles at equilibrium. This, in turn contributes to the changes in cmc. Fujio (1998) [13] found that spherical micelles associated to form into rod-like micelles when salt concentration exceeded a threshold concentration. Salts decrease the cmc in the order: $MgSO_4 < Na_2SO_4$. Here Mg^{++} is least effective in decreasing the cmc due to small size and large hydrated radius and would act as a water-structure promoter decreasing the availability of water to the micelles. Therefore, upon addition of $MgSO_4$ and Na_2SO_4 in CTAB, Na_2SO_4 is more effective in reducing the cmc of CTAB. Hence in our case Na_2SO_4 decreases the cmc of CTAB more than $MgSO_4$ (Table 2).

The surface tension of CTAB in the presence and absence of Na_2SO_4 and $MgSO_4$ were calculated from equation (3) and were tabulated in Table 3. The graphical representations of the surface tension of CTAB in the presence and absence of Na_2SO_4 and $MgSO_4$ with log [CTAB] are shown in Figs. 4-6. Since, there was sharp decrease of surface tension on increase of surfactant concentrations. According to the experimental calculations and determinations, the surface tension was found to be decreased in presence of salts .i.e. Na_2SO_4 and $MgSO_4$.The surface tension value was high in case of water because of absence of externally added salts. Since, on the addition of inorganic salts, affect surfactant aggregation mainly through reducing the electrostatic interaction among the surfactant head groups and consequently decrease the surface tension of the surfactant molecules.

Table 1: Viscosity of CTAB in absence and presence of MgSO4 and Na_2SO_4 at room temperature

Solvent	Concentration(mol/l)	Viscosity(cp)
Distilled water	0.00315	0.91643
	0.00271	0.90422
	0.00235	0.89231
	0.00204	0.88256
	0.00176	0.87561
	0.00153	0.86825
	0.00133	0.85967
	0.00116	0.85272
	0.00103	0.84782
	0.00086	0.84921
	0.00074	0.84920
	0.00065	0.84919
	0.00056	0.84919
	0.00048	0.84918
Solvent	Concentration(mol/l)	Viscosity(cp)
$MgSO_4$-Water	0.00210	0.89079
	0.00181	0.88780
	0.00157	0.88380
	0.00136	0.88050
	0.00118	0.87800
	0.00100	0.87500
	0.00085	0.86900
	0.00077	0.86500
	0.00066	0.85100
	0.00057	0.85100
	0.00050	0.85100
	0.00043	0.85100
Solvent	Concentration(mol/l)	Viscosity(cp)
Na_2SO_4-Water	0.00170	0.92019
	0.00156	0.91475
	0.00135	0.90722
	0.00118	0.89900
	0.00104	0.89433
	0.00074	0.88079
	0.00052	0.86689
	0.00040	0.86025
	0.00031	0.85300
	0.00025	0.85300
	0.00020	0.85300

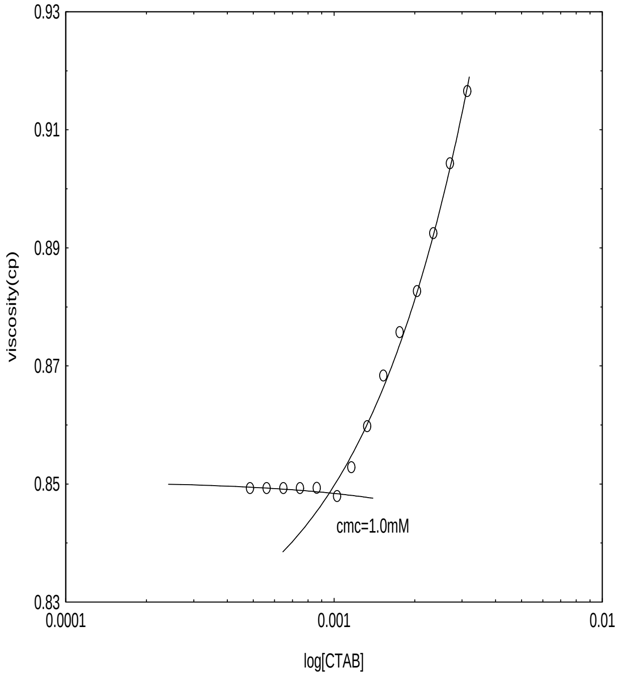

Fig. 1: Variation of Viscosity with log[CTAB] in distilled water at room temperature.

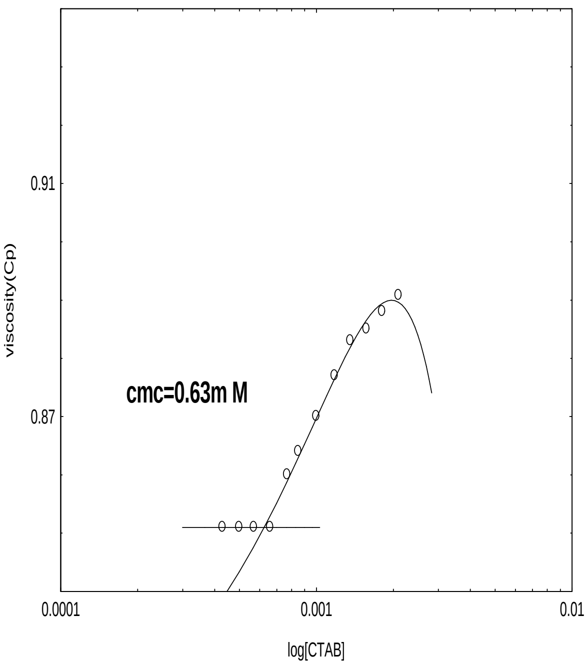

Fig. 2: Variation of Viscosity with log[CTAB] in $MgSO_4$-Water at room temperature.

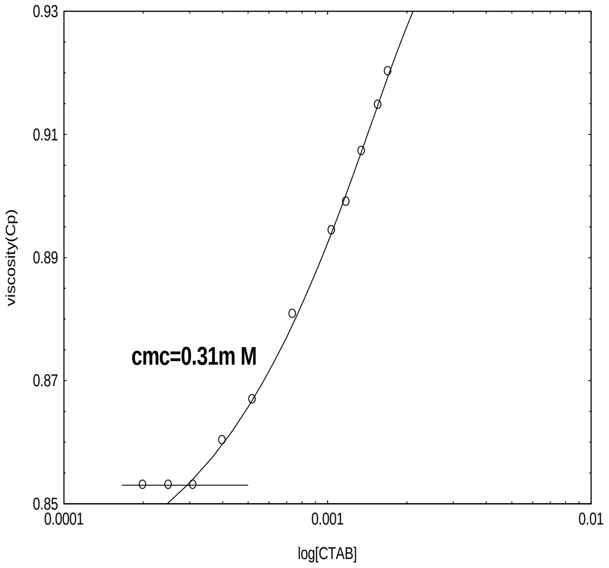

Fig.3: Variation of Viscosity with log[CTAB] in Na_2SO_4-Water at room temperature.

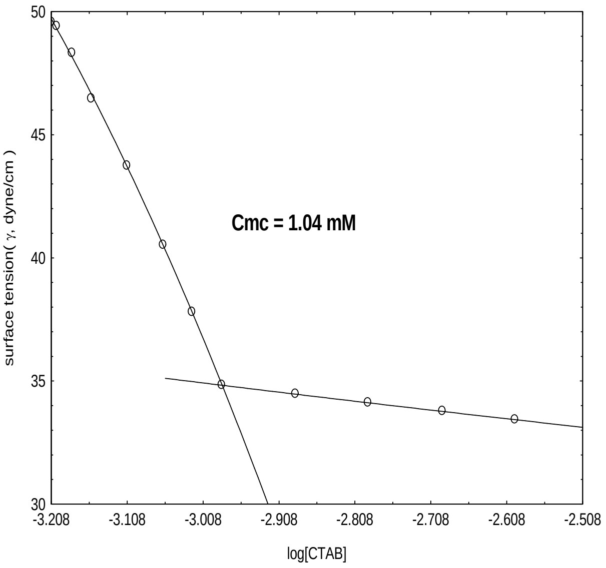

Fig. 4: Variation of surface tension with log[CTAB] in distilled water at room temperature.

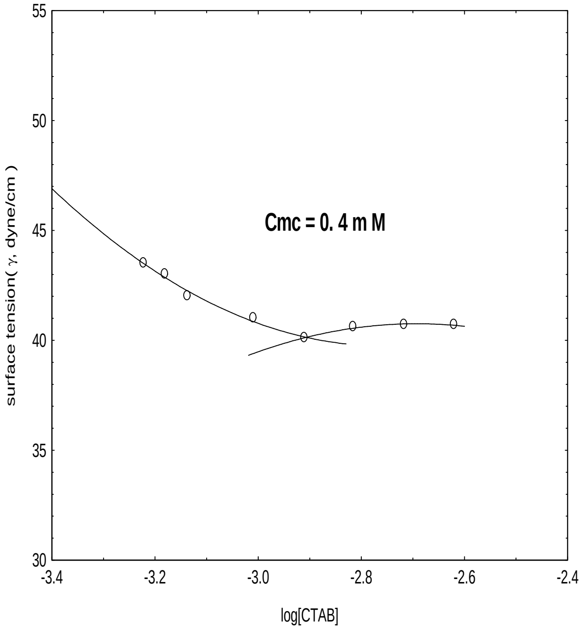

Fig. 5 : Variation of surface tension with log[CTAB] in Na_2SO_4-Water at room temperature.

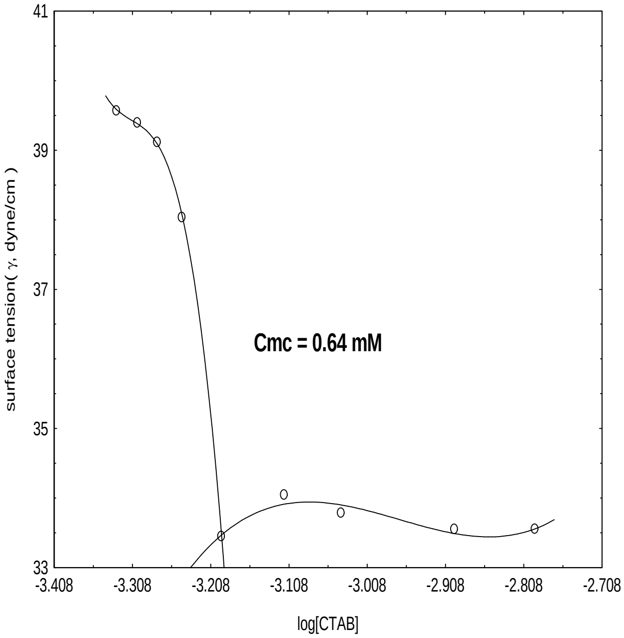

Fig. 6: Variation of surface tension with log[CTAB] in $MgSO_4$- water at room temperature.

Table 2. Critical micellar Concentration (Cmc) obtained from Viscometry of CTAB in presence and in absence of Na_2SO_4 and $MgSO_4$ in aqueous media at room temperature

Distilled water cmc (mM)	Na_2SO_4-Water cmc (mM)	$MgSO_4$-Water cmc (mM)
1.08	0.31	0.63

In the case of Na_2SO_4 and $MgSO_4$, the sodium ion (Na+) is larger than the Magnesium ion (Mg^{2+}) because the Magnesium cation, Mg^{2+} has a greater cationic charge than the Na+ cation. The surface tension of CTAB in presence of Na_2SO_4 is more than in presence of MgSO4 because the smaller ions are strongly hydrated, so they need to pull more water molecules with them which make them less mobile. Thus, due to Magnesium ions (Mg^{2+}) .i.e. counter ions reduced largely the electrostatic interaction among the surfactant molecules and decreased surface tension largely. When surface tension of a solution is plotted against log[C], where C is the concentration of surfactant. The results showed a sharp decrease in surface tension with increase in concentration of cetyltrimethylammonium bromide in presence and absence of Na_2SO_4 and $MgSO_4$ and then minimum surface tension has been observed and again the small increase in surface tension has been noticed and finally the almost flat curves were obtained. The intersection between two curves gives the critical micelle concentration. The critical micelle concentration of the surfactant decreased in presence of Na_2SO_4 and $MgSO_4$, the decrease in cmc depended upon the concentration of added salts. Our calculation of cmc of CTAB in distilled water at room temperature found to be 1.04 mM which is almost matching with 1.102 mM by surface tension method [14]. When surfactant and salt are mixed in solution, salting-out phenomenon often happens [15-18]. According to hydration theory [19] 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 [20-21].

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 [22-23].

Salts decrease the cmc in the order: MgSO4< Na_2SO_4 as like viscosity measurements. (Table 4).

Table 3: The surface tension of CTAB in presence and absence of Na_2SO_4 and $MgSO_4$.

Solvent	Concentration(mol/l)	Surface tension(dyne/cm)
Distilled water	0.00253	33.43
	0.00203	33.77
	0.00162	34.11
	0.00130	34.47
	0.00104	34.83
	0.00095	37.79
	0.00087	40.52
	0.00078	43.73
	0.00070	46.46
	0.00066	48.31
	0.00063	49.40
Na_2SO_4-Water	0.00073	40.70
	0.00066	40.70
	0.00060	40.60
	0.00040	40.10
	0.00030	41.00
	0.00020	42.00
	0.00010	43.00
	0.00009	43.50
$MgSO_4$-Water	0.00161	33.55
	0.00127	33.54
	0.00091	33.78
	0.00077	34.03
	0.00064	33.44
	0.00057	38.02
	0.00053	39.11
	0.00050	39.38
	0.00047	39.55
	0.00044	40.14

Table 4: Critical micellar Concentration (Cmc) obtained from Tensiometry of CTAB in presence and in absence of Na_2SO_4 and $MgSO_4$

Distilled water cmc (mM)	Na_2SO_4-Water cmc (mM)	$MgSO_4$-Water cmc (mM)
1.04	0.40	0.64

4. Conclusions

The following conclusions have been drawn from above results and discussion. The results showed an increase in viscosity of cetyltrimethylammonium bromide with addition of salts where as decrease in surface tension of cetyltrimethylammonium bromide with addition of salts. The viscosity of cetyltrimethylammonium bromide is found more in presence of Na_2SO_4 than $MgSO_4$ in aqueous media whereas the surface tension of cetyltrimethylammonium bromide is found less in presence of $MgSO_4$ than Na_2SO_4 in aqueous media. In the presence of Na_2SO_4, the cmc of cetyltrimethylammonium bromide decreases more in comparison with presence of $MgSO_4$ for both viscosity and surface tension measurements. The calculations of cmc from both systems seem to be equal.

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