

# Measurement of Critical Micelle Concentration of Technical Grade Non-ionic Detergent Tween-40 in Presence of Chloramine-T by Ultrasonic Velocity Measurements

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**Abstract**— The phenomenon of solubilization of nonionic surfactant Tween-40 has been studied through the influence of additive Chloramine-T in aqueous medium by measuring the ultrasonic velocity of the pure surfactant and with Chloramine-T. The ultrasonic velocity of pure surfactant as well as mixed system was found to be increased with increase in temperature. By keeping the surfactant concentration equal to its CMC, for mixed system the CMC found to be increased with the addition of Chloramine-T. This is mainly due to increased micelle concentrations. The CMC for pure or mixed system found to be decreased with increase in temperature. The influence of additive Chloramine-T on the CMC and acoustical parameters of nonionic surfactant is a clear indication that the phenomenon of micellization is associated with the different micelles coalescing. The CMC of pure and mixed system decreases with increase in temperature. This decrease in CMC may be due to change in free energy of the system with increase in temperature. Findings of the present work support to the probable evidence of electrolyte surfactant interactions in aqueous medium.

**Index Terms**— Chloramine-T (CAT), Micellization, Tween-40 (TW-40), Ultrasonic velocity.

## I. INTRODUCTION

Several research workers have studied the molecular interactions in surfactants in the presence of added electrolytes [1]-[4]. Surfactants contain two distinct grouping in their structure. Strongly polar or charged group at one end of surfactant molecule is the “head group” which is hydrophilic in nature and long chain of alkyl or aryl group is the “tail” which is hydrophobic in nature. When surfactants are added to water at low concentration, they are dispersed as discrete molecules. However, at a particular concentration, surfactant molecules get associated to form aggregates or micelles [5]-[7]. This concentration is known as critical micellar concentration (CMC) which is an important property of surfactant. Above CMC, the surfactants exist as aggregates or micelles. CMC of a surfactant is determined by several methods such as conductance, surface tension, solubilization, turbidity, light scattering, diffusion, ultrasonic velocity measurement etc. There are merits as well as demerits in all

these methods. Polysorbates are a class of emulsifiers used in some pharmaceuticals and food preparations. They are often used in cosmetics to solubilize essential oils in to water based products. Tween-40 (TW-40) is one of the polysorbate. TW-40 is nonionic detergent used for cell lysis, nuclei isolation and cell fractionation. It is also widely used in cosmetics and some pharmaceutical preparations. It has been shown earlier that by the addition of electrolyte, CMC of non ionic surfactant is affected [8]. Some inorganic and organic compounds are added to detergents in order to make detergent cheap, user friendly and to boost its power [9], these compounds are called “builders”. Chloramine-T (CAT) is used as a disinfectant, algicide, bactericide, germicide, for parasite control and for drinking water disinfection. Due to these properties, CAT can be used as a “builder” in detergents.

The ultrasonic velocity technique has been used for studying solute-solvent interactions in a number of systems including organic liquids [10], dilute solutions in organic acids [11] and complexes [12]-[13]. The propagation of ultrasonic waves and the measurement of their velocity [14]-[16] has been used to determine the nature of molecular interactions in the systems. Acoustical Impedance ( $Z$ ), Adiabatic Compressibility ( $\beta_{ad}$ ), Intermolecular Free length ( $L_f$ ), Molar Volume ( $V_m$ ), Molar Sound Velocity ( $R_M$ ), Surface Tension ( $\gamma$ ) are functions of ultrasonic velocity. As these parameters throw more light on ion-ion and ion- solvent interactions, an ultrasonic study of CAT- surfactant mixed and pure system has been made at various temperatures and at 2 MHz frequency.

In this paper, the effect on the CMC of pure TW-40 and in presence CAT at various temperatures has been reported. These studies are important in the field of medicinal preparations, agrochemicals, detergents etc.

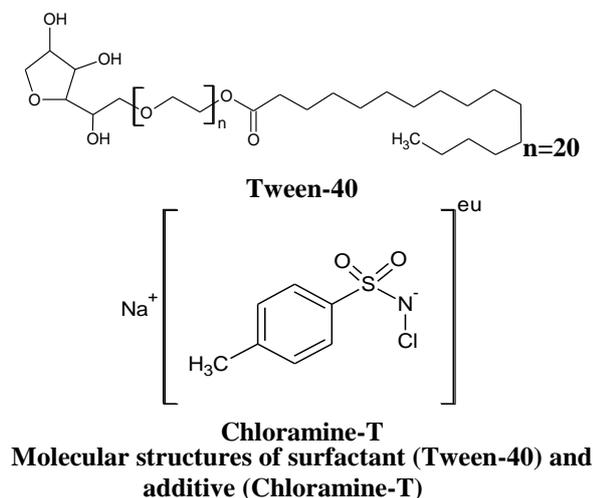
## II. MATERIALS AND METHODS

The nonionic surfactant Tween-40 (M.Wt. 1283.65) and Chloramine-T.Trihydrate (M.Wt. 281.69) were the products of SIGMA-ALDRICH, USA. and these were used as received. Doubly distilled water with Specific Conductance  $2 - 4 \mu S cm^{-1}$  at 303.15 K was used in the preparation of all solutions of different concentrations.

In present investigation, the speed of sound was measured with an uncertainty of  $\pm 0.2\%$  using a single crystal variable path ultrasonic interferometer F-81 operating at 2MHz. This manual instrument is converted in to fully automatic microprocessor controlled, software based instrument-having

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facility to record digital reading of maxima or minima on digital panel and in computer. The accuracy in ultrasound velocity measurement was checked by comparing the observed velocity values of water (1496.4 m/s) and acetone (1164.2 m/s) with those of their literature values (1496 m/s)[17] and (1165 m/s)[18] respectively. In order to maintain the uncertainty of the measurement several maxima and minima are allowed to pass and their number  $n$  is counted. All maxima and minima are recorded with the help of microprocessor operated computerized system graphically.



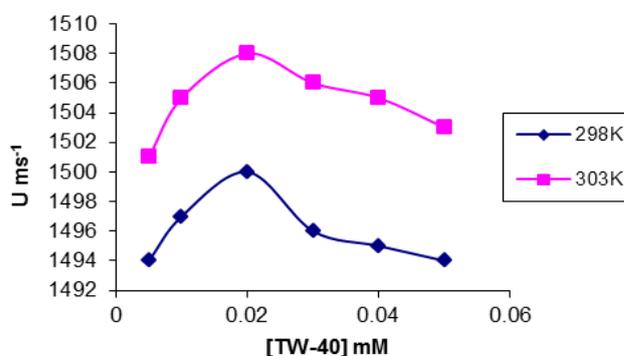
## III. RESULTS AND DISCUSSION

### A. Ultrasonic Velocity Studies of Pure Tween-40:

In the present investigation, CMC values of nonionic surfactants TW-40 is determined by ultrasonic method as formulated in Table 1.

As ultrasonic waves are high frequency mechanical waves, their velocity in the medium depends[19] inversely on the density and the compressibility of the medium. From above data it is clear that as temperature increases, density and adiabatic compressibility decreases hence ultrasonic velocity increases for a particular concentration aqueous solution of nonionic surfactant. Plot of ultrasonic velocity ( $U$ ) in  $\text{ms}^{-1}$  Vs Concentration in mM of nonionic surfactant are given in Fig. 1 for TW-40.

**Fig.1: Plots of Ultrasonic velocity Vs [TW-40] at 298K and 303K temperatures.**



**Table-1 : Acoustic parameters of aqueous TW-40 at various concentrations and at 298K,303K temperatures.**

Conc. (mM)	Density ( $\rho$ ) $\text{kgm}^{-3}$	Ultrasonic Velocity ( $U$ ) $\text{ms}^{-1}$	Adiabatic Compressibility ( $\beta_{ad}$ ) $\times 10^{-10}$ $\text{Kg}^{-1}\text{ms}^{-2}$	Intermolecular Free length ( $L_f$ ) $\text{A}^\circ$	Acoustic Impedance ( $Z$ ) $\times 10^6$ $\text{Kgm}^{-2}\text{s}^{-1}$	Molar Volume ( $V_m$ ) $\times 10^{-3}$ $\text{L.mol}^{-1}$	Molar Sound Velocity ( $R_M$ ) $\times 10^{-4}$ $\text{mmol}^{-1} (\text{N/m}^{1/2})^{-1/3}$	Surface Tension ( $\gamma$ ) $\times 10^4$ $\text{Nm}^{-1}$
<b>298K</b>								
0.005	997.3745	1494	4.4920	0.4167	1.4901	29.63064	338.73	3.628
0.01	997.5046	1497	4.4734	0.4159	1.4933	41.20853	471.41	3.640
0.02	997.6317	1500	4.4550	0.4150	1.4964	64.36383	736.78	3.651
0.03	997.7559	1496	4.4783	0.4161	1.4926	87.51349	1000.89	3.637
0.04	997.9521	1495	4.4834	0.4163	1.4919	110.64940	1265.21	3.634
0.05	998.0792	1494	4.4888	0.4166	1.4911	133.78547	1529.42	3.631
<b>303K</b>								
0.005	997.3607	1501	4.4503	0.4187	1.4970	29.63106	339.27	3.654
0.01	997.4900	1505	4.4261	0.4176	1.5012	41.20913	472.25	3.669
0.02	997.6179	1508	4.4079	0.4168	1.5044	64.36472	738.10	3.680
0.03	997.7421	1506	4.4191	0.4173	1.5026	87.51470	1003.13	3.674
0.04	997.9376	1505	4.4241	0.4175	1.5019	110.65101	1268.04	3.671
0.05	998.0647	1503	4.4353	0.4180	1.5001	133.78742	1532.50	3.664

From the above plots it is clear that the ultrasonic velocity initially increased, acquires a maximum value at CMC and then starts decreasing as the concentration of nonionic surfactant is increased. At CMC aggregation of monomers to form aggregates known as micelles take place hence at CMC ultrasonic velocity is maximum. This observation suggest

that the ultrasonic velocity measurement can be relied upon to yield meaningful information about the micelle aggregation in aqueous solution. The CMC values of nonionic surfactants are very close to the reported values[20],[21].

To study the effect of temperature, the ultrasonic velocity measurements were made at two different temperatures 298K and 303 K. Fig.1 clearly shows that the CMC decreases with increase in temperature for pure nonionic surfactant

solutions[22]-[25], however this decrease is very small. This decrease in CMC may be due to the reason that with the increase in temperature the free energy of the system is affected. Due to this overall changes in free energy, the CMC decreases. Further the change in shape of the micelles from cylindrical/rod to spherical like with the increase in temperature of the system can also be one of the reason for such decrease. Lowering of CMC values with increase in temperature is also in line with the inverse temperature solubility relation of nonionic detergents as presented in Table-3.

**B. Ultrasonic Velocity Studies of Mixed Surfactant Systems:**

The ultrasonic velocity and density values are measured for aqueous solutions of the surfactant in presence of added CAT having different concentrations at 298K and 303K temperature. The surfactant concentration is maintained at the CMC value in these measurements. The acoustical parameters such as adiabatic compressibility, intermolecular free length, acoustic impedance, molar volume, molar sound velocity and surface tension at different concentration of CAT and surfactant concentration at CMC value of pure surfactant are presented in Table 2 for TW-40 (0.02mM).

**Table-2: Acoustic parameters of aqueous 0.02 mM [TW-40] with various [CAT] at 298K and 303K temperatures.**

CAT Conc. (mM)	Density ( $\rho$ ) $\text{kgm}^{-3}$	Ultrasonic Velocity (U) $\text{ms}^{-1}$	Adiabatic Compressibility ( $\beta_{ad}$ ) $\times 10^{-10}\text{Kg}^{-1}\text{ms}^2$	Intermolecular Free length ( $L_f$ ) $\text{A}^\circ$	Acoustic Impedance (Z) $\times 10^6\text{Kg}^{-2}\text{s}^{-1}$	Molar Volume ( $V_m$ ) $\times 10^{-3}\text{L.mol}^{-1}$	Molar Sound Velocity( $R_M$ ) $\times 10^{-4}\text{mmol}^{-1}(\text{N/m}^{1/2})^{-1/3}$	Surface Tension( $\gamma$ ) $\times 10^4\text{Nm}^{-1}$
<b>298K</b>								
0.02	997.5692	1495	4.4851	0.4164	1.4914	56.48955	645.92	3.633
0.04	997.8889	1498	4.4657	0.4155	1.4948	66.63375	762.43	3.645
0.06	998.0175	1500	4.4533	0.4149	1.4970	76.78615	878.98	3.653
0.08	998.0807	1496	4.4768	0.4160	1.4931	86.94163	994.35	3.638
0.1	998.2078	1496	4.4763	0.4160	1.4933	97.08960	1110.41	3.639
<b>303K</b>								
0.02	997.5547	1508	4.4082	0.4168	1.5043	56.49038	647.80	3.680
0.04	997.8758	1508	4.4068	0.4167	1.5048	66.63462	764.13	3.681
0.06	998.0029	1510	4.3945	0.4161	1.5070	76.78727	880.94	3.689
0.08	998.0662	1506	4.4176	0.4172	1.5031	86.94289	996.57	3.675
0.1	998.1940	1504	4.4288	0.4177	1.5013	97.09094	1112.40	3.668

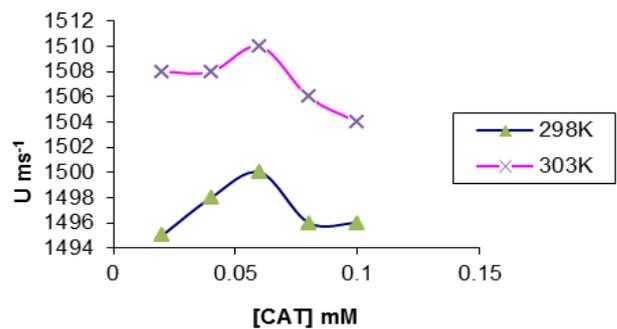
From the above table it is clear that for a given concentration of nonionic surfactant (their CMC values) and additive CAT, the ultrasonic velocity, intermolecular free length, acoustic impedance, molar volume, molar sound velocity and surface tension increases with increase in temperature but adiabatic compressibility decreases with increase in temperature. This is due to decrease in density with increase in temperature as explained earlier. The variation of sound velocity with concentration of surfactant is given by relation[26].

$$dU/dc = - (U/2) [(1/\rho)(d\rho/dc) + (1/\beta_{ad})(d\beta_{ad}/dc)]$$

According to Eyring and Kincaid model for soundwave propagation, the sound velocity increases as inter-molecular free length decreases as a result of mixing of components. This is further supported by expected decrease in  $\beta_{ad}$  with increased concentration of surfactant, signifies the probable interaction between the solute and solvent[27].

For a given concentration of nonionic surfactant which is equal to its CMC value, plots of ultrasonic velocity (U) Vs concentration of CAT at 298K and 303K for TW-40 (0.02mM) is represented in fig.2. This plot show that the maximum interactions exists at a characteristic concentration (at maximum ultrasonic velocity). The concentration of CAT at which the interactions are maximum at 298K and 303K for mixed system of TW-40 with CAT is presented below in Table-3.

**Fig.2:Plots of Ultrasonic velocity Vs [CAT] at 298K and 303K for 0.02 mM aqueous [TW-40] and CAT mixed system.**



**Table-3: [CAT]<sub>max</sub>/CMC values for TW-40 pure nonionic surfactant and mixed system with CAT at 298K and 303K temperatures.**

Temp.K	TW-40	0.02 mM TW-40 and CAT mixed system
298	0.021	0.06
303	0.020	0.059

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The trend in the acoustical parameters with concentration of detergents suggest that aggregation of surfactant molecules is taking place at CMC and there is influence of Chloramine-T on detergent action. The influence of additive Chloramine-T on the CMC and acoustical parameters of nonionic surfactant is a clear indication that the phenomenon of micellization is associated with the different micelles coalescing. From the above table it is also inferred that the CMC of any mixed system decreases with increase in temperature. This decrease in CMC may be due to change in free energy of the system with increase in temperature. Further the change in shape of the micelles from cylindrical or rod like to spherical with the increase in temperature of the system [22],[24],[25] can also be one of the reason for such decrease.

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