Research Article

A Study of Influence of Chloramine-T on the CMC of non-ionic surfactant TritonX-100 by Ultrasonic Velocity Measurements

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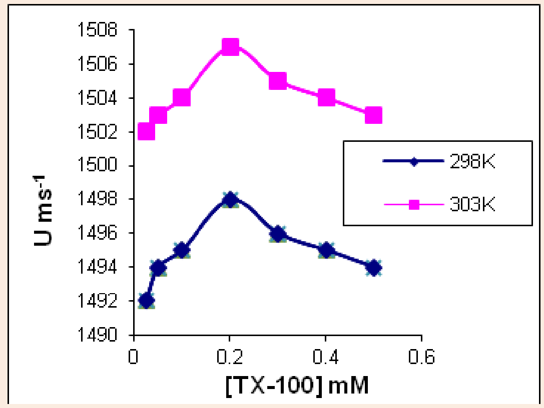
Abstract

The phenomenon of solubilization of nonionic surfactant TritonX-100 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 surfactnat 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.



Keywords: Chloramine-T (CAT), Micellization, TritonX-100 (TX-100), ultrasonic velocity

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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.

TX-100 widely used as detergent in molecular biology [8] and for pre-concentration in analytical chemistry. The principle use of TX-100 surfactant is in industrial and household detergent applications and in emulsifying agents. It is used almost in every type of liquid, paste, and powdered cleaning compound, ranging from heavy-duty industrial products to gentle detergents for fine fabrics. TX-100 is also important ingredients of primary emulsifier mixtures used in the manufacture of emulsion polymers, stabilizers in latex polymers and emulsifiers for agricultural emulsion concentrates and wettable powders. It has been shown earlier that by the addition of electrolyte, CMC of TX-100 is affected by the additives [9]. Some inorganic and organic compounds are added to detergents in order to make detergent cheap, user friendly and to boost its power[10],these compounds are called “builders”. Chloramine-T (CAT) is used as an disinfectant, algaecide, bactericide, germicide, for parasite control and for drinking water disinfection. Due to these properties, CAT can be used as a “builder” in detergents.

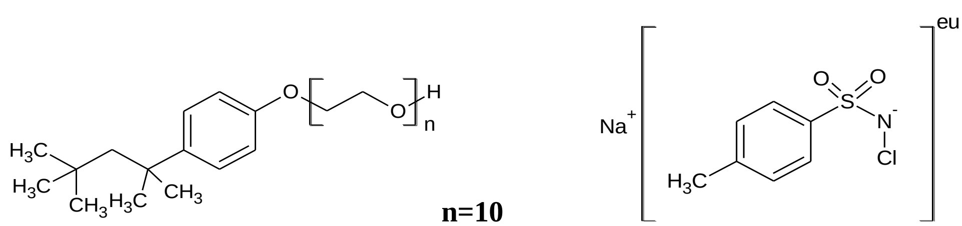
The ultrasonic velocity technique has been used for studying solute-solvent interactions in a number of systems including organic liquids [11], dilute solutions in organic acids[12] and complexes [13-14]. The propagation of ultrasonic waves and the measurement of their velocity[15-17]has been used to determine the nature of molecular interactions in the systems. Acoustical Impedance (Z), Adiabatic Compressibility (β_{ad}), Intermolecular Free length (L_f), Molar Volume (V_m), Molar Sound Velocity (R_M), Surface Tension (γ) 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 TX-100and in presence CAT at various temperatures has been reported. These studies are important in the field of medicinal preparations, agrochemicals, detergents etc.

Experimental

The nonionic surfactant TritonX-100 (M.Wt. 646) 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 μ 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 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)[18]and (1165 m/s)[19]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.



n=10

TritonX-100 **Chloramine-T**

Molecular structures of surfactant (Triton X-100) and additive (Chloramine-T)

Results and Discussion

(*A*) Ultrasonic Velocity Studies of Pure TritonX-100:

In the present investigation, CMC values of nonionic sufactants TX-100 is determined by ultrasonic method as formulated in **Table 1**.

As ultrasonic waves are high frequency mechanical waves, their velocity in the medium depends[20]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 ultrsonic velocity increases for a particular concentration aqueous solution of nonionic surfactant. Plot of ultrasonic velocity (U) in ms^{-1} Vs Concentration in mM of nonionic surfactant are given in **Figure 1** for TX-100.

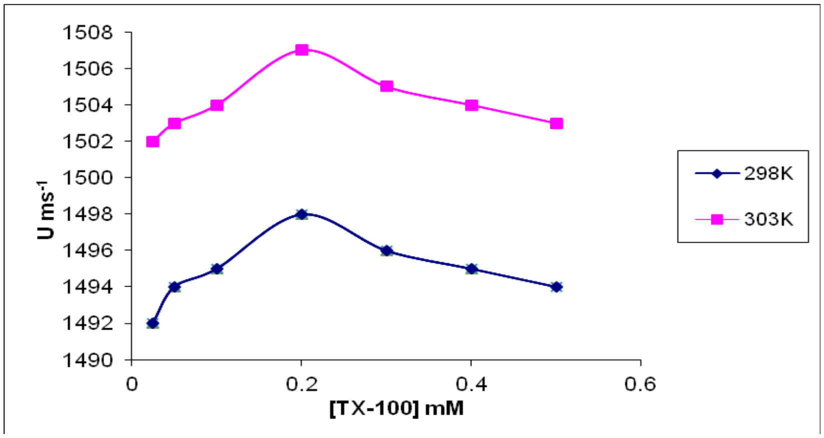


Figure 1 Plots of Ultrasonic velocity Vs [TX-100] at 298K and 303K temperatures

Table 1 Acoustic parameters of aqueous TX-100 at various concentrations and at 298K,303K temperatures

Conc. (mM)	Density (ρ) kgm^{-3}	Ultrasonic Velocity (U) ms^{-1}	Adiabatic Compressibility (β_{ad}) x 10^{-10} $Kg^{-1}ms^2$	Intermolecular Free length (L_f) A°	Acoustic Impedance (Z) x 10^6 $Kgm^{-2}s^{-1}$	Molar Volume (V_m)x10^{-3} $L.mol^{-1}$	Molar Sound Velocity(R_M) x10^{-4} $mmol^{-1}$ $(N/m^{1/2})^{-1/3}$	Surface Tension (γ) x 10^4 Nm^{-1}
298K								
0.025	996.7374	1492	4.5069	0.4174	1.4871	47.22408	539.62	3.619
0.05	996.9299	1494	4.4940	0.4168	1.4894	76.37448	873.10	3.627
0.1	997.1224	1495	4.4871	0.4165	1.4907	134.66752	1539.84	3.631
0.2	997.2466	1498	4.4686	0.4156	1.4939	251.25179	2874.84	3.643
0.3	997.4384	1496	4.4797	0.4162	1.4922	367.78209	4206.31	3.636
0.4	997.6310	1495	4.4848	0.4164	1.4915	484.26724	5537.31	3.633
0.5	997.8206	1494	4.4900	0.4166	1.4907	600.70919	6867.22	3.630
303K								
0.025	996.7250	1502	4.4472	0.4186	1.4971	47.22466	540.83	3.655
0.05	996.9153	1503	4.4404	0.4183	1.4984	76.37559	874.86	3.660
0.1	997.1071	1504	4.4337	0.4180	1.4996	134.66958	1542.95	3.664
0.2	997.2321	1507	4.4155	0.4171	1.5028	251.25545	2880.62	3.675
0.3	997.4239	1505	4.4264	0.4176	1.5011	367.78745	4214.79	3.669
0.4	997.6164	1504	4.4314	0.4179	1.5004	484.27430	5548.48	3.666
0.5	997.8061	1503	4.4365	0.4181	1.4997	600.71794	6881.09	3.663

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. These observations 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[21,22].

To study the effect of temperature, the ultrasonic velocity measurements were made at two different temperatures 298K and 303 K. **Figure 1**clearly shows that the CMC decreases with increase in temperature for pure nonionic surfactant solutions[23-26], however this decreases 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 reasons 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 **Table3**.

*(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 TX-100 (0.2mM).

Table 2 Acoustic parameters of aqueous 0.2 mM [TX-100] with various [CAT] at 298K and 303K temperatures

CAT Conc. (mM)	Density (ρ) kgm^{-3}	Ultrasonic Velocity (U) ms^{-1}	Adiabatic Compressibility $(\beta_{ad})x10^{-10}Kg^{-1}ms^2$	Intermolecular Free length (L_f) A°	Acoustic Impedance (Z)X 10^6 $Kgm^{-2}s^{-1}$	Molar Volume $(V_m)x10^{-3}$ $L.mol^{-1}$	Molar Sound Velocity(R_M)x 10^{-4} $mmol^{-1}$ $(N/m^{1/2})^{-1/3}$	Surface Tension(γ)x 10^4Nm^{-1}
298K								
0.2	997.1210	1492	4.5052	0.4173	1.4877	334.93269	3827.19	3.620
0.4	997.3113	1496	4.4803	0.4162	1.4920	436.55055	4992.81	3.636
0.6	997.5700	1494	4.4911	0.4167	1.4904	538.09279	6151.40	3.629
0.8	997.8882	1493	4.4957	0.4169	1.4898	639.54421	7309.55	3.627
1	998.1403	1492	4.5006	0.4171	1.4892	740.98002	8467.00	3.624
303K								
0.2	997.1071	1504	4.4337	0.4180	1.4996	334.93732	3837.48	3.664
0.4	997.2968	1507	4.4152	0.4171	1.5029	436.55691	5005.09	3.676
0.6	997.5561	1504	4.4317	0.4179	1.5003	538.10024	6165.18	3.666
0.8	997.8729	1502	4.4421	0.4184	1.4988	639.55400	7324.32	3.659
1	998.1257	1501.5	4.4439	0.4184	1.4987	740.99083	8485.05	3.659

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[27].

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

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 β_{ad} with increased concentration of surfactant, signifies the probable interaction between the solute and solvent[28].

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 TX-100(0.2mM) is represented in **Figure 2**. This plot show that the maximum interactions exist 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 TX-100 with CAT is presented below in **Table3**.

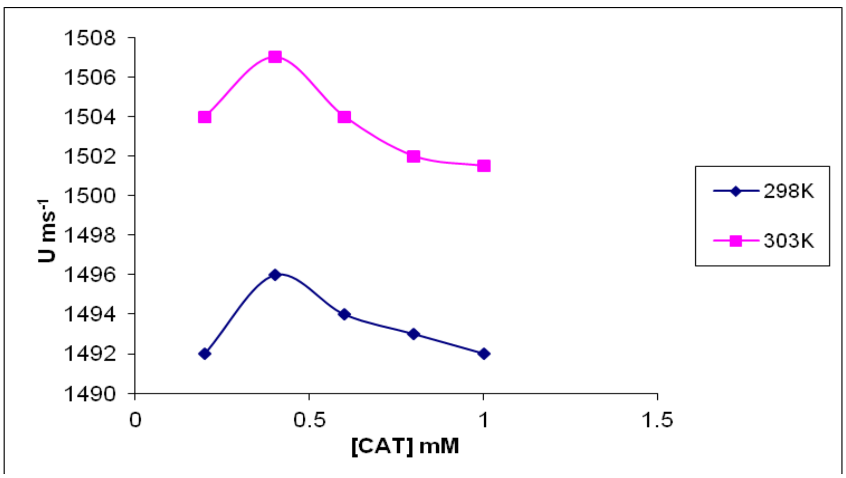


Figure 2 Plots of Ultrasonic velocity Vs [CAT] at 298K and 303K for 0.2 mM aqueous [TX-100] and CAT mixed system

Table 3 $[CAT]_{max}$/CMC values for TX-100 pure nonionic surfactantand mixed system with CAT at 298K and 303K temperatures

Temp.K	TX-100	0.2 mMTX-100 and CAT mixed system
298	0.215	0.425
303	0.205	0.41

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 [23,25,26] can also be one of the reason for such decrease.

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