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Research Article

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The study of influence of chloramine-T on CMC of nonionic surfactant TritonX-114 by ultrasonic velocity measurements

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ABSTRACT

The phenomenon of solubilization of nonionic surfactant TritonX-114 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 decreses 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.

Key words: Micellization, ultrasonic velocity, TritonX-114 (TX-114), Chloramine-T (CAT)

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. 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-114 used for pre-concentration in analytical chemistry [8]. The principle use of TX-114 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-114 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-114 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.

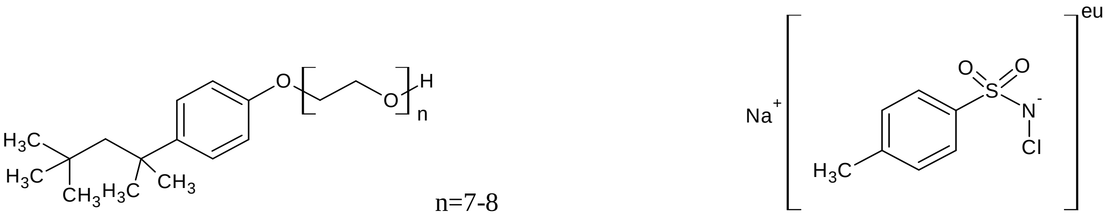
The ultrasonic velocity technique has been used for studying solute-solvent interactions in a number of systems including organic liquids [11], dilute solutions in organic acids [12] and complexes [13-14]. The propagation of ultrasonic waves and the measurement of their velocity [15-17] has been used 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-114 and in presence CAT at various temperatures has been reported. These studies are important in the field of medicinal preparations, agrochemicals, detergents etc.

EXPERIMENTAL SECTION

The nonionic surfactant TritonX-114 (M.Wt. 537) 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 ±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.



TritonX-114 **Chloramine-T**

Molecular structures of surfactant (Triton X-114) and additive (Chloramine-T)

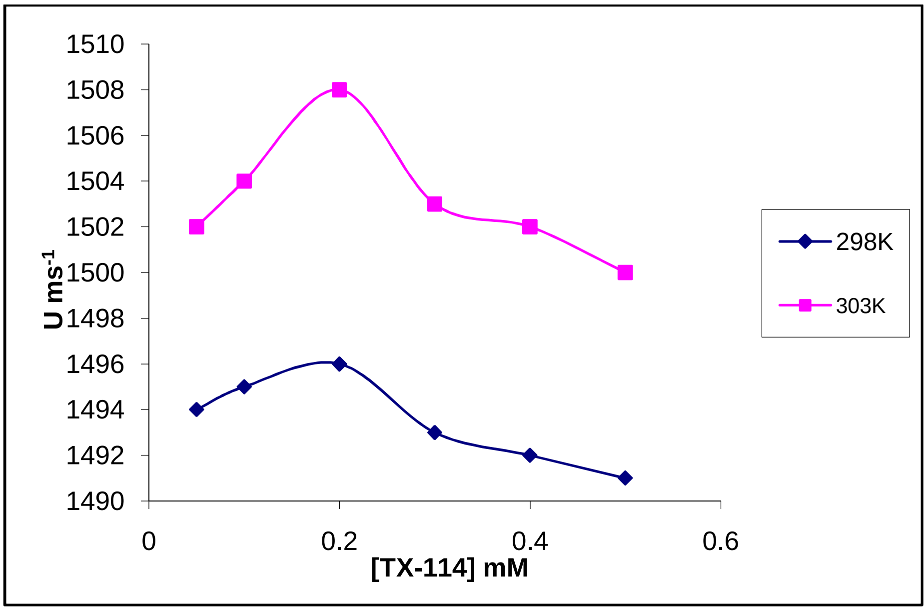
RESULTS AND DISCUSSION

(*A*) Ultrasonic Velocity Studies of Pure TritonX-114 :

In the present investigation, CMC values of nonionic sufactants TX-114 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 meidum. 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 Fig. 1 for TX-114.

Fig.1:Plots of Ultrasonic velocity Vs [TX-114] at 298K and 303K temperatures



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 [21,22].

Table-1 : Acoustic parameters of aqueous TX-114 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								
0.05	998.5519	1494	4.4867	0.4165	1.4918	66.4261	759.37	3.633
0.1	998.6769	1495	4.4802	0.4162	1.4930	114.811	1312.81	3.637
0.2	998.8110	1496	4.4736	0.4159	1.4942	211.571	2419.74	3.641
0.3	998.9375	1493	4.4910	0.4167	1.4914	308.307	3523.74	3.631
0.4	999.0038	1492	4.4967	0.4170	1.4905	405.043	4628.33	3.627
0.5	999.1326	1491	4.5022	0.4172	1.4897	501.735	5731.92	3.624
303K								
0.05	998.5375	1502	4.4391	0.4182	1.4998	66.4271	760.74	3.662
0.1	998.6633	1504	4.4268	0.4176	1.5020	114.813	1315.45	3.670
0.2	998.7959	1508	4.4027	0.4165	1.5062	211.574	2426.22	3.685
0.3	998.9232	1503	4.4315	0.4179	1.5014	308.312	3531.64	3.667
0.4	998.9895	1502	4.4371	0.4181	1.5005	405.049	4638.72	3.664
0.5	999.1176	1500	4.4484	0.4187	1.4987	501.743	5743.52	3.657

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 [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 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 TX-114 (0.2mM).

Table-2: Acoustic parameters of aqueous 0.2 mM [TX-114] with various [CAT] at 298K and 303K temperatures.

CAT Conc. (mM)	Density (ρ) kgm^{-3}	Ultrasonic Velocity (U) ms^{-1}	Adiabatic Compressibility (β_{ad})x10^{-10}Kg^{-1}ms^{2}	Intermolecular Free length (L_f) A^o	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^{4}Nm^{-1}
298K								
0.2	999.1974	1490	4.5079	0.4175	1.4888	294.96513	3368.99	3.621
0.4	999.2622	1492	4.4956	0.4169	1.4909	396.42929	4529.90	3.628
0.6	999.3277	1493	4.4892	0.4166	1.4920	497.87991	5690.42	3.632
0.8	999.3903	1494	4.4829	0.4163	1.4931	599.31903	6851.33	3.636
1	999.4581	1491	4.5007	0.4171	1.4902	700.74177	8005.42	3.625
303K								
0.2	999.1838	1500	4.4481	0.4186	1.4988	294.96914	3376.55	3.657
0.4	999.2486	1502	4.4359	0.4181	1.5009	396.43467	4540.06	3.665
0.6	999.3127	1505	4.4180	0.4172	1.5040	497.88742	5705.71	3.676
0.8	999.3759	1508	4.4002	0.4164	1.5071	599.32762	6872.76	3.687
1	999.4437	1504	4.4233	0.4175	1.5032	700.75181	8028.73	3.673

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-114(0.2mM) 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 TX-114 with CAT is presented below in Table-3.

Fig.1:Plots of Ultrasonic velocity Vs [TX-114] at 298K and 303K temperatures

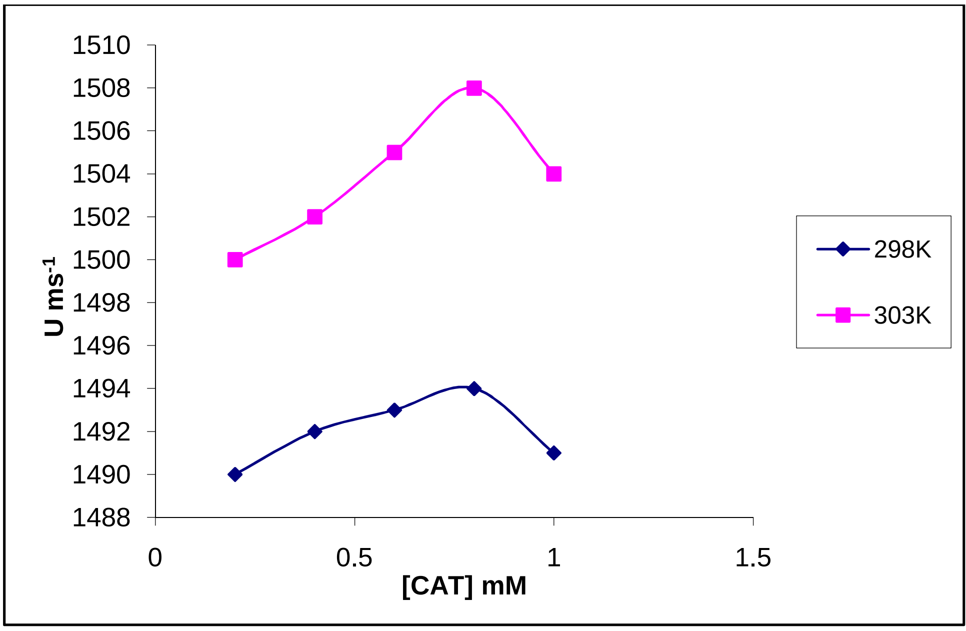


Table-3: [CAT]$_{max}$/CMC values for TX-114 pure nonionic surfactant and mixed system with CAT at 298K and303K temperatures.

Temp.K	TX-114	0.2 mM TX-114 and CAT mixed system
298	0.21	0.8
303	0.2	0.79

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 decreses 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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REFERENCES

[1] J.Miller and A.J.Parker, *J.Am.Chem.Soc.*, **1961**, 83, 117
[2] K.Ramabrahaman, *Indian J. Pure Appl. Phys.*, **1968**, 6,75
[3] M.M.Chauhan and R.K.Shukla, *J. Pure Appl. Ultrasonics*, **1996**, 18,118
[4] K.N.Mehrotra and S.Gupta, *Acoustica*, **1998**, 84,167
[5] J.W.Mcbain, *Trans.Farad.Soc.*, **1913**, 9,99
[6] M.Almgren and S.Swarup, *J.Phy.Chem.*, **1982**,86,4212
[7] J.R.Bellare,T.Kaneko and D.F.Evans, *Langmuir*, **1988**,4,1066
[8] Pinto CG, Perez Pavon JL, Cordero BM,*Anal Chem.*, **1992**, 64,2334
[9] L.Koshy, A.H.Saiyad, A.K.Rakshit, *Colloid Polym.Sci*. **1996**, 274,582
[10] P.G.T.Fogg *J.Chem.Soc*. **1958**, 83,117
[11] C.V.Chatruvedi and S.Prakash, *Acustica*, **1972**, 27, 248
[12] K.Gopal and N.P.Rao, *Acoustic letters*, **1981**, 4, 164

[13] T.N.Srivastava, R.P.Singh and B.Swaroop, *Ind. J. Pure Appl. Phys*., **1983**, 21,67
[14] K.N.Mehrotra, Mamata Jain, *Colloids Surf. A*.. **1995,** 95 (2/3), 229 (Eng.)
[15] A. Kumar, *Tenside Surf. Deteg*., **1997**, 34, 259
[16] L.Chandreshwar, S.Verghese and K.Smriti, *Tenside Surf. Deteg*., **2002**, 39(5), 150
[17] K.N.Mehrotra, A. Kumar and S.P.Verghese, *Tenside Surf. Deteg*., **2002**, 39(3), 25
[18] J.A.Riddlick, W.B.Bunger and T.K.Sakano, “Organic Solvents: Physical Properties and Methods of Purification, Techniques of Chemistry”, 4th Edi, Wiley-Interscience, New York, **1986**, Vol.II, 336
[19] J.Nath and A.P.Dixit, *J.Chem.Eng.Data*, **1984**, 29, 313
[20] S.P.Moulik, Md.E.Haque, P.K.Jana and A.R.Das, *J.Phys.Chem*., **1996**, 100, 701
[21] S.K.Hait and S.P.Moulik, *J.of Surfactants and Detergents*, **2001**, 4(3), 303
[22] S.Kothai, *Asian J.of Chemistry*, **2007**, 19 (1), 264
[23] M.K.Baloch, G.Hameed and A.Bano, *Jour.Chem.Soc.Pak*, **2002**, 24(2), 77,
[24] M.J.Schick, *J.Phys. Chem*., **1963**, 67(9), 1796
[25] E.A.G.Aniansson, S.N.Wall, M.Almgleh, H.Hoffmann, I.Kielmann, Wulbricht, R.Zans, J.Lang and C.Tandre, *J.Phys.Chem*., **1976**, 80, 905
[26] K.S.Birdi, S.O.Eiatsager, S.Bacldund, *J.Chem.Soc.Faraday TransI*, **1980**, 76, 2035
[27] P.S.Nikam, V.M.Kapade and M.Hassan, *Indian J.Pure Appl.Phys*., **2000**, 38, 170
[28] B.Sundarson and A.Shrinivasarao, *Polym. J*., **1994**, 26, 1286