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# Ultrasonic Studies on Certain Surfactants

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Ultrasonic velocities (u) and densities (ρ) have been measured for the aqueous solutions of three surfactants in presence of chloramine-T at various concentrations and at 303 K. Acoustical parameters such as adiabatic compressibility (κ), free length ($L_f$), surface tension (γ), molar surface energy (E) and surface area (Y) are evaluated. The trend in the acoustical parameters and the surface properties of surfactants with various concentrations of detergents suggest the aggregation of surfactant molecules at critical micellar concentration. The trend in the influence of chloramine-T on detergent action on the three surfactants at 303 K in aqueous solutions are investigated.

**Key Words: Surfactants, Chloramine-T, Acoustical parameters.**

## INTRODUCTION

In recent years, several research workers have investigated the molecular interactions in soaps, metallic soaps and detergents in the presence of added electrolytes[1–4]. Surfactants contain two distinct moieties in aqueous solution. The hydrophilic moiety of a surfactant is the 'head group' and is either strongly polar or charged. The hydrophobic group is the 'tail' and is normally a long chain alkyl or aryl group. In aqueous and organic solvents, amphiphiles self-assemble into a variety of microstructures, which, by physical interaction forces, hold together. These microstructures are monolayer micelles, bilayers and liposomes.

When surfactants are added to water at low concentration, they are dispersed as discrete molecules. However, at a particular concentration, characteristic of the surfactant, the molecules tend to associate to form particles, namely, aggregates or micelles[5–7]. This concentration is known as critical micellar concentration (CMC) and it is an important property of a surfactant. Above CMC, the surfactant exists as aggregates or micelles. Ultrasonic relaxation[8, 9], P-jump, NMR and EPR spectral methods[10] can be used to study the formation of micelles. Bulk properties such as conductance, light scattering, surface tension, diffusion, turbidity, magnetic resonance and osmotic pressure support the aggregation of surfactants above CMC. CMC of a surfactant can be determined by several methods such as surface tension, conductance, light scattering, solubilization, auto diffusion and pH methods. There are merits as well as demerits in these methods. In order to make the detergents cheap and user friendly, inorganic and organic diluting agents are added to study the effect of additives[11]. These are called 'builders' and they enhance the detergency action and these compounds are relatively cheap, resulting in the utility of fewer amounts of more expensive detergents of high activity.

## EXPERIMENTAL

AnalaR grade (SDS) samples of sodium lauryl sulphate (SDS), cetyl-NNN-trimethyl ammonium bromide (CTAB), triton X-100 (TX100), chloramine-T (CAT) were used as such and triple distilled water was prepared by distillation technique. Accurately weighed amounts of the sample were dissolved in triple distilled water to obtain solutions of various concentrations. The ultrasonic velocities of the solutions were measured using an ultrasonic interferometer (F-81) with a single crystal at a frequency of 2 MHz. The accuracy in the velocity measurement is $\pm 0.5\%$[12]. The densities of solutions were measured at 303 K using specific gravity bottles with an accuracy of $\pm 0.001 kg/m^3$. The cell temperature was maintained constant at 303 K by an ultra-thermostat (Julabo U-3) maintained at an accuracy of $\pm 0.1$ K.

**Theoretical formulations:** The acoustical parameters such as adiabatic compressibility ($\kappa$), free length ($L_f$), surface tension ($\gamma$), molar surface energy (E) and surface area (Y) were calculated from the measured ultrasonic velocity (u) and density ($\rho$) of aqueous solutions of the surfactants, in presence of CAT at 303 K. The following equations were used in these calculations:

Adiabatic compressibility $\kappa = (1/U^2\rho)\ kg^{-1}\ m\ s^2$ (1)

Free length $L_f = k \times (\kappa)^{1/2}$ Å (2)

Surface tension $\gamma = (U^{3/2}) \times (6.3 \times 10^{-4}) \times \rho\ N\ m^{-1}$ (3)

Molar surface energy $E = \gamma \times V_m^{2/3}\ J\ mol^{-1}$ (4)

Surface area $Y = (36\pi N V_a)^{1/3}\ m^2\ mol^{-1}$ (5)

where U = ultrasonic velocity (m/s), $\rho$ = density ($kg/m^3$), $V_m$ = molar volume ($m^3$), $V_a$ = available volume ($m^3$), k = Jacobson's constant.

## RESULTS AND DISCUSSION

In the present investigation, CMC values of the three surfactants are determined by ultrasonic method. Of the three surfactants chosen for investigation, one is anionic, another is cationic and the third one is neutral. The following surfactants are used in the investigation:

Sodium lauryl sulphate [SDS]

(anionic surfactant; $CH_3(CH_2)_{10}CH_2OSO_3Na$).

Cetyl-N,N,N-trimethyl ammonium bromide [CTAB]

(cationic surfactant; $[CH_3(CH_2)_{15}N(CH_3)_3]^+Br^-$).

Triton X-100, [TX100]

(non-ionic surfactant; *p*-tertiary octyl phenol poly $(oxyethylene)_{92}$).

The surfactants chosen for the present study are popular in detergent industries. SDS has good detergent action because it has wetting power and high emulsification efficiency. Besides, CTAB has good antiseptic property due to its surface-active character. TX100 is used in biological study because it does not denature the integral proteins and it is found to be biodegradable. The influence of CAT on the three surfactants is also investigated.

A survey of literature indicates that the studies on CAT are quite diverse in nature. CAT derivatives have been widely used in the kinetics of the various reactions involving different substrates and also as an oxidant in different analytical procedures[13, 14]. Its rich potentiality is quite well exploited in several synthetic, industrial and biological applications. CAT and its derivatives are employed as antiseptic, disinfectant, bactericide, fungicide and immunoreactive materials and their multifarious functions in leather industries. CAT is a strong oxidizing agent. It spreads on the walls of bacteria and septum, hence it is used as an antiseptic. It may influence the detergent action of surfactants by changing the surface tension (γ) and molar surface energy (E). It is necessary to investigate the interaction between the surfactant and CAT molecules. The ultrasonic velocity and density values are measured for aqueous solutions of the surfactant at 303 K in the presence of added CAT at different concentrations. The concentration of the surfactants is maintained at the CMC value in these measurements.

The critical micellar concentratiosn (CMC) of the three surfactants, SDS (anionic), CTAB (cationic) and TX100 (neutral) determined by the ultrasonic methods are given below:

| Detergent | CMC (mM) at 303 K |
|---|---|
| SDS | 8.10 |
| CTAB | 0.33 |
| TX100 | 0.20 |

These values are comparable to the values determined by other methods by earlier workers[15].

The acoustical parameters, surface tension, molar surface energy and molar surface area at different concentrations of CAT for the three systems are presented in Tables 1–3. Plots of ultrasonic velocity (U) *vs.* concentration of CAT are given in Fig. 1. These plots show that the maximum interaction exists at a characteristic concentration. Fig. 2 contains plots of adiabatic compressibility (κ) *vs.* various concentrations of CAT. The adiabatic compressibility (κ) values are minimum at

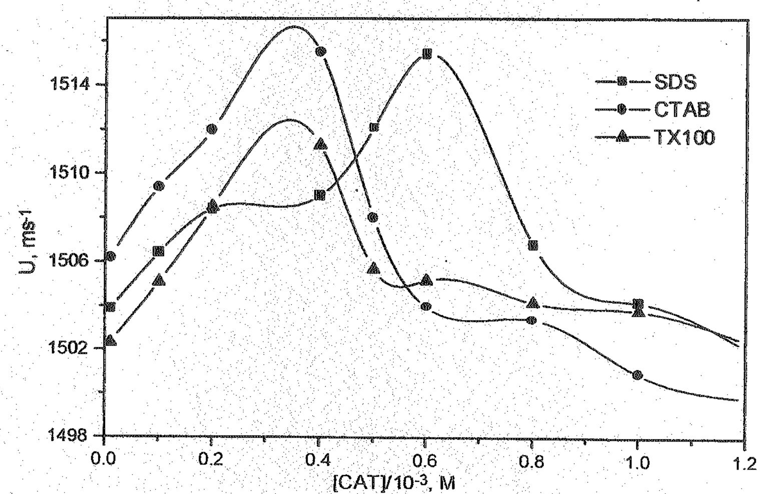


Fig. 1. Plots of ultrasonic velocity *vs.* concentration of CAT at 303 K

a particular concentration of CAT, indicating that there are strong molecular interactions between surfactant molecules and the added CAT molecules in the solution.

Plots of surface tension (γ) *vs*. concentration of CAT (Fig. 3) and plots of molar surface energy (E) *vs*. concentration of CAT (Fig. 4) show that the surface tension (γ) and molar surface energy (E) are maximum at the concentration at which the molecular interactions are maximum. Molar surface area (Y) is maximum at these concentrations. While free length ($L_f$) values are minimum as given in Tables 1–3. The concentrations of CAT at which the interactions are maximum are presented below :

| Detergent with CAT | [CAT] (mM) at 303 K |
|---|---|
| SDS | 0.8 |
| CTAB | 0.5 |
| TX100 | 0.5 |

From the values of $[CAT]_{max}$, it may be inferred that the interaction between CAT and SDS is less than the interaction between CAT and CTAB or with CAT and TX100. The trend in the acoustical parameters and the surface properties with concentration of detergents suggest the aggregation of surfactant molecules at CMC.

TABLE-1

ULTRASONIC VELOCITIES (u), DENSITIES (ρ), ADIABATIC COMPRESSIBILITIES (κ), FREE LENGTHS ($L_f$), SURFACE TENSIONS (γ), MOLAR SURFACE ENERGIES (E) AND SURFACE AREAS (Y) OF AQUEOUS SOLUTION OF SDS WITH VARIOUS CONCENTRATIONS OF CAT.

[SDS] = 8.1 mM, Temp. = 303 K

| $[CAT]/10^{-3}$ (M) | U ($ms^{-1}$) | ρ, ($kg\ m^{-3}$) | $κ/10^{-10}$ ($kg^{-1}\ m\ s^2$) | $L_f$ (Å) | $γ/10^{-4}$ ($N\ m^{-1}$) | E [molar]/$10^2$ ($J\ mol^{-1}$) | $Y/10^9$ ($m^2\ mol^{-1}$) |
|---|---|---|---|---|---|---|---|
| 0.01 | 1503.9 | 999.0 | 4.426 | 0.417 | 3.671 | 27.69 | 53.60 |
| 0.10 | 1506.4 | 999.9 | 4.407 | 0.417 | 3.683 | 27.77 | 53.66 |
| 0.20 | 1508.4 | 1000.7 | 4.392 | 0.416 | 3.693 | 27.83 | 53.71 |
| 0.40 | 1509.0 | 1000.7 | 4.388 | 0.416 | 3.696 | 27.85 | 53.72 |
| 0.50 | 1512.1 | 1001.0 | 4.369 | 0.415 | 3.708 | 27.94 | 53.79 |
| 0.60 | 1515.4 | 1001.3 | 4.349 | 0.414 | 3.721 | 28.03 | 53.87 |
| 0.80 | 1506.8 | 1002.1 | 4.395 | 0.416 | 3.692 | 27.80 | 53.67 |
| 1.00 | 1504.2 | 1002.5 | 4.409 | 0.417 | 3.685 | 27.74 | 53.61 |
| 1.20 | 1502.1 | 1002.7 | 4.420 | 0.417 | 3.677 | 27.68 | 53.56 |
| 10.00 | 1501.4 | 1002.7 | 4.424 | 0.417 | 3.675 | 27.66 | 53.54 |

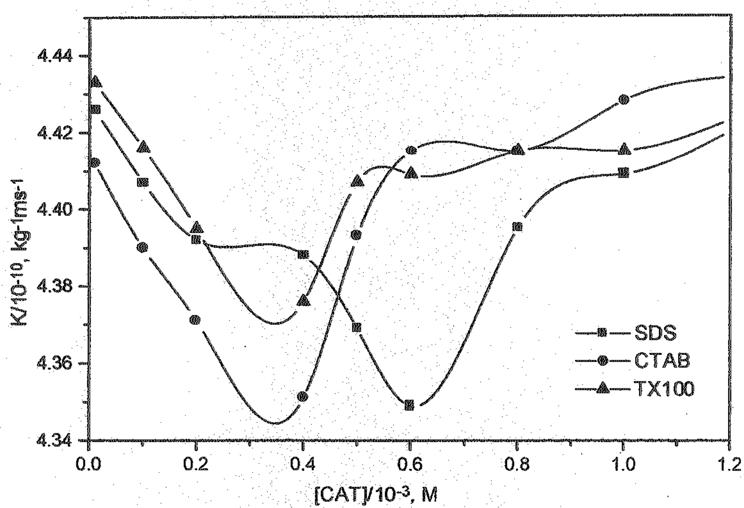


Fig. 2. Plots of adiabatic compressibility *vs.* concentration of CAT at 303 K

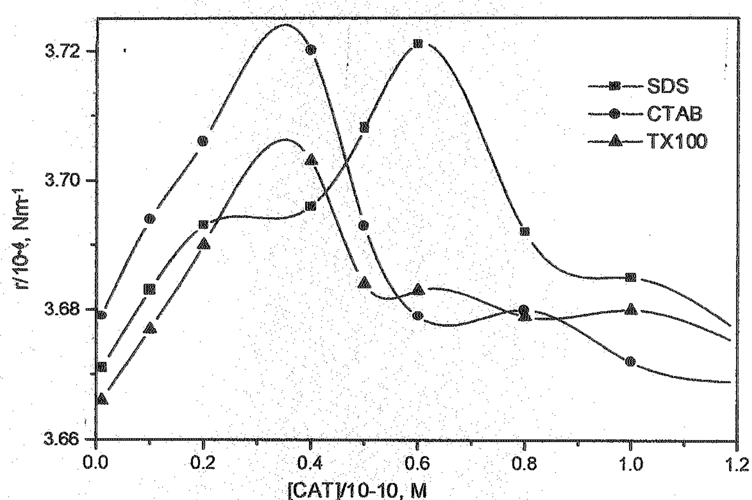


Fig. 3. Plots of surface tension *vs.* concentration of CAT at 303 K

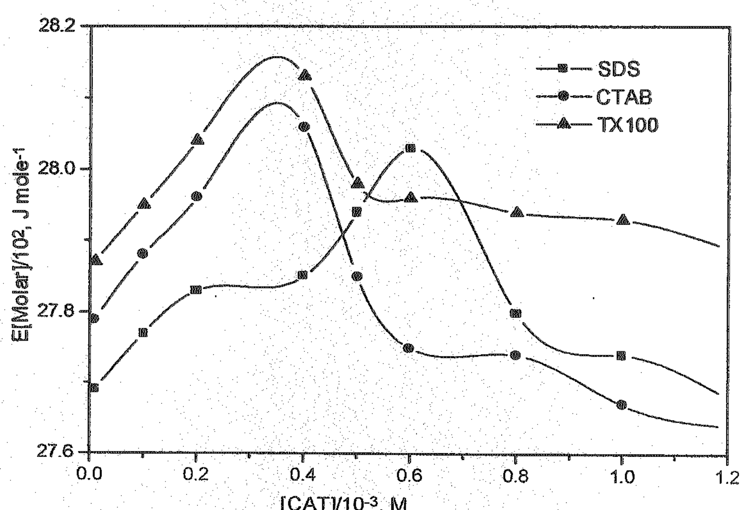


Fig. 4. Plots of molar surface energy *vs.* concentration of CAT at 303 K

TABLE-2
ULTRASONIC VELOCITIES (u), DENSITIES (ρ), ADIABATIC COMPRESSIBILITIES (κ), FREE LENGTHS ($L_F$), SURFACE TENSIONS (γ), MOLAR SURFACE ENERGIES (E) AND SURFACE AREAS (Y) OF AQUEOUS SOLUTION OF CTAB WITH VARIOUS CONCENTRATIONS OF CAT

[CTAB] = 0.33 mM; Temp = 303 K

| [CAT]/$10^{-3}$ (M) | U ($ms^{-1}$) | ρ, (kg $m^{-3}$) | κ/$10^{-10}$ ($kg^{-1}$ m $s^2$) | $L_f$ (Å) | γ/$10^{-4}$ (N $m^{-1}$) | E [molar]/$10^2$ (J $mol^{-1}$) | Y/$10^9$ ($m^2$ $mol^{-1}$) |
|---|---|---|---|---|---|---|---|
| 0.01 | 1506.2 | 999.0 | 4.412 | 0.417 | 3.679 | 27.79 | 53.65 |
| 0.10 | 1509.4 | 999.9 | 4.390 | 0.416 | 3.694 | 27.88 | 53.73 |
| 0.20 | 1512.0 | 1000.7 | 4.371 | 0.415 | 3.706 | 27.96 | 53.79 |
| 0.40 | 1515.5 | 1000.7 | 4.351 | 0.414 | 3.720 | 28.06 | 53.87 |
| 0.50 | 1508.0 | 1001.0 | 4.393 | 0.416 | 3.693 | 27.85 | 53.70 |
| 0.60 | 1504.0 | 1001.3 | 4.415 | 0.417 | 3.679 | 27.75 | 53.60 |
| 0.80 | 1503.4 | 1002.1 | 4.415 | 0.417 | 3.680 | 27.74 | 53.59 |
| 1.00 | 1500.9 | 1002.5 | 4.428 | 0.418 | 3.672 | 27.67 | 53.53 |
| 1.20 | 1499.8 | 1002.7 | 4.434 | 0.418 | 3.669 | 27.64 | 53.50 |
| 10.00 | 1498.4 | 1002.7 | 4.442 | 0.418 | 3.664 | 27.60 | 53.47 |

TABLE-3
ULTRASONIC VELOCITIES (u), DENSITIES (ρ), ADIABATIC COMPRESSIBILITIES (κ), FREE LENGTHS ($L_F$), SURFACE TENSIONS (γ), MOLAR SURFACE ENERGIES (E) AND SURFACE AREAS (Y) OF AQUEOUS SOLUTION OF TX100 WITH VARIOUS CONCENTRATIONS OF CAT

[TX100] = 0.2 mM; Temp = 303

| [CAT]/$10^{-3}$ (M) | U ($ms^{-1}$) | ρ, (kg $m^{-3}$) | κ/$10^{-10}$ ($kg^{-1}$ m $s^2$) | $L_f$ (Å) | γ/$10^{-4}$ (N $m^{-1}$) | E [molar]/$10^2$ (J $mol^{-1}$) | Y/$10^9$ ($m^2$ $mol^{-1}$) |
|---|---|---|---|---|---|---|---|
| 0.01 | 1502.3 | 999.4 | 4.433 | 0.418 | 3.666 | 27.87 | 53.56 |
| 0.10 | 1505.1 | 999.5 | 4.416 | 0.417 | 3.677 | 27.95 | 53.63 |
| 0.20 | 1508.5 | 999.8 | 4.395 | 0.416 | 3.690 | 28.04 | 53.71 |
| 0.40 | 1511.3 | 1000.5 | 4.376 | 0.415 | 3.703 | 28.13 | 53.78 |
| 0.50 | 1505.7 | 1000.9 | 4.407 | 0.417 | 3.684 | 27.98 | 53.64 |
| 0.60 | 1505.2 | 1001.0 | 4.409 | 0.417 | 3.683 | 27.96 | 53.63 |
| 0.80 | 1504.2 | 1001.1 | 4.415 | 0.417 | 3.679 | 27.94 | 53.61 |
| 1.00 | 1503.8 | 1001.6 | 4.415 | 0.417 | 3.680 | 27.93 | 53.60 |
| 1.20 | 1502.4 | 1001.8 | 4.423 | 0.417 | 3.675 | 27.89 | 53.56 |
| 10.00 | 1501.2 | 1001.8 | 4.430 | 0.418 | 3.671 | 27.86 | 53.54 |

## Conclusion

Ultrasonic velocity and density studies are employed on the three surfactants in presence of chloramine-T at 303 K in aqueous solutions. The trend in the acoustical and surface parameters suggests the aggregation of surfactant molecules at CMC and the influence of chloramine-T on detergent action.

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