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Acoustical studies on the effect of urea on the micelles of aqueous surfactants

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Abstract Acoustical studies are undertaken in aqueous solutions of sodium oleate and sodium taurocholate, which form micelles in aqueous solution. The ultrasonic velocity and attenuation are measured in these solutions in the concentration range 0.001–0.04 molar by adding 0.1 and 0.2 molar urea using a Time Intervalometer (Model-101) at 303 K. From the measured ultrasonic velocity (C) and attenuation $(\alpha/f^2)_{obs}$, various other parameters namely adiabatic compressibility (β_s), freelength (L_f) and excess absorption $(\alpha/f^2)_{ex}$ are calculated and reported. The velocity studies show that the variation of ultrasonic velocity with concentration exhibits a break at the critical micelle concentration (CMC) of the surfactants in water. These studies further establish that the addition of urea shifts the CMC of aqueous surfactants. The results are discussed on the basis of micelle formation and structure breaking nature of urea.

Keywords Surfactants, urea, micelles, acoustical studies

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1. Introduction

Our earlier ultrasonic studies in aqueous solutions of potassium and sodium oleate [1] clearly brought out the process of micellar aggregation taking place in aqueous solutions of these surfactants. The effect of additives on micelle formation, critical micelle concentration (CMC) and on thermodynamic parameters of the surfactants has been the interest of many researchers [2–5]. It has been well established that the properties of aqueous micellar solutions are modified by the addition of additives such as electrolytes, non-electrolytes and polymers. These additives can affect in many ways the delicate balance of hydrophobic and hydrophilic interactions of micelle forming surfactants. Several studies related to the effect of urea [2–4,6] and alkyl urea [7] on the aggregation of surfactants have been reported in literature. It has been established that urea acting as statistical structure breaker destabilizes the water structure. It has pronounced ability towards protein denaturation. From a survey of literature, it has been found that the studies on effect of urea on the aqueous solutions of sodium oleate and a biological detergent sodium taurocholate are scandy. Hence, the present study has been undertaken to throw more light on the effect of urea on the micelles formed by sodium oleate and sodium taurocholate.

2. Experimental

The surfactants and urea used here are AR/BDH grade and are used without further purification. The surfactant solutions having different concentrations are prepared by dissolving the required amounts of surfactants and urea in double distilled water. The ultrasonic velocity and absorption are measured using an ultrasonic time intervalometer (Model 101, Innovative Instruments, Hyderabad) using a pulse echo overlap technique at an RF frequency of 10 MHz and at a temperature of 303 K. The accuracy of velocity measurement is ±2 parts in 10^4. Shear viscosities are measured using an Ostwald's viscometer and the densities at different concentrations of surfactants and urea are determined using a graduated dilatometer. From the measured values of velocity, density, viscosity and observed absorption, various other parameters such as adiabatic compressibility, intermolecular freelength and classical absorption are calculated using standard equations.

3. Results and Discussion

Ultrasonic velocity and absorption studies are undertaken in aqueous solutions of sodium oleate and sodium taurocholate in the concentration range 0.001 to 0.014 molar (for sodium oleate) and 0.005 to 0.04 molar (for sodium taurocholate) with the addition of 0.1 and 0.2 molar urea at 303 K. The measured parameters and the derived parameters for these aqueous solutions of surfactants without urea and with the addition of urea are presented in Tables 1–6. The variation of ultrasonic velocity and adiabatic compressibility with concentration of these surfactants in water and urea-water mixture are shown in Figures 1–4.

Table 1. Ultrasonic parameters for aqueous solutions of sodium oleate at 303 K

X molar	C ms^{-1}	ρ kg m^{-3}	β_s 10^{-10} N^{-1}m^2	η_s 10^{-4} Nsm^{-2}	$(\alpha/f^2)_{cl}$	$(\alpha/f^2)_{obs}$	$(\alpha/f^2)_{ex}$	L_f Å
						10^{-15} Npm^{-1}s^{-2}		
0.001	1502.9	990.2	4.44	8.07	6.3	156.1	149.7	0.421
0.002	1498	992.4	4.47	8.10	6.3	179.4	173.9	0.422
0.003	1494	994.2	4.49	8.18	6.4	228.0	221.6	0.423
0.004	1490	996.2	4.51	8.17	6.5	247.2	240.7	0.424
0.005	1486	998.2	4.54	8.28	6.6	322.4	315.7	0.425
0.006	1479.9	999.8	4.57	8.88	7.2	386.4	379.2	0.427
0.007	1497.6	1000.7	4.46	8.24	6.3	169.4	163.1	0.422
0.008	1510.6	1002.5	4.38	8.17	6.2	140.2	134.0	0.418

Table 2. Ultrasonic parameters for aqueous solutions of sodium oleate + 0.1 molar urea at 303 K

X molar	C ms^{-1}	ρ kg m^{-3}	β_s 10^{-10} N^{-1}m^2	η_s 10^{-4} Nsm^{-2}	$(\alpha/f^2)_{cl}$	$(\alpha/f^2)_{obs}$	$(\alpha/f^2)_{ex}$	L_f Å
						10^{-15} Npm^{-1}s^{-2}		
0.002	1514	998.5	4.36	6.58	4.9	477.8	472.9	0.413
0.004	1579.9	1001.3	4.32	6.83	4.9	464.6	459.6	0.416
0.006	1524.8	1002.5	4.28	7.29	5.3	386.7	381.4	0.412
0.008	1529.8	1005.7	4.24	7.46	5.4	340.0	334.6	0.410
0.010	1539.9	1009.6	4.17	7.55	5.3	347.8	342.5	0.407
0.012	1550.7	1013.7	4.10	7.68	5.3	360.0	354.7	0.403
0.014	1560.6	1019.4	4.02	7.90	5.3	391.3	386.0	0.399

Table 3. Ultrasonic parameters for aqueous solutions of sodium oleate + 0.2 molar urea at 303 K

X molar	C ms^{-1}	ρ kg m^{-3}	β_s 10^{-10} N^{-1}m^2	η_s 10^{-4} Nsm^{-2}	$(\alpha/f^2)_{cl}$	$(\alpha/f^2)_{obs}$	$(\alpha/f^2)_{ex}$	L_f Å
						10^{-15} Npm^{-1}s^{-2}		
0.002	1517	1000.0	4.34	6.98	5.2	567.7	562.5	0.415
0.004	1524.6	1003.5	4.28	7.16	5.2	550.1	544.9	0.412
0.006	1530.9	1007.2	4.23	7.24	5.2	518.3	513.1	0.410
0.008	1537.3	1010.4	4.18	7.34	5.2	476.9	471.7	0.407
0.010	1542.8	1013.8	4.14	7.48	5.2	469.6	464.4	0.405
0.012	1568.9	1017.6	3.99	8.56	5.8	521.6	515.8	0.400
0.014	1597.8	1021.8	3.83	9.39	5.9	534.4	528.5	0.390

Table 4. Ultrasonic parameters for aqueous solutions of sodium taurocholate at 303 K

X molar	C ms^{-1}	ρ $kg\,m^{-3}$	β_s $10^{-10}\,N^{-1}m^2$	η_s $10^{-4}\,Nsm^{-2}$	$(\alpha/f^2)_{cl}$	$(\alpha/f^2)_{obs}$	$(\alpha/f^2)_{ex}$	L_f Å
						$10^{-15}\,Npm^{-1}s^{-2}$		
0.005	1504.56	997.3	4.42	7.86	6.0	677.2	671.2	0.420
0.010	1510.27	997.9	4.39	7.79	5.9	636.3	630.4	0.419
0.015	1513.65	998.6	4.37	8.04	6.0	638.8	632.8	0.416
0.020	1516.50	999.6	4.34	8.16	6.1	640.4	634.3	0.414
0.030	1521.30	1000.4	4.31	8.16	6.3	643.5	637.2	0.413
0.040	1526.87	1002.3	4.27	8.55	6.2	647.4	641.2	0.411

Table 5. Ultrasonic parameters for aqueous solutions of sodium taurocholate + 0.1 molar urea at 303 K

X molar	C ms^{-1}	ρ $kg\,m^{-3}$	β_s $10^{-10}\,N^{-1}m^2$	η_s $10^{-4}\,Nsm^{-2}$	$(\alpha/f^2)_{cl}$	$(\alpha/f^2)_{obs}$	$(\alpha/f^2)_{ex}$	L_f Å
						$10^{-15}\,Npm^{-1}s^{-2}$		
0.002	1503.0	997.0	4.43	7.46	5.7	736.0	730.2	0.420
0.004	1507.3	997.8	4.41	7.50	5.7	710.1	704.4	0.418
0.006	1512.0	998.3	4.38	7.72	5.8	690.2	684.4	0.416
0.008	1516.5	998.8	4.35	7.77	5.8	672.3	666.5	0.415
0.010	1520.2	999.2	4.32	7.84	5.8	658.0	652.2	0.414
0.012	1522.4	999.9	4.31	7.97	5.9	649.0	643.1	0.413
0.015	1524.4	1000.5	4.30	8.07	5.9	655.5	649.6	0.413
0.018	1527.6	1001.4	4.27	8.21	6.0	667.7	661.7	0.412

Table 6. Ultrasonic parameters for aqueous solutions of sodium taurocholate + 0.2 molar urea at 303 K

X molar	C ms^{-1}	ρ $kg\,m^{-3}$	β_s $10^{-10}\,N^{-1}m^2$	η_s $10^{-4}\,Nsm^{-2}$	$(\alpha/f^2)_{cl}$	$(\alpha/f^2)_{obs}$	$(\alpha/f^2)_{ex}$	L_f Å
						$10^{-15}\,Npm^{-1}s^{-2}$		
0.002	1507.4	997.8	4.41	6.88	5.2	819.9	814.7	0.418
0.004	1511.8	998.2	4.38	7.08	5.4	801.9	796.5	0.417
0.006	1516.1	999.1	4.35	7.28	5.5	783.6	778.1	0.415
0.008	1521.2	1000.2	4.31	7.41	5.5	768.9	763.4	0.414
0.010	1525.9	1001.3	4.28	7.53	5.5	749.2	743.7	0.412
0.012	1531.0	1002	4.25	7.59	5.5	734.7	729.2	0.410
0.015	1533.8	1003.3	4.23	7.74	5.6	758.4	752.8	0.410
0.018	1536.4	1004.4	4.21	7.83	5.6	789.7	784.1	0.405

X – Concentration; C – Ultrasonic velocity; ρ – Density of the solution; β_s – Adiabatic compressibility; η_s – Shear viscosity; $(\alpha/f^2)_{cl}$ – Classical absorption; $(\alpha/f^2)_{obs}$ – Observed absorption; $(\alpha/f^2)_{ex}$ – Excess absorption; L_f – Freelength

Aqueous solutions of sodium oleate :

From Figure 1, it can be seen that the ultrasonic velocity in aqueous solutions of sodium oleate decreases with increase of concentration of sodium oleate up to 0.006 molar and thereafter the ultrasonic velocity increases with further increase in concentration of sodium oleate.

With the addition of 0.1 and 0.2 molar urea to these aqueous solutions of sodium oleate, the ultrasonic velocity also increases with increase of concentration of sodium oleate and urea. These results can be explained by resorting to flickering cluster model of water. According to this model, water is supposed to consist of hydrogen bonded clusters called 'open structures' and dense monomers called 'close packed structures'. Water is a dynamic mixture of these two. The close and open packed structure of water plays an important role in micellisation.

In aqueous medium, sodium oleate dissociates as

$$\text{R–COONa} \rightleftharpoons \text{RCOO}^- + \text{Na}^+.$$

The Na^+ ion thus obtained has a water structure making property [8]. This Na^+ ion restricts the overall motional freedom of dense monomers, and thereby the water clusters try to aggregate around the hydrophobic oleate ion due to hydrophobic interaction. So, the medium becomes more compressible and hence the velocity decreases and the adiabatic compressibility increases. This indicates that the hydrophobic interaction might be dominating over the structure making property of Na^+ ions in aqueous solutions of sodium oleate upto a concentration of 0.006 molar.

The increase in ultrasonic velocity after 0.006 molar concentration of sodium oleate, may be due to micelle formation taking place in these solutions. The velocity and compressibility curves can be regarded as the intersection of two straight lines at a definite concentration of 0.006 molar. This shows that 0.006 molar is the critical micelle concentration (CMC) of sodium oleate in water. The increase of ultrasonic velocity after 0.006 molar *i.e.*, after CMC, may be explained on the basis of the fact that the oleate ions in

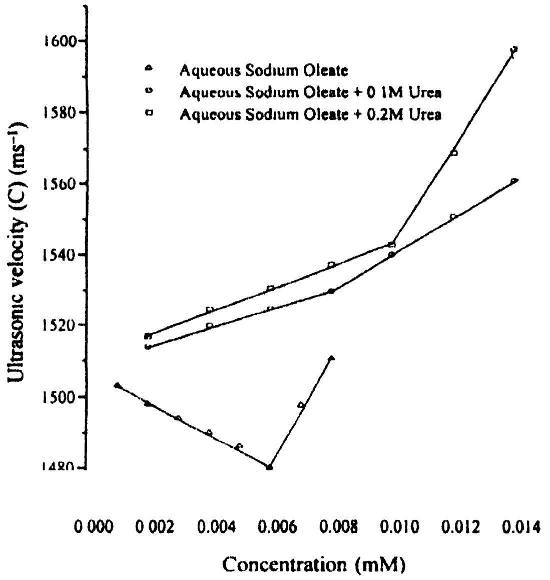

Figure 1. Variation of ultrasonic velocity with concentration of sodium oleate in urea-water mixture.

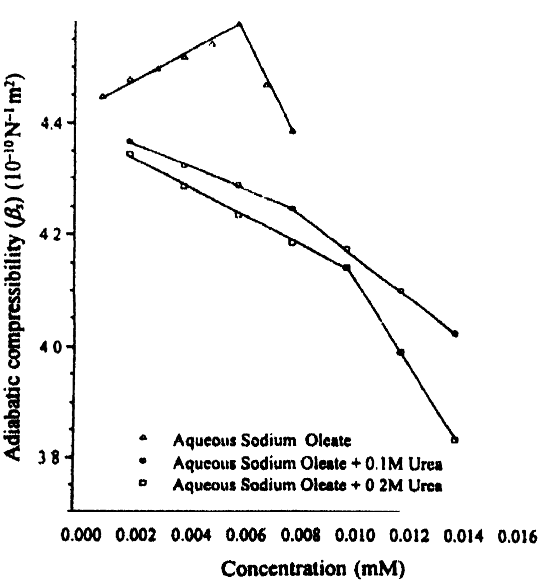

Figure 2. Variation of adiabatic compressibility with concentration of sodium oleate in urea-water mixture.

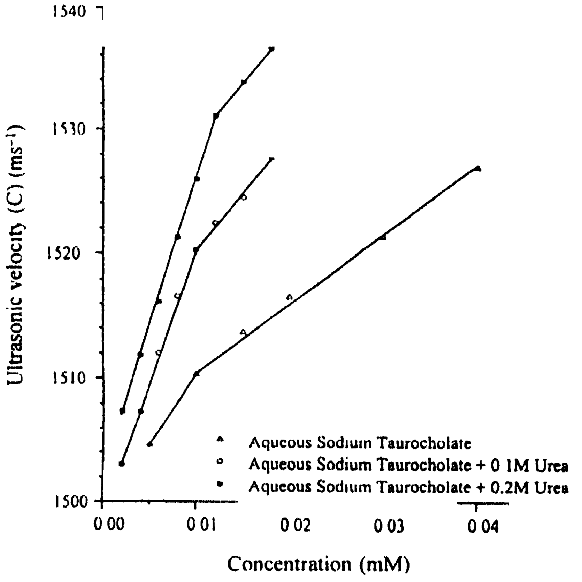

Figure 3. Variation of ultrasonic velocity with concentration of sodium taurocholate in urea-water mixture

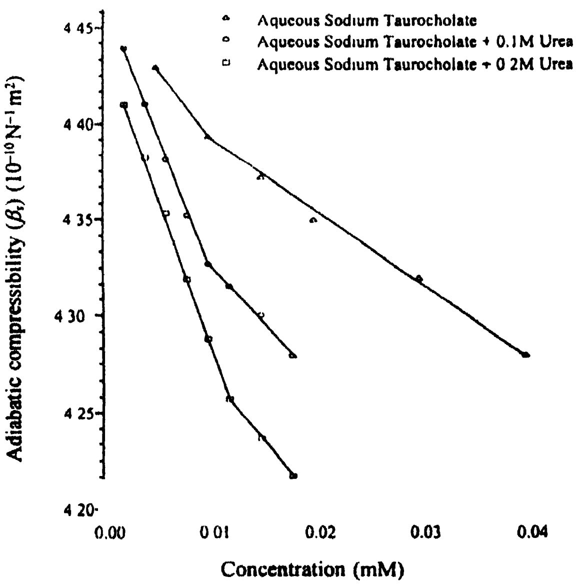

Figure 4. Variation of adiabatic compressibility with concentration of sodium taurocholate in urea-water mixture.

the solutions are surrounded by layer of solvent molecules firmly bound and oriented towards the hydrophilic head and the hydrophobic tail forming the core of the micelle. The electrostatic field of the oleate ions influences the orientation of the solvent molecules around it and results in increase of internal pressure and lowering of compressibility (Figure 2) of the solutions, *i.e.*, the solutions became harder to compress. This indicates that there is a significant surfactant-solvent interaction, due to which the structural arrangement has been considerably affected [1,9].

lqueous solutions of sodium oleate with urea :

With the addition of 0.1 and 0.2 molar urea to aqueous solutions of sodium oleate, the ultrasonic velocity also increases. From Figure 1, it can be seen that the ultrasonic velocity for a particular concentration of sodium oleate is higher in the solutions with 0.2 molar urea than in the solutions with 0.1 molar urea. Moreover, the velocity curves for the aqueous solutions of sodium oleate with 0.1 and 0.2 molar urea can be seen as the intersection of two straight lines at a particular concentration of sodium oleate, *i.e.*, the critical micelle concentration. The present study indicates that the CMC is 0.008 molar and 0.010 molar for aqueous solutions of sodium oleate with 0.1 and 0.2 molar urea, respectively.

The variation of ultrasonic velocity with increasing concentration of sodium oleate in 0 1 and 0.2 molar urea-water mixtures may be explained as follows :

In urea-water mixture, the urea being a water structure breaker disrupts the less dense water clusters releasing dense monomers. When sodium oleate is added to these mixture, the sodium ion (Na^+) obtained due to the dissociation of sodium oleate, restricts the overall motional freedom of the water molecules released by urea. This increases the cohesion in the medium and thereby leading to an increase in ultrasonic velocity and decrease in adiabatic compressibility upto 0.008 and 0.010 molar concentration of sodium oleate in 0.1 and 0.2 molar area-water mixture.

The ultrasonic velocity increases when the concentration of sodium oleate is further increased above CMC in 0.1 and 0 2 molar urea-water mixture. This behavior is similar to the variation of ultrasonic velocity above CMC in aqueous solutions of sodium oleate. Hence, the explanation offered for the increase of ultrasonic velocity with increasing concentration of sodium oleate in water above CMC may be extended too to this observed increase in the ultrasonic velocity above CMC in aqueous solutions of sodium oleate with 0.1 and 0.2 molar urea.

It is observed from the present study that the CMC's of aqueous solutions of sodium oleate with 0.1 and 0.2 molar urea is being shifted to 0.008 (shift of 0.002 M) and to 0.01 molar (a shift of 0.004 M) compared to 0.006 molar of aqueous sodium oleate without urea. This may be attributed to the water structure breaking effect of urea. It has been established that the CMC is increased when the additive (i) is a structure breaker, (ii) lowers the dielectric constant of the medium and (iii) undergoes partial micelle penetration [2]. In the present study, although, the addition of urea may increase the dielectric constant of the medium, still there is appreciable shift in CMC towards higher concentration. This may be due to the fact that, the structure breaking effect may be predominating over the increase of dielectric constant of the medium.

The ultrasonic absorption measurements undertaken in aqueous solutions of sodium oleate with 0.1 and 0.2 molar urea shows a change of slope at CMC thereby supporting the explanation offered for the velocity studies.

Aqueous solutions of sodium taurocholate :

From Figure 3, it can be seen that the ultrasonic velocity increases with increasing concentration of sodium taurocholate in water. Further, it may be inferred from Figure 3, that the CMC of sodium taurocholate in water is 0.01 molar. The increase of ultrasonic velocity in aqueous solutions of sodium taurocholate may be due to the formation of hydrogen bonds between the hydroxyl groups of sodium taurocholate and the water molecules. In addition, the Na^+ ion obtained due to the dissociation of sodium taurocholate in aqueous medium may also contribute towards the increase of ultrasonic velocity by its water structure making property.

The increase of ultrasonic velocity when the concentration of sodium taurocholate is increased beyond CMC may be due to the aggregation of taurocholate molecules leading to micelle formation. Above CMC, aggregation of molecules can take place by polyfunctional hydrogen bonding. Since, the taurocholate molecule has both residual hydrogen bond donor and acceptor groups, polyfunctional hydrogen bonding may be possible and this may perhaps lead to the formation of higher aggregates [10]. The formation of higher aggregates leads to increase of ultrasonic velocity and decrease of adiabatic compressibility as shown in Figures 3 and 4.

Aqueous solutions of sodium taurocholate with urea :

In Figure 3, the ultrasonic velocity increases with increasing concentration of sodium taurocholate in 0.1 and 0.2 molar urea-water mixture. This is similar to the velocity variation observed in aqueous solutions of sodium taruocholate. So, the explanation offered for the variation of ultrasonic velocity in aqueous solutions of sodium taurocholate also holds good for the variation of velocity with concentration of sodium taurocholate in 0.1 and 0.2 molar urea-water mixture.

From Figure 3, it can also be inferred that the critical micelle concentration of sodium taurocholate in 0.2 molar urea-water mixture is 0.012 molar, which is 0.002 M higher than the CMC of sodium taurocholate in water. However, the CMC of sodium taurocholate in 0.1 molar urea-water mixture remains unchanged at 0.01 M. This may be due to the fact that the structure breaking strength of 0.1 molar urea may not be sufficient to shift the CMC of sodium taurocholate to higher concentrations. The shift of CMC of sodium taurocholate in 0.2 molar urea-water mixture may be attributed to the structure breaking property of urea as in the case of aqueous sodium oleate with urea. Hence, the explanation offered for the shift of CMC of sodium oleate in urea-water mixture may be extended to sodium taurocholate in urea-water mixture.

The velocity studies undertaken in aqueous solutions of sodium taurocholate with 0.1 and 0.2 molar urea are supported by the ultrasonic attenuation measurements. The excess absorption calculated in these solutions also exhibits a break at CMC.

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