9.1. Introduction

Solutions resulting from the surfactant self-assembly sometimes form viscoelastic wormlike micelles, which display interesting rheological behavior useful as drag-reducing agents or thickeners for personal and home care products. These wormlike micelles have received considerable attention during the past decade [1-3]. Cationic surfactants such as cetyltrimethylammonium bromide/chloride, cetyletrimethylpyridinium bromide form rod- or wormlike micelles at concentrations much above the critical micelle concentration (CMC) or in the presence of salts like NaCl, NaBr, NaNO₃ and NaClO₃ [4-9]. Formation of such micelles also prove for surfactants have strongly bound organic counterions such as salicylate, tosylate [5,10,11] and also for mixed cationic + anionic and cationic + nonionic surfactant system having different chain length [12,13]. These micelles are much like polymers and entangle above a critical concentration making viscoelastic solutions but with a difference that these are in dynamic equilibrium. Narayanan et al and Müller et al [14] observed that cetyltrimethylammonium tosylate (CTAT) forms wormlike micelles even at much lower concentrations. With anionic sodium dodecylbenzene sulfonate in aqueous solution CTAT form unilamellar vesicles spontaneously without substantial input of energy. This viscoelastic behavior observed in aqueous solutions of surfactant mixture provides evidence for the presence of rodlike micellar structures [16,17].

Mixed surfactant systems have been extensively studied due to technological importance as they possess better stability and rheology of dispersion/suspension in many industrial formulations such as in food, cosmetics, pharmaceuticals, pesticides, paints, and detergents. Mixtures of two or more surfactants of same or different types (anionic, cationic, nonionic or zwitterionic) often exhibit cooperative interactions and show synergism due to nonideal mixing. This results in lower CMC and higher surface activity, altered micelle size/shape as compared to unmixed surfactant alone. Thus, mixed systems reduce the total amount of surfactant and hence the cost and environmental impact [18,19]. Of all classes of mixed surfactant systems, oppositely charged (cationic-anionic)
mixtures show strongest synergism that at certain mole ratios sometimes form vesicular structure. Such mixtures exhibit unique interfacial activity, different aggregate morphologies and liquid crystalline phases and insoluble precipitates due to the strong electrostatic attraction. However, in many cases mixtures of oppositely charged surfactants are avoided as they undergo phase separation (form precipitates or coacervates) due to neutralization of charges of the polar head groups.

The solution behavior of anionic-cationic mixed surfactant systems depends mainly on attraction of polar heads which alters with composition and the total surfactant concentration, temperature and the presence of additives like electrolytes and non-electrolytes [20-24]. It is generally known that weak attraction in oppositely charged polar head groups leads to only small growth in micelles, moderate attraction would result in remarkable micellar growth leading to long rod- or worm-like micelles, while strong attraction forms vesicles or form precipitates or coacervates.

Since electrostatic interactions dictate colloid-chemical behavior of mixed cationic-anionic systems, the presence of added salt is likely to modify both intramicellar and intermicellar interactions due electrostatic screening and thus affect the performance properties. Superior properties viz. high surface activity, low CMC, various self-assembled structures such as micelles of different geometries, rich phase behavior and formation of aqueous two phase micellar systems make these mixed systems very promising both from fundamental and applied view point. Several anionic-cationic mixed surfactant systems have been investigated in past two decades employing a variety of physic-chemical methods and modern instrumental techniques viz thermal [23,25],scattering[20,26], microscopic [27,28], rheology[29,30] etc. to understand different aspects of their solution chemistry. Strong interaction in such oppositely charged mixed systems as shown by large negative value of Rubingh interaction parameter (β) has been shown [31]. This strong synergism in mixed surfactants thus accounts for the nonideality. Thermodynamic treatments have also been developed to calculate micellar composition, Gibbs energy of micellization (Maeda’s approaches) and
the prediction interactions [31]. A difference in the lengths of the nonpolar chains from two surfactants stabilizes vesicles relative to liquid crystalline structures and formation of precipitates. The formation of large elongated micelles and vesicles have been found in mixed systems of oppositely charged surfactants systems. Bergström and Pedersen [33] in mixtures of sodium dodecylsulfate (SDS) and dodecyltrimethylammonium bromide (DTAB) showed elongated and flexible ribbon-like structures. Mixtures of cetyltrimethylammonium bromide (CTAB)-sodium butyl benzene sulfonate at constant total concentration showed a maximum in aggregation number when the composition is changed [34].

There have also been few reports on mixed system of cetyltrimethylammonium bromide (CTAB) and bile salt [40]. The presence of bile salt affects the micellar properties in mixed systems; while NaC forms smaller micelles with CTAB, large micelles were seen in the presence of NaDC. The dihydroxy salts were found to favour micellar growth and formed precipitate in the 1:1 molar ratio.

CTAT is a quaternary salts based cationic surfactant that forms giant micelles in aqueous solutions and above certain concentration exhibit remarkable viscoelasticity [29]. The micellization and rheology of CTAT solutions has been studied before [41]. The effect of polymers on the rheological behavior of CTAT has also been examined [42].

Bile salts are natural biosurfactants, which act as solubilizer and emulsifier for cholesterol, lipids and proteins in the intestine. They have a remarkable ability to transform lamellar arrays of lipids into mixed micelles. Bile salts are typical anionic amphiphilic substances that form micelles through primary and secondary association. Bile salts play an important role in digestion of fat in animals and form as a result of metabolism of cholesterol. NaC and NaDC are commonly known bile salts from di and trihydric family that aggregates in aqueous solution and help in lipid solubilization [43,44,45]. The physiological and therapeutic properties of some bile salts such as
solubilizing agents are due to their ability to form micellar aggregates, which facilitate the dissolution and transportation of lipophilic substances.

To visualizing the significance of structural transition of ionic micelles and to understand CTAT + bile salt system, I undertook this work as a systematic study on the effect of three bile salts (differing in number of hydroxyl groups or substitution) on the structural transitions of wormlike cationic CTAT micelles. The objective of this study was to investigate the mixed cationic/anionic systems, and to observe the effect of presence of bile salt on the transition and microstructure of CTAT micelles.

9.2 Materials

Cetyltrimethyammonium toluene sulfonate (CTAT) was from Sigma Chemical Company (USA) and bile salts sodium cholate (NaC) and sodium deoxycholate were obtained from fluka and used as received. Solutions were prepared in triply distilled water for viscosity and cryo-TEM measurements. For 2D NOESY experiments solutions were prepared in D2O( form Sigma).

9.3. Methods

9.3.1 Viscosity

The viscosities of solution were measured using an Ubbelohde suspended level capillary viscometer. The CTAT concentration chooses was such that solutions showed Newtonian flow. The viscometer was vertically suspended in a thermostat at 30 °C unless stated otherwise. The viscometer was cleaned and dried every time before and after each measurement.

9.3.2 Cryogenic-transmission electron microscopy (Cryo-TEM)

Cryo - TEM measurements were performed with Philips CM 120 TEM and a Tecnai 12 G2 TEM (FEI). Digital images were recorded using Gatan 791 or a Gatan Ultrascan 1000 cooled CCD camera maintain at magnification of 48k. To prevent electron beam radiation damage low dose imaging was used [46,47]. Before recording image sample solutions were maintain at 30°C in a water bath, then transferred to
controlled environment vitrification system (CEVS) where same temperature was sustain. Sample drop was placed on a perforated carbon grid (Ted Pella) held by tweezers inside the CEVS, and blotted to form a thin film of the sample (100–200 nm thick). After relaxation time of 75-80 seconds the sample was plunged into liquid ethane (held just above its freezing point) to be converted into vitreous form and then stored in to liquid nitrogen. Throughout the experiment samples were prevented from atmospheric conditions.

9.3.3 Small angle neutron scattering (SANS)

SANS measurements on 20mM CTAT solution in presence of various concentration of TBCF87 were performed at Dhruva reactor, BARC, India [48]. The sample solutions were prepared in D₂O and kept overnight for equilibration. The mean wavelength of the incident neutron beam was 5.2 Å with a wavelength resolution of approximately 15% obtained by SANS diffractometer with polycrystalline beryllium oxide (BeO) filter as monochromator. The angular distribution of the scattered neutron was recorded by a linear 1 meter long He³ position sensitive detector (PSD), in the Q range 0.017–0.34 Å⁻¹. The data, corrected for the background and solvent contribution were normalized to the cross-sectional unit using standard procedures. The scattering cross section per unit volume measured, as a function of scattering wave vector, gives the micellar parameters for the monodispersed surfactant system [49].

In SANS experiment, the differential scattering cross-section per unit volume as a function of scattering vector Q is obtained, and for monodisperse system of micelles it can be expressed as [49].

\[
\frac{d\Sigma}{d\Omega} = n_m V_m^2 (\rho_m - \rho_s)^2 [\langle F^2(Q) \rangle + \langle F(Q) \rangle^2 [S(Q) - 1]] + B \tag{1}
\]

Here \(n_m\) is the number density of the micelles, \(\rho_m\) and \(\rho_s\) are the scattering length densities of the micelle and solvent, respectively, \(V_m\) is the volume of micelle, and \((\rho_m - \rho_s)^2\) is a contrast factor that represents the difference between the average scattering length density of the micelle and solvent. \(F(Q)\) and \(S(Q)\) are single particle form factor.
and the inter-particle structure factor, respectively. The inter-particle structure factor \( S(Q) \) depends upon the spatial arrangement of particles and hence gives information about the inter-particle interaction. B is a constant term that represents the incoherent scattering background, which is mainly due to the hydrogen atoms in the sample.

### 9.3.4 2-D nuclear overhauser enhancement spectroscopy (NOESY)

2D-NOESY is a noninvasive technique that can be used to determine the locus of solubilizates in micelles or its interaction with micelle. This technique does not require an aromatic molecule or added paramagnetic agents to determine the position of solubilizates in surfactant solutions.

### 9.4 Results and discussion

#### 9.4.1 Viscosity

The viscosities of CTAT solutions of different concentrations (5-20mM) at 30 °C are shown in Fig. 9.1(a), the temperature dependence of viscosity of 20 mM CTAT is shown in Fig. 9.1(b). All CTAT solutions were 5 or more times concentrated than at CMC. It can be clearly seen from Fig. 9.1 (a) that the relative viscosity of CTAT increases with concentration but solutions showed a remarkable increase around 15 mM which attributed the shape transition of CTAT micelle from sphere to rodlike at critical rod concentration (CRC). This is in agreement with literature [50]. With increase in concentration of CTAT, micelles grow in length (wormlike micelle) and further increase leads to entanglement or overlapping of wormlike micelle which form network structure of micelle hence with increase in concentration of CTAT viscosity of solutions increased[40,51-53]. For CTAT, the counterion \( p \)-toluenesulfonate (tosylate) being competitively large organic counterion [52] is able to penetrate in micelle surface by hydrophobic interaction (low value of counterion dissociation (\( \alpha \)) =0.13). This accounts for higher viscosity in absence of salt for relatively lower concentration of CTAT as compare to CTAB.

At 20 mM, CTAT forms network structure similar to polymer solutions but with a difference. The surfactant micelles are in dynamic equilibrium with monomer and hence
network structure of micelles is rather different from polymeric network. Further, as it involves dynamic equilibrium, effect of temperature is quite important. With this aim, viscosity measurements of aqueous 20 mM CTAT solution in the temperature range 30°C-60°C with increment of 2°C were carried out. As shown in Fig. 9.1 (b) viscosity decreases exponentially with temperature which is in agreement with literature [54]. For ionic surfactant rise in temperature leads to demicellization, hence diminished growth of micelle which tends to decrease viscosity of surfactant solution. With increase in temperature, CTAT monomer jump more rapidly between cylindrical body and hemispherical end-cap of worm, thus at higher temperature end-cap restriction is less; suppresses the growth of worm [55].

Fig. 9.1 Relative viscosity of CTAT solutions of different concentration (a) at 30 °C and (b) 20 mM CTAT solution at different temperatures

The effect of salts (NaCl, NaBr) on the viscosity of 5 mM CTAT solution at 30 °C is shown in Fig. 2. With increasing content of salt relative viscosity of 5 mM CTAT
solution increases initially and then decreases slightly and then increases. The presence of salt screens head group charge, reduces electrostatic repulsion, allows the headgroup to come closer [56] and thus facilitates formation of worm- like micelles even in 5mM solution. The growth of worm- like micelle (entangled structure) caused by presence of salt is evident by initial increase in viscosity [56,57]. For CTAT, limit between the dilute and semi-dilute regime or overlapping concentration is about 6- 11 mM (0.3- 0.5 wt %) as reported by other authors [52,59]. According to Torres et al.[56] in presence of salt overlapping concentration decreases up to around 4 mM (0.2 wt %) which results in initial increase in viscosity at about 0.1M NaCl/NaBr. The slight decrease in viscosity with further addition of salt was because of increase of flexible worm-like micelle that leads to formation of more compact coils formation [42]. At higher salt concentration, further increase in viscosity is also supported by the results of Frapp study by Narayanan and co-workers [14], which attributes the further growth of worm-like micelle due to salting out effect with decrease in overlapping concentration. However, in presence NaBr increase in viscosity was more pronounced than with NaCl. This is because of relatively more hydrated size of Cl\(^-\) Hence presence of NaCl is less dominant in decreasing head group charge repulsion as compared to NaBr [60].
Fig. 9.2 Relative viscosity of 5 mM CTAT in presence of different concentration (0.1-1M) of (●) NaBr and (■) NaCl at 30 °C.

The viscosities of CTAT solutions at fixed concentrations (5-20 mM) but in the presence of varying concentrations of three bile salts are shown in Fig. 9.3 (a and b) and Fig. 9.4. It is evident from these results that dihydroxy bile salts (NaC and NaTC) drastically decrease the viscosity of CTAT solutions bringing down the value close that of water at higher concentrations without any precipitation at equimolar concentrations. The effect of NaDC on the viscosity of CTAT solutions was altogether different and a maximum is observed at ~3 mM NaDC.

CTAT, a cationic surfactant forms highly viscoelastic solution in water even at concentration few tens of its CMC while other CTAX (X= Cl, Br, NO₃, SO₄) form spherical micelles with viscosity slightly higher than water. This viscoelastic effect of CTAT solution diminishes on addition of little bile salt NaC (a typical anionic surfactant) which does not form precipitate for mixed system with equimolar composition. The
wormlike CTAT micelles transform to small spherical mixed micelles in the presence of NaC.

Fig. 9.3 Relative viscosity of CTAT solutions (●) 5mM, ( ■) 10 mM, ( ▲) 15 mM and (♦) 20mM at varying concentrations of trihydroxy bile salts (a) NaC and (b) NaTC at 30 °C

The viscosity of CTAT/NaDC mixed system passes through a peak on increasing NaDC concentration in isotropic single-phase region. The viscosity peak might result from the transformation of linear micelles to branched wormlike micelles [30,16]. Branched wormlike micelles have been shown theoretically to have lowered viscosity [61]. As branching progresses, the viscosity decreases and the tendency for phase separation increases. Another explanation is that the wormlike micelles grow up to the peak and shrink beyond the peak [62,63].
The studies on the effect of NaBr on the viscosities of the 5 mM CTAT in the presence of varying concentration of bile salts is shown in Fig. 9.5. No precipitation was seen even for equimolar concentration of NaDC as observed in water.

For some CTAB/NaBr systems, a viscosity peak was obtained in the presence of bile salt. Though, the peak position is at quite higher concentration for NaC as compared to NaDC. This viscosity peak arises due to a shift from linear wormlike aggregates to branched wormlike aggregates. The formation of long wormlike aggregates is closely related to the interaction between the oppositely charged surfactants.

The stronger counterion binding between Br\(^-\) and CTA\(^+\) than that between Na\(^+\) and cholate\(^-\) results in stronger influence to the interactions between the headgroups in mixed micelles. Therefore, the addition of NaDC to mixed CTAT/NaBr micelles induces stronger effect on the viscosity peak at the isotropic single-phase region with excess CTAT, and weaker effect on that with excess cholate.
Fig 9.5. Relative viscosity of 5 mM CTAT in 1M NaBr in presence of varying concentration of bile salt ●NaDC and ○ NaC at 30 °C.

9.4.2 Cryo-TEM Characterization of micelle shape

The surfactant concentration was (20 mM) where the solution exhibited isotropic behavior. At this CTAT concentration, the cryogenic-temperature-transmission electron microscopy (cryo-TEM) was used to image microstructures in the presence of varying concentration of bile salts. Such images were taken on 20mM CTAT solution in the presence of NaC and NaDC. As shown in Fig. 9.6 (a) clear rod-like as well as thread-like micelle (few branching between thread also observed) seen for pure 20mM CTAT solution, close observation of this figure also supports the co-existence of very few spherical micelles. The addition of 1mNaC in 20 mM CTAT reduces the size of rod/thread-like micelle (see Fig. 9.6b) and increase the number density of spherical. Further increase in concentration of NaC (6mM) reduces rod/thread-like micelle (Fig.
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9.6c) and raise number of spherical micelle. Thus, the microstructures observed were rod or thread-like micelles that changed to spheroidal micelles as the concentration NaC was increased. This trend exactly explains why viscosity reduces with increase concentration of NaC for 20mM CTAT. On the contrary, as demonstrated in Fig. 9.7 with increasing concentration of NaDC thread-like micelle of 20mM CTAT now convert to flexible and branched worm-like micelle the generate a network like structure. As the NaDC added initially at 3mM (Fig. 9.7b) thread-like micelles became more flexible and form branching, (formation of some loops also evident). This situation is corresponds to peak in relative viscosity plots for same system. Spherical micelles were still present, but their number density was significantly reduced, and no disk-like structures were observed. In Fig. 9.7c (7mM NaDC) as compared to Fig. 9.7(a) and 9.7(b) thread-like micelles are now contorted, shorter and have some Y-junction (evidence of branching). At higher amount of NaDC (12 mM Fig 9.7d) micelles still contorted and more shorter (micelle were short up to 100mM). Thread-like micelles were short (up to 200 nm).

![Fig. 9.6](image)

Fig. 9.6 (a) 20 mM CTAT (b)20mM CTAT +1mM NaC black arrow indicate spherical micelle while white arrow indicate worm / rod like micelle (c) 20mM CTAT+ 6mM NaC (only spherical micelle are present) at 30°C.

The branching of wormlike micelle was the reason behind the decrease in viscosity of CTAT –NaDC system at higher concentration of NaDC. The branches are highly mobile and free to slide along the cylindrical micelles. At higher concentration of
NaDC, the network structure of micelle gets saturated with branched micelles resulting in shrinkage and leading to phase separation into a concentrated and a dilute phase.

**Fig. 9.7** (a) 20 mM CTAT (b) 20mM CTAT +3mM NaDC (black and white short arrow indicate branching and loop formation respectively) (c) 20mM CTAT + 7mM NaDC (d) 20mM CTAT+ 12mM NaDC at 30°C

### 9.4.3 Micelle shape/size from SANS

In order to quantify observation from viscosity and cryo-TEM, a corresponding SANS study was carried out. Fig. 9.8 shows SANS results for 20 mM CTAT in D$_2$O as well as in solution at different concentration of NaC. All SANS plots are in log-log scale. CTAT-NaDC mixed systems could not be analyzed by SANS.

The parameters in the SANS analysis were optimized by the means of nonlinear least-square fitting program (solid lines in the figure represent fitting data) [64]. The data obtained from fitting are listed in Table 9.1. The SANS distribution of the micellar
solution for ionic surfactants generally shows a correlation peak [65] that corresponds to a peak in interparticle structure factor $S(Q)$ and indicates the presence of repulsive interaction between micelles and specifies the correlation between the centers of the micelle. Since $S(Q)$ depends on both the shape and the orientation of the particles, its calculation is quite complicated for any shape other than spheres. Hence, for simplification, prolate ellipsoidal micelles are assumed to be equivalent to spherical micelles. We have calculated $S(Q)$ as derived by Hayter and Penfold [66] using the Ornstein–Zernike equation and the mean spherical approximation.

Fig. 9.8 Plot of normalized neutron scattering cross-section $(d\Sigma/d\Omega)$ vs. the scattering vector $Q$ for 20 mM CTAT in (○) $D_2O$, (●) 3mM NaC (■) 6mM NaC and (▲) 10 mM NaC at 30°C

The SANS plot for 20 mM CTAT shown in Fig. 9.8 indicates that the SANS data asymptote to a slope close to -1 at low $Q$ and resembles those from long
cylindrical/rodlike micelles [67]. This observation clearly supports the cryo-TEM image as well as high \( \eta \)\textsubscript{rel} values of 20 mM CTAT solution. Fig. 9.8 clearly demonstrates that with increasing concentration of NaC, the scattering intensity of CTAT solution decreases and slope at low \( Q \) increases and tends to zero. Further, a shift in the correlation peak is found towards the high \( Q \) region, which indicates decrease in the micelle size and intermicellar distance (\( Q_m = \frac{2\pi}{d} \), where \( Q_m \) is the value of \( Q \) at the peak position). Also, the normalized neutron scattering cross-section (\( \frac{d\Sigma}{d\Omega} \)) gradually decreases in the presence of NaC. All these factors suggest a decrease in micelle size with increasing concentration of NaC; micelles transform to ellipsoidal shape from long cylinder (rod like). This is also supported by decrease in aggregation number for CTAT (Aggregation number, was calculated by equation \( N_{agg} = \frac{4\pi ab^2}{3v} \), where \( v \) is the volume of the surfactant monomer \( a \) and \( b \) are semi major and semi minor axis of micelle respectively). (Table 9.1). These observations are in accordance with viscosity results and cryo-TEM images.

**Table 9.1** Parameters obtained from the SANS fits for 20 mM CTAT in presence of NaC at 30°C

<table>
<thead>
<tr>
<th>[NaC] mM</th>
<th>a Å</th>
<th>b Å</th>
<th>( N_{agg} ) CTAT</th>
<th>( N_{agg} ) NaC</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>107.5 ± 1.8</td>
<td>18.2 ± 0.5</td>
<td>1234 ± 15</td>
<td>185 ± 10</td>
</tr>
<tr>
<td>4</td>
<td>54.5 ± 1.6</td>
<td>17.8 ± 0.5</td>
<td>540 ± 8</td>
<td>162 ± 8</td>
</tr>
<tr>
<td>6</td>
<td>31.9 ± 1.2</td>
<td>16.4 ± 0.5</td>
<td>233 ± 5</td>
<td>117 ± 7</td>
</tr>
</tbody>
</table>

**9.4.4 Location of bile salt molecule in CTAT micelle by 2D-NOESY**

In Fig. 9.9 (a and b) the NOESY spectra are presented for CTAT-NaC and CTAT-NaDC systems, respectively. From the comparative inspection of these spectra, it is apparent that there are more number of cross peaks between CTAT and NaC molecules and only few cross peaks are observed for CTAT-NaDC system. This is a strong indication that there is more interaction of CTAT molecules with NaC molecules as
compared to that of NaDC. Close observation of Fig. 9.9 (a) (CTAT-NaC system) suggests that there are intense cross peaks between methyl and methylene protons of NaC and N-CH$_3$ as well as N-CH$_2$ protons of CTAT around 0.9 ppm. Further, there are also cross peaks between tosylate head group protons and methyl protons of NaC at around 4 ppm. There is no evidence of interaction between inner protons of CTAT (protons of CTAT micelle core) and protons of NaC. Such observations suggest that NaC molecules are only able to interact with the head group protons of the CTAT. In contrast, from the examination of the NOESY spectrum of CTAT-NaDC systems there are clear cross peaks between methyl protons of NaDC and inner methylene protons of CTAT (tail protons that form core region of micelle) around 1 ppm. Such observation suggests that NaC molecules most probably are placed flat on the surface of CTAT micelle such that their hydroxyl and carboxylate group remain in contact with bulk water and hydrocarbon segments of the steroid backbone in contact with micelle surface. NaDC molecules penetrate in micelle core such that their methyl protons remain towards micelle core. These observations also go in line with anticipation of George et al [68].

According to Vethamuthu et al [38, 39] the distinction in interaction of NaC and NaDC with CTAT is based on difference in their structure. NaC has the $\alpha$ hydroxyl groups at the 3, 7, and 12 positions on the same concave side of the molecule. NaDC has hydroxyl groups at both the $3\alpha$ and $12\alpha$ positions on the concave side. The presences of hydrophilic hydroxyl (-OH) groups and the carboxylate (-COO) group, and a hydrophobic nonpolar face made up of hydrocarbon segments of the steroid backbone results in amphiphilic character of bile salts. In the case of NaC, three –OH and a –COO group in contact with bulk water provide flat position for NaC molecules on micelle water interface. Such orientation of NaC increases the average area of the head group ($\alpha$) or the curvature (due to the large area taken up by the cholate ion when placed flat at the interface of the micelle). As a consequence, micelle size decreases with addition of NaC (see Fig. 9.6). Based on this explanation decrease in viscosity of CTAT solution with addition of NaC could be understood.
On the other hand, the presence of only two –OH groups (and a –COO group) does not facilitate such orientation for NaDC molecule. In case of NaDC, deoxycholate anion inserts in cationic micelles such that only the negatively charged –COO group remains near to the head-group region protrudes at the micellar interface. Such location (packing) of NaDC molecules between the charged (cationic) head groups screens the charge (due to location of negatively charged –COO group between head groups), reduces repulsion between them and weakens their hydration and overall charge on micelle surface. This results decrease in the average area of the head group (a). In
addition, accommodation of the shorter and bulkier bile body into the micellar core would increase the volume $V$ but reduce the effective length by averaging out the contribution of the longer hydrocarbon chain. An increase in Israelachvilli (packing) parameter ($P= \frac{V}{al}$; where $V$ and $l$ is the volume and length of hydrophobic chain of the surfactant monomer respectively, $a$ is the surface area occupied per surfactant head group [69]) or decrease in micelle curvature, results in micellar growth and formation of rod/cylindrical and even wormlike structures. However, at higher concentration of NaDC rod like micelles transform into small spherical micelles and the viscosity attains values comparable to the CTAT + NaC system. Above explanation is in accordance with viscosity results and cryo-TEM image for CTAT-NaDC system (Fig. 9.7).

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Work described in this chapter will be communicated to **Langmuir**