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1-Hexanol triggered structural characterization of the worm-like micelle to vesicle transitions in cetyltrimethylammonium tosylate solutions

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The cationic surfactant cetyltrimethylammonium tosylate (CTAT) forms highly viscous/viscoelastic solutions and worm-like micelles at relatively low concentrations. The effect of 1-alkanols with short to long alkyl chains *viz.* ethanol, 1-butanol, 1-hexanol and 1-octanol on CTAT micelles was examined. In particular, a detailed study on the effect of 1-hexanol was carried out by viscosity, cryogenic transmission electron microscopy (cryo-TEM), nuclear magnetic resonance (NMR) and small-angle neutron scattering (SANS) to observe microstructural changes in CTAT micelles. 1-Hexanol displays a distinct interaction with CTAT micelles strongly dependent on CTAT concentration. Up to a certain critical CTAT concentration, 1-hexanol molecules penetrate into the micelles and show growth. Characterization by direct cryo-TEM imaging implies that upon progressive addition of 1-hexanol, worm-like CTAT micelles first grow and finally transform into vesicles. The course of vesicle formation was followed by SANS measurements. The site of 1-hexanol in the micelles close to the palisade layer was evaluated using 2D NMR. This study devotes a fundamental knowledge for controlling the shape and size of worm-like micelles that find many industrial applications particularly in personal- and home-care products.

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1. Introduction

In aqueous solution, quaternary ammonium salt based cationic surfactants *viz.* cetyltrimethylammonium bromide (CTAB) form rod- or worm-like micelles, much above the critical micelle concentration (CMC) or in the presence of salts such as NaCl, NaBr, NaNO₃ and NaClO₃ even at concentrations close to CMC.^{1–3} The presence of salt screens the electrostatic repulsion between the charged head groups and facilitates micellar growth.^{4,5} However, cationic surfactants with strongly bound hydrophobic counterions such as cetyltrimethylammonium tosylate (*p*-toluenesulfonate) (CTAT) can form worm-like micelles even in the absence of salt and at a much lower concentration.^{6–8} The CMC of CTAT is relatively low (0.3 mM), rod-like micelles form at about 15 mM and transform into

viscoelastic gels around 70 mM.^{9–13} The solution behavior of CTAT is comparable to that of high molecular weight polymer solutions where molecules entangle above their coil-overlap concentration.^{14,15} Here, tosylate counterions insert between the head groups in micelles and promote micellar growth to worm-like micelles and viscoelasticity. Worm-like micelles are sometimes called living polymers due to the fact that they are in dynamic equilibrium with monomers.¹⁶ Such micellar systems exhibit peculiar rheological properties and find applications in diverse fields ranging from personal care products to drilling fluids for enhanced oil recovery, drag reduction, as templates for material synthesis, cosmetics, paints, fracturing fluids in oil production and are also ideal candidates for the study of complex flow phenomenon.^{17–22}

The rheological properties of aqueous CTAT solutions can be influenced by the presence of anionic surfactant,^{5,15} salts,^{23–25} polymers^{12,26–28} and by temperature.^{25,29} Koehler *et al.*⁵ studied the effect of sodium dodecylbenzene sulfonate (SDBS) on CTAT solution and observed growth of worm-like micelles, though at higher concentrations strong mutual interactions between the oppositely charged surfactants facilitated a transition from linear micelles to branched micellar network of low viscosity. Rojas *et al.*³⁰ studied the effect of hydroxyethyl cellulose (HEC) and hydrophobically modified hydroxyethyl celluloses (HMHEC) with different molecular weights on the shear viscosity of CTAT solution. Their results show that the shear

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viscosity of HEC/CTAT solutions is higher than the viscosities of the surfactant or polymer solutions at the same concentrations, but are lower compared with the HMHEC/CTAT system. In addition, surface tension measurements manifest complex formation between CTAT and HMHEC but not for CTAT/HEC system.

In our previous study, we have examined the effect of Pluronic® F87, a hydrophilic nonmicellar PEO-PPO-PEO tri-block copolymer, on worm-like micelles of CTAT.²⁸ In the presence of F87, a sharp decrease in the CTAT solution viscosity was due to transformation of worm-like micelles into smaller micelles. Here, PPO segments of F87 inserts towards hydrophobic core of CTAT micelles. The PPO moieties contain significant amount of water and PEO is heavily hydrated and this results in increase in hydrophilicity. These additives are often used to modify the properties of surfactants solutions, allowing them to be utilized in diverse applications such as lubrication, oil-wetting cleaners, pharmaceuticals, cosmetics, food and detergent formulations, which require the use of surfactants in a water-poor medium.³¹⁻³³

Short/medium/long chain alcohols have been of interest due their important role as co-solvents/co-surfactants in micro-emulsions. It is generally noticed that short chain alcohols (C_1-C_3) remain in the aqueous bulk phase, medium chain alcohols (C_4-C_6) partition between the micellar and bulk phases and long chain alcohols (C_7 and above) are solubilized within the micelle with polar hydroxyl group protruding towards the micelle surface and inducing the microstructural changes in the system. Bahadur and coworkers³⁴⁻⁴¹ have extensively studied the effect of different alcohols on aqueous surfactant solutions. 1-Hexanol is a weakly amphiphilic alcohol with low aqueous solubility, which is known to penetrate into micelles and promote their growth. There have been other reports on the effect of 1-hexanol on several surfactants *viz.* cationic,³⁴ gemini,^{36,42} sugar surfactant,⁴³ Triton X-100³⁷ and Pluronics® with varying hydrophobicity.³⁸⁻⁴¹ Few studies demonstrate that addition of hydrophobic alcohol leads to growth of worm-like micelle^{44,45} followed by vesicle formation.⁴⁶⁻⁴⁸ Sreejith *et al.*⁴⁹ observed 1-octanol induced a micelle-to-vesicle transition in CTAB/KBr system that was dependent on the alcohol concentration and temperature. These vesicular structures are extensively studied due to their prime importance in numerous applications.⁴⁹⁻⁵¹ Generally, vesicles are formed by interaction of two oppositely charged surfactants. The formation of vesicular structures has also been reported for CTAT micelles in the presence of anionic surfactant SDBS.^{52,53} Kaler *et al.*⁵² demonstrated the spontaneous formation of equilibrium vesicle of CTAT in the presence of SDBS and it was proposed that vesicle size can readily be tuned by changing the composition of both the surfactants. However, a study involving additive induced vesicle formation in salt-free CTAT in aqueous solution has not been attempted yet.

Herein, we report on the aqueous solution behavior of CTAT in the presence of 1-hexanol accompanied by worm-like micelles-to-vesicles transition. Microstructural changes are function of 1-hexanol and CTAT concentrations and are scrutinized by viscosity, cryo-TEM and SANS. Ethanol, 1-butanol and

1-octanol were used to compare the viscosity behavior of CTAT. Location of 1-hexanol in micelles was elucidated from NOESY. The present study offers a simple way of getting desired morphology of worm-like micelles easily tuned up by 1-hexanol.

2. Experimental

2.1 Materials

Cetyltrimethylammonium tosylate (CTAT) was purchased from Sigma Aldrich and used without further purification. Ethanol, 1-butanol, 1-hexanol and 1-octanol were obtained from Spectrochem, India and used as received. Deionized water from a Millipore Milli-Q system was used to prepare samples for viscosity and cryo-TEM measurements. The solutions for SANS and NMR were prepared in D_2O (99.9% pure).

2.2 Methods

2.2.1 Viscosity. The absolute viscosity of solutions was measured by using size 50, 150, 300 and 500 calibrated Cannon Ubbelohde viscometers suspended vertically in a thermostat with a temperature stability of ± 0.1 °C. The viscometer constants are 0.004093, 0.03462, 0.2530 and 7.495 centi-stokes s^{-1} , respectively. The kinematic viscosity of the solutions in centi-stokes were obtained by multiplying the measured flow time in seconds by the viscometer constant. These kinematic viscosities were then multiplied by the water density (1 g cm^{-3}) to get viscosity in centi-poise. Relative viscosities of the solutions were calculated by dividing the obtained viscosities with viscosity of water.⁵⁴

2.2.2 Cryogenic transmission electron microscopy (cryo-TEM). Cryo-TEM measurements were performed using a Philips CM 120 TEM and a Tecnai 12 G² TEM (FEI) at Technion, Haifa, Israel. Digital images were recorded using Gatan 791 or Gatan Ultrascan 1000 cooled CCD cameras at magnifications of up to 48k. To prevent electron beam radiation damage low dose imaging was used.⁵⁵⁻⁵⁷ The solutions were maintained at 30 °C in a water bath and then transferred to the controlled environment vitrification system (CEVS) for preparation. A 5 μ l drop was placed on a perforated carbon grid (Ted Pella) and blotted to form a thin film of sample. After relaxation time of 15–45 s to overcome shearing effects, even in highly viscous solutions, the sample was plunged into liquid ethane (held just above its freezing point) to be converted into a vitreous specimen and then stored in liquid nitrogen. Throughout the experiment, samples were prevented from atmospheric conditions.

2.2.3 Small angle neutron scattering (SANS). SANS experiments were performed at the SANS diffractometer at the Guide Tube Laboratory, Dhruva reactor, BARC, Mumbai, India. The sample solutions were prepared in D_2O (99.9%). The mean incident neutron wavelength was 5.2 Å with $\Delta\lambda/\lambda = 15\%$. The scattering data were measured in the wave vector transfer ($Q = 4\pi \sin(\theta/2)/\lambda$, where θ is scattering angle) range of 0.017 to 0.35 Å⁻¹. Sample temperature was kept constant at 30 °C for all measurements. The measured SANS data were corrected for the background, empty cell contribution and the transmission and



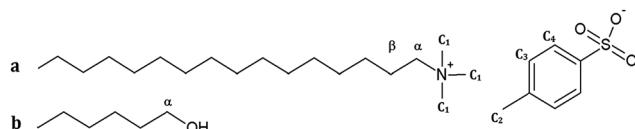


Fig. 1 Chemical structures and proton labeling of (a) cetyltrimethylammonium tosylate (b) 1-hexanol.

normalized to absolute cross-sectional unit using standard protocols.

2.2.4 Nuclear magnetic resonance (NMR). NMR experiments (1D and 2D) were performed on a Bruker Avance-II 400 MHz NMR spectrometer at St. Francis Xavier University, Canada. The spectrum was calibrated by setting the HDO peak at a chemical shift of 4.65 ppm at 298 K. Solvent suppression eliminated the HDO peak due to residual water. For the 2D NMR experiments the mixing times and the delay times were estimated from the spin-lattice relaxation times. In all cases, an acquisition delay of $\gg 3 \times T_1$ and a mixing time of $\gg 1 \times T_1$ were used to obtain the NOESY spectra.

2.3 Results and discussion

2.3.1 Relative viscosity. CTAT forms worm-like micelles at a much lower concentration than conventional surfactants like CTAB or CTAC. Such morphology of surfactant micelle has a tremendous effect on the solution viscosity. An abrupt increase in the viscosity is observed due to the formation of worm-like micelles in CTAT solution (data not shown).²⁸ Viscometry is a classical but important technique to study growth/transition in surfactant micelles. In order to perceive the influence of chain length of some short and medium chain 1-alkanols on size/shape, viscosities of 15 mM CTAT solution were measured as a function of 1-alkanol concentrations at 30 °C. Here, concentration of CTAT is selected in such a way that solution contains worm-like micelles and it can take up some 1-alkanol and present growth of worm-like micelle (critical rod concentration for CTAT is 15 mM). At higher [CTAT], micelles are more compact which will not allow 1-alkanols to penetrate inside (Fig. 3). Data displayed in Fig. 2 show that addition of 1-alkanols produces a viscosity maximum in all cases. In the presence of ethanol, a maximum appears at a relatively high concentration (approximately at 0.6%) but the viscosity still remains high enough even up to 2% ethanol. For 1-butanol, peak in the viscosity is observed at 0.3%. The addition of 0.2% of 1-hexanol causes sharp increase in the viscosity and at 0.5% concentration the solution has a water-like viscosity. For 1-octanol, a remarkably high increase in the viscosity is observed with a sharper peak and a maximum at 0.1%. These observations manifest that with increase in chain length of 1-alkanols, the peak concentration shifts to lower 1-alkanol concentrations.

In earlier studies, such micellar growth has been observed in the presence of an oppositely charged surfactant or when inorganic salt was added to surfactant solutions. For ionic surfactants, the electrostatic repulsions between the polar groups are strong which leads to a large effective head group

and favor the formation of relatively smaller micelles. However, the added salt or oppositely charged amphiphile screens net surface charge and thus decreases the effective area per head group and favors micellar growth/transition.^{4,5} In the present case, due to hydrophobic tosylate counterion, worm-like (linear) micelles exist even in the absence of salt, which results in a high solution viscosity. These propose that the viscosity of CTAT solution in the presence of alcohols is influenced by an additional factor.

The effect of alcohols chain length on the viscosity of cationic surfactant can be explained by their ability to partition between the aqueous bulk phase and the pseudomicellar phase. The longer chain (more hydrophobic) alcohols are efficiently solubilized in the micelle compared to shorter chain (more hydrophilic) alcohols which mostly affect solvent properties. As indicated from CMC values of surfactants in presence of alcohols, hydrophobic alcohols cause a larger decrease in the CMC than hydrophilic ones.³⁶ Alternatively, more hydrophobic alcohols have higher partition coefficient and they get solubilized in surfactant micelles at much lower concentrations than the shorter chain alcohols.⁵⁸

It is well documented that short chain hydrophilic alcohols (like ethanol) behave as water structure breakers (co-solvents) and affect the micelle stability by altering the water dielectric constant.³⁶ Their presence makes water (solvent) more affable for the hydrocarbon portion of the surfactant, resulting in increasing destruction of the micelles.⁵⁹ Based on this explanation, the trend observed in the viscosity of CTAT solutions as

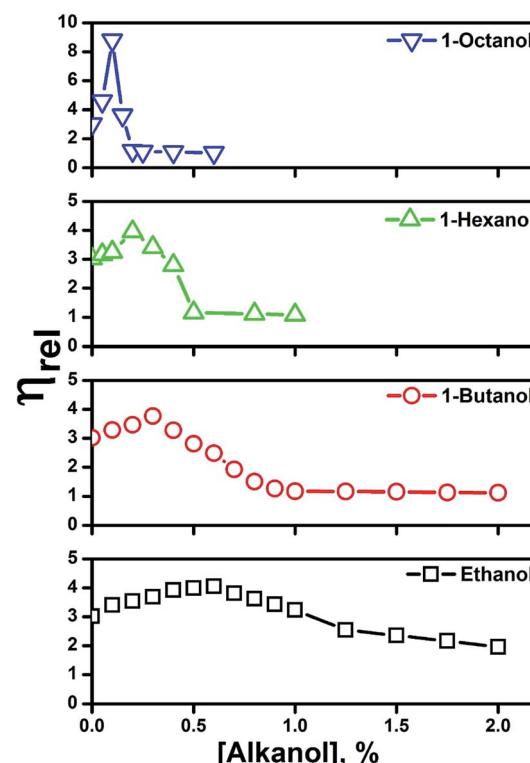


Fig. 2 Relative viscosity of 15 mM CTAT as a function of alkanol concentration at 30 °C.



a function of ethanol concentration can be understood. At 15 mM CTAT micelles are already large; small addition of ethanol transforms these micelles to a less compact state (*i.e.*, micelle size increases), which is reflected as an increase in the viscosity. Above 0.6% of added ethanol, the large and less compact micelles slowly convert into smaller micelles, which is reflected in the drop in the viscosity. In the present study, the concentration of ethanol used is below its aqueous solubility so there is not any possibility of its penetration inside CTAT micelles which can lead to any morphological changes. Due to much lower dielectric constant of ethanol, its presence weakens the hydrophobic effect of CTAT and hence energy of system required for vesicle formation is not attained.⁶⁰ So it can be inferred that ethanol is not capable of forming vesicle from CTAT. It can also be correlated with lower value of octanol-water partition co-efficient ($P_{o/w}$) ~ 0.49 for ethanol which opposes its penetration inside CTAT micelles.³⁶ There is no report on ethanol induced micellar growth which leads to formation of branched worm-like micelles or vesicles formation of single surfactant at higher concentration so it was safely concluded that disintegration of micelles to smaller size is responsible for lowering of solution viscosity at higher ethanol concentration. As compared to ethanol, in the presence of 1-butanol, the peak viscosity appears at relatively lower concentration. Since the hydrophobicity of the micellar interior is high (due to insertion of the tosylate counterion) and 1-butanol is relatively more hydrophobic and has higher $P_{o/w}$ compared to ethanol, it partitions between the micellar and the bulk phases at a lower concentrations. Such a partition increases micellar size and stimulates slight increase in the solution viscosity. However, with increase in 1-butanol concentrations, the solubility of the nonpolar tail of CTAT is increased; hence, the hydrophobic interactions between the surfactant tails are reduced which will affect the amount of surfactant assembling into micelles. This will lead to a decrease in the micellar size and consequently a decrease in the viscosity is observed. At higher concentration, 1-butanol also behaves as co-solvent similar to ethanol and does not contribute to vesicular formation at all concentrations.³⁴ So it was expected that worm-like CTAT micelles are transformed to smaller micelles at higher 1-butanol concentrations responsible for lower solution viscosity. However, 1-hexanol with higher $P_{o/w}$ (~ 107), intercalates between the head group of CTAT micelles at lower concentrations and reduces surface charge density and promotes micellar growth, which is reflected in higher solution viscosity. It is reported that 1-hexanol is capable of inducing the growth of wormlike micelles that can be transformed into vesicles at higher concentrations.⁴² Similarly, in the present study, a dramatic loss in solution viscosity at higher [1-hexanol] is observed which suggests that such a transition is accompanied by variety of microstructures. Such observations prompted us to study the effect of 1-hexanol on CTAT solution in detail. A detailed study on formation of vesicles from CTAB micelles in the presence of KBr has been reported for 1-octanol and it was concluded that sudden drop in viscosity after maximum is due to formation of vesicles.⁴⁹ It is well reported that 1-octanol increases the aggregation number by forming mixed

micelles.^{45,49} It is obvious from above observations that 1-hexanol and 1-octanol are capable of forming vesicles from single surfactant solution while ethanol and 1-butanol are not. In the present study, due to more hydrophobic nature of 1-octanol, it intercalates between CTAT charged head groups and leads to a large increase in viscosity than 1-hexanol at much lower concentration. Consequently, viscosity maximum appears at 0.1% for 1-octanol. So it can be concluded that extent of penetration of 1-alkanols which contributes to higher solution viscosity is greater for 1-alkanols having alkyl chain length higher than 1-butanol so viscosity maximum is shifted to lower 1-alkanol concentration and the magnitude of increase in viscosity follows the order 1-octanol $>$ 1-hexanol $>$ 1-butanol $>$ ethanol.

The microstructures formed have been found to be the function of CTAT concentration as well. In this context, viscosity measurements were performed by varying CTAT concentration in the presence of 1-hexanol; the results are shown in Fig. 3. The critical rod concentration (CRC) for CTAT is 15 mM.^{9,10} Below the CRC, the addition of 1-hexanol does not lead to large increase in viscosity and we get a good viscosity graph at 20 mM CTAT expecting variety of microstructures formed so we performed detailed study this concentration. Addition of 1-hexanol to 20 mM CTAT solution has a striking effect on the solution viscosity showing a maximum at 0.25% 1-hexanol. With increase in [CTAT], the maximum shifts to lower 1-hexanol concentration.⁴⁹ In 30 mM CTAT, the viscosity directly decreases without showing any maximum. This may be due to a more compact packing of micelles at higher [CTAT] which does not allow 1-hexanol molecules to penetrate.

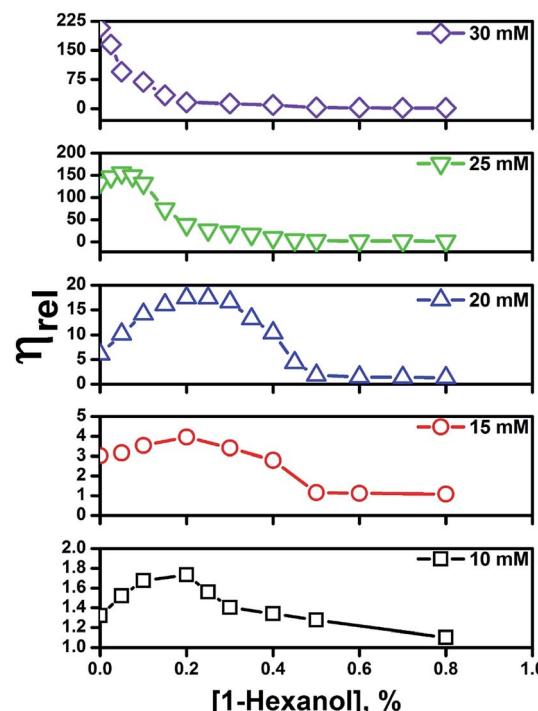


Fig. 3 Effect of 1-hexanol on relative viscosity of CTAT solution at 30 °C.



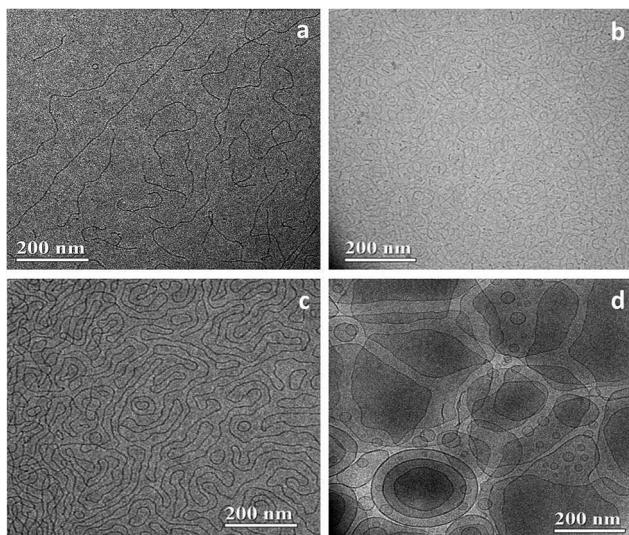


Fig. 4 Cryo-TEM images of 20 mM CTAT in the presence of (a) 0.0% (b) 0.25% (c) 0.5% (d) 1.5% 1-hexanol at 30 °C.

Such a dramatic changes in viscosity is a clear indication of transition in the micellar architecture in the system. Agarwal *et al.*⁶¹ have examined the effect of phenolic compounds on CTAB micellar solutions; the nonpolar moiety of these solutes interacts with the surfactant tail and the polar phenolic group with water. Phenol and cresol induced a sphere-to-rod-to worm-like micelles while 4-ethyl phenol and 4-butyl phenol showed a sphere to worm-like to multilamellar vesicle transitions. Zhang *et al.*⁶² reported that benzyl alcohol is solubilized in interfacial region and promotes growth of wormlike salted CTAB micelles while their transformation into small rods and then spherical ones at higher level of solubilization is responsible for peak in viscosity. In literature, a concept of vesicle formation has been claimed for peak in viscosity.^{42,49} 1-Hexanol induced micelle-to-vesicle transition *via* formation of elongated micelles has been reported for the cationic gemini surfactant ethyl- α,ω -bis(dodecyldimethylammonium bromide).⁴² A study on the effect of alkanols ranging from C_3 to C_9 on sucrose monohexadecanoate (sugar surfactant) showing a similar micellar transition has also been reported.⁶³ These results demonstrate that the length of worm-like micelles can easily be controlled by the addition of alkanols.

The focus of the present study is on the influence of 1-hexanol on CTAT worm-like micelles and formation of vesicular structures; a detailed study was performed at 20 mM surfactant concentration. At this concentration the solution contains worm-like micelles that are able to take up some 1-hexanol, hence at a lower 1-hexanol concentration an increase in the viscosity is observed followed by a sudden drop in viscosity at higher 1-hexanol concentration.⁴² Such a dramatical change in the viscosity is attributed to morphological changes in the system and is further quantified by cryo-TEM and SANS.

2.3.2 Cryo-TEM. To gain a microscopic view of the different microstructures formed as proposed by the viscosity measurements, cryo-TEM experiments of 20 mM CTAT solutions in the presence of 1-hexanol were performed. Cryo-TEM is a powerful

tool for direct imaging of micellar systems.^{2,55,64-67} The prime importance of applying this methodology here is the ability to identify in addition to the structure, structural transitions and coexistence of range of nanostructures present in the system. Fig. 4a-d systematically follows the micellar morphologies at increasing 1-hexanol concentrations. The existence of worm-like micelles in 20 mM CTAT solution has already been shown earlier.²⁸ The close inspection of Fig. 4a suggests the co-existence of short rod-like and spherical micelles. An overlapping of worm-like structures is seen as branched wormlike micelles. In the presence of 0.25% 1-hexanol, spherical micelles no longer exist, and the solution is dominated by elongated worm-like micelles and closed loop structures. Here, 1-hexanol is not only acts as co-surfactants, but also provides the possibility to avoid ends by creating loops. It is important to note that closed loops are formed at much lower 1-hexanol concentration. These observations clearly validate a link between the initial increase in the viscosity and the presence of multiple morphologies. Fig. 4c shows that in the presence of 0.5% 1-hexanol, branched worm-like micelles are present (further confirmed by SANS). This branching is the probable cause for the decrease in viscosity found with increasing 1-hexanol concentration.^{4,5,18,42,68,69} A few unilamellar vesicles are also observed at 0.5% 1-hexanol (further proved by SANS). At 1.5% 1-hexanol, solution mainly comprises of uni- and multilamellar vesicles (Fig. 4d). Thus overall, cryo-TEM shows that in the present system branching of worm-like micelles followed by vesicle formation are responsible for the drop in the viscosity from the peak value back to water-like viscosity. The plausible mechanism of 1-hexanol induced aggregate transformations can thus be explained as follows. Cetyltrimethylammonium tosylate (20 mM) solution contains worm-like micelles. At lower concentration, 1-hexanol behaves as co-surfactant. 1-Hexanol is medium chain alkanol and it partition between CTAT ionic head group thereby decreases surface charge density and favors micellar growth. So worm-like CTAT micelles get elongated. With increase in concentration of 1-hexanol, CTAT micelles are elongated to its maximum length. A spontaneous decrease in curvature with increase in concentration of 1-hexanol results in

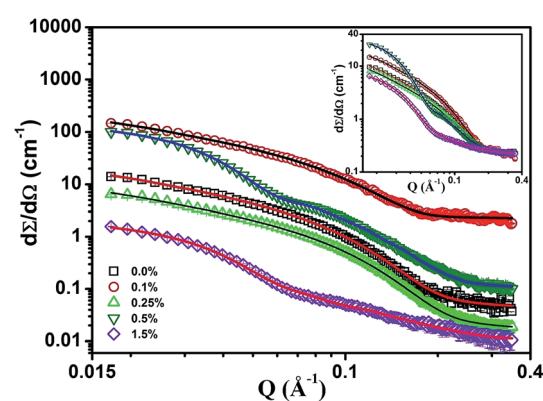


Fig. 5 SANS data of 20 mM CTAT as a function of 1-hexanol concentration at 30 °C. The data have been shifted vertically for clarity. Inset shows the data as measured.



Table 1 Micellar parameters for 20 mM CTAT in the presence of 1-hexanol obtained from SANS data analysis

| [1-Hexanol] (%) | Cross-sectional radius of worm-like micelles ^a R (Å) | Vesicle thickness t (Å) | Shape |
|--------------------|---|------------------------------|---|
| 0 | 17.6 ± 0.3 | — | Worm-like |
| 0.1 | 17.5 ± 0.3 | — | Worm-like |
| 0.25 | 17.5 ± 0.3 | — | Worm-like |
| 0.5 | 17.3 ± 0.3 | 54.6 ± 0.8 | Worm-like + unilamellar vesicles |
| 1.5 | 17.3 ± 0.6 | 55.2 ± 0.8 | Worm-like + unilamellar vesicles + multilamellar vesicles |

^a Worm-like micelles: Kuhn length (b) > $2\pi/Q_{\min} \sim 430$ Å and contour length (L) ≫ b .

formation of branched worm-like micelles and vesicular structure.⁴²

2.3.3 SANS. To gain further information on the microstructures formed by 1-hexanol, SANS measurements analogous to the viscosity and cryo-TEM measurements were performed. SANS scattering profiles for 20 mM CTAT in the presence of varying concentration of 1-hexanol are shown in Fig. 5. For 20 mM CTAT, a typical slope of (−1) at low- Q region in the log-log plot of SANS data clearly designates the presence of worm/rod-like micelles in the solution (correlates with the cryo-TEM Fig. 4a).^{28,70}

In the presence of 0.25% 1-hexanol, the scattering intensity of CTAT solution as well as the slope at low- Q remain almost same. This is consistent with the formation of elongated worm-like CTAT micelles at 0.25% 1-hexanol was proposed by cryo-TEM (Fig. 4b). On the basis of cryo-TEM and the observed increase in the viscosity and cryo-TEM image, it is evident that worm-like CTAT micelles elongate with increasing concentration of 1-hexanol. For worm-like micellar model, the chain of contour length L (total length) can be described a chain of some number of locally stiff segments (length l_p). The persistence length l_p is the length along the cylinder over which the flexible cylinder can be considered as a rigid rod. The Kuhn length (b) used in the model is also used to describe the stiffness of a chain, and is simply $b = 2l_p$. At 0.5% 1-hexanol a sharp increase in the scattering intensity in the low- Q region suggests of the presence of larger structures. It was debated that the formation of branched worm-like micelles and/or vesicles is responsible for the sudden drop in the viscosity (cryo-TEM Fig. 4c). SANS plot showing slope of (−2) on log-log scale is a clear indication of the presence of vesicular structures at this concentration.^{71,72} There is dramatic decrease (about a factor of 5) in the magnitude of scattering with 1.5% 1-hexanol, suggesting some kind of phase separation because of the formation of much larger structures (perhaps multilamellar vesicles). These large structures could not be measured prior to their phase separation as the time for the SANS measurements (~ 5 h) is much larger than over the period they exists. The fitted structural parameters from SANS data are shown in Table 1. The systems consist of worm-like micelles mostly upto 0.25%

1-hexanol. Unilamellar vesicles coexist with the worm-like micelles at 0.5% 1-hexanol. At further higher concentrations of 1-hexanol, the system also shows phase separation (multilamellar vesicles). The location of 1-hexanol is a deciding factor to induce such microstructural changes in CTAT micelles which is further evaluated using NMR spectroscopy.

2.3.4 NMR. ¹H NMR is a beneficial technique to observe the changes in the local environment of the surfactant molecules. Surfactant protons are extremely sensitive to the change in microenvironment/polarity in the solution. Interaction of 1-hexanol with CTAT micelles can also be followed by studying their ¹H NMR spectrum. ¹H NMR experiments were performed to get better insight on the influence of 1-hexanol on CTAT micelle. 1-Hexanol induced microstructural changes can be counted from changes in the chemical shift of CTAT protons, which are extremely sensitive to the change in polarity of their microenvironment. Protons are labeled and are shown in Fig. 1. ¹H NMR spectra for 20 mM CTAT in the absence and the presence of varying concentrations of 1-hexanol are depicted in Fig. 6. For CTAT, the chemical shifts for head group protons ($-\text{CH}_3$) and α -protons are found ~ 3 ppm and cannot be identified separately as they are overlapped. While the protons from hydrophobic part of CTAT micelles, give NMR signals in the upfield region. The internal chain protons and the β -protons of CTAT give NMR signals at ~ 1.2 ppm but they are in much close proximity of each other and hence overlapped and merged. Methyl protons ($-\text{CH}_3$) of tosylate counterion of CTAT (C_2) show chemical shift at ~ 2.1 ppm. The terminal protons of CTAT which form hydrophobic core produce chemical shift at more upfield region at ~ 0.9 ppm. The chemical shifts of aromatic protons (C_3 and C_4) of tosylate counterion are observed at ~ 7 ppm and 7.5 ppm, respectively. The α -proton of 1-hexanol gives an intense NMR signal at ~ 3.5 ppm. The internal and terminal chain protons of 1-hexanol show intense signals in the more upfield region at ~ 1.2 and 0.8 ppm, respectively.

In the presence of 0.25% 1-hexanol, an intense NMR signals at ~ 3.6 , ~ 1.2 , 0.8 ppm corresponding to α , internal and terminal protons of 1-hexanol, respectively are observed. But at 0.5% the intensity of these signals is decreased clearly indicating that these protons are more shielded and experiences a more hydrophobic environment. It manifests penetration of 1-hexanol inside CTAT micelles at higher level of solubilization. At 0.25% 1-hexanol, intensity of head group protons remains unaffected but at 0.5% 1-hexanol it sharply increases. It reveals that these protons experience more hydrophilic environment possibly due to formation of few vesicles at 0.5% 1-hexanol which provide internal cavity made up of water (cryo-TEM Fig. 4c). In the presence of 1-hexanol, the intensities of the aromatic protons and C_2 protons of CTAT are decreased, suggesting that they are more shielded and feel a hydrophobic environment probably due to the vicinity to the 1-hexanol hydrocarbon chain. It clearly manifests that penetrated 1-hexanol molecules reside below head group of CTAT micelle and are in close proximity of tosylate counterion/near the palisade layer and induces micellar growth. It is reflected in merging of NMR signals of internal chain protons clearly suggesting the strong interaction in this region of CTAT



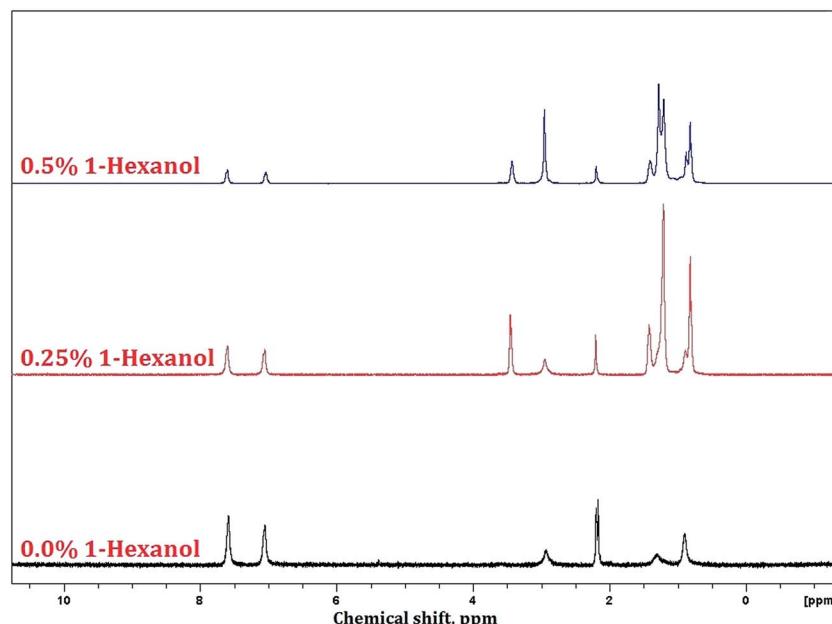


Fig. 6 NMR spectra of 20 mM CTAT in the presence of 1-hexanol at 30 °C.

micelles.^{73,74} Similarly, terminal protons reveal broadening and merging showing interaction due to bending of CTAT hydrocarbon chain.⁷² From the NMR study it is concluded that 1-hexanol displays strong interactions with internal chain protons of CTAT depicting the location of 1-hexanol between micelle–water interface and palisade layer of CTAT micelle. To get better insight on sight of location and interaction of 1-hexanol molecules in CTAT micelles, NOESY experiments were performed.

2.3.5 NOESY. The two dimensional-nuclear overhauser enhancement spectroscopy (NOESY) is an established non-invasive technique mainly used to examine micellar solutions and it provides the information about intra and inter molecular interactions between the surfactant and solubilizate molecules.^{75,76} When the protons are close enough (<5 Å), they produce intra- and inter-crosspeaks in the NOESY spectra.⁷⁷ The positive cross peaks in NOESY spectra signify the closeness of surfactant and solute protons accompanied with crosspeaks and their arrangement in the micelle. In the NOESY spectrum, intensity of crosspeaks can be analyzed to get the distance between the protons responsible for crosspeaks.^{77,78} The existence of the crosspeaks provides vital information regarding the locus of solubilization in micelles and hence, we used NOESY to acquire the location of 1-hexanol and extent of interaction between 1-hexanol and CTAT protons. The location of 1-hexanol in CTAT micelles can be of crucial importance in modulating the microstructures present in the system.

The NOESY contour plot for the 20 mM CTAT in the presence of 0.25% 1-hexanol is presented in Fig. 7a. Intra- and intermolecular cross peaks are observed in the spectra suggesting the strong interactions of 1-hexanol with CTAT protons. The closeness of protons is deciding factor for intensity of cross peaks; the intensity of cross peak is high if two protons are much closer. It is clear from Fig. 7a that there are no crosspeaks

between head group protons of CTAT with α -proton of 1-hexanol which conclude that 1-hexanol do not interact with CTAT head group at 0.25% concentration. Weak intramolecular crosspeaks are observed for aromatic protons. Crosspeaks are observed between C_2 protons of CTAT and aromatic protons. Intense crosspeaks are observed between α -proton of 1-hexanol with β -protons and internal chain protons of CTAT which indicates the strong interaction in this region of CTAT micelles. Many overlapping crosspeaks are observed for internal and terminal chain protons of CTAT and 1-hexanol presenting strong interaction between them. The appearance of many crosspeaks in the NOESY spectra at 0.5% 1-hexanol clearly reveals that it exhibits concentration dependent interaction with CTAT micelles (Fig. 7b). A close inspection of NOESY spectra suggests that there is an intra-molecular crosspeak between head group protons, aromatic protons and aromatic protons with $-CH_3$ protons (C_2) of tosylate counterion of CTAT. Low intensed cross peaks are observed for head group protons and internal chain protons of CTAT. There is no cross peak between α -proton of 1-hexanol with C_2 protons or aromatic proton of tosylate ion indicating that $-OH$ group of 1-hexanol is not in palisade layer of CTAT micelles. A weak crosspeak is observed between C_4 proton and head group protons of CTAT which may be due to penetration of tosylate counter ion inside micelle. A weak crosspeaks between α -proton of 1-hexanol with β -protons of CTAT were also noticed. It suggests that $-OH$ group of 1-hexanol remains slightly inside the micelle, away from head group. Intense crosspeaks between α -proton and terminal chain protons of 1-hexanol with internal chain proton of CTAT were observed, suggesting strong interactions between them. A cross peak between C_2 protons of CTAT and internal chain proton of 1-hexanol is also observed. It manifests the location of 1-hexanol close to the palisade layer and below the head group inside the CTAT micelle. An intense cross peak between α and



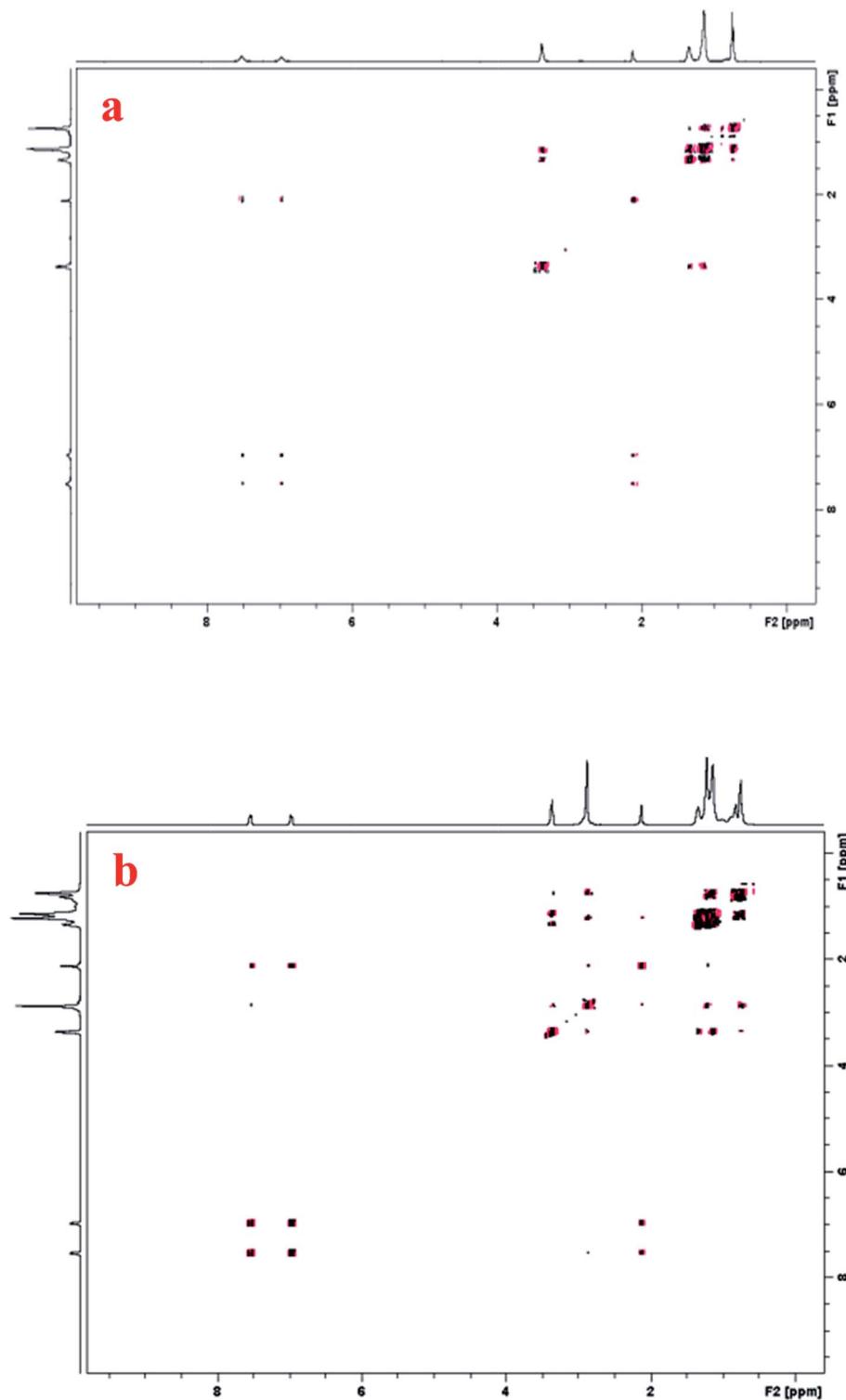


Fig. 7 NOESY spectra of 20 mM CTAT in presence of (a) 0.25 and (b) 0.5% 1-hexanol at 30 °C.

terminal protons of 1-hexanol suggest intra-molecular interaction or bending of 1-hexanol chain. From the NOESY study, it is concluded that 1-hexanol resides near the palisade layer and below the head group, inside CTAT micelles. 1-Hexanol exhibits concentration dependent interactions with different region of CTAT micelles and accordingly alter micellar morphology.

3. Conclusions

The effect of *n*-alkanols on CTAT worm-like micelles was examined by viscosity, SANS, cryo-TEM, NMR and NOESY experiments. Studies show that 1-alkanols majorly influence CTAT micelles. Longer chain *n*-alkanols are more efficient in

promoting micellar growth compared to shorter chain *n*-alkanols.

The motivation of the present study was to examine 1-hexanol aided microstructural transitions of worm-like CTAT micelles. A typical peak in viscosity is ascribed to elongation of the worm-like micelles and co-existence of short rod-like micelles with other structures. With further increase in 1-hexanol concentration length of worm-like micelles is sufficient to allow branching and micellar segments sliding on each other. Branched worm-like micelles accompanied by few vesicular structures are formed which is reflected in a sudden drop in the viscosity. Further addition of 1-hexanol up to its maximum solubility leads to the formation of vesicular dispersions. A complete course of vesicles formation from worm-like CTAT micelles *via* elongated and branched worm-like micelles and short rod-like micelles was successfully monitored by cryo-TEM. It is well confirmed by SANS. NOESY experiments disclose that 1-hexanol resides close to palisade layer and below the head group inside CTAT micelles. Doping with 1-hexanol offers a simple and easy method of controlling the size and shape of CTAT micelles from worm-like to vesicles that find many industrial applications as well as applications in personal and home care products and in templated synthesis of mesoporous materials^{42,79-81} and can also be utilized for micellar-enhanced ultrafiltration process.

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