Structural investigation of viscoelastic micellar water/CTAB/NaNO$_3$ solutions

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Abstract. A highly viscoelastic worm-like micellar solution is formed in hexadecyltrimethylammonium bromide (CTAB) in the presence of sodium nitrate (NaNO$_3$). A gradual increase in micellar length with increasing NaNO$_3$ was assumed from the rheological measurements where the zero-shear viscosity (η_0) versus NaNO$_3$ concentration curve exhibits a maximum. However, upon increase in temperature, the viscosity decreases. Changes in the structural parameters of the micelles with addition of NaNO$_3$ were inferred from small angle neutron scattering measurements (SANS). The intensity of scattered neutrons in the low q region was found to increase with increasing NaNO$_3$ concentration. This suggests an increase in the size of the micelles and/or decrease of intermicellar interaction with increasing salt concentration. Analysis of the SANS data using prolate ellipsoidal structure and Yukawa form of interaction potential between micelles indicate that addition of NaNO$_3$ leads to a decrease in the surface charge of the ellipsoidal micelles which induces micellar growth. Cryo-TEM measurements support the presence of thread-like micelles in CTAB and NaNO$_3$.

Keywords. Worm-like micelles; viscoelasticity; small angle neutron scattering; cryo-TEM.

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1. Introduction

Worm-like micellar structures in water have garnered a great deal of attention over the past two decades [1,2]. It is well-known that in aqueous solutions of cationic surfactants, for example, hexadecyltrimethylammonium bromide (CTAB), long worm-like micelles form upon addition of some salts, strongly binding counterions or cosurfactants [3–8] or upon mixing with anionic surfactants [9,10]. The one-dimensional micellar growth in such systems is attributed to the screening of the head–head repulsion between amphiphiles, thereby reducing the interfacial curvature of the aggregate. In these systems, the low shear viscosity often displays a

maximum when plotted as a function of additives. The increase in the zero shear viscosity at low additive concentration is due to the growth of spherical micelles into long worm-like micelles. As a consequence, the viscosity is raised and micelles become entangled. In contrast, the decrease in the viscosity is thought to result from the formation of fluid cross-links leading to a network of branched micelles, showing weak rheological response [11,12].

In this work, the effect of adding $NaNO_3$ to aqueous solution of CTAB is investigated. Bulk properties and dynamics are measured by rheological measurements while a detailed structural investigation of micellar shape and size was done using small angle neutron scattering. Cryo-TEM was used for the direct visualization of the surfactant aggregates [13].

2. Materials

Hexadecyltrimethylammonium bromide (CTAB, purity >99%) was purchased from Fluka. Sodium nitrate ($NaNO_3$, purity >98%) was obtained from Sigma. All chemicals were used as received. Millipore-filtered water was used for the preparation of all the samples except for neutron scattering measurements for which heavy water (D_2O) was used.

3. Methods

Small angle neutron scattering measurements (SANS): SANS experiments were carried out in the instrument installed in the Guide Tube (GT) Laboratory in the Dhruva reactor hall at BARC, Trombay, India. Details about the SANS instruments and analysis procedure can be found elsewhere [14,15].

Rheological measurements: The rheological measurements were performed in a stress-controlled rheometer, AR-G2 (TA Instrument) using cone-plate geometry with the plate temperature controlled by a peltier unit.

Cryo-TEM studies: Cryo-TEM samples were prepared in the controlled-environment vitrification system at a controlled temperature, and at saturation. Relaxation times of 20–45 s were allowed before vitrification in liquid ethane. Samples were examined in a CM120 TEM at cryogenic temperatures, using the low-dose software to avoid electron beam radiation damage.

4. Results and discussion

Rheological measurements: The changes in the zero shear viscosity (η_0) of the water/CTAB/$NaNO_3$ system are shown in figure 1 at various temperatures. In aqueous CTAB solutions, upon increasing the $NaNO_3$ content, a slow and then a sharp increase of the viscosity is found, until it reaches a maximum. This is followed by a slight decrease when the salt concentration is increased further. It is generally agreed that increasing the salt concentration leads to an increase in the curvature energy of the surfactant molecules in the end-cap relative to that in the cylindrical
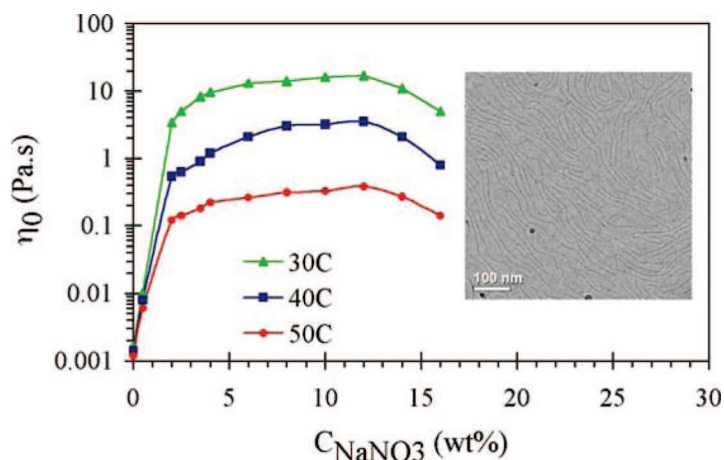
Figure 1. Plots of the zero-shear viscosity (η_0) for 0.15 M CTAB aqueous solutions as a function of $NaNO_3$ concentration, at different temperatures (30, 40 and 50°C). Lines are only visual guides. Cryo-TEM image of 0.15 M CTAB and 0.025 M $NaNO_3$ is shown as inset in the figure, indicating the presence of elongated micelles.
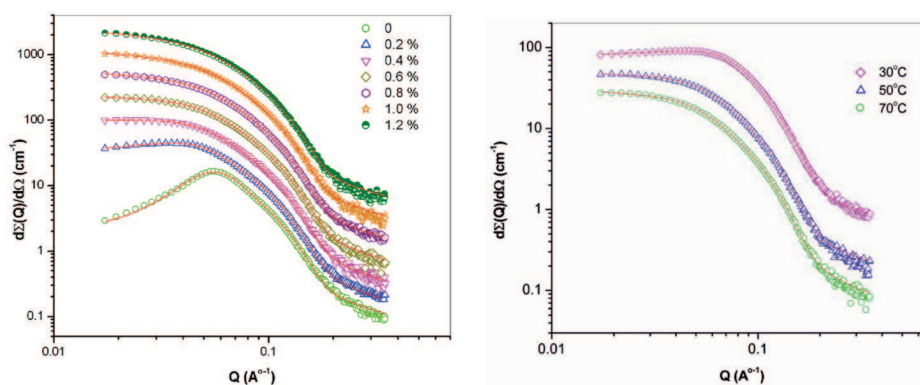

Figure 2. Left: SANS spectra for (left) 0.15M CTAB in the presence of different $NaNO_3$ concentrations ($T = 30°C$). Each spectrum has been shifted vertically by multiplying with a factor of 2 for the clarity of presentation. Right: SANS spectra for 0.15 M CTAB in the presence of 0.6% $NaNO_3$ at various temperatures.

body. At a fixed CTAB concentration, an increase in the salt content leads to the formation of rod-like micelles resulting in a viscosity increase. The cryo-TEM image (figure 1, inset) provides the direct evidence for the existence of these elongated micelles. When the length of the rod-like micelles increases further so that they are flexible and can curve freely, the micelles become worm-like, which can result in a rapid increase of the viscosity, and attains the maximum value. Thereafter, the micelles are thought to form branches rather than to continue growing axially

Table 1. Parameters obtained from the SANS fit for 0.15 M CTAB in the presence of different $NaNO_3$ concentrations.

$NaNO_3$ (wt%)	Temperature (°C)	r_a (Å)	r_b (Å)	α	N_{agg}
0	30	45.7	22.8	0.14	177.3
0.2	30	110.8	22.8	0.08	429.6
0.4	30	130.3	22.8	0.08	505.0
0.6	30	132.7	22.8	0.08	514.7
0.8	30	135.8	22.8	0.08	526.5
1.0	30	135.9	22.8	0.08	527.0
1.2	30	137.4	22.8	0.08	532.8
0.6	50	110.2	22.0	0.08	398.8
0.6	70	45.7	21.0	0.11	160.5

r_a = semi-major axis, r_b = semi-minor axis, α = fractional charge, N_{agg} = aggregation number.

[11,12]. As branching proceeds, the viscosity drops because the branch points are not fixed, and they are free to slide along the micelle providing an additional mode of stress relaxation. When a worm-like micellar solution is heated, the micellar contour length L decays with temperature according to [16–18]. The reduction in the micellar length, in turn, leads to a decrease in the viscosity.

Small-angle neutron scattering: SANS measurements were carried out on aqueous solutions of CTAB (0.15 M) and increasing $NaNO_3$ content (0 to 1.2 wt%) as shown in figure 2(left), in order to obtain detailed structural information. The scattered intensity in the low Q region increases with increasing $NaNO_3$ concentration indicating possible micellar growth. The SANS data were analysed using prolate ellipsoidal model. The solid lines in figure 2 represent the calculated scattering patterns. In the absence of $NaNO_3$, the spectrum shows a characteristic correlation peak. This indicates the presence of repulsive intermicellar interaction between the charged CTAB micelles. The correlation peak usually occurs at $Q_{max} \sim 2\pi/d$, where d is the average distance between the micelles and Q_{max} is the value of Q at the peak position [19]. With the addition of $NaNO_3$ this correlation peak broadens as well as shifts to lower Q values. The broadening of the correlation peak at constant volume fraction of the micelles is an indication of a decrease in the range of electrostatic interactions. This may be attributed to the decrease in the Debye screening length due to an increase in the ionic strength of the medium by the addition of $NaNO_3$. The shift in Q_{max} towards lower Q suggests an increase in the value of d with the addition of salt. For the analysis, all the three parameters, i.e., semi-major axis (r_a), semi-minor-axis (r_b) and fractional charge (α) were used as fitting variables. The values obtained from the fit are shown in table 1. It was noted that in order to obtain a good fit, a polydispersity in the semi-minor axis was necessary and was included using Schultz distribution. In all the samples a polydispersity parameter $z = 35$ was used in the semi-minor axis. The semi-major axis and hence the aggregation number calculated by the relation $N = 4\pi ab^2/3v$,

(where v is the surfactant monomer volume) was found to increase with increasing NaNO$_3$ concentration. The fractional charge for 0.15 M CTAB obtained by analysing SANS data is 0.14 and is consistent with previous reports [20]. The fractional charge was kept constant ($\alpha = 0.08$) for all successive salt concentrations and only the semi-major axis was used as a variable.

We also carried out SANS measurements on 0.15 M CTAB solutions containing 0.6% NaNO$_3$, at different temperatures (figure 2(right)). The intensity of the scattered neutrons, at low q limit, was found to decrease with increasing temperature, suggesting that the size of the micelles decreases with increasing temperature as supported by the rheological measurements discussed earlier. Quantitative estimate of the micellar parameters (table 1) suggests that the aggregation number as well as the semi-major axis decrease with increase in the temperature.

5. Conclusions

Highly flexible and elongated viscoelastic worm-like micellar solutions form in aqueous solutions of CTAB in the presence NaNO$_3$. Our structural investigations by SANS confirm the micellar elongation with increase in salt concentration while increase in temperature shows reduction in the micellar length.

Acknowledgements

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