

# Growth of Cetyltrimethylammonium Tosylate Micelles—A Frapp Study

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The growth and entanglement of cetyltrimethylammonium tosylate (CTAT) micelles with and without added salt are investigated using the fluorescence recovery after fringe pattern photobleaching (FRAPP) technique. In the absence of salt the micelles grow slowly in the concentration range 0.06–0.7 wt % and get entangled beyond an overlap concentration of 0.7 wt %. With added salt of 0.1 and 1 M KBr, the slow growth is not observed and the entanglement seems to exist right from the lowest concentration used in this study (0.07 wt %). The variation of self diffusion coefficient with concentration in the presence of salt is found to be in accordance with the recent theoretical predictions for the scaling of the diffusion constant with concentration. The modes of micellar diffusion are discussed under the purview of these scaling laws.

## Introduction

Cationic surfactants like cetyltrimethylammonium bromide (CTAB) on addition of strongly binding counterions like salicylate (sal) form long threadlike micelles and produce strongly viscoelastic gels at volume fractions of about 1%.<sup>1,2</sup> These properties arise out of the small hydrophobic portions of salicylate ions which get bound in the micelle and alter the packing.<sup>3</sup> Once the importance of this hydrophobic part is realized, one can design several similar gels by using the proper choice of anions, for example, tosylate,<sup>4</sup> heptanesulfonate,<sup>5</sup> and chlorobenzoate.<sup>6</sup> Reference 1 gives a list of systems which are observed to show viscoelasticity.

In this paper we investigate cetyltrimethylammonium tosylate (CTAT), which belongs to a special class of surfactants with no conventional small ions like Cl<sup>-</sup>, Br<sup>-</sup>, etc. These surfactants form micelles which have a small surface charge but large Debye screening length in view of the weak dissociation of counterions. Recent studies on CTAT by Soltero et al.<sup>7</sup> have shown that the electrical conductivity of a CTAT–water system is an order of magnitude lower than that of KBr at the same concentration. We investigate the mechanism of the growth of micelles in this system using fluorescence recovery after fringe pattern photobleaching (FRAPP) and study the effect of salt, which drastically alters the Debye screening length.

## Materials and Methods

CTAT obtained from Sigma chemicals was recrystallized from a 1:1 mixture of ethanol and acetone. KBr (Prolabo product) was used as received. However, it was heated to 100 °C for 24 h to remove traces of water, if any. All measurements were made at 24.5 °C, well above the Kraft temperature, 23 °C, of CTAT.<sup>7</sup> 5-Dodecyl-dodecanol aminofluorescein was used as the fluorescent probe.

Fluorescent probes homogeneously dissolved in the sample get embedded in the micelle, since they are also surfactant molecules with the polar head being a fluorescein group. The mass ratio of fluorescent material to CTAT was kept very low (about 0.05 wt %) so that the probe molecules do not alter the micellar structure. In the FRAPP experiment, the sample is illuminated by a short pulse from a powerful laser beam and the fluorescence property of the probes in the beam area is destroyed (photobleaching). Subsequently a weak laser beam (about 10<sup>4</sup> times less intense) is used to monitor the photobleached region and excite any unbleached probes diffusing in from other regions. The fluorescence recovery is monitored to calculate the diffusion coefficient of the probe. If the probes are considered as held fixed to the micelles, the diffusion coefficient measured will be the self-diffusion coefficient,  $D$ , of the micelles. Both the bleaching and the monitoring beams are divided and superposed in a fringe geometry. At the end of the bleaching pulse, a piezoelectric crystal makes the monitoring beam sweep the fringes in the bleached sample. This reduces the noise to signal ratio in the fluorescence recovery signal. The self-diffusion coefficient,  $D$ , is obtained from the characteristic time  $\tau$  of the fluorescence recovery curve with an error smaller than 5%. The recovery curves are fitted by an exponential function  $f(t) = A \exp(-t/\tau) + B$ , where  $1/\tau = 4\pi^2 D/l^2$ ,  $l$  being the fringe spacing (10–75  $\mu\text{m}$ ).  $D$  is deduced from a plot of  $1/\tau$  vs  $l^2$  ( $\equiv 4\pi^2/l^2$ ). The bleaching pulse duration was 50 ms, and the bleaching power in the sample was 400 mW. The samples were kept in Helma quartz cells of 1 mm path length and thermostated at 24.5 °C ( $\pm 0.1$  °C). More details on the experimental setup have been published elsewhere.<sup>8</sup>

## Results and Discussions

**CTAT with No Added Salt.** Figure 1 shows the results of the FRAPP experiment on a CTAT–water system in the concentration range 0.06%–2% by weight. This region was chosen on the basis of the results of Soltero et al.,<sup>7</sup> who have found the first cmc to be 0.011 wt % and the second cmc corresponding to a transition from spherical

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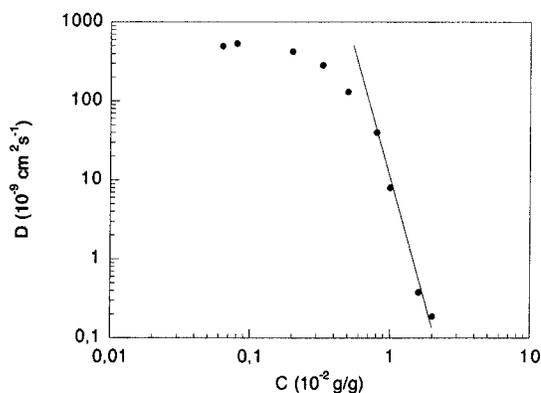
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**Figure 1.** Log-log plot of self-diffusion coefficient vs concentration of CTAT with no added salt.

to cylindrical micelles to be 0.04 wt %. Therefore, in the concentration range chosen by us the micelles would already be cylindrical and their growth and entanglement could be elucidated.

The self-diffusion coefficient measured as a function of concentration could be conveniently divided into three regions.

In the region  $0.06 < C < 0.2$  wt %, the self-diffusion coefficient is constant and is approximately  $5 \times 10^{-7}$  cm<sup>2</sup>/s. The apparent hydrodynamic radius,  $R$ , calculated from the Stokes-Einstein equation

$$D = \frac{k_B T}{6\pi\eta R} \quad (1)$$

is  $R \sim 45$  Å. This indicates that the micelles are small.

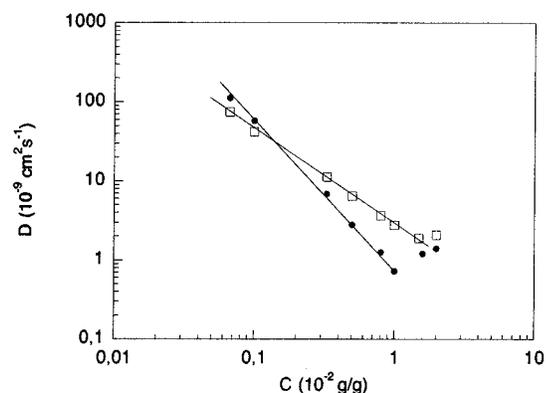
For a dilute system of inflexible micellar rods the number density of rods of length  $L$  is given by

$$c(L) \propto \exp(-L/L) \quad (2)$$

where  $L$  is the average micellar length.<sup>2</sup> Thus there is a finite but very small probability for huge micelles in dilute solutions. Kaler et al.<sup>4</sup> have observed very long micelles of diameter 50 Å and persistence length about 1 μm for a 0.1 wt % CTAT solution using freeze-fracture transmission electron microscopy. Transient electric birefringence results<sup>9</sup> on CTAT of 0.2 wt % at 25.5 °C show a rotational relaxation time constant of 1.5 μs, which corresponds to a length of 400 Å for a cylindrical micelle of diameter 50 Å. For a cylindrical micelle of this size, the value of the hydrodynamic radius works out to be ~100 Å. Thus we find that the micellar size remains small in the dilute regime.

In the region  $0.2 < C < 0.7$  wt %, the self-diffusion coefficient starts decreasing slowly with increasing concentration. The micellar size starts growing slowly, and the effective  $R$  increases to about 500 Å. These are the average dimensions of the micelles.

In the region  $0.7 < C < 2$  wt % the self-diffusion coefficient decreases drastically with increasing concentration. This is the semidilute region and corresponds to the entanglement of the micelles. The rheological study by Soltero et al.<sup>7</sup> indicates the formation of viscoelastic gels around 0.9 wt %. In the electric birefringence study<sup>9</sup> the anomalous birefringence signal is found to exist in a narrow concentration range of  $0.6 < C < 0.9$  wt % with a peak at 0.7 wt %. Thus 0.7 wt % seems to represent  $C^*$ , the overlap concentration beyond which the micelles get entangled and the solution enters the semidilute regime exhibiting viscoelastic properties. In contrast, in cetylpy-



**Figure 2.** Log-log plot of self-diffusion coefficient vs concentration of CTAT for 0.1 M (circles) and 1 M (squares) KBr.

ridinium chlorate (CPClO<sub>3</sub>) with no added salt the onset of the semidilute regime is found to be around 6 wt %, <sup>10</sup> an order of magnitude higher. This shows that the micellar growth is much more rapid in CTAT. This must be due to strong binding of the hydrophobic counterion (tosylate) to the micellar surface, which decreases the electrostatic repulsions between the head groups and helps in micellar growth.

In the semidilute regime, the self-diffusion coefficient decreases with a power law  $D \sim C^{-\delta}$ . The value of  $\delta$  is found to be 6. In this region, as remarked above, the Debye screening lengths are expected to be large, and there are no theories, at present, which can be used to interpret our results. Due to weak screening of the electrostatic field, the micelles may behave as stiff rods, and hence with increasing concentration the diffusion may be hindered. The rapid decrease of the self-diffusion coefficient is a manifestation of this effect. On adding salts, these effects should reduce and a weak dependence on concentration is expected. In order to verify this, we have used two salt concentrations. Fortunately for these screened micellar systems some experiments for comparison and theoretical models exist.<sup>10-14</sup>

**Effect of Salt.** Figure 2 gives the log-log plot of  $D$  vs  $C$  for CTAT micelles in the presence of 0.1 and 1 M KBr. Two regions can be distinguished—a semidilute regime where  $D$  decreases sharply with a power law  $C^{-\delta}$  and a concentrated regime where  $D$  increases slightly with surfactant concentration. One can observe a drastic reduction in  $D$ , indicating an increase in micellar size which is expected in view of the salting out effect. No plateau or slow decrease in  $D$  with  $C$  could be observed, as in the case of CTAT with no added salt, though the concentration range studied was the same. This shows that long wormlike micelles are formed at very low concentrations and the overlap concentration  $C^*$  has moved to very low values. Further,  $D \sim C^{-\delta}$  but with  $\delta = 1.9$  and 1.1 for KBr concentrations of 0.1 and 1 M, respectively. In order to understand this drastic lowering of the exponents, we consider theories for the semidilute region.

For a semidilute micellar solution the equilibrium size distribution is given by<sup>2</sup>

$$c(L) \propto \exp(-L/L) \\ L = \exp\left(\frac{E}{2k_B T\phi^y}\right) \quad (3)$$

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where  $E$  is the scission energy (the energy required to create two end caps from a semiinfinite cylinder),  $\phi$  is the volume fraction, and  $y \sim 0.6$ . For the formation of very long flexible micelles at low concentrations the scission energy must be very high. This seems to be the case with the CTAT–KBr system.

In the Cates model for micellar growth,<sup>12</sup> it is assumed that scission can occur anywhere along the chain with equal probability  $k$  per unit length per unit time on all the chains and that the chains may recombine at a rate independent of their size. The average scission or breaking time (also equal to the lifetime of a free chain before recombination) is

$$\tau_{\text{break}} = 1/(kL) \quad (4)$$

The diffusion of the micelles in the semidilute regime is described by the reptation model, in which it is assumed that any macromolecule can move only along a tube formed by the surrounding chains. The duration of a full disentanglement by curvilinear diffusion (reptation) in the tube is  $\tau_{\text{rep}}$ . If  $\tau_{\text{break}} < \tau_{\text{rep}}$ , the disengagement of a whole micelle from its tube of constraints is disrupted by a transfer of mass with other micelles.

Three kinetics of mass transfer can be distinguished<sup>14</sup> (i) reversible scission, (ii) end interchange (where a free chain attacks and breaks an interior bond of another chain and one part of the broken chain recombines with the attacking end), and (iii) bond interchange (fusion process of two chains to form a four-armed star and subsequent separation into two chains by exchanging segments). Turner et al.<sup>14</sup> have obtained the scaling laws for the self-diffusion coefficient for the above three processes in the reptative regime and the breathing regime (diffusion along the tube by means of tube length fluctuations) of chain motion. For the three kinetics of mass transfer mentioned above, the self-diffusion coefficient  $D$  is shown to scale with the surfactant concentration as  $C^{-1.7}$  (reversible scission),  $C^{-1.6}$  (end interchange), and  $C^{-1.4}$  (bond interchange) for the reptative regime and  $C^{-1.4}$  (reversible scission),  $C^{-1.2}$  (end interchange), and  $C^{-0.8}$  (bond interchange) for the breathing regime of the chain motion.

In our FRAPP study on the CTAT–KBr system, the self-diffusion coefficient is found to scale as  $C^{-1.9}$  for 0.1 M and  $C^{-1.1}$  for 1 M salt (Figure 2). Comparing these results with the theoretical predictions, we find that the micellar diffusion in 0.1 M salt can be described by the reversible-scission process in the reptative regime. The exponent  $\delta = 1.9$  for this salinity is very close to the  $\delta = 1.7$  predicted for ionic surfactants with high salt concentration.<sup>12</sup> In 1 M salt the exponent  $\delta = 1.1$  obtained is consistent with the end-interchange process in the breathing regime as per the scaling laws mentioned above. This suggests that at this salinity the micellar diffusion is not by pure reptation but by tube length fluctuations associated with the end-interchange kinetics of mass transfer.

In Figure 2 we find that beyond a concentration  $C^{**}$  the self-diffusion coefficient increases slightly with surfactant concentration. Morie et al.<sup>10</sup> have given two possible explanations for this phenomenon.

(i) *The micelles remain disconnected.* But at high surfactant concentration the micelle motion slows down. In this case the probe diffusion relative to the micelle cannot be ignored. The diffusion of the probe along the micelle may become faster than the curvilinear motion of the micelle in the tube of constraints. Since in FRAPP the diffusion of the probe is monitored,  $D$  is found to increase, though actually the micellar diffusion may be slower. In this case, if  $\tau_{\text{break}} > \tau_{\text{Rouse}}$ , for  $C < C^{**}$ , i.e., in the semidilute regime, the diffusion of the micelles would be by pure reptation.  $\tau_{\text{Rouse}}$  is the time scale for the breathing motion of the chain. However, if  $\tau_{\text{break}} > \tau_{\text{Rouse}}$ , for  $C < C^{**}$ , the micellar diffusion would be by tube length fluctuations.

Comparing our FRAPP results with this picture, at 0.1 M salinity, for CTAT micelles,  $\tau_{\text{break}} > \tau_{\text{Rouse}}$ , and at 1 M salinity,  $\tau_{\text{break}} < \tau_{\text{Rouse}}$ . Thus there seems to be a transition from pure reptation to Rouse motion as the salinity increases from 0.1 to 1 M.

(ii) *The micelles are connected.* The existence of connections affects the rheological properties of the micellar solutions.<sup>15</sup> It has been shown theoretically that it may lead to a reduction of the zero-shear viscosity and of its surfactant concentration dependence.<sup>16</sup> It is likely that, upon increasing the surfactant concentration in the presence of excess salt, a structural change occurs whereby cross-links are formed resulting from fusion of micelles. Contrary to the case of ordinary branched polymers where the branch points have fixed positions on the polymer backbone, in branched micelles the connections can move along the cylindrical part of the micelles, which speeds up the diffusion of the micelle within the tube. This may lead to an increased fluidity of the system, and hence the self-diffusion coefficient may increase.

Soltero et al.<sup>7</sup> have found that, around 0.2%, the zero-frequency complex viscosity of the CTAT–water system increases sharply with concentration and reaches a constant value for high concentrations. To our knowledge there is no data on the zero-shear viscosity of CTAT in the presence of salt. Hence it is difficult to conclude whether the micelles form a connected network or not when salt is added.

## Conclusions

In this paper we have investigated the growth and entanglement of CTAT micelles using the FRAPP technique. We find the following:

(a) In the absence of added salt, the variation of the self-diffusion coefficient with concentration shows three regions corresponding to the formation of large micelles, their growth, and entanglement. A rapid decrease,  $D \sim C^{-6}$ , in self-diffusion coefficient on entanglement possibly indicates that the micelles are stiff. No theories exist to explain the scaling law in this region. The CTAT micelles are much larger and grow more rapidly than CPClO<sub>3</sub> micelles.<sup>10</sup>

(b) Addition of salt results in an increase in size of the micelles due to the salting out effect with the overlap concentration shifting to very low values. The decrease in the self-diffusion coefficient for 0.1 and 1 M KBr follows scaling laws that are consistent with those obtained by

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Turner et al.<sup>14</sup> Following their analysis, the FRAPP data for CTAT-KBr in the semidilute regime suggest that the micellar diffusion is by a reversible-scission process in the reptative regime of chain motion for 0.1 M salinity and by an end-interchange process in the breathing regime for 1 M salinity.

(c) A slight increase in the self-diffusion coefficient with concentration is observed in the presence of salt at high volume fractions. If it is assumed that micelles are entangled but remain unconnected in this region, an

increase of salinity seems to produce a transition from diffusion by pure reptation to that by Rouse motion.

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