Diffusion of Probe Particles in Surfactant Gels: Dynamic Light Scattering Study

P. A. Hassan and C. Manohar*

Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400 085, India

Received: March 25, 1998; In Final Form: June 3, 1998

The growth and entanglement of certain aqueous surfactant solutions were studied by the concept of probe particle diffusion in polymeric networks. The cetyl trimethylammonium tosylate(CTAT)−water system forms elongated micelles, in the absence of any added electrolytes, at low and intermediate concentrations. The diffusion coefficients of spherical polystyrene particles embedded in CTAT micelles were measured using dynamic light scattering (DLS). The diffusion coefficient changes drastically near the overlap concentration of the micelles, and anomalous diffusion of the probe particle takes place in the entangled network of the micelles. The measured diffusion coefficient is shown to reflect the growth of CTAT micelles as investigated by other techniques such as fluorescence recovery after fringe pattern photobleaching (FRAP). The diffusion coefficients of the probe particles follow the same qualitative behavior as those of the self-diffusion coefficients of the micelles measured by FRAP. The effect of breakage of micelles with temperature and consequent decrease of the characteristic pore size of the network has been monitored. From the measured diffusion coefficient data, the microviscosity of the probe particles was calculated and is found to follow a rapid increase in the microviscosity above the overlap concentration as is expected for the bulk zero shear viscosity. The effects of hydrophobicity of the alkyl chain on the growth of micelles in cationic−anionic surfactant mixtures were studied in a mixture of monoalkylated disulfonated diphenyl oxide surfactants (C_nMADS) and dodecyl trimethylammonium bromide (DDTAB). The increased hydrophobicity of the long alkyl chain anionics seems to have an increased growth rate and hence low overlap concentration in the presence of DDTAB. Possible relevance of this technique in application is pointed out.

Introduction

The structure and dynamics of viscoelastic surfactant solutions have been of great interest in the past few years.[1,2] This interest arises from a number of possible applications, apart from the challenge in basic research, which are offered by these systems. Some of the applications are in the area of drag reduction, cleaning formulations, detergent applications, etc.[3,4] These systems have been named as "living polymers" in view of the dynamic nature of the wormlike micelles that constitute this system.[5,6] The relaxation behavior is not only by reptation, as in conventional polymer systems, but by new mechanisms such as breaking and remaking of the wormlike micelles, which are special to this class of systems.

The interesting rheology of these systems should provide new applications in using these solutions as the media for other purposes such as water-based paints, inks, etc. In view of this, it is interesting to investigate the diffusion of particles deliberately added to the system. Such approaches, in conventional polymeric systems, have given valuable information on the structure of the medium.[7−9] The present paper is an attempt to investigate the diffusion of deliberately added monodisperse polystyrene latex (PS) particles in surfactant solutions that are known to form wormlike micelles.[10−12] In fact, there is enough experimental evidence to support the existence of long flexible polymer-like micelles in many different surfactant solutions.[13−17] In view of this, it is of considerable interest to check the details of entanglement formation and assess the conditions at which they occur. The study of dynamics of entangled micelles was mostly done by techniques such as rheology, dynamic light scattering (DLS), fluorescence recovery after fringe pattern photobleaching (FRAP), etc.

In the present work, we report on the diffusion characteristics of spherical polystyrene particles in an entangled network of surfactant assemblies. We use DLS to observe the translational diffusion of monodisperse PS particles embedded in a micellar solution. The big advantage one gets in this technique is the high scattering intensity of PS over the background of long micelles. We used the properties of the diffusing probes to explore the growth behavior of various surfactant assemblies. We should anticipate that once the PS particles are diffusing through a network of wormlike micelles, the diffusion coefficient of these particles reduces drastically, responding to the changes taking place in the medium. Thus, by observing the diffusion of the particles in a multiconnected network, it is possible to understand indirectly the topological structure and physical properties of the media. The variation of the diffusion coefficients of the probe particle can provide information regarding the local microviscosity within the pores of the network of micelles. The effects of varying the chain length of one of the surfactants in a surfactant mixture on the formation of viscoelastic surfactant phases were investigated. This method could act as a powerful method of monitoring the diffusion of not only PS but also other pigment particles such as TiO_2 which have high scattering power and would have implications in the stability of dispersions.

Materials and Methods

Cetyl trimethylammonium tosylate (CTAT), dodecyl trimethylammonium bromide (DDTAB), and cetyl trimethylammonium bromide (CTAB) were obtained from Sigma Chemicals, and

---

* To whom correspondence should be addressed.

monoalkylated disulfonated diphenyl oxide surfactants (C_n-MADS), where $n = 6, 10, 12,$ and 16, were obtained from Dow Chemical Co. All chemicals were used as such without further purification. The measurements in this paper were made by choosing the 100 nm diameter standard PS particles from Duke Scientific. Dust-free distilled water was used as the solvent. Prior to the preparation of the sample, a small amount of concentrated PS particles was added to the surfactant solution along with the required quantity of water, and the solution was kept overnight for equilibration. In all the samples the concentration of PS particles was kept constant and were chosen such a way that the scattering intensity measured to be 50 times higher than that of surfactant solution. Measurements of the scattered intensity correlation functions were performed with the use of a standard Brookhaven light-scattering instrument BI-90 with a 5 mW He−Ne laser (6328 Å), the angle of scattering being 90°.

Theoretical Background

The normalized time correlation function of the scattered intensity, $g^{(2)}(\tau)$ can be written as

$$g^{(2)}(\tau) = \frac{\langle I(0)\ I(\tau)\rangle}{\langle I\rangle^2} \tag{1}$$

For photocounts obeying Gaussian statistics, $g^{(2)}(\tau)$ is related to the time correlation function of the electric field, $g^{(1)}(\tau)$, by the Siegert relationship

$$g^{(2)}(\tau) = \beta + A|g^{(1)}(\tau)|^2 \tag{2}$$

where β is the baseline and A is an adjustable parameter dependent on the scattering geometry and independent of τ. For a suspension of monodisperse, rigid, spherical particles undergoing Brownian diffusion, the correlation function decays exponentially and is given as

$$g^{(1)}(\tau) = \exp(-Dq^2\tau) \tag{3}$$

where D is the translational diffusion coefficient and q is the magnitude of the scattering wave vector given by

$$q = (4\pi n/\lambda)\ \sin(\theta/2) \tag{4}$$

n being the refractive index of the solvent, λ the wavelength of light, and θ the scattering angle.

For small, dilute, noninteracting spheres the hydrodynamic radius, R_h, can be obtained from the translational diffusion coefficient using the Stokes−Einstein relationship

$$D = kT/(6\pi\eta R_h) \tag{5}$$

where k is the Boltzmann constant, η is the solvent viscosity, and T is the absolute temperature.

When a broad distribution of diffusion coefficient is present in the system, eq 3 must be modified before data analysis of the measured autocorrelation function can proceed. Each D contributes its own exponential, and the mathematical problem becomes

$$g^{(1)}(\tau) = \int_0^\infty G(\Gamma)\ \exp(-\Gamma\tau)\ d\Gamma \tag{6}$$

where $\Gamma = Dq^2$. Thus $G(\Gamma)$ can be obtained by performing an inverse Laplace transform on the above equation, but a much simpler method, known as the method of cumulants,[18] has been used traditionally. The first and second cumulant, respectively,
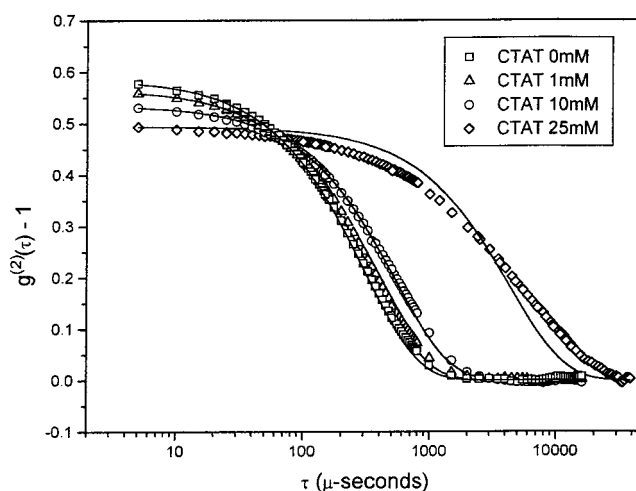

Figure 1. Correlation function versus time (semilogarithmic) for the scattered light intensity from polystyrene latex beads embedded in CTAT micellar solutions at surfactant concentrations below and above the gelation threshold. The solid lines are fit to the experimental data with a single-exponential decay.

give the mean and variance of the distribution $G(\Gamma)$. By fitting the experimentally observed $g^{(1)}(\tau)$ to a quadratic in τ, we can get the mean, $\bar{\Gamma}$, and the variance, μ_2.

Results and Discussion

1. Growth of CTAT Micelles. Figure 1 shows representative curves of the normalized time correlation function of the light intensity scattered at an angle of 90° from 100 nm standard polystyrene particles embedded in CTAT micellar solutions for different concentrations of the surfactant. Since the data acquisition is carried out with simple linear channel spacing, a single run with one sampling time, $\Delta\tau$, cannot provide the correlation function over a wide time range sufficient for data analysis. Therefore, we collected the data repeatedly by varying $\Delta\tau$ by different orders of magnitude. Finally, the composite curve is obtained from superposition of all the data collected at various $\Delta\tau$ values. A few of the composite curves, thus obtained, are shown in Figure 1 as typical examples.

Since the scattered light intensity from the probe particles is much higher than that of the micelles alone, we can assume that the correlation function measured here is directly related to the movement of the probes and has no significant contribution from the micelles. Owing to the strong scattering power of PS particles, their scattering intensity was found to be around 50 times higher than that of pure micellar solution, and this ensures that the above assumption was justified. As seen from the Figure 1, the time profiles are well-represented by a single relaxation time for concentrations less than around 10 mM. The solid lines in this figure correspond to the decay patterns of the correlation function calculated from expressions 2 and 3, assuming a single-exponential decay. These lines are drawn from a best least-squares fit analysis to the data with a single diffusion coefficient, D. The squares correspond to the correlation function of the scattered light intensity from PS particles in water without any surfactants present. The data fits fairly well with a single D value, and the measured D matches with the value expected for 100 nm particles in water at 298 K. As the concentration of the surfactant is increased to around 10 mM, the correlation function shifts to the right, indicating a decrease in the diffusion coefficient of the probe. Below 10 mM, the D values are more or less constant and are comparable to the value obtained for PS particles in water without any surfactants present. We can also see that above 10 mM the
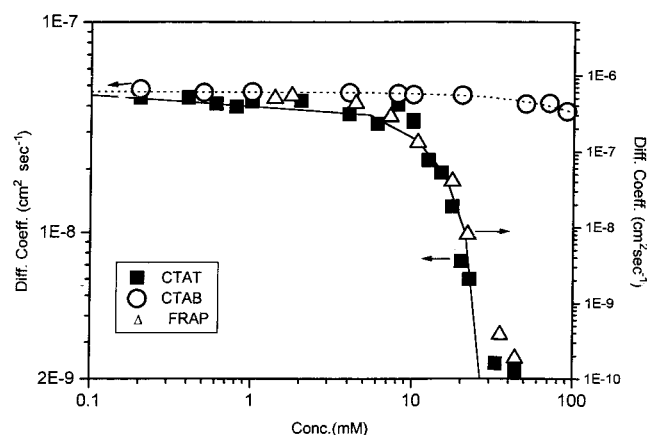
Figure 2. (a) Diffusion coefficient of standard polystyrene particles (100 nm diameter) incorporated in wormlike micellar solution of CTAT plotted against surfactant concentration (squares). (b) Diffusion coefficient data for PS particles in CTAB micelles vs surfactant concentration (circles). All the experimental conditions are same as in (a). (c) Self-diffusion coefficient of CTAT micelles as measured by FRAP technique (triangles); the data are taken from ref 17.

correlation function slowly deviates from the single-exponential decay, indicating a broad distribution in the diffusion coefficient. This picture indicates that the diffusion process of PS particles in samples above 10 mM differs from normal free diffusion.

Figure 2 shows the average diffusion coefficient obtained for PS particles in CTAT and CTAB solutions at different concentrations of the surfactant. The drastic reduction of the diffusion coefficient of PS in CTAT as the concentration approaches above 10 mM is clearly seen in Figure 2. To rule out the possibility of any chemical bond formation or electrostatic interaction between the probe particles and the surfactant assemblies, we measured the diffusion coefficient of PS particles in CTAB micelles too. In both CTAT and CTAB, the amphiphilic moiety was the same, that is, CTA^+, and only the counterion was different, namely tosylate (Tos^-) and bromide (Br^-), respectively. Owing to its hydrophobic nature, Tos^- adsorbs strongly on the micellar surface, like salicylate,[19] and induces a structural change in the aggregates. Since the amphiphilic moiety is the same in both cases, (i.e., in CTAT and CTAB), the nature of charge and hence the electrostatic interaction between the probe and the headgroup is expected to be the same. Under these conditions we expect that any type of interaction, if it exists, between the probe particles and CTAT micelles that would affect the diffusion of the probe particles should be present in CTAB micelles also. This tempted us to compare the diffusion coefficient of PS particles in CTAB micelles with CTAT, and the results are shown in Figure 2. It is found that there is no significant decrease of diffusion coefficient in CTAB solution, in contrast to that in the CTAT solution for the same concentration range.

In CTAT there is a drastic decrease in the diffusion coefficient of PS particles as the concentration of CTAT approaches around 10 mM. This suggests that a structural change is taking place in CTAT micelles at around 10 mM. Rheological investigation on the phase behavior and linear viscoelastic behavior of the CTAT−water system were done by Soltero et al.[11] It has been observed that it forms elongated micelles and exhibit strong viscoelasticity at low concentrations (1% w/w) without the addition of any electrolytes. Thus the abrupt change in the diffusion coefficient can be attributed to a transition from dilute to semidilute regimes of micellar solutions. In the dilute regime the micellar solution consists of identifiable, rodlike micelles that are singly dispersed in the solvent, whereas in the semidilute

regime it consists of a transient network of entangled wormlike micelles. Recently, the formation and growth of CTAT micelles at low and intermediate concentration ranges were investigated by using FRAP.[20] From FRAP measurements it is observed that the self-diffusion coefficient of the micelles decreases drastically at around 10 mM CTAT, and this has been attributed to the formation of entangled network of long threadlike micelles. The self-diffusion coefficients of micelles formed in CTAT/water system as measured by the FRAP technique are included in Figure 2 for comparison. As is seen from the figure, it is possible to superimpose one data over the other by properly scaling the ordinate. It is worth mentioning that in FRAP it is the self-diffusion coefficient of the micelles which is being measured whereas here we measure the diffusion coefficient of the probe particles incorporated in the micellar solutions. This explains why the actual magnitude of diffusion coefficient varies from the self-diffusion coefficient values. Thus, the observation of probe particle diffusion in surfactant assemblies reflects the growth and phase behavior of self-assembled system. In the case of polymer-like micelles the crossover from dilute to semidilute regime can easily be detected from an examination of the diffusion of the probe particles embedded in the system.

Anomalous diffusion of probe particles in semidilute polymer solutions has been studied by Nishio et al.[8] DLS has an associated probing distance equal to the inverse of the scattering vector, q. In measurements with inert noninteracting particles embedded in polymer network, the scattered intensity fluctuations can be divided into two parts; one from the diffusion of the freely diffusing particles and the other from the particles entrapped in the network. Thus the scattered intensity fluctuation depends on the fraction of the particles that are free to diffuse over the probing distance. Information regarding the charcteristic pore size distribution in an entangled network can be obtained from the measurements of the autocorrelation functions of the scattered intensity from probe particles. It is observed that abnormal diffusion of the particles take place when $(1/q) + d$ is greater than the characteristic mesh size (ξ) of the network, where d is the diameter of the probe particle. When $(1/q) + d$ is smaller than ξ, the diffusion of the particle seems like a normal diffusion. It is found that as the surfactant concentration approaches the overlap threshold, the slope of the correlation function tends to decrease, indicating a decrease in the diffusion coefficient. Such a decrease of the diffusion coefficient with an increase of surfactant concentration indicates that the diffusion of the particle deviates from the normal diffusion and the structure of the assemblies in the solution becomes different.

The abnormal diffusion of the particles embedded in a polymer-like network can also be envisaged from the deviation of the decay of the correlation function from the single-exponential decay (cf. Figure 1). The solid line in Figure 1 is drawn by a least-squares fit to the observed correlation spectra assuming a single-exponential deacy. As is seen from the figure, as the surfactant concentration increases, the diffusion coefficient of the probe particle decreases above a threshold concentration of the surfactant, and above this concentration the autocorrelation function deviates from single-exponential decay. The abnormal growth of the micelles above a critical volume fraction (ϕ^*) is predicted from the mean field models,[1] and it is shown that for uncharged micelles the mean micelle aggregation number N_{av} increases with the square root of the surfactant volume fraction according to

$$N_{av} = \phi^{1/2} \exp(E_c/2kT)$$

Diffusion of Probe Particles in Surfactant Gels

J. Phys. Chem. B, Vol. 102, No. 37, 1998 **7123**
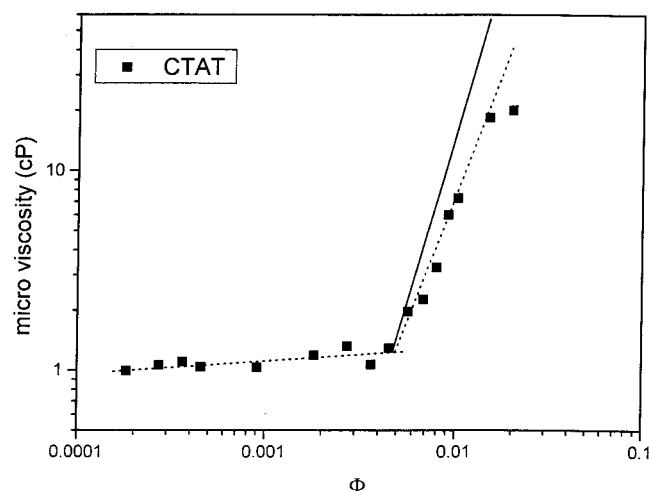
Figure 3. Change in the microviscosity, as calculated from the diffusion coefficient data, of the CTAT solution undergoing gelation. Solid line (slope 3.5) drawn in the semidilute regime has been obtained from the calculation of the micellar length for "living polymers", using the theory of Cates.[5] The dashed line (experimental) in the semidilute regime has a slope of 2.5.

where E_c is the end cap energy of the micelles. In the case of CTAT micelles, the abnormal diffusion of the probe particles can be attributed to the rapid growth of the micelles in the semidilute regime as predicted by the mean field approach and subsequent entanglements of the long micelles. Thus the change in the diffusion coefficient of the probe particles reflects the crossover from dilute to semidilute regimes. In the semidilute regime above the threshold concentration, rodlike micelles overlap and entangle together like a network, and the behavior of the solution is described by its characteristic pore size or mesh size of the network.

Madonia et al.[21] have used DLS as a probe of microviscosity in gels such as sickle cell hemoglobin. The diffusion coefficients of the latex particles embedded in hemoglobin solution were measured using DLS. From the diffusion coefficient values and the known hydrodynamic radius of the particle, they obtained the microviscosity of the solution near the probe environment using the Stokes−Einstein equation (cf. eq 5). Meaningful values of the locally measured viscosity are obtained, which they called the microviscosity, and they observed a change in the apparent microviscosity of hemoglobin solution in the vicinity of the gelation point. They interpreted the rapid increase in microviscosity as being caused by trapping of particles in the polymer network and regarded the point at which the microviscosity diverged as the gelation point. Figure 3 shows the apparent microviscosity of the CTAT solution as calculated from the average diffusion coefficient and hydrodynamic radius of PS particles using the Stokes−Einstein equation. The microviscosity shows an abrupt increase above a critical volume fraction, and this volume fraction is identified as the gelation threshold.

The rapid increase of the microviscosity above the gelation threshold can be attributed to the simultaneous onset of micellar growth and of the semidilute regime. The growth behavior and the dynamics of the "living polymer" solution have been studied extensively by Cates.[5] The behavior of the system differs from the predictions of the conventional polymer theory because of two reasons. First, the average micellar length, L, is itself a function of surfactant volume fraction, Φ, in these self-organizing systems with $L \sim \Phi^{1/2}$. Second, the process of disentanglement in a micellar network is enhanced by the presence of breaking and recombination reactions. The theory

of Cates, which takes into account both these effects, predicts a dependence on Φ of the viscosity as $\eta \sim L\Phi^3 \sim \Phi^\alpha$, where $\alpha = 3.5$. The solid line in Figure 3 drawn in the semidilute regime has been obtained from the variation of the micellar length calculated from the Cates theory, which has a slope of 3.5. The dashed line is a guide to the experimental data and has a slope of 2.5. It is to be noted that the value of $\alpha = 3.5$ as predicted by Cates theory is for the behavior of uncharged micelles. In the case of charged system the growth law has been modified by Safran and MacKintosh et al.[22] The effect of electrostatic interactions in the aggregates increases the rate of growth of the micelles. These effects can still lead to a power law growth but with a new increased exponent relating η and Φ. In view of these, it is seen that the observed value of the exponent $\alpha = 2.5$ is inconsistent with the theoretically expected values. A possible reason for this decreased exponent is the fact that by probe particle diffusion what we measure is the apparent microviscosity whereas the theoretically predicted exponent is for the bulk viscosity, which is obtained from rheological measurements. Owing to these facts, with the present state of knowledge, a quantitative statement about the validity of the theory to the observed microviscosity of the solution cannot be made. However, the experimental results do conclusively show that microviscosity is related to the bulk viscosity and the need for a proper theory for interpreting these results.

2. Effect of Temperature. The diffusion coefficient of the polystyrene probe particles entrapped in a network of micelles above the critical concentration is studied as a function of temperature. It is observed that in the case of polymer-like self-organized assemblies, the micellar length is a strong function of temperature, unlike unbreakable polymers. This strong dependence of the micellar length with temperature arises from the fact that the micelles are dynamic species that undergo breaking and recombination within characteristic time scales. An increase of temperature favors the breakage of the micelles, and subsequent decrease of the average micellar length is observed. This decrease in the average length of the micelles shifts the overlap concentration to higher volume fractions, and hence the fraction of the probe particles trapped in the network of the micelles decreases with an increase of temperature. This will be reflected as an increase in the average diffusion coefficient of the probe particles.

The diffusion coefficient of a free particle undergoing Brownian motion can also be affected by a change in temperature. An increase in temperature will lead to an increase in the thermal velocity of the particle undergoing diffusion and hence leads to an increased diffusion coefficient. To overcome this fact, the observed diffusion coefficients of the particle (D) are divided by the diffusion coefficient for a free particle (D_0) at that temperture to obtain the reduced diffusion coefficient. Figure 4 shows the variation of the reduced diffusion coefficient (D/D_0) as a function of temperature for a solution of 25 mM CTAT. It is observed that above 310 K the reduced diffusion coefficient increases rapidly and takes an almost constant value at around 340 K. In other words, an increase of temperature induces a breakage of the micelles and subsequent increase of the characteristic pore size of the network. As the temperature reaches 340 K, the micellar length become small enough to push the system to a dilute regime. In the dilute regime the diffusion coefficient is virtually constant, and hence above this temperature we find a constant plateau for the reduced diffusion coefficient. Looking into the reduced diffusion coefficient more closely by replotting D/D_0 against $1/T$ semilogarithmically, we
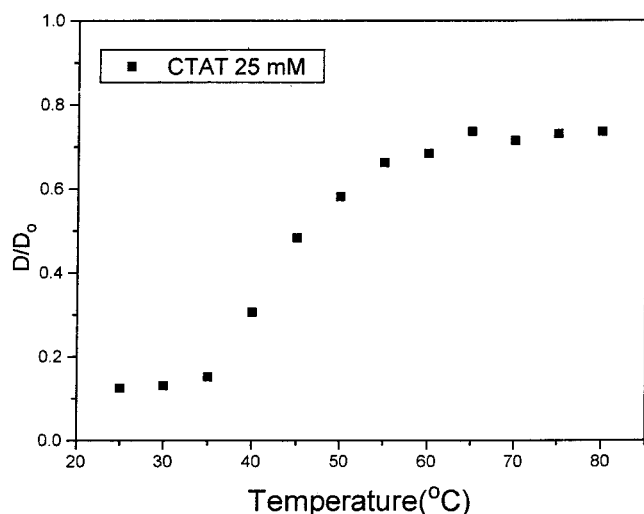
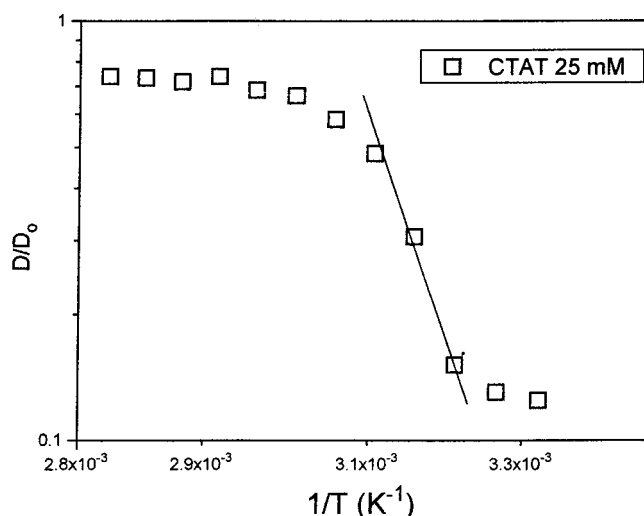**Figure 4.** Variation of the reduced diffusion coefficient (D/D_0) with temperature for 25 mM CTAT.

Figure 5. Variation of the reduced diffusion coefficient (D/D_0) (log scale) versus $1/T$ for 25 mM CTAT.

can identify two different regimes where one can have a nearly constant value of D/D_0 and a region where a sudden increase in D/D_0 is observed (Figure 5). In the regime where a rapid change in D/D_0 is observed, behavior is found to be Arrhenian type, and this type of functional dependence is expected for the self-diffusion coefficient of the micelles in the semidilute regime owing to the breakage of the micelles with an increase in temperature.

3. Growth of Micelles in Cationic−Anionic Mixtures. Formation of elongated micelles in a combination of cationic surfactant with a suitable anionic salt or hydrotrope has attracted considerable interest. Here we investigate the formation of viscoelastic surfactant phases in a combination of cationic and anionic surfactants and the effect of surfactant chain length on the growth behavior of the micelles. The anionic surfactant chosen was a doubly charged single chain surfactant designated as the disodium salt of monoalkylated disulfonated diphenyl oxide (C_nMADS) with variable alkyl chain length (i.e., $n = 6$, 10, 12, and 16). The chemical structure of the surfactant is given in Figure 6. The cationic surfactant chosen was DDTAB, and the volume fraction of the anionic surfactant is kept as 2% w/w in all the measurements.

The growth of C_nMADS micelles by the addition of a cationic surfactant DDTAB has been studied by the technique of probe
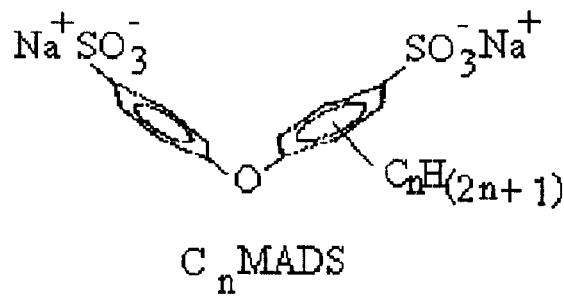

Figure 6. Chemical structure of the monoalkylated disulfonated diphenyl oxide (C_nMADS) surfactant.
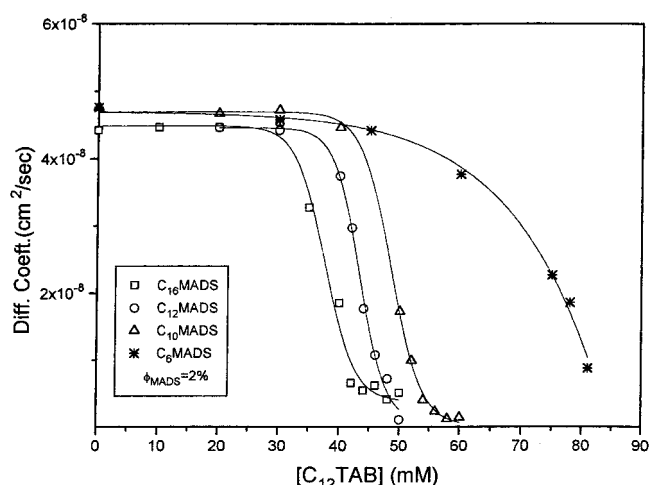

Figure 7. Variation of the diffusion coefficient of PS particles in C_nMADS with varying amounts of DDTAB.

particle diffusion in surfactant assemblies. Figure 7 depicts the variation of the diffusion coefficient of PS particles in C_nMADS surfactant solutions with varying DDTAB concentration. It is to be noted that the diffusion coefficient of the probe particles decreases drastically above a threshold concentration that depends on the length of the alkyl chain of C_nMADS. The decrease of D indicates that the addition of DDTAB induces the growth of C_nMADS micelles, which results in the formation of an entangled network of micelles. Moreover, the crossover concentration from dilute to semidilute regime is a function of the length of the alkyl chain on the surfactant. Since the concentration of the C_nMADS is kept as 2% w/w in all the samples, there exist a slight decrease in the number of moles of anionic surfactant as n increases from 6 to 16 because of the increase in the molecular weight. To account for this difference in the number of moles of the anionic surfactant taken, we have calculated the ratio of the number of moles of DDTAB at the overlap threshold to the concentration of C_nMADS taken. This ratio of [DDTAB]/[C_nMADS] is plotted in Figure 8 as a function of the number of carbon atoms in the alkyl chain, n. It can be seen that for lower alkyl chain lengths, the ratio is higher than those observed for longer chains. If only packing considerations are important in deciding the growth of these micelles, one would expect that the ratio to be same for all surfactant mixtures.[23] But an increase in the ratio for lower chain anionics suggests that the hydrophobicity of the surfactant also plays a role in deciding the structure of the aggregate and growth of the micelles. The growth of the micelle in the dilute regime is found to be faster in the case of more hydrophobic surfactant $C_{16}MADS$ compared to a less hydrophobic C_6MADS. This shows the importance of hydrophobicity of the surfactants in the growth of micelles in mixed cationic−anionic systems.

Diffusion of Probe Particles in Surfactant Gels

J. Phys. Chem. B, Vol. 102, No. 37, 1998 **7125**
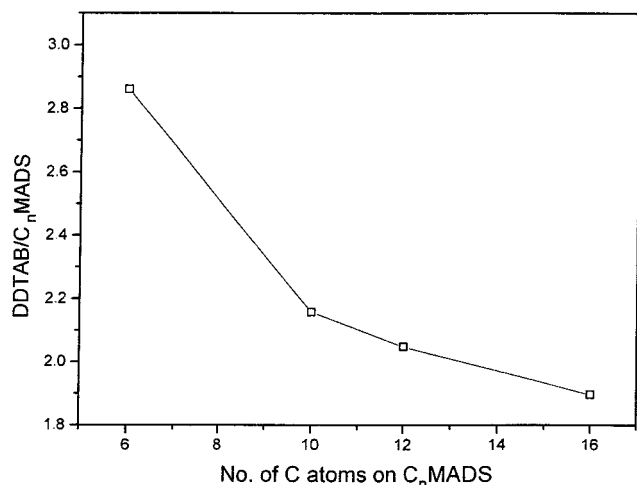
Figure 8. Ratio of DDTAB to C_nMADS at the overlap concentration versus the number of carbon atoms on the alkyl chain of C_nMADS.

Conclusion

In summary, we have demonstrated that the concept of probe particle diffusion in polymer gels can be applied to surfactant assemblies to characterize the growth behavior of micelles. It is found that the growth of CTAT micelles with an increase in the volume fraction of the surfactant, in the absence of any added electrolyte, can be conveniently monitored by a change in the diffusion coefficient of the added PS particles in the micellar solution. The diffusion of the particles in threadlike micelles obeys qualitatively the same behavior as that of the self-diffusion coefficient of the micelles. Thus the crossover from dilute to semidilute regime of long threadlike micelles can be obtained from the diffusion coefficient data. The effect of micellar length and the characteristic pore size of the network on the diffusion of incorporated spherical particles can also be reflected in the temperature dependence of the diffusion coefficient data. Further, the variation of the microviscosity of the probe particle shows an abrupt change at the overlap threshold similar to the bulk zero shear viscosity of the system. The method of probe particle diffusion has been used efficiently to monitor the growth and overlap of micelles in cationic−anionic surfactant mixtures. The growth behavior suggests that an increased hydrophobicity of the surfactant leads to a higher growth rate for the micelles in the dilute regime. This in combination with the packing

parameter would lead to better understanding of the growth behavior of micelles in oppositely charged surfactant mixtures.

References and Notes

(1) Cates, M. E.; Candau, S. J. *J. Phys.: Condens. Matter* **1990**, *2*, 6869.

(2) Rehage, H.; Hoffmann, H. *Mol. Phys.* **1991**, *74*, 933.

(3) Harwigsson, I.; Khan, A.; Hellsten, M. *Tenside Deterg.* **1993**, *30*, 74.

(4) Ohlendorf, D.; Interthal, W.; Hoffmann, H. *Rheol. Acta* **1986**, *25*, 468.

(5) (a)Cates, M. E. *Macromolecules* **1987**, *20*, 2289. (b) Cates, M. E.; Turner, M. *Europhys. Lett.* **1990**, *11*, 68.

(6) Messager, R.; Ott, A.; Chatenay, D.; Urbach, W.; Langevin, D. *Phys Rev. Lett.* **1988**, *60*, 1410.

(7) Langevin, D.; Rondelez, F. *Polymer* **1978**, *19*, 875.

(8) Nishio, I.; Reina, J. C.; Bansil, R. *Phys Rev. Lett.* **1987**, *59*, 684.

(9) Bucci, S.; Hoffmann, H.; Platz, G. *Prog. Colloid Polym. Sci.* **1990**, *81*, 87.

(10) Kaler, E. W.; Herrington, K. L.; Murthy, A. K.; Zasadzinski, J. A. N. *J. Phys. Chem.* **1992**, *96*, 6698.

(11) Soltero, J. F. A.; Puig, J. E.; Manero, O.; Schulz, P. C. *Langmuir* **1995**, *11*, 3337.

(12) Narayanan, J.; Mendes, E.; Manohar, C. *J. Phys. Chem.* **1996**, *100*, 18524.

(13) Porte, G.; Appell, J. *J. Phys. Chem.* **1981**, *85*, 2511.

(14) Schurtenberger, P.; Scartazzini, R.; Magid, L. J.; Leser, M. E.; Luisi, P. L. *J. Phys. Chem.* **1990**, *94*, 3695.

(15) Olsson, U.; Soderman, O.; Guering, P. *J. Phys. Chem.* **1986**, *90*, 5223.

(16) Missel, P. J.; Mazer, N. A.; Carey, M. C.; Benedek, G. B. *J. Phys. Chem.* **1989**, *83*, 8354.

(17) Ozeki, S.; Ikeda, S. *J. Colloid Interface Sci.* **1982**, *87*, 424.

(18) Brown, J. C.; Pusey P. N.; Dietz, R. *J. Chem. Phys.* **1975**, *62*, 1136.

(19) Manohar, C.; Rao, U. R. K.; Valaulikar, B. S.; Iyer, R. M. *J. Chem. Soc., Chem. Commun.* **1986**, 379.

(20) Narayanan, J.; Manohar, C.; Langevin, D.; Urbach, W. *Langmuir* **1997**, *13*, 398.

(21) Madonia, F.; San Biagio, P. L.; Palma, M. U.; Schiliro, G.; Musumeci, M.; Russo, G. *Nature* **1982**, *302*, 412.

(22) Safran, S. A.; Pincus, P. A.; Cates, M. E.; MacKintosh, F. C. *J. Phys. France* **1990**, *51*, 503.

(23) Mishra, S.; Mishra, B. K.; Chokappa, D. K.; Shah, D. O.; Manohar, C. *Bull. Mater. Sci.* **1994**, *17*, 1103.