

Effect of Poly(ethylene glycol)s on Micellar Stability of Sodium Dodecyl Sulfate

Dibakar Dhara and Dinesh O. Shah*

Center for Surface Science and Engineering, Departments of Chemical Engineering and Anesthesiology, University of Florida, Gainesville, Florida 32611

Received July 20, 2000. In Final Form: November 9, 2000

The effects of poly(ethylene glycol)s of different molecular weights on the micellar stability of sodium dodecyl sulfate in the concentration range from 50 to 600 mM were investigated. The presence of polymer was found to decrease micellar stability drastically. The decreased stability of micelles is explained by the increased population of small aggregates in the presence of polymer. This decreases the value of "resistance" for the micellar formation–dissolution process. The foaming property of SDS solutions in the presence of poly(ethylene glycol) was related to micellar stability.

Introduction

Surfactant–polymer systems in aqueous solution find extensive industrial applications in areas related to medicine, cosmetics, food, detergency, mineral processing, enhanced oil recovery, and so forth. The interaction between surfactants and polymers has been the subject of active research for the last three decades, and this subject has been the focus of some of the recent reviews.^{1,2} Investigations into these systems are important also in relevance to many biological systems, such as biomembranes and vesicles, and also to biological processes, for example, lipid–protein interactions and so forth. The well-explored systems till now are those containing nonionic water-soluble polymers and anionic surfactants, or polyelectrolytes and oppositely charged surfactants. There are plenty of references^{3–6} describing interactions between polymers and surfactants, but most of them are based upon equilibrium data, for example the effect of polymers on the critical micellar concentration (CMC) of the surfactant and the aggregation number of the micelles. However, in most of the technological processes involving surfactants, such as foaming, wetting, emulsification, solubilization, and detergency, the equilibrium concentrations are never attained at the interface and the actual interfacial tension is much higher. In these processes the stability of micelles should play an important role. For example, the stability of micelles has been found to play an important role in various technological processes such as foaming,⁷ bubble dynamics,⁸ wetting time of cotton,⁹ solubilization and detergency,¹⁰ emulsion droplet size,¹¹ and thin film stability.¹²

Shah and co-workers showed that the stability of sodium dodecyl sulfate micelles can be tuned by additives such as short and long chain alcohols,^{13,14} oppositely charged

surfactants,¹⁵ tetraalkylammonium chlorides,¹⁶ and antifoams.¹⁷ However, the effect of polymers on the micellar stability has not been studied well. Such a study is worthwhile in understanding the fundamentals of polymer–surfactant interaction and also useful in tailoring the micellar stability. The effect of poly(ethylene glycol) (PEG), poly(*N*-vinylpyrrolidone) (PVP), and bovine serum albumin (BSA) on the stability of sodium dodecyl sulfate micelles has been studied by Wyn Jones et al.¹⁸ by the p-jump method while Tondre¹⁹ has used the T-jump method for studying the poly(ethylene oxide) (PEO)–SDS system. Both the studies were performed at low concentration of surfactants in solution. This paper aims to study the effect of polymers on the micellar stability over a wide range of surfactant concentrations. Here, we report the effect of poly(ethylene glycol)s of different molecular weights on the micellar relaxation time of sodium dodecyl sulfate in the concentration range 50–600 mM and its relevance to the foaming properties of surfactant solutions.

Experimental Section

Materials. SDS (99% purity), from Sigma Chemical Co., was used as received. The source and average molecular weights of the PEGs used are listed in Table 1. The molecular weights are given by the suppliers; polydispersity data are not available. Deionized water was used for all the experiments.

Pressure Jump. The slow relaxation time τ_2 was measured using a pressure-jump apparatus with conductivity detection from Dia-Log GmbH (Duesseldorf, Germany) with a pressure jump of 100–130 bar. The conductivity of the surfactant solution held in the conductivity cell attached to the pressure chamber was compared to that of a reference cell filled with KCl solution. All τ_2 values were obtained at a constant temperature of 25 °C.

* Corresponding author. Phone: (352) 392-0877. Fax: (352) 392-0127. E-mail: shah@che.ufl.edu.

(1) Goddard, E. D. *Colloids Surf.* **1986**, *19*, 255.

(2) Lindman, B.; Thalberg, K. In *Interactions of Surfactants with Polymers and Proteins*; Goddard, E. D., Ananthapadmanabhan, K. P., Eds.; CRC Press: Boca Raton, FL, 1993; p 203.

(3) Jones, M. N. *J. Colloid Interface Sci.* **1967**, *23*, 36.

(4) Schwuger, M. J. *J. Colloid Interface Sci.* **1973**, *43*, 491.

(5) Gao, Z.; Wasylisen, R. E.; Kwak, J. C. T. *J. Phys. Chem.* **1991**, *95*, 462.

(6) Dubin, P. L.; Gruber, J. H.; Xia, J.; Zhang, H. *J. Colloid Interface Sci.* **1992**, *148*, 92.

(7) Oh, S. G.; Shah, D. O. *Langmuir* **1991**, *7*, 1316.

(8) Oh, S. G.; Klein, S. P.; Shah, D. O. *AIChE J.* **1992**, *38*, 149.

(9) Oh, S. G.; Shah, D. O. *Langmuir* **1992**, *8*, 1232.

(10) Oh, S. G.; Shah, D. O. *J. Am. Oil. Chem. Soc.* **1993**, *70*, 673.

(11) Oh, S. G.; Jobalia, M.; Shah, D. O. *J. Colloid Interface Sci.* **1993**, *156*, 511.

(12) Patel, S. S.; Kumar, K.; Shah, D. O.; Delfino, J. *J. Colloid Interface Sci.* **1996**, *183*, 603.

(13) Leung, R.; Shah, D. O. *J. Colloid Interface Sci.* **1986**, *113*, 484.

(14) Patist, A.; Axelberd, T.; Shah, D. O. *J. Colloid Interface Sci.* **1998**, *208*, 259.

(15) Patist, A.; Chhabra, V.; Pagidipati, R.; Shah, R.; Shah, D. O. *Langmuir* **1997**, *13*, 432.

(16) Patist, A.; Huibers, P. D. T.; Deneka, B.; Shah, D. O. *Langmuir* **1998**, *14*, 4471.

(17) Jha, B. K.; Patist, A.; Shah, D. O. *Langmuir* **1999**, *15*, 3042.

(18) Bloor, D. M.; Wyn-Jones, E. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 657.

(19) Tondre, C. *J. Phys. Chem.* **1985**, *89*, 5101.

Table 1. PEGs/PEOs Used in This Study

molecular weight	source
600	Scientific Polymer Products
1000	Scientific Polymer Products
1500	Scientific Polymer Products
3400	Scientific Polymer Products
4000	PolyScience
6800	Scientific Polymer Products
8000	Aldrich
10000	Aldrich
35000	Fluka
100000	Aldrich
900000	Aldrich
4000000	Aldrich

Foaming. A quartz column, 3.5 cm in diameter, was used to acquire the foamability measurements. At the base of the cylinder a single capillary, 2.5 mm in diameter, was used to generate the bubbles. Fifty milliliters of the sample solution was poured into the column using a long funnel that reached to the bottom to ensure that the walls of the cylinder remained dry and could not act as an additional supplier of surfactant molecules, which would increase foamability. The air was then turned on at a constant flow rate of 158.2 cm³/min. The foam volume produced after 1 min was recorded. All the experiments were performed at least four times at ambient temperature, 23 ± 1 °C. Results reported in this study are an average of four measurements.

Surface tension of the polymer solutions was measured by the Wilhelmy plate method, consisting of a platinum blade suspended from a force transducer with output connected to a voltmeter for digital display. Before each measurement, the platinum plate was cleaned by heating it to a red/orange color with a Bunsen burner. The readings were noted when there was no significant change in the value of the transducer readout.

Results and Discussion

One of the most widely studied systems of nonionic polymer and ionic surfactant is SDS-PEG/PEO. In our study, initially PEG 6800 was chosen because it is known that the interaction of SDS with PEG does not differ significantly when the PEG molecular weight is above 4000. Figure 1 shows the effect of different amounts of PEG 6800 on the slow relaxation time τ_2 of SDS micelles in the concentration range 50–600 mM. In the absence of polymer, τ_2 shows initially an increase with increasing SDS concentration but starts decreasing after 200 mM SDS. These results are well in agreement with previous investigations.^{7,20} The appearance of a maximum in τ_2 has been explained by the onset of formation of non-spherical micelles. As SDS concentration increases, the number of micelles steadily increases. The increasing electrostatic repulsion between the micelles contributes to their increasing stability. At 200 mM, the maximum packing density of the spherical micelles is reached and a transition to nonspherical (cylindrical) form occurs.¹⁰ As more and more micelles convert to cylindrical form, the distance between the remaining spherical micelles increases, and thus a drop in τ_2 is observed. From Figure 1 it is evident that addition of PEG decreases the stability of SDS micelles for all concentrations, and this effect increases with the amount of the polymer. This decrease in τ_2 , and hence the micellar stability, is most significant in the case of 200 mM SDS, which formed the most stable micelle in the absence of PEG.

The accepted view regarding interactions in the SDS-PEG system is that, when the surfactant concentration exceeds a certain critical value, known as the critical aggregation concentration (CAC), the surfactant molecules start binding to the polymer.^{1,2} The CAC is generally lower

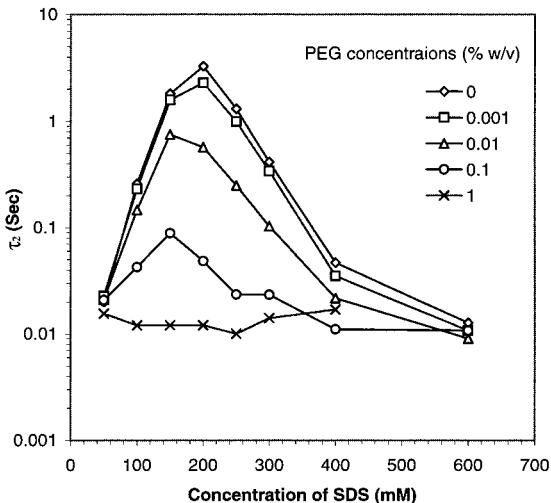


Figure 1. Effect of different concentrations of PEG 6800 on the slow relaxation time (τ_2) of SDS micelles.

than the normal critical micellar concentration (CMC) in a polymer-free solution under otherwise identical conditions. The extent of binding between polymer and surfactant increases with increase in concentration of the surfactant up to a particular concentration, known as the polymer saturation point (PSP), after which the polymer becomes saturated with surfactants. It is fairly well established that the CAC is independent of, or very slightly dependent on, the concentration of a particular polymer, whereas the PSP is directly proportional to the concentration of the polymer.

Micelles are often drawn as static structures of spherical aggregates of oriented surfactant molecules, but in reality they are in dynamic equilibrium. Dynamic properties of micelles are characterized by two relaxation processes. The first relaxation time τ_1 , which is of the order of microseconds, is associated with the monomer-micelle exchange process. The slow relaxation time τ_2 is associated with the complete micelle dissolution-formation process and is of the order of milliseconds to minutes depending upon the structure and concentration of surfactant. The two relaxation times can be used to calculate two important statistical parameters of the micellar system, namely, the "residence time" of a surfactant in micelles and the average "lifetime" of micelles. The kinetics of these processes has been evaluated by Aniansson and co-workers.^{21,22} The "residence time" of the surfactant monomer in micelles is related to τ_1 and is equal to n/k^- , where n is the mean aggregation number and k^- is the rate constant of dissociation of a surfactant from a micelle. The average micellar lifetime is given by the following expression²¹

$$\frac{1}{\tau_2} = \frac{n^2}{A_1 R} \left\{ 1 + \frac{\sigma^2}{n} a \right\}^{-1}$$

$$T_M = \tau_2 \frac{na}{1 + (\sigma^2/n)a}$$

where T_M is the average micellar lifetime, n is the aggregation number, σ is the half-width of the Gaussian distribution curve of micellar population, and $a = (A_{tot} - A_1)/A_1$, where A_{tot} is the total surfactant concentration and A_1 is the mean monomer concentration, which is

(21) Aniansson, E. A. G.; Wall, S. N. *J. Phys. Chem.* **1974**, 78, 1024.

(22) Aniansson, E. A. G.; Wall, S. N.; Almgren, M.; Hoffmann, H.; Kielmann, I.; Ulbricht, W.; Zana, R.; Lang, J.; Tondre, C. *J. Phys. Chem.* **1976**, 80, 905.

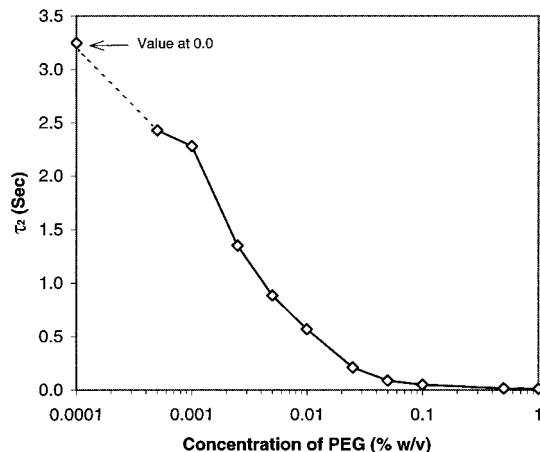


Figure 2. Effect of different concentrations of PEG 6800 on the slow relaxation time (τ_2) of 200 mM SDS.

often approximated as the CMC. Aniansson and Wall defined the “resistance” R by

$$R = \sum_{s=s_1+1}^{s_2} 1/(k_s^- A_s)$$

where s is the aggregation number of a particular aggregate and k_s^- is the dissociation rate constant of the aggregate having an aggregation number s . When the concentration of surfactant is much greater than the cmc, T_M is approximately equal to m_2 . Thus, the slow relaxation time can be directly related to the stability (or lifetime) of the micelles. The dependence of τ_2 on ionic strength, concentration, temperature, and other variables can be interpreted in terms of their effect on R . Since during the slow relaxation process the reaction path from monomers to micelles follows sequential addition of monomers to premicellar aggregates, increased population of these intermediate premicellar species will facilitate the micellar formation–dissolution process and decrease the value of τ_2 .

It is likely that in the presence of polymer there would be formation of small aggregates of SDS by adsorbing on the polymer chain; that is, there will be an increase in the population of smaller surfactant aggregates. This will result in a decrease in the values of R . As R is considered to be the “resistance” for micellization–dissolution process, then with reduction in the value of R would decrease the stability of the micelles. We believe that this is the reason for the decreased stability of SDS micelles in the presence of polymers. The greater the amount of added polymer, the greater is the effect. The effect is observed mostly in the case of 200 mM SDS because at this concentration the stability of SDS micelles is maximum. So any perturbation in the stability would be reflected most significantly at this concentration.

The following reason can also be given for such an observation. On addition of PEG to SDS solution, some SDS micelles get bound to (or adsorbed on) the polymer chain. The hydrophilic groups of the PEG chain form an ion–dipole association with the ionic headgroups of SDS, and the hydrophobic segments of PEG are in contact with the “exposed” hydrocarbon areas of the micelles because of their screened charges. This, in effect, results in screening of the electrical charge of the micellar headgroups and reduction in the extent of the hydrocarbon area of the micelle “exposed” to water.^{23,24} Now, these polymer-bound micelles exert less electrostatic repulsion

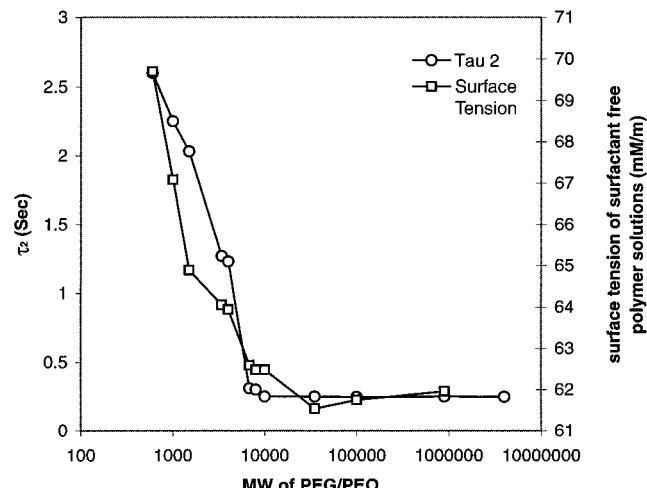


Figure 3. Relation between the surface activity of the PEGs of different molecular weights and their effect on the slow relaxation time (τ_2) of 200 mM SDS.

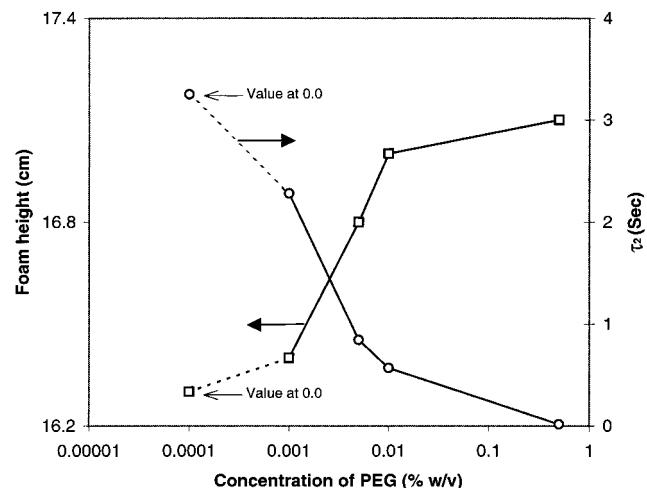


Figure 4. Relation between foamability and the micellar stability of 200 mM SDS in the presence of PEG.

forces to the free micelles. Due to this reduction in the intermicellar repulsion, the stability of the micelles decreases. The more polymer present in the solution, the more is the reduction of intermicellar repulsion and hence the lower is the micellar stability. The intermicellar electrostatic repulsion is maximum in the case of 200 mM SDS, and as expected, the reduction of τ_2 on addition of PEG is maximum in the case of 200 mM SDS, as shown in Figure 1.

Figure 2 shows the change in τ_2 of 200 mM SDS for different PEG concentrations. One of the interesting observations is that τ_2 decreases significantly even in the presence of a very small amount (0.002 wt %) of PEG. This shows that the interaction between PEG and SDS occurs even in the presence of such a small amount of PEG in solution. Most of the references concerning polymer–surfactant interactions using methods such as surface tension, viscometry, NMR, EPR, light scattering, microcalorimetry, and so forth^{1,2,25–27} report polymer–surfactant interaction at relatively higher polymer concentration.

Figure 3 shows the effect of molecular weights of PEG/PEO on the stability of SDS micelles along with the surface tension values (of surfactant free polymer solutions) for

(23) Cabane, B. *J. Phys. Chem.* **1977**, *81*, 1639.

(24) Zana, R.; Lianos, P.; Lang, J. *J. Phys. Chem.* **1985**, *89*, 41.

the polymers. The concentration of PEG in all of the solutions was 0.02% w/v. A good correlation between surface tension and τ_2 values is observed. It may be possible that the lower molecular weight PEGs are not hydrophobic enough to bind with a SDS molecule and as a result the stability is not decreased significantly. As the surface activity increases, polymer chains will bind to SDS molecules.

Oh and Shah⁷ have shown that the foamability of a micellar solution is influenced by the average lifetime of micelles. This is because the micelles have to be broken into the monomers for adsorption onto newly created surfaces of bubbles. Without this process, foam cannot be generated. Figure 4 shows the correlation between foam-

ability and micellar relaxation time in the presence of polymer for a 200 mM SDS solution. Foamability increases with a decrease in the micellar stability. Relatively unstable micelles would disintegrate faster into monomers, which can rapidly adsorb onto the newly created surface. This enhances the foamability of micellar solutions.

In summary, the results discussed in this paper suggest that the stability (or slow relaxation time τ_2) of SDS micelles decreases in the presence of poly(ethylene glycol)s, which strongly interact with SDS. The foamability of SDS solution in the presence of polymer increases with a decrease in micellar stability.

Acknowledgment. The authors thank the NSF—Engineering Research Center for Particle Science & Technology (Grant No. 9402989) for their support.

LA001030I

(25) Zana, R.; Lang, J.; Lianos, P. In *Microdomains in Polymer Solutions*; Dubin, P., Eds.; Plenum: New York, 1985; p 369.

(26) Wang, Y.; Lu, D.; Yan, H.; Thomas, R. K. *J. Phys. Chem. B* **1997**, *101*, 3953.

(27) Wang, G.; Olofsson, G. *J. Phys. Chem. B* **1998**, *102*, 9276.