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# Stability of Sodium Dodecyl Sulfate Micelles in the Presence of a Range of Water-Soluble Polymers: A Pressure-Jump Study

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The effects of a range of nonionic and ionic water-soluble polymers on the micellar stability of sodium dodecyl sulfate were investigated by the pressure-jump method. The presence of polymer that interacts with SDS was found to decrease the micellar stability drastically. Surface activity of the polymers was correlated with their ability to reduce the micellar stability. The decrease in micellar stability was explained by the formation of premicellar aggregates (or submicelles) of surfactants in the presence of polymer, which facilitated the micelle formation—disintegration process.

#### Introduction

In any situation where surfactant must adsorb at a newly created interface, whether it is at air/liquid or solid/liquid interface, it is supplied to the new interface by the diffusion of monomer molecules. When a surface is suddenly expanded, the stability of the micelles affect the ability of the solution to supply the monomers to the new surface. The less stable the micelles, the greater the monomer flux to the new surface/interface will be. Hence, the stability of micelles should play a significant role in processes where new interfaces are constantly generated. It has been experimentally verified that the micellar stability indeed plays an important role in various technological processes such as foaming,1 bubble dynamics,2 wetting time of cotton,3 solubilization and detergency,4 emulsion droplet size,5 and thin film stability.6 Therefore, understanding the factors affecting micellar stability is key to influencing the dynamic surface or interfacial tension and also the technological processes controlled by them.

Shah and co-workers have showed that the stability of sodium dodecyl sulfate micelles can be affected by additives such as short and long chain alcohols, <sup>7,8</sup> oppositely charged surfactants, <sup>9</sup> tetraalkylammonium chlorides, <sup>10</sup> and antifoams. <sup>11</sup> However, the effect of polymers on the micellar stability has not been explored well. Since the polymers are added in various surfactant formulations, it will be very interesting to investigate the dynamic behavior of surfactant micelles in the presence of polymers.

Besides, the surfactant—polymer systems in aqueous solution are also intriguing from both fundamental as well as practical points of view. These complex mixtures find extensive industrial applications in areas related to mineral processing, foaming control, medicine, food, detergency, enhanced oil recovery, etc. They are also of interest in formulation and conditioning of cosmetics, biological, pharmaceutical, and fine chemistry applications. From the fundamental point of view, understanding the nature of the surfactant—polymer interactions that lead to the formation of a complex and the physical structure and stability of this complex is fascinating and not clearly established

yet. Thus interaction between surfactants and polymers has been the subject of active research for the last three decades and it has also been focused on in some of the recent reviews. 12,13 Most studies on polymer-surfactant interaction are based upon equilibrium data, i.e., the effect of polymers on the critical micellar concentration of the surfactant and the aggregation number of the micelles. 14-17 The effect of polymers on the dynamic behavior of micellar solutions has not been studied in depth.<sup>18-21</sup> Such a study is important in understanding the dynamic behavior of surfactant micelles in the presence of polymers and also in understanding the fundamentals of polymer-surfactant interaction. In a recent paper we have reported the effect of poly(ethylene glycols) on sodium dodecyl sulfate micelles in the concentration range of 50-600 mM.<sup>22</sup> The present paper is an extension of that work, intended as a detailed study of the effect of a range of water-soluble polymers on the micellar stability over a wide range of surfactant concentrations.

### **Experimental Section**

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

**Pressure-Jump Experiments.** The slow relaxation time  $(\tau_2)$  of SDS micelles was measured using a pressure-jump apparatus with conductivity detection from Dia-Log GmbH (Duesseldorf, Germany) by recording the change in conductivity that results from micelle formation or disintegration. The surfactant solution was pressurized up to 100-130 bar and the solution was allowed to reach its new equilibrium state (at high cmc). Subsequently, the pressure was suddenly released to ambient pressure (initial cmc). The slow relaxation time  $\tau_2$  was then calculated from the exponential decay in electrical conductivity. The conductivity of the surfactant sample solution held in the conductivity cell attached to the pressure chamber was compared to a reference cell containing KCl solution of the same conductivity. In the pressure-jump instrument used here, the pressure falls following the rupture of a thin metal diaphram,

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TABLE 1: Sources and Molecular Weights of Polymers and Proteins Used in This Study

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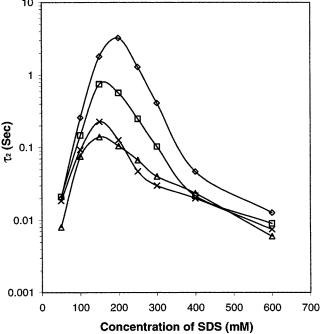
**Figure 1.** Mechanism for the two relaxation times,  $\tau_1$  and  $\tau_2$ , for a surfactant solution above critical micelle concentration (cmc).

which takes  $50-100~\mu s$ . So it is not possible to measure the fast relaxation time ( $\tau_1$ ) (which is on the order of microseconds) with our instrument. Moreover, we are mainly interested in  $\tau_2$ , because it is related to the micellar stability. All  $\tau_2$  values were obtained at 25 °C.

**Surface tensions** of the polymer solutions were 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 to a red/orange color with a Bunsen burner.

#### Results and Discussion

Dynamic properties of micelles are characterized by two relaxation processes (Figure 1). The first relaxation time  $(\tau_1)$ , which is on the order of microseconds, is associated with the exchange of monomers with micellar aggregates. The slow relaxation time  $(\tau_2)$ , which is on the order of milliseconds to seconds, is associated with complete formation—disintegration of micelles.  $\tau_1$  and  $\tau_2$  are related with two important statistical parameters of the micellar system, namely, the "residence time" of a surfactant in micelles and the stability (average "lifetime") of micelles, respectively.



**Figure 2.** Effect of PEG, MC, and PNIPA on the slow relaxation time  $(\tau_2)$  of SDS of different concentrations:  $(\diamondsuit)$  SDS only,  $(\Box)$  PEG (0.01%),  $(\times)$  PNIPA (0.01%), and  $(\triangle)$  MC (0.01%).

Figure 2 shows the effect of PEG, MC, and PNIPA on the slow relaxation time  $\tau_2$  of SDS micelles in the concentration range of 50–600 mM. All three polymers are reported to interact strongly with SDS. $^{12-16,26-29}$  In the absence of polymer,  $\tau_2$  showed an initial increase with increasing SDS concentration but started decreasing above 200 mM. These results are well in agreement with previous investigations. $^{1,30}$  The appearance of a maxima in  $\tau_2$  has been explained by the onset of formation of nonspherical micelles. $^1$  Another explanation for the occurrence of the maximum at 200 mM was provided by Kahlweit et al. $^{30}$  They represent the reaction path for the formation of micelles by two parallel resistors,  $R_1$  and  $R_2$ , where  $R_1$  refers

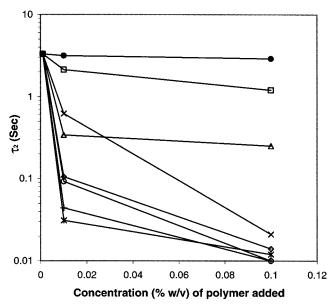
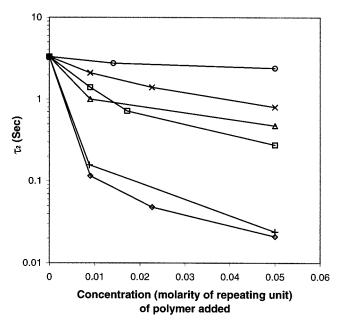


Figure 3. Effect of cellulose derivatives at different concentration on the slow relaxation time  $(\tau_2)$  of 200 mM SDS:  $(\bullet)$  dextran,  $(\Box)$  HEC,  $(\triangle)$  E230,  $(\times)$  E411,  $(\diamondsuit)$  MC, (\*) HPC,  $(\bigcirc)$  HPMC, and (+) HBMC.

to the formation of micelle by stepwise addition of monomers and R<sub>2</sub> refers to micelle formation by coagulation of submicellar aggregates. At low concentrations, R2 is very high due to electrostatic repulsion between the submicellar aggregates, and therefore,  $R_1$  determines the  $\tau_2$ . However,  $R_1$  increases with an increase in counterion concentration, whereas R2 decreases due to a decrease in electrostatic repulsion between submicellar aggregates. Within a limited concentration range, both resistors become comparable and  $\tau_2$  passes through a maximum. Figure 2 shows that the addition of polymers decreases the stability of SDS micelles for all concentrations and this decrease in  $\tau_2$  is most effective in the case of 200 mM SDS, which formed the most stable micelle in the absence of any polymer. Therefore, to compare this micelle destabilizing effect of different polymers, further experiments with other polymers were restricted on 200 mM SDS solution. It is to be mentioned that addition of salts actually did not reduce the maximum value of  $\tau_2$ , instead addition of salt shifted the SDS concentrations lower, until, at high salt concentrations,  $\tau_2$  appears to decrease starting from the cmc onward.  $^{30,31}$ 

In Figure 2 it appears to be that the maximum in  $\tau_2$  is shifted from 200 mM for the binary SDS/water system to nearly 150 mM SDS as PEG, MC, and PNINA are added to the solution. This could possibly be due to formation of nonspherical micelles at 150 mM SDS in the presence of polymers. Synthetic macromolecules do not possess any preferential three-dimensional geometry; they are more flexible to assume any random conformation. For example, a PEG chain in aqueous solution behaves as a highly mobile molecule with a large exclusion volume.32 Upon SDS binding, the hydrodynamic volume of polymer chains is expected to increase further due to polyelectrolyte behavior. Thus, in the presence of polymer the effective free volume of water available for the free micelles to disperse is considerably less compared to polymer-free solution; as a result, the maximum packing of spherical micelles and subsequent nonspherical micelle formation are expected to be at lower concentration than 200 mM SDS.

Figure 3 plots  $\tau_2$  of 200 mM SDS as function of concentration of various cellulose derivatives and dextran. All the polymers decreased  $\tau_2$  drastically, except dextran and HEC. Among these polymers, only dextran and HEC reportedly do not interact or



**Figure 4.** Slow relaxation time ( $\tau_2$ ) of 200 mM SDS as a function of molarity of repeating unit of synthetic polymers (vinylic): (O) PAAm, (\*) PVA, ( $\triangle$ ) PVP, ( $\square$ ) PPG, (+) PNIPA, and ( $\diamondsuit$ ) PEG.

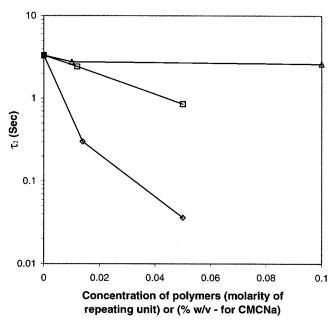
very weekly interact with SDS.<sup>33–35</sup> The cellulose derivatives and dextran can be ranked according to their ability to affect the  $\tau_2$  of SDS as follows: HPC > HBMC > HPMC > MC >  $E230 > E411 \gg HEC > dextran.$ 

As stated above, the polymers interacting strongly with SDS decrease  $\tau_2$ . So the above ranking of the polymers should also be applicable to their strength of interaction with SDS in water. This ranking more or less tally with the critical aggregation concentration (cac) values (defined as the critical surfactant concentration for the start of aggregation) in the presence of these polymers.<sup>33</sup>

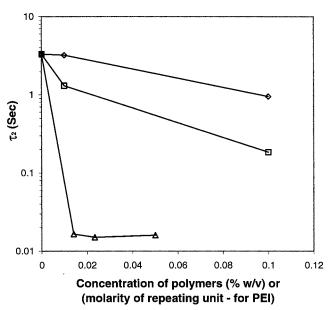
Figure 4 shows the effect of various synthetic polymers (vinylic) on the  $\tau_2$  of 200 mM SDS. In this case the molarity of polymer repeating units was used for proper comparison among the polymers. PNIPA and PEG reduced  $\tau_2$  drastically; PVP, PPG, and PVA moderately, and PAAm not at all. Interaction of SDS with PEG, PNIPA, PVP, PPG, and PVA is welldocumented. 12,26,36-37 These polymers can be ranked according to their effect on the  $\tau_2$  of 200 mM SDS as follows: PEG  $\sim$  $PNIPA \gg PPG > PVP > PVA \gg PAAm$ .

As in the case of cellulose derivatives, this ranking should also be applicable to their strength of interaction with SDS. This ranking is fairly comparable with the cac values in the presence of these polymers, except for the pair PEG/PVP. 12,26,38 It can be mentioned that PVP is known to have a lower cac than PEG, which was attributed to the greater hydrophobicity of PVP.<sup>13</sup> But the hydrophobicity of PVP is not so different than that of PEG (as shown later in Figure 8), which can only be responsible for the low cac of PVP. While studying the gel-electrophoretic behavior of the PEG-SDS complex, it was reported that unlike PEGs, PVPs could not be separated according to their molecular weight by SDS-poly(acrylamide) gel electrophoresis due to the weaker nature of the PVP-SDS complex than the PEG-SDS complex.  $^{39,40}$  The  $\tau_2$  results reported here are consistent with this interpretation.

Figure 5 shows the effect of anionic polymers on the stability of 200 mM SDS. While PAA decreased the relaxation time, the effect of PAA Na and CMC Na was not significant. Somasundaran et al.41 reported the presence of a definite interaction between PAA and SDS; it has also been reported



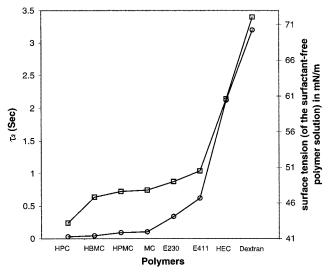
**Figure 5.** Effect of anionic polymers as a function of molarity of repeating unit of polymers on the slow relaxation time  $(\tau_2)$  of 200 mM SDS:  $(\triangle)$  CMC Na,  $(\square)$  PAA Na, and  $(\diamondsuit)$  PAA.



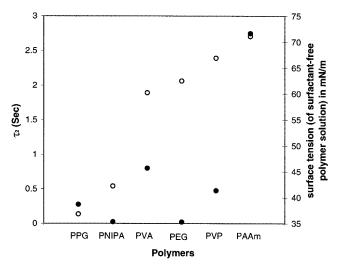
**Figure 6.** Effect of cationic polymers at different concentration on the slow relaxation time  $(\tau_2)$  of 200 mM SDS:  $(\diamondsuit)$  LM-200,  $(\Box)$  JR 400, and  $(\triangle)$  PEI.

that SDS does not interact with PAA Na and CMC Na by Zana et, al. 42 and Schwuger et al., 43 respectively. These results again indicate that the polymers that interact strongly with SDS decrease its micellar stability. Figure 6 shows the effect of cationic polymers on the stability of 200 mM SDS. All the three polymers reduced the stability, the effect being a maximum for PEI. The strong interaction between PEI and SDS is well-studied by Winnik and co-workers 44 and Wyn-Jones et al.; 45 interactions between JR 400 and LM-200 with SDS are also reported. 46,47 The strong interaction between oppositely charged polymers and SDS is not surprising, since very strong electrostatic forces of attraction are involved.

The kinetics of these processes has been evaluated by Aniansson and co-workers.<sup>48,49</sup> The "residence time" of the surfactant monomer in micelles is related to  $\tau_1$  and is equal to  $n/k^-$ , where n is the mean aggregation number and  $k^-$  is the



**Figure 7.** Relation between surface activity of cellulose derivatives and their effect on the slow relaxation time  $(\tau_2)$  of 200 mM SDS:  $(\Box)$   $\tau_2$  and  $(\bigcirc)$  surface tension.



**Figure 8.** Relation between surface activity of the synthetic polymers and their effect on the slow relaxation time  $(\tau_2)$  of 200 mM SDS:  $(\bullet)$   $\tau_2$  and  $(\bigcirc)$  surface tension.

rate constant of dissociation of a surfactant from a micelle.  $\tau_2$  is given by the following expression<sup>48</sup>

$$\frac{1}{\tau_2} = \frac{n^2}{R} \left[ A_1 + \frac{\rho^2}{n} (A_{\text{tot}} - A_1) \right]^{-1}$$

where n is the aggregation number,  $\rho$  is the half-width of the Gaussian distribution curve of micellar population,  $A_{\text{tot}}$  is the total surfactant concentration, and  $A_1$  is the mean monomer concentration, which is often approximated as the cmc. Aninasson and Wall defined "resistance" R by

$$R = \sum_{s=s_1+1}^{s_2} \frac{1}{k_s^-[A_s]}$$

where  $A_s$  and  $k_s^-$  are the equilibrium concentration and the dissociation rate constant of the premicellar aggregates having aggregation number s, respectively. The overall rate is assumed to be limited by a set of slow steps involving several of the least stable aggregates, that is, values of s in a range of species of aggregation number  $s_1 + 1 < r < s_2$ , where  $s_1$  represents monomer and  $s_2$  the start of true micelle formation. Therefore,

as per the model,  $\tau_2$  value should be sensitive to the concentration of premicellar aggregates. Since during the slow relaxation process the reaction path from monomers to micelles follows sequential addition of monomers to premicellar aggregates, the increased population of these intermediate premicellar species will facilitate the micelle formation—dissolution process and decrease the value of  $\tau_2$ .

It is likely that in the presence of a polymer there would be formation of small aggregates of SDS by adsorption on the polymer chain, i.e., there will be an increase in the population of smaller surfactant aggregates. This will result in a decrease in the values of "R" and consequently the stability of micelles. This could be the reason for the decreased stability of SDS micelles in the presence of polymers. The greater the amount of added polymer, the greater the effect. The effect is observed mostly in the case of 200 mM SDS, because at this concentration the stability of SDS micelles is a maximum. So any perturbation in the stability would be reflected most significantly at this concentration. This effect should be expected to be greater is case of more hydrophobic polymers, because SDS would bind more to the more hydrophobic polymers.

The polymer-bound surfactant aggregates have a higher degree of dissociation compared to the normal micelles.<sup>50</sup> So addition of polymers could also result in more free counterions in the solution and an increase in the ionic strength. According to Kalhweit's model, this could also be the reason for the decrease in the micellar stability due to the greater probability of coagulation between premicellar aggregates. But, as mentioned earlier, it was reported that the addition of salts shifted the maxima of  $\tau_2$ , the value of the maximum  $\tau_2$  being the same. In the present case the maximum value of  $\tau_2$  is decreased. Moreover, addition of CMC Na and PAA Na did not affect the micellar stability considerably. This observation supported that the decrease in micellar stability is because of polymer-induced formation of small surfactant aggregates. Figure 7 shows the value  $\tau_2$  of 200 mM SDS in the presence of 0.01% (w/v) cellulose derivatives along with their surface tension values (of surfactant-free polymer solutions). A direct relation between the surface activity of the polymer and its ability to reduce the stability of SDS micelles is observed. The greater the surface activity of the polymer, the greater will be the binding of SDS on to the polymer and the value of  $\tau_2$  would decrease. Figure 8 shows the value  $\tau_2$  of 200 mM SDS in the presence of 0.1% nonionic synthetic polymers along with their surface tension values (of surfactant-free polymer solutions). In this case there is no direct relation between the surface activity of the polymer and  $\tau_2$  values. This indicates that the interaction between these synthetic polymers and SDS is not governed by the hydrophobicity of the polymers alone. Rather, electrostatic and/or specific interaction between the surfactant headgroup and the polar group present in the polymer molecule could be determining the strength of interaction between SDS and these synthetic polymers.

#### Conclusion

The results presented here on the effect of a range of water-soluble polymers on the micellar stability of sodium dodecyl micelles suggest that the polymers that interact strongly with SDS decrease its micellar stability drastically. In fact this can be used as a tool to probe the interacting ability of various polymers with SDS in aqueous medium. For the nonionic cellulose derivatives, surface activity determines their ability to interact with SDS and consequently their ability to make micelles more labile. For synthetic polymers (vinylic) either

specific interactions or electrostatic interactions between polymer and SDS determine their ability to affect micellar stability. The decrease in the micellar stability on interaction with polymer is explained by the increased population of premicellar aggregates of SDS on binding with the polymers.

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