

# Effect of Polyethyleneoxide and Sodium Chloride Over the Micellization Behavior of Sodium Dodecyl Sulfate

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**ABSTRACT:** Micellization behavior of sodium dodecyl sulfate (SDS) and its mixture with polyethylene oxide (PEO) are investigated using surface tension and light scattering techniques. The data are presented and interpreted in a novel way, which provides more and reliable information about the interaction of the components. The concentration of SDS corresponding to the initiation of interaction with PEO ( $T_1$ ) and the saturation point ( $T_3$ ) are well identified in this way. It has been observed that the concentration span

between  $T_1$  and  $T_3$  is not much affected by the amount of PEO added. The detail investigation of data concludes that SDS and PEO interactions are in one to one ratio at molecular level and CMC decreases with the addition of salt to the system and the micelles become more compact. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1444–1448, 2009

**Key words:** PEO; SDS; electrolytes; micellization; dynamic light scattering; surfactants

## INTRODUCTION

Surfactants and water-soluble polymers are used together in many formulations and industrial processes to boost the properties of the surfactant by the addition of polymer.<sup>1–10</sup> This has greatly stimulated the interest in polymer/surfactant system and investigation of interactions among them has become the major issue in these days.<sup>2,3–13</sup> Neutral water-soluble polymers are considered to be less complicated than charged ones. Nevertheless, the interaction between neutral polymers and surfactants is less well understood and needs further investigation.<sup>14–20</sup> It is generally observed that the surfactants self-associate cooperatively at the so-called critical aggregation concentration (CAC). The CAC is usually lower than the critical micellization concentration (CMC) of the surfactant by a factor say between 1 and 10.<sup>11,12,20–22</sup> This is in contrast with polyelectrolyte/ oppositely charged surfactant systems, where the CAC may be 102–104 times lower than the CMC.<sup>22</sup> The strength of the interaction between a polymer and a surfactant can be characterized by the CAC/CMC ratio, even though it gives only a semiquantitative idea.<sup>23</sup> Polyethylene oxide (PEO) has high water solubility and unique applications in human life; hence, it is mostly investigated water-soluble polymer.<sup>24–26</sup> Its exceptional high water solubility and low-critical tempera-

ture is considered to be due to its conformation that allows a hydrating water molecule to bridge two ether linkages as shown in Figure 1.<sup>25–29</sup>

In this report, we have studied the extent and nature of interactions among PEO and surfactant and how these are affected by the addition of electrolytes. For this purpose, different techniques have been used and some new methods have been proposed for the determination of degree of interactions.

## EXPERIMENTAL SECTION

### Materials

PEO having average molecular mass 4000 g/mole was used for investigation. The surfactant and electrolyte used were sodium dodecyl sulfate (SDS) and sodium chloride, respectively. Both were obtained from E. Merck, Germany, being of analytical grade used without further purification. Deionized water was used as solvent, which had the conductance of 5–7  $\mu\text{S}$ .

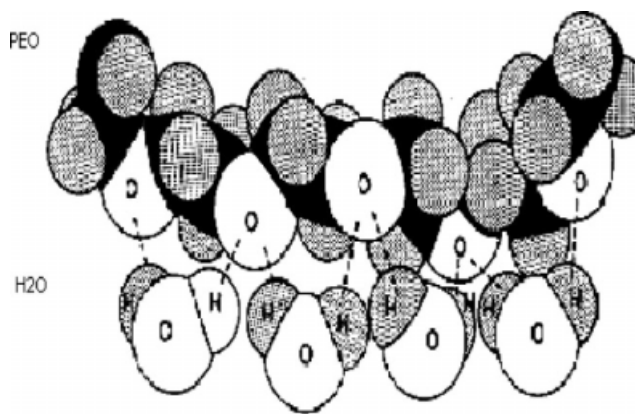
### Sample preparation

Known concentration of SDS, PEO, and NaCl was prepared in deionized water as a stock solution. Solutions of different concentration were obtained by diluting the stock solution.

### Surface tension measurement

The surface tension was measured using TE3 LAUDA tensiometer, supplied by LAUDA, Germany. All measurements were made sufficiently slowly so as to

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**Figure 1** Schematic representation of hydrated polyethyleneoxide, the dark black area showing the PEO, dotted circles are hydrogen atoms, and white circles are the oxygen atoms.

ensure equilibrium conditions. The measurements were made for different concentrations and at constant (25°C) temperature. The temperature was maintained using Ecoline Circulation Thermostat Model E 015T, Germany, which retained the temperature to  $\pm 0.01^\circ\text{C}$ .

#### Laser light scattering measurement

The aggregation behavior of PEO in water was studied by static and dynamic laser light scattering techniques. The measurement was made at different concentrations while temperature was kept constant. Before LLS measurements, all samples were filtered using a filter of 0.02  $\mu\text{m}$  and 0.25  $\mu\text{m}$  pore size for the solvent and solution, respectively. Instrument used for the purpose was DAWN EOS/ QELS supplied by Wyatt, USA, with helium-neon laser of 632.8 nm wavelength as light source. A cylindrical cell (SV) of 2 cm diameter was used for the purpose.

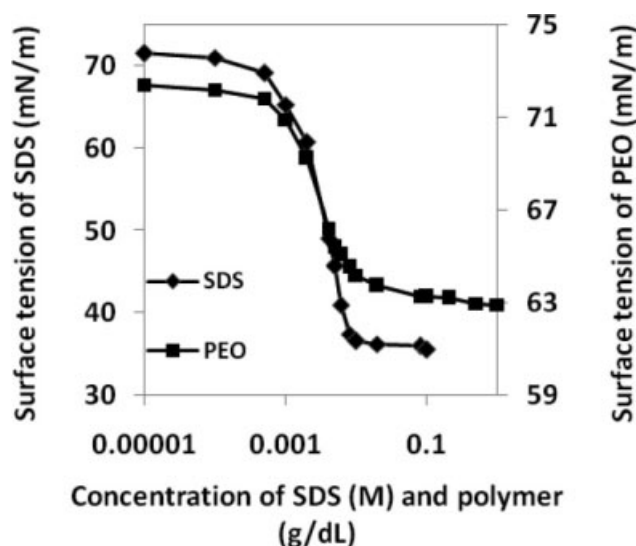
### RESULTS AND DISCUSSION

The surface tension of SDS and PEO obtained in water is depicted in Figure 2. The results show a typical trend expected for such systems. The addition of surfactants to the aqueous solution decreases the surface tension up to concentration called critical association concentration for pure substance ( $CAC_p$ ). Further addition of surfactants resulted in an abrupt decrease in surface tension. This decrease in surface tension continued up to critical micelles concentration (CMC) and further addition of surfactant did not affect the surface tension as expected. This phenomenon has been discussed and reviewed in detail by Taylor et al.<sup>11</sup> According to them it is due to accumulation of surfactant at the air–water interface and micellization. Further increase in concentration of surfactant does not alter the surface tension; how-

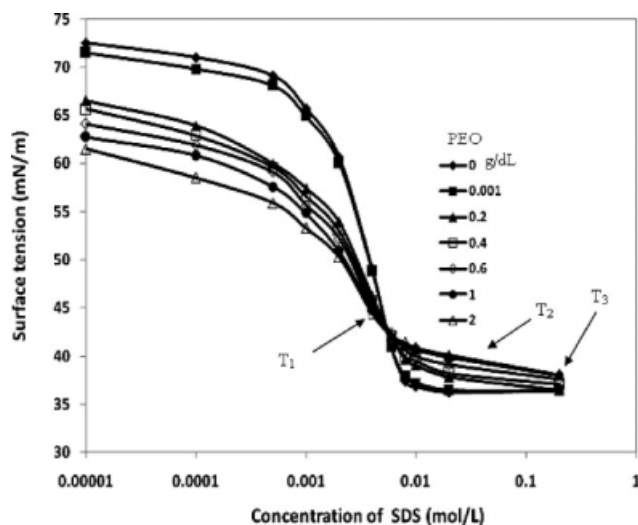
ever, it can increase size and change the shape of micelles. The same trend is observed by pure PEO; however, the decrease in surface tension and the span of concentration between  $CAC_p$  and CMC is small when compared with surfactant. This can be attributed to the longer chain (high molecular mass) and nonionic nature of PEO. The CMC obtained through Figure 2 is 0.008 mol/L and 0.01 g/dL for SDS and PEO, respectively. Because the average molecular mass of PEO is 4000 g/mole, hence CMC in terms of mol/L is  $2.5 \times 10^{-5}$ . It can be noted (Fig. 2) that although the CMC of PEO is less than SDS, it is more surface active and has significant impact over the surface tension. This may be due to the fact that SDS is ionic in nature and has great effect over  $\Delta G$  which is related to CMC through eq. (1). Furthermore, PEO enhances hydrogen bonding through interactions, as shown schematically in Figure 1.<sup>25–29</sup>

$$\Delta G = RT \log(\text{CMC}) \quad (1)$$

To see the combined effect of SDS and PEO over the surface tension of water, different amount of polymer was added (0–2%) to the SDS solution and the surface tension of the mixture was measured, which is plotted in Figure 3. The SDS being an anionic and PEO nonionic show weak interactions.<sup>26–28</sup> The difference in SDS pure and PEO-added system is due to PEO-surfactant interactions, which forms a complex structure. In the absence of polymer, the surface tension behavior of SDS is typical, showing a single break point at CMC (0.008M); however, by the addition of polymer two break points are observed, which are related to the beginning of surfactant binding to the polymer, called the CAC and the saturation point of the polymer by the surfactant, called polymer saturation point and labeled as  $T_1$ .<sup>11</sup>

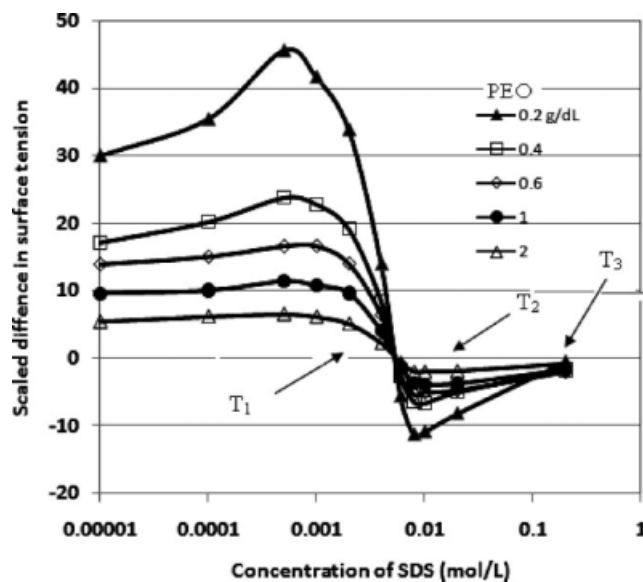


**Figure 2** Surface tension of SDS and PEO as a function of their concentration.



**Figure 3** Surface-active behavior of SDS in the absence and presence of PEO at 25°C.

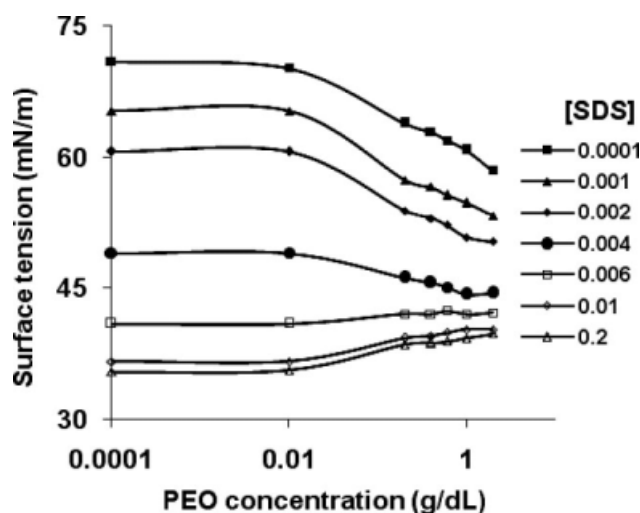
In the presence of polymer, the surface tension decreases, which is due to adsorption of surfactant molecules at the surface, and hence, the effect seems to be additive although there will be interactions among the polymer and surfactant molecules and these will be more pronounced at the surface.<sup>30-34</sup> This phenomenon continues until the polymer is saturated with surfactant and entire surface is covered with the surfactant molecules. With further increase in surfactant concentration, no distinct change in surface tension is observed and ultimately the surface tension of mixture becomes equal to that of surfactant. This point is marked as  $T_3$ . To identify these two points in explicit way, scaled difference in surface tension (surface tension of surfactant – surface tension of mixture)/polymer concentration) versus SDS concentration is plotted in Figure 4. It can be noted that this effect is not only well pronounced but also easy to identify as  $T_1$  and  $T_3$ . The surfactant concentration span among  $T_1$  and  $T_3$  does not change with polymer concentration indicating low interactions among polymer and surfactant, which is contrary to the observation made by Capalbi and La Mesa<sup>12</sup> for other systems. The curves also show that for lower polymer and surfactant concentration, the difference in surface tension is highest and it decreases with surfactant as well as polymer concentration. The comparison of Figures 2, 3, and 4 concludes that the concentration of surfactant corresponding to maximum difference in surface tension correspond to the  $CAC_p$  of surfactant, the concentration at which an accumulation at the surface begins. These results also conclude that when the polymer concentration is low the added surfactant gets adsorbed at the surface and reduces the surface tension; however, in case of high polymer concentration, the added surfactant gets adsorbed over the polymer



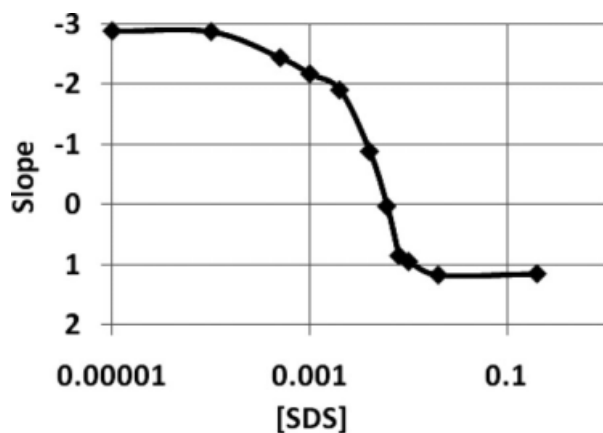
**Figure 4** Difference in surface tension of surfactant and mixture divided by concentration of polymer.

and shows little effect over the surface tension until it reaches to  $T_1$ , as stated before.<sup>25</sup>

The same data of surface tension have been plotted as a function of polymer concentration to understand the absorbance of surfactant and polymer molecules at the surface of water (Fig. 5). The data reveal that in case of low-surfactant concentration the surface tension decreases with the increase in polymer concentration, which means that almost all the polymer is adsorbed at the surface. However, if SDS is in high concentration the added polymer and SDS interact with each other and lower the concentration of SDS over the surface, which either decrease or increase surface tension of the system and the curves converge to a single point at a polymer concentration equal to



**Figure 5** Variation in surface tension of polymer-SDS mixture with respect to PEO concentration.

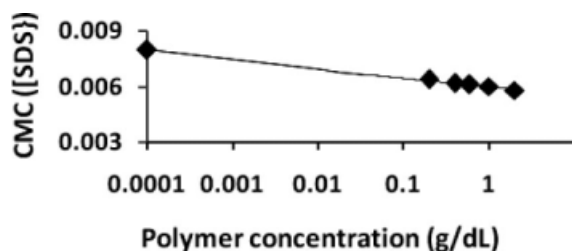


**Figure 6** Slope (=change in surface tension/log (change in concentration of PEO)) of the plots shown in Figure 5.

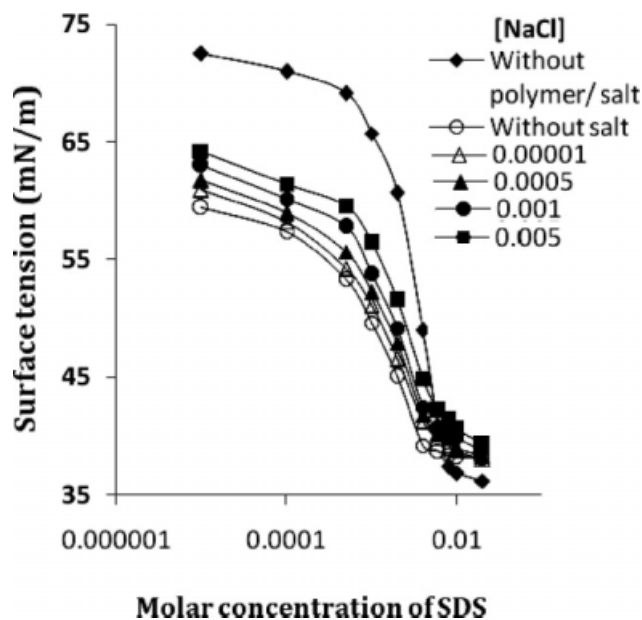
$0.008 \pm 0.001$  mol/L (not shown), which is located over a plot of SDS concentration equal to  $0.008$  mol/L (= CMC of pure SDS) having slope equal to zero. It probably means that the polymer–surfactant interactions at molecular level are in one to one ratio and not much affected by polymer concentration as is concluded from Figure 4. The slope of the curves is obtained and plotted in Figure 6. It can be seen that the value approaches to zero and the effect of added polymer is nullified as the SDS concentration equals to CMC. However, for SDS concentration higher than CMC, the slope becomes positive and increases with the concentration.

We have also calculated CMC from the data displayed in Figure 4 and plotted in Figure 7 as a function of PEO concentration, which decreases with the polymer concentration as concluded from Figure 3. This phenomenon is attributed to the decrease in dissolution of SDS with the addition of PEO.

The surface tension of mixture of SDS,  $0.6$  g/dL polymer, and NaCl is plotted in Figure 8. It is observed that the addition of electrolyte to polymer–surfactant solution increases the surface tension. This phenomenon can be explained through variation in electrostatic forces of the system as salt screens out the charges of the surfactant<sup>35</sup> resulting in a decrease in solubility and surface activity of SDS. This explanation is further supported by the decreases in CMC of



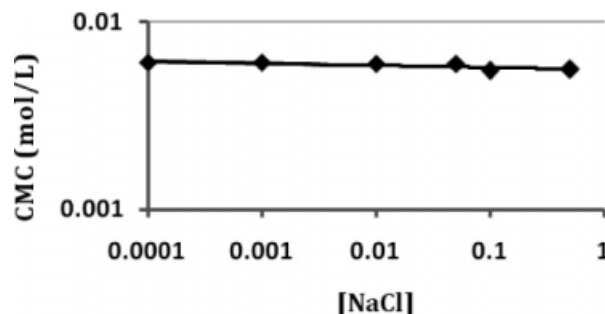
**Figure 7** CMC of the polymer–SDS mixture plotted against polymer concentration.



**Figure 8** Variation in surface tension of SDS solution containing different salt and fixed ( $0.6$  g/dL) polymer concentration.

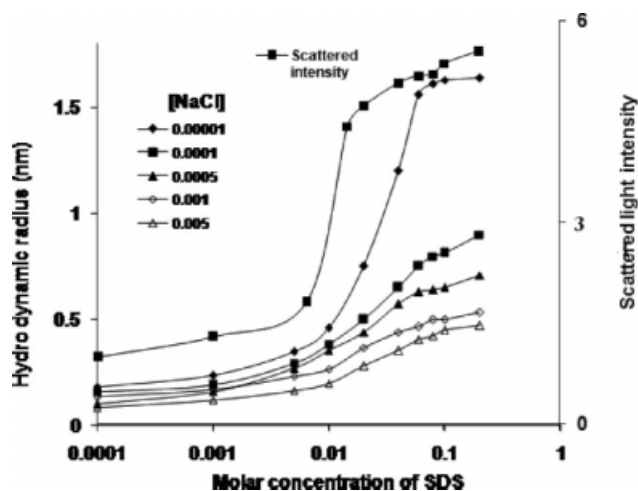
polymer–surfactant system with the increase in salt concentration (Fig. 9) as observed by others.<sup>1</sup>

The hydrodynamic size obtained through dynamic light scattering technique is plotted in Figure 10. It can be noticed that the hydrodynamic size is small and not much affected by the increase in SDS concentration in its lower concentration region. The hydrodynamic size increases very fast as the SDS concentration approaches to CAC ( $T_1$ ) or CMC due to micellization. Further increase in SDS leads to increase in size of micelles/aggregation number. This phenomenon leads to sharp change in size of micelles, and hence, the rate of change in micelles size decreases with the concentration when compared with earlier portion of concentration. This concentration corresponds to saturation point ( $T_3$ ). It concludes that the addition of SDS leads to change in conformation of the micelles rather than the size.<sup>21,22,35</sup> It may be noted from the figure that the size of micelles for a particular SDS concentration



**Figure 9** CMC of SDS as a function of sodium chloride concentration having  $0.6$  d/dL PEO.





**Figure 10** Hydrodynamic radius of micelles of SDS plus 0.6 g/dL PEO as a function of SDS and NaCl concentration. The scattered light intensity measured at  $90^\circ$  with respect to incident light of the same system having 0.0001M salt in it is also displayed.

decreases with the increase in the salt concentration, that can be attributed to the fact that the free ions of the salt compress the surfactant–polymer complex to smaller size as it screen out the charges and increases the polymer–surfactant interactions and decreases surfactant–water interactions. It can be, therefore, concluded that salt is responsible for decrease in CMC.<sup>21,35,36</sup> Figure 10 also shows static light scattered intensity for 0.0001M NaCl, fixed PEO concentration, and shows a similar trend with clear indication of  $T_1$  and  $T_3$  points.

## CONCLUSIONS

It has been shown that the data presented in terms of difference in surface tension provide better measurement of  $T_1$  and  $T_3$  points and offers more information. From the obtained results, it can be concluded that polymer–surfactant interactions at molecular level are most probably in one to one ratio. Both the techniques that are surface tension and light scattering measurement conclude the reduction in CMC of SDS by the addition of PEO and NaCl.

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