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ORIGINAL CONTRIBUTION

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# Aggregation of sodium dodecyl sulfate in poly(ethylene glycol) aqueous solution studied by $^1$H NMR spectroscopy

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**Abstract** $^1$H NMR self-diffusion coefficient, spin–spin relaxation and two-dimensional nuclear Overhauser enhancement spectroscopy measurements of sodium dodecyl sulfate (SDS) in poly(ethylene glycol) (PEG) aqueous solution show that SDS molecules start to self-aggregate at a concentration of 3.3 mM, which is well below the normal critical micellar concentration (cmc). SDS micelles are formed when the cmc is reached with PEG solubilized in their hydrophobic micellar cores.

**Keywords** Sodium dodecyl sulfate · Poly(ethylene glycol) · Interaction · $^1$H NMR · Self-diffusion coefficient · Spin-spin relaxation · 2D NOESY

## Introduction

The study of the interaction between sodium dodecyl sulfate (SDS) and poly(ethylene glycol) (PEG) in aqueous solutions has received great attention since Jones et al. [1] reported two discontinuities instead of one in the surface tension curve when SDS was added to a PEG solution of fixed concentration. The first discontinuity was attributed to the beginning of SDS binding with PEG, defined as the critical aggregation concentration (cac), and the second to the beginning of the formation of self-aggregated SDS micelles when PEG is completely exhausted, defined as $c_2$. Different methods (surface tension [2, 3], etc. [4]) were used to determine the molar ratio of SDS to PEG monomer units in the coaggregate at the second discontinuity. Meanwhile, intensive studies, especially by NMR methods.[3, 5, 6], concerning the structure of the coaggregate of PEG and SDS, i.e. the structure of the mixed micelle were reported. From the variation of the $^{13}$C chemical shift and relaxation measurements of SDS aqueous solution at a concentration of 97 mM with the variation of the PEG concentration, Cabane [3] suggested that PEG wrapped around the self-aggregated SDS micelles with some of the ethylene oxide units of PEG directly adsorbed on the hydrocarbon/water interface and most of the remaining units form loops in the solution. Using the NMR paramagnetic relaxation method, Gao et al. [5] determined the apparent distribution coefficient of poly(ethylene oxide) (PEO) in SDS micelles and in the solution at a total SDS concentration of 240 mM and suggested from the relaxation behavior of the polymer protons that PEG resides in the SDS micelles. Gjerde et al. [6] showed that PEG penetrates into the interior of the SDS micelles by a two-dimensional nuclear Overhauser enhancement spectroscopy (2D NOESY) experiment on a solution of 15.3 mM SDS and 2 gl$^{-1}$ PEG.[6] A cross-correlation peak between the protons of PEG and the methylene protons of the hydrophobic hydrocarbon chain of SDS was observed. However, there are also other suggestions for the structure of the coaggregate, such as a linear necklace [7] and a swollen cage [8], which seem to be less possible. It is obvious from the studies mentioned that attention was mostly paid to the interaction of PEG with SDS at concentrations of SDS well above its critical micellar concentration (cmc). Zana et al. [9] observed that SDS starts to aggregate on the polymer strand in POE aqueous solution well below its normal cmc, and showed that the aggregation number of this aggregate gradually increases with the total SDS concentration. The behaviors of PEG and SDS in dilute solution of SDS (below its cmc) have been studied by Gjerde et al. [10], recently, by NMR self-diffusion coefficient and relaxation measurements, etc. However, the study of the interaction between SDS and the polymer was not attacked at a molecular level. All the studies mentioned were based on the assumption that SDS starts to interact with PEO at the cac, the first discontinuity, although there was not any direct evidence for the interaction between SDS and the polymer at a molecular level. What is the structure of the SDS–PEO coaggregate if it really exists? It seems necessary to get deeper insight into the interaction between these two components in dilute solutions of SDS (below its cmc). Our successful characterization of the hydrophobic and hydrophilic chain packing of various types of surfactant micelles[11, 12] shows that the combination of $^1$H NMR relaxation with the 2D NOESY experiment is an efficient approach to the study of self-aggregation of surfactant molecules. The same method was used to elucidate the interaction between surfactant and partially hydrolyzed poly(acrylamide) and the interaction between different kinds of surfactants [13, 14]. We expect that the use of this method with a comprehensive study of the behaviors of both the polymer and the surfactant will give a reasonable description of the interaction between SDS and PEG in the concentration range from lower than the first to higher than the second discontinuities.

## Experimental

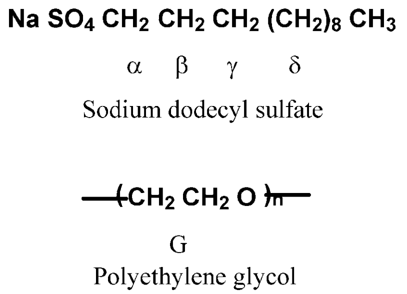
SDS was the electrophoresis reagent of Acros Co.,USA, and the PEG4000 was the chromatographic pure product of the Shanghai Chemical Plant. Its molecular weight is 4,000 Da. $D_2O$ (99.6% deuterated) was produced by the Beijing Chemical Factory of China. The chemicals were used as received without any purification. All the $^1$H NMR measurements were performed using a Bruker ARX-500 with a $^1$H frequency of 500.13 MHz. A Carr–Purcell–Meiboom–Gill pulse sequence was used for spin–spin relaxation time ($T_2$) measurements at 25 °C. Thirty-two accumulations were normally collected. $D_2O$ was used as a solvent instead of water in order to weaken the water signal. Meanwhile, a presaturation method was used to further suppress the proton signal of the solvent. The self-diffusion coefficients were measured using the longitudinal Eddy-current delay with bipolar pulse pair sequence [15]. 2D NOESY experiments were performed with the standard three-pulse sequence [16]. A mixing time of 1.5 s was chosen for systems at concentrations of 3.3 and 4.8 mM SDS and to avoid spin diffusion effect a mixing time of 600 ms was used for the solutions with 17.3, 34.6 and 69.2 mM SDS with the addition of 2 gl$^{-1}$ PEG, respectively, and 64 runs were collected.

## Results

Little information could be extracted from the chemical shift variations of the protons of either SDS and PEG measured in this study or of $^{13}$C [3] because they are too small. However we can make use of the dynamic properties of the protons in this system to elucidate the interaction between SDS and PEG. We have shown that the self-diffusion coefficient, $D$, the spin–lattice and the spin–spin relaxation times ($T_1$, $T_2$) of the hydrophobic methylene protons near the polar head of the surfactant (sodium dodecyl sulfonate, cetyltrimethylammonium bromide and Triton X-100) decrease abruptly upon micellization [17]. The existence of turning points in the variation in these parameters with the concentration of these surfactants is an indication of their self-aggregation. The turning points of these parameters for other surfactant molecules may also show sharp changes in their environments.

The chemical formulas of SDS and PEG with proton numbering are given in Fig. 1.

The variation in the self-diffusion coefficientsof SDS (average values of the self-diffusion coefficients measured for each of the resonance peaks of SDS) and PEG in the mixed solutions over a large range of concentrations of SDS (from 2.4 to 69.2 mM) with and without the addition of PEG (2 gl$^{-1}$) is shown in Fig. 2. The value of D of SDS aqueous solution free of PEG remains constant until the concentration of SDS reaches 6.5 mM, then it decreases abruptly and approaches a constant value after the concentration reaches 17.3 mM. In the presence of PEG in the solution $D$ of SDS starts to decrease after the concentration of SDS reaches 3.3 mM and gradually decreases until a sharp turning point occurs at 17.3 mM. However, the $D$ value of PEG


$$\underset{\phantom{\alpha}}{\mathrm{Na\,SO_4}}\;\underset{\alpha}{\mathrm{CH_2}}\;\underset{\beta}{\mathrm{CH_2}}\;\underset{\gamma}{\mathrm{CH_2}}\;\underset{\delta}{\mathrm{(CH_2)_8}}\;\mathrm{CH_3}$$

$$-\!\!\left(\underset{G}{\mathrm{CH_2\,CH_2\,O}}\right)_{\!n}\!\!-$$

**Fig. 1** Chemical formulae of sodium dodecyl sulfate (*SDS*) and poly(ethylene glycol) (*PEG*) with proton labeling stays constant at 13 mM SDS. A turning point also exists at 17.3 mM SDS.

The variation in the $T_2$ with the concentration of SDS for the $\beta$ protons of SDS with and without the addition of PEG (2 $gl^{-1}$) and that of PEG protons are shown in Fig. 3. The spin–spin relaxation time of the $\beta$ protons of SDS remains unchanged until the concentration of SDS reaches 6.5 mM, then it decreases abruptly and approaches a constant value after the concentration reaches 17.3 mM. In the presence of PEG the $T_2$ of the $\beta$ protons starts to decrease earlier (3.3 mM) and a sharp turning point at a SDS concentration of 17.3 mM follows. However, the $T_2$ of the PEG protons remains unchanged up to 6.5 mM SDS, and decreases abruptly to 17.3 mM, then slowly approaches a constant value. The tendencies of the $T_2$ versus the SDS concentration for SDS protons other than the $\beta$ protons are similar and are presented in Table 1.

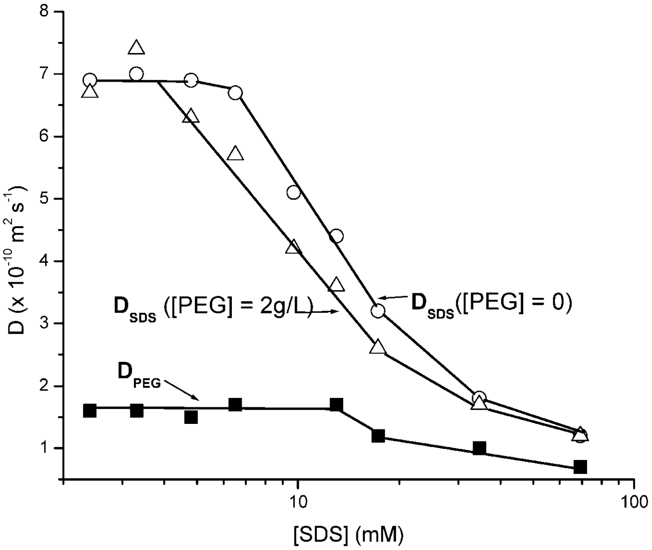


**Fig. 2** Self-diffusion coefficient ($D/\times10^{-10}$ $m^2s^{-1}$) dependence of SDS and PEG molecules on the concentration of SDS in solutions without and with the addition of 2 $gl^{-1}$ PEG

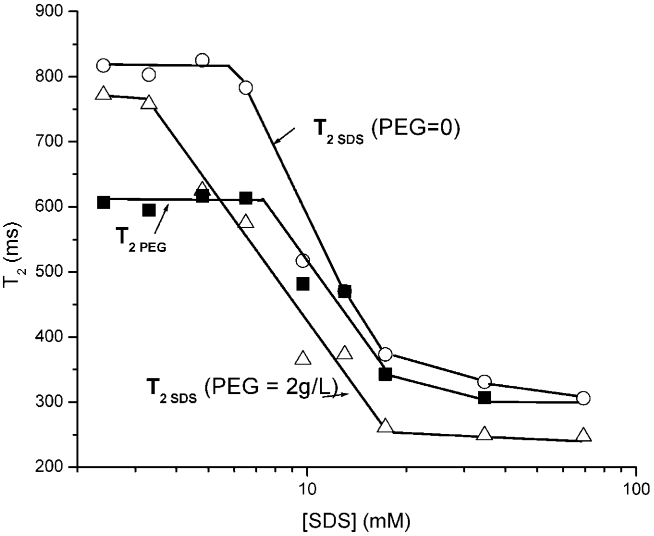


**Fig. 3** Spin–spin relaxation time ($T_2$/ms) dependence of protons of SDS and protons of PEG on the concentration of SDS in solutions without and with the addition of 2 $gl^{-1}$ PEG

The 2D NOESY spectra of SDS at concentrations of 3.3, 4.8, 17.3, 34.6 and 69.2 mM with the addition of 2 $gl^{-1}$ PEG are given in Fig. 4a–e, respectively. Cross-correlation between PEG protons and the $\delta$ protons of SDS are found for the systems with SDS at concentrations of 17.3, 34.6 and 69.2 mM with the addition of PEG (Fig. 4c–e, respectively).

## Discussion

It is obvious from Figs 2 and 3, respectively, that the $D$ and $T_2$ values of the $\beta$ protons of SDS remain unchanged up to 6.5 mM SDS in the PEG-free solution. Abrupt turning points of both the $D$ and $T_2$ values occur over the concentration range from 6.5 to 17.3 mM. These are typical micellization curves for solutions of various types of surfactants[17]. The plateaus of the diffusion coefficient and of the $T_2$ of SDS resemble the monomer state at concentrations below its cmc and the remarkable turning points show the micelle formation when the concentration reaches the cmc. The size of the micelle is more than 60 times larger than a SDS free molecule. This causes a significant decrease in the self-diffusion coefficient. The hydrophobic chain of the SDS molecules involved in the micellar core are densely packed, resulting in an increase in the dipolar interaction between protons attached to the hydrocarbon chain, and consequently, a decrease in $T_2$. No sharp turning points at the cmc, as in the case of the surface tension curve, can be obtained for NMR curves, since the observed NMR parameters are the weighted averages of all of the species, such as the monomers and the micelles. The further increase in the total concentration of SDS results in an increase in the number of micellar SDS molecules. This makes the contribution of the monomer molecules to the weighted average (observed) value less and less important. So, the $D$ and $T_2$ values decrease slowly after the cmc is reached.

The $D$ and $T_2$ dependences on the concentration of SDS in the presence of PEG show different characteristics from those of the PEG-free solution. Both these values of SDS in the PEG aqueous solution start to decrease significantly earlier (3.3 mM) than in the PEG-free solution (6.5 mM) and then uniformly decrease with the increase in the total concentration of SDS. After a significant turning point at 17.3 mM they approach constant values almost equal to those in the PEG-free solution. The start of the decrease in the self-diffusion

**Table 1** $^1$H spin–spin relaxation times ($T_2$/ms) of α, γ, δ and $CH_3$ protons of sodium dodecyl sulfate (*SDS*) in aqueous solutions over a wide range of concentrations of SDS without and with the addition of 2 gl$^{-1}$ PEG

| SDS concentration (mM) | α | | γ | | δ | | $CH_3$ | |
|---|---|---|---|---|---|---|---|---|
| | Without 2 gl$^{-1}$ PEG | With 2 gl$^{-1}$ PEG | Without 2 gl$^{-1}$ PEG | With 2 gl$^{-1}$ PEG | Without 2 gl$^{-1}$ PEG | With 2 gl$^{-1}$ PEG | Without 2 gl$^{-1}$ PEG | With 2 gl$^{-1}$ PEG |
| 2.4 | 801 | 639 | 890 | 865 | 1,001 | 968 | 1,708 | 1,734 |
| 3.3 | 712 | 596 | 869 | 858 | 980 | 952 | 1,763 | 1,627 |
| 4.8 | 661 | 519 | 913 | 692 | 1,001 | 791 | 1,638 | 1,372 |
| 6.5 | 654 | 444 | 849 | 673 | 930 | 752 | 1,589 | 1,269 |
| 9.7 | 431 | 367 | 601 | – | 608 | 424 | 1,129 | 681 |
| 13.0 | 382 | 329 | 522 | – | 597 | 418 | 996 | – |
| 17.3 | 222 | 262 | 395 | 277 | 446 | 338 | 752 | 692 |
| 34.6 | 301 | 258 | 313 | 235 | 387 | 295 | 697 | 601 |
| 69.2 | 297 | 243 | 315 | 259 | 353 | 296 | 679 | 581 |

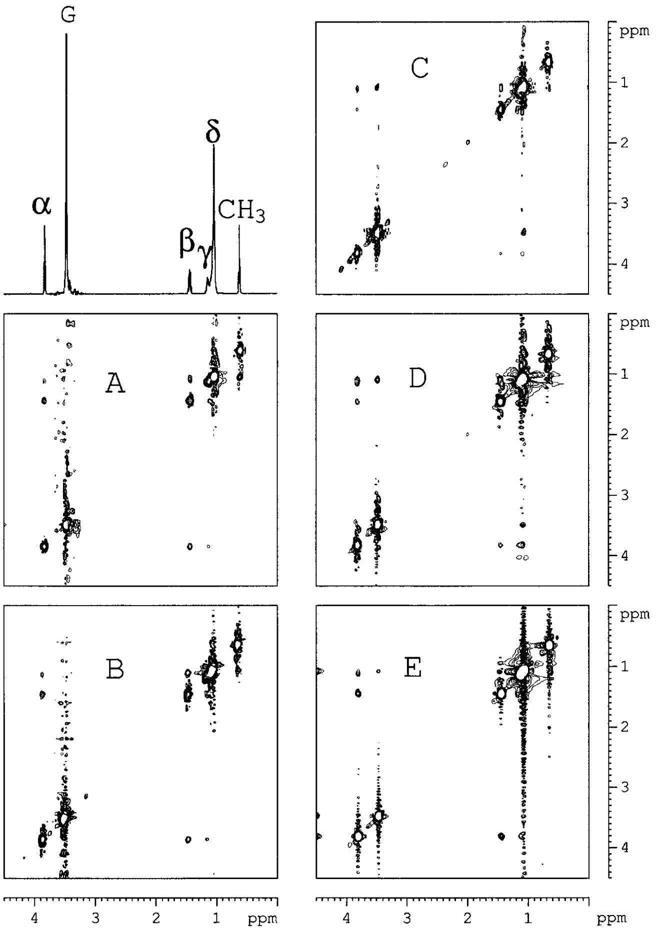


**Fig. 4** Contour plots of the 2D NOESY experiments of SDS in PEG (2 gl$^{-1}$) aqueous solutions at different concentrations of SDS: **a** 3.3 mM, **b** 4.8 mM, **c** 17.3 mM, **d** 34.6 mM and **e** 69.2 mM

coefficient and the spin–spin relaxation times of SDS implies that SDS molecules begin to aggregate in a PEG aqueous solution; however this does not indicate that the aggregated SDS molecules should start to combine with PEG. It is analogous to the case of the surface tension curve, where the turning point, cac, only gives the information that the concentration of the free SDS monomers starts to become lower than the total concentration but it cannot tell how the rest of the SDS molecules are aggregated, i.e. whether they are bound to the polymer or self-aggregated. The further decrease of these two parameters should be attributed to an increase in the aggregate size, as shown by Zana et al. [9], and to the increase in the degree of the packing of the hydrophobic chain with the increase in the total concentration of SDS. After the normal cmc is reached, SDS micelles are formed and the $D$ and $T_2$ values decrease slowly as in the case of PEG-free solution.

It is evident from these observations that the variations of the self-diffusion coefficient and the spin–spin relaxation time of SDS with the SDS concentration in the PEG solution can only give the information that the presence of PEG causes the SDS molecules to start to aggregate earlier. We expect that the measurement of $D$ and $T_2$ of PEG in the solution will give further insight into the interaction between SDS and PEG. If the aggregation of SDS in the solution in a concentration range between the cac and the cmc is the association of SDS with PEG, the $D$ and $T_2$ values of the PEG protons should also show a response. Unfortunately, they stay unchanged and show definite decreases only after the cmc of SDS is reached. The variations of these two curves are almost parallel to those of SDS in the PEG-free solution. However, the difference between the self-diffusion coefficients of uncombined PEG ($1.7\times10^{-10}$ m$^2$s$^{-1}$) and that of combined PEG ($0.9\times10^{-10}$ m$^2$s$^{-1}$) seems to be too small to give high enough sensitivity as in the case of SDS (from $6.5\times10^{-10}$ m$^2$s$^{-1}$ for the monomer to $1.2\times10^{-10}$ m$^2$s$^{-1}$ for the micelle) to decide whether there is any changes in the self-diffusion coefficient of PEG in this range of concentration of SDS. However, the difference between the $T_2$ values of the uncombined PEG protons (607 ms) and the combined PEG protons (302 ms) is not so small compared with the difference between those of the monomer (772 ms) and the micellar (247 ms) SDS protons. Although the population of the uncombined PEG monomer unit seems to change slightly, the influence of the SDS association with the PEG monomer unit on the $T_2$ value sounds quite large. A monomer unit of PEG with a mass of 44 becomes a unit with a mass of 332 after its association with one molecule of SDS, because the $T_2$ is influenced by slow molecular motions, and these motions are a function of the size of the molecular aggregate. That is why we see a remarkable difference in the $T_2$ of the combined and uncombined PEG (303 ms) in Fig. 3. Therefore, the sensitivity in the $T_2$ versus SDS concentration curve should be enough to draw the reliable conclusion that SDS molecules are self-aggregated in aqueous solutions at concentrations in the range between the cac and the cmc. The abrupt decrease in the $D$ and $T_2$ values of PEG by the further increase of the total concentration of SDS above its cmc shows that PEG is associated with the SDS micelles.

The spin–spin relaxation study shows that PEG is unaffected by SDS in aqueous solution in a concentration range of SDS from above the cac to below the cmc. Direct evidence for the space relationship between SDS molecules and the PEG polymer chains will help to confirm the existence of the interaction. This can be achieved by performing the 2D NOESY experiment to show the near vicinity of protons in different kinds of molecules [18]. Contour plots of the 2D NOESY spectra for the mixed solutions over a wide range of concentrations of SDS show that cross-peaks among the SDS protons evolved even in the dilute solution (3.3 mM) of SDS in the presence of PEG, but that no cross-peaks between any SDS protons and those of PEG could be found in solutions at concentrations of 3.3 (Fig. 4a) or 4.8 mM (Fig. 4b) SDS (above the cac and below the normal cmc), although definite cross-peaks exist between the $\delta$ protons of SDS and the PEG protons for solutions at concentrations of 17.3, 34.6 and 69.2 mM SDS (Fig. 4c–e, respectively) where the cmc is reached. These facts suggest that SDS molecules are self-aggregated at concentrations between the cac and cmc and that the PEG protons are near the $\delta$ methylene protons of SDS micelles in solutions at concentrations above the normal cmc of SDS, i.e. solubilization of PEG into the SDS micelles occurred. The absence of cross-correlation peaks between any protons of SDS and those of PEG in solutions at SDS concentrations of 3.3 and 4.8 mM indicates that the protons of SDS are far apart from those of the PEG protons in these solutions, because the appearance of the correlation cross-peaks is the result of the dipolar interaction of proton pairs which are separated by less than 5 Å in space. It is difficult to imagine that the two species are interacting if they are far apart from each other. The intensity of these cross-peaks depends not only on the distances of the interacting protons but also on the number of these proton pairs of interest. It is evident that 3.3 mM SDS in the PEG solution is sensitive enough to observe the cross-peaks between the $\alpha$ and the $\delta$ SDS protons (Fig. 4a) which should originate from the intermolecular interaction, i.e. the self-aggregation of SDS molecules, because the intramolecular nuclear distance between these two protons is far greater than 5 Å. Cross-peaks between the aggregated SDS protons and those of PEG should also be observed in the solution at a concentration of 4.8 mM SDS, if there is any interaction between the SDS molecules and PEG because the number of PEG protons is larger than that of the $\alpha$ protons of SDS. Besides, cross-peaks between SDS protons and those of PEG were not observed either even in the solution with a concentration of 6.5 mM SDS (below the cmc) and 4 $\mathrm{gl}^{-1}$ PEG (not shown here).

The $^1$H $T_2$, 2D NOESY and self-diffusion coefficient measurements for both PEG and SDS in the mixed solution over a wide range of SDS concentrations could not confirm the existence of the interaction between SDS and PEG below the normal cmc of SDS, while there is evidence for the self-aggregation of SDS when its concentration is above the cac and below the cmc. PEG is involved with the SDS micelles when the normal cmc is reached. With the increase of the total concentration of SDS more and more SDS micelles are formed and less and less PEG will participate in each SDS micelle because the exchange rate of the molecules in different environments is fast in the solution. It is difficult to imagine that PEG molecules saturate some of the SDS micelles and leave the other micelles unsolubilized when SDS is in excess. It seems that the $c_2$ will not be easily detected.

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