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ORIGINAL CONTRIBUTION

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Interaction between poly(ethylene oxide) and sodium dodecyl sulfonate as studied by surface tension, conductivity, viscosity, electron spin resonance and nuclear magnetic resonance

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Abstract The aggregation of sodium dodecyl sulfonate (AS) in aqueous solution containing various amounts of poly(ethylene oxide) (PEO) has been investigated by different experimental techniques. The experimental techniques include surface tension, conductivity, viscosity, electron spin resonance (ESR) and nuclear magnetic resonance (NMR). The critical aggregate concentration of AS on polymer strands as well as the concentration where the polymer becomes saturated with surfactant has been determined. Both ESR and NMR results indicate that the AS–PEO complex forms a more "open" structure and that PEO may penetrate into the interior of the micelles.

Key words Poly(ethylene oxide) · Sodium dodecyl sulfonate · Critical aggregation concentration · Polymer saturation

Introduction

The interaction of surfactants with water-soluble polymers has been studied for many years, due to the application of mixed surfactant/polymer systems in various fields [1]. Most of the studies published on surfactant–polymer interactions in aqueous solution have been for a neutral polymer and an anionic surfactant. Several reviews on the topic have also been published [2, 3]. Some water-soluble uncharged polymers, such as poly(ethylene oxide) (PEO), poly (vinylpyrrolidone) (PVP), hydrophobically modified polyacylamide, (ethylhydroxyethyl cellulose), etc., interact with surfactants in aqueous solution and give the systems special rheological properties [4] and biological phenomena involving surfactants and proteins such as the inactivation of bacterial metabolism by synthetic detergents [5]. It is well known that the combination of alkyl sulfonate with polymer has been applied in cosmetics, paints and tertiary oil recovery. In tertiary oil recovery the combination of surfactants and polymers has been widely used to control the mobility characteristics of polymer buffers. Therefore, in order to enhance the efficiency of the micellar/alkaline/polymer chemical flooding, how the surfactants interact with polymers must be understood so this chemical system can be designed properly for various crude oils.

So far most studies relate to the interactions between nonionic polymer (PEO, PVP) and ionic surfactants, particularly with sodium dodecyl sulfate (SDS). A variety of experimental techniques have been used, including surface tension [6], conductivity [7], viscosity [8], dye solubilization [9], neutron and light scattering [10], fluorescence [11], calorimetry [12], nuclear magnetic resonance (NMR) [13] and electron spin resonance (ESR) [14].

For SDS–PEO systems, the characteristics of the interaction have been investigated extensively. At constant polymer concentration and increasing amounts of SDS, two critical concentrations, viz., the critical aggregation concentration (cac) and c_2 of the surfactant appear. The cac represents the concentration at which interaction between surfactant and polymer first occurs, and c_2 represents the concentration at which the polymer becomes saturated with surfactant. At the cac the surfactant forms micellelike aggregates and clusters on the polymer [15]. Jones [16] has demonstrated that the cac is only weakly dependent on the amount of polymer in solution. The concentration of surfactant for "aggregate" formation is mainly a function of surfactant concentration for a particular polymer. On the other hand, the values of c_2 are directly proportional to the polymer concentration; at this point, the SDS molecules can either be free monomers in water, bound to the polymer as surfactant aggregates, or start to reside in normal micelles. Several mechanisms [17] for the formation of the polymer–surfactant complex have been proposed, which include

1. A reduction in the hydrocarbon/water contact area of the alkyl chains of the dissolved surfactant.
2. Ion-dipole interaction between the polymer and the surfactant head groups.
3. A hydrophobic interaction between the polymer and the hydrocarbon of the surfactant.

So it is expected that the effect of the surfactant structure on the organization of molecules in the self-assembly is of interest.

As already mentioned, the studies on the interaction between alkyl sulfonate and polymer are very important, but the investigation of the variation of the surfactant structure has been limited. Although alkyl sulfonate is a typical kind of anionic surfactant and is widely used in Chinese enhanced oil recovery, to our knowledge there are few reports on the interaction between alkyl sulfonate and polymers.

The work of Tokiwa and Tsujii [18] clearly shows that sodium alkylbenzene sulfonate interacts with PEO in much the same way as SDS does. In our work, the structure of the surfactant–polymer complex is studied by various methods, and sodium dodecyl sulfonate (AS) has been used because it is very similar to SDS in many physicochemical properties, such as the critical micelle concentration (cmc) and the micelle aggregate number [19]. Its structure is, however, very different from SDS, so in order to explore the nature of the interaction between AS and PEO, we compare the behavior of the interaction between SDS or AS with PEO and determine whether the structure difference between AS and SDS can lead to a different mechanism for the formation of the surfactant–polymer complex. We expect that this study will serve as a useful basis for analyzing systems containing alkyl sulfonate and polymer, and will provide a clue for the formulation design for detergents, cosmetics and chemical flooding.

Experimental

Materials

As (purity better than 99%) was obtained from the Chemical Reagent Company, Beijing, China. Before use it was recrystallized 3 times from a mixed solvent of water and ethanol (water:ethanol = 1:9 v/v). PEO with an average molecular mass of 20,000 and of a quality for gas chromatography was obtained from Merck. D_2O (99.95 atom% isotopic purity) was purchased from the Chemical Reagent Factory, Beijing, China. The Department of Chemistry, Lanzhou University, supplied the spin probe, C_{12}-Tempo (4-dodecanoyloxyl-2,2,6,6-tetramethyl-piperdine-1-oxyl). Its purity was analyzed and was confirmed to satisfy all experimental requirements.

Methods

Surface tension

The surface tension was measured using a model CBVP-A3 tensiometer (Kyowa-kaimenkagaku Co). This method was based on the principle of the Wilhelmy plate. Water was distilled 3 times. The surface tension of the water at 298 K was taken to be 71.6 dyn/cm.

Conductivity measurement

The conductivity measurements were carried out on a DDS-11D conductometer with platinum electrodes, manufactured by the Shanghai Leici instrument factory, Shanghai, China. The solution was contained in a double-walled glass vessel thermostated at 40 ± 0.2 °C. A DJS-1 conductivity cell (with a constant of $1.01\ cm^{-1}$) was used in all the measurements.

The specific conductivity was plotted versus SDS concentration and the slopes obtained both above and below the cac (cmc for AS in water without polymer) and c_2 were found by the use of linear regression. In the experiments, the conductivity was measured by keeping the polymer concentration constant. In another series of measurements, the conductivity was measured at constant AS concentration and increasing PEO concentration. All experiments were performed without salt. The specific conductivity was 2×10^{-7} S/cm for pure water.

Viscosity

The viscosity measurements were carried out with a Ubbelohde viscometer. The apparatus was thermostated at 40 ± 0.2 °C and the reproducibility of the flow time was 0.05%. All solutions were prepared by weight with distilled, deionized and degassed water.

Electron spin resonance

The ESR measurements were performed on a Varian E-115 X-band spectrometer. All samples for the ESR measurements contained 1.2×10^{-4} M C_{12}-Tempo and were deoxygenated with nitrogen before measurement.

^{13}C NMR spectra

All samples for the ^{13}C NMR measurements contained D_2O and a trace of sodium(trimethylsilyl)-1-propane sulfonate. The latter was used as the internal reference. The numbering of the carbon atoms of AS is given as follows:

$$Na^{+}\ ^{-}SO_3\text{-}\overset{1}{CH_2}\text{-}\overset{2}{CH_2}\text{-}\overset{3}{CH_2}\text{-}(CH_2)_6\text{-}\overset{10}{CH_2}\text{-}\overset{11}{CH_2}\text{-}\overset{12}{CH_3}$$

Results

Surface tension

The surface-tension method was applied to a mixture of a highly surface active species, the surfactant, and a feebly surface of active species, the polymer, because of the simplicity of this method. The effect of PEO on the surface tension of AS is shown in Fig. 1. In the presence of different PEO concentrations, two critical surfactant concentrations (cac and c_2) are found. The first break at c_{AS}(AS concentration) = cac < cmc, is generally considered as the onset of the binding of AS onto the polymer. The second one at $c_{AS} = c_2 >$ cmc, is assumed to correspond to the polymer saturation in AS. They exhibit the features described above for SDS–PEO [7]. The first critical concentration decreases with increasing polymer concentration (c_W) as shown Fig. 1. On the other hand, c_2 is an increasing function of c_W. From Fig. 1, cac and c_2 are obtained at two polymer concentrations, and they are listed in Table 1.

Figure 2 shows that the addition of PEO to an AS micellar solution (0.02 M) results in an increase in the surface tension. This means that at low polymer concentration, AS may interact with PEO, which leads to a decrease in surfactant monomer concentration; however, at high c_W values, the surface tension remained unchanged, so the surfactant monomer concentration remains constant, and the polymer does not absorb significantly on the surface.

Conductivity

Conductivity was used extensively to study the interaction between nonionic polymers and ionic surfactants. In an aqueous solution of surfactant, the micellization is revealed by a break in the plot of the specific conductivity, κ, as a function of concentration, as shown in Fig. 3. In the system with only AS and water, but no added PEO, two linear regions appear. The intercept is a normal cmc, 9.6×10^{-3} M, in agreement with the result of the surface-tension method (Table 1). The conductivity of AS with PEO added shows three linear regions connected by two breakpoints. The first break is taken to be the cac, and the second one is regarded as the concentration c_2. The cac and c_2 values thus determined are also presented in Table 1 for various polymer concentrations.

The specific conductivity is plotted versus AS concentration and the slopes obtained both above and below the cac (cmc for AS in water without polymer)

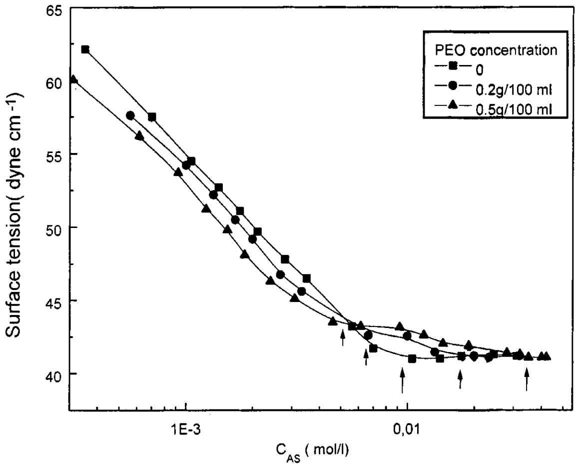


Fig. 1 Surface tension/concentration plot of sodium dodecyl sulfonate (*AS*) in the presence of poly(ethylene oxide) (*PEO*) at various concentrations

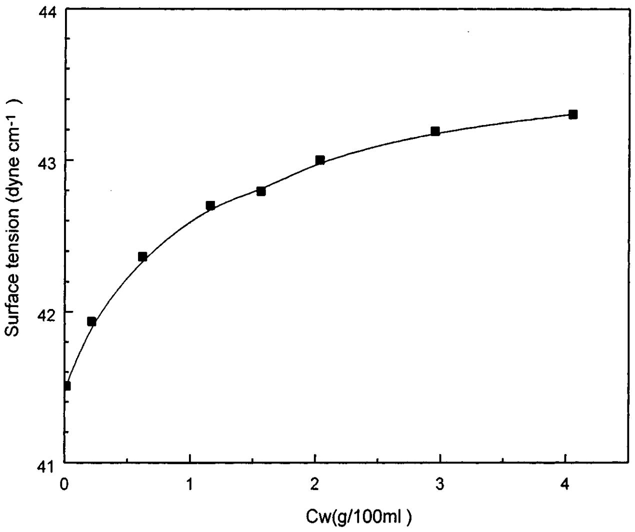


Fig. 2 Variation of surface tension of an AS (0.02 M) micellar solution versus the concentration of PEO added

Table 1 The critical aggregation concentration (*cac*) and c_2 values (M/10^3) of sodium dodecyl sulfonate in the presence of poly(ethylene oxide) (*PEO*) at various polymer concentrations determined by conductivity, surface tension and viscosity

Experimental technique	No polymer cmc	PEO concentration, c_W (g/100 ml)							
		0.2		0.4		0.5		1.0	
		cac	c_2	cac	c_2	cac	c_2	cac	c_2
Surface tension	9.1	6.0	14.5	–	–	4.9	34.2	–	–
Conductivity	9.6	6.3	14.2	5.5	25.4	4.8	33.8	5.0	42.5
Viscosity	9.8	6.0	14.6	5.3	25.7	4.5	34.6	5.1	44.5
Average (0.2)	9.5	6.1	14.4	5.4	25.5	4.6	34.3	5.3	43.0

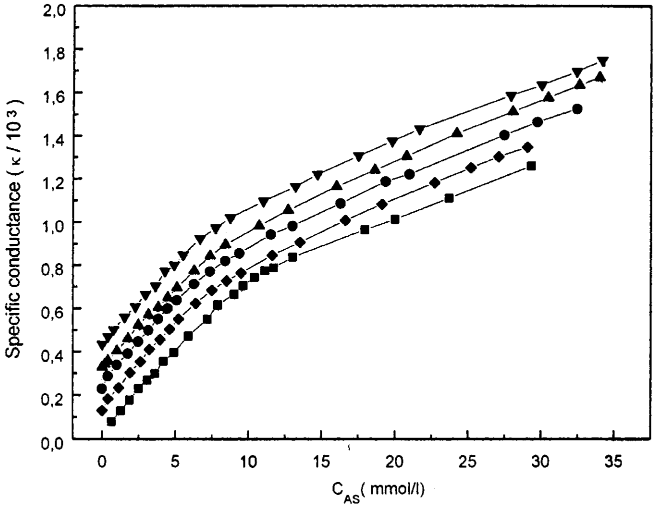


Fig. 3 Variation of the specific conductivity as a function of different AS concentrations. From *bottom* to *top*: c_W = 0, 0.2, 0.4, 0.5 and 1.0 g/100 ml. All the curves start at the origin. They have been shifted for better readability

and c_2 are found by use of linear regression. The slope ratio is taken as the degrees of ionization α_1 and α_2, which represent the degrees of ionization of bound polymer and of ordinary micelles in a polymer solution, respectively [15]. The ratio of the slope in the second region of the conductivity plot to that in the first region up to the cac is defined as α_1, and α_2 is the ratio of the slope in the third region of the conductivity plot to that in the first region up to the cac. The α_1 and α_2 values are listed in Table 2.

The results obtained when c_{AS} is kept constant, and c_W is increased are shown in Fig. 4. It is observed that when c_{AS} is close to the cmc, the addition of PEO induces a slight loss of conductivity. On the other hand, when c_{AS} is higher than the cmc, the conductivity increases at lower c_W values and then passes through a maximum.

Viscosity

The curves of the variation of the flow time versus c_{AS} in the absence and presence of PEO were obtained from viscosity measurements. The curves (the raw data are not shown) exhibit a breakpoint (cmc) for pure AS in water, and exhibit two breakpoints in the presence of PEO, just as for the conductivity and surface-tension results. The first break corresponds to the cac and the second one is c_2, and the values are listed in Table 1. These values are close to the cac and c_2 determined by surface-tension and conductivity measurements, and represent the same phenomena.

Table 2 The degrees of ionization, α_1 and α_2, found from conductivity measurements

PEO concentration (c_W, g/100 ml)	α_1	α_2
No PEO	0.36[a]	–
0.2	0.52	0.37
0.4	0.56	0.41
0.5	0.52	0.39
1.0	0.49	0.38

[a] The degree of ionization of the ordinary micelles without PEO

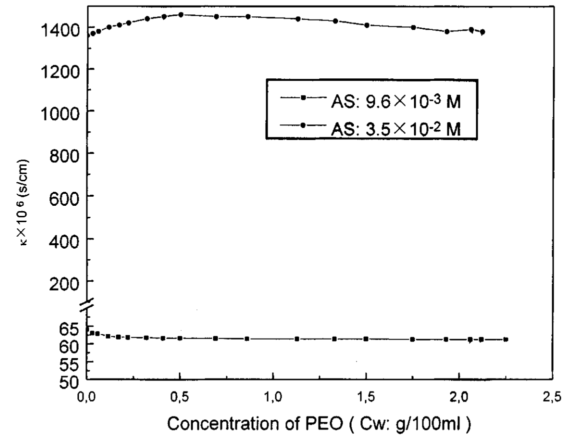


Fig. 4 Variation of the specific concentration versus the concentration of PEO for two AS concentrations

ESR studies

In order to understand the structure of the surfactant–PEO complex, ESR experiments were carried out to confirm the presence of an interaction between AS and PEO. The rotational correlation time τ_C measured from the ESR spectrum is characteristic of the probe mobility and can be used to monitor changes in the microviscosity experienced by the probe. The values of τ_C may be regarded as the time needed for a molecule to rotate by an angle of π. From the ESR spectra, the rotational correlation time can be calculated by the following equation [20]:

$$\tau_C = 6.5 \times 10^{-10} W_o[(h_0/h_{-1})^{1/2} + (h_0/h_{+1})^{1/2} - 2] ,$$

where W_o represents the peak-to-peak line width of the ESR midfield, and h_{-1}, h_0, h_{+1} are the peak-to-peak heights of the low-, mid- and highfield lines, respectively. A large τ_C value means a large microviscosity.

The hyperfine coupling constant A_N can give information on the micropolarity of the microenvironment sensed by the nitroxide probe. A more polar environment produces larger values of A_N due to a greater electron density at the nitrogen [21].

The changes in the ESR spectra of C_{12}-Tempo in AS aqueous solution are shown in Fig. 5. We can see that the changes occurring at the cmc are very sharp. Below the cmc, the spectra are composed of three narrow lines corresponding to free-probe molecular tumbling in the bulk solution; at and above the cmc, the lines become broader because of a slower motion. The ESR spectra of C_{12}-Tempo in a PEO–AS solution are similar to those in the AS aqueous solution (Fig. 6). From Figs. 5 and 6, the τ_C and A_N values are obtained and are shown as a function of c_{AS} in Fig. 7. In each system, there is a pronounced increase in τ_C at the onset of micelle or aggregate formation, which corresponds to the cmc or cac (in the presence of PEO) of AS, respectively. In the presence of PEO, at about 0.025 M AS, the τ_C values do not increase anymore, which corresponds to the polymer saturation in AS–PEO aqueous solution. It is observed that the τ_C values in the AS–PEO system are lower than these in the pure AS system.

Information about the average location of PEO in the polymer–surfactant complex can be derived from the chemical shift of the ^{13}C resonance of PEO. If PEO resides predominantly outside the aggregates, or is embedded into the surface palisade region only, in close proximity to the C1 and C2 methylene groups of AS, a very small ^{13}C chemical shift for PEO should be observed. On the other hand, if PEO penetrates into the interior of the aggregate, a substantial ^{13}C chemical shift may be expected. The ^{13}C spectra of PEO (2 g/100 ml) at various AS concentrations are shown in Fig. 8. A substantial upfield shift for the ^{13}C resonance is observed when the AS concentration is increased.

The ^{13}C chemical shift of AS at different PEO concentrations is shown in Fig. 9. It is found that the C1 and C2 chemical shifts do not change significantly, but the C12 chemical shift changes greatly when c_W is increased. This implies that PEO might penetrate into the AS micelles, and then shield the end carbon (C12) of AS.

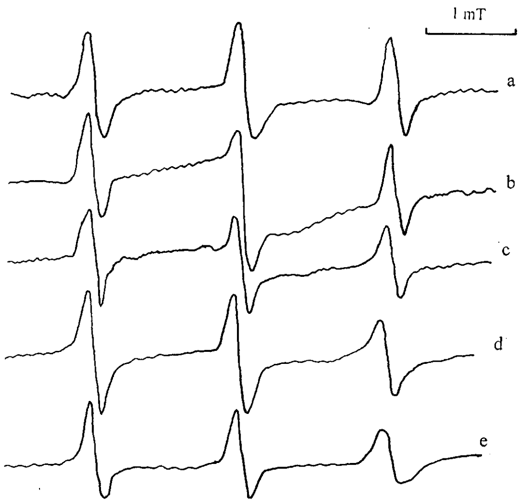


Fig. 6 Representative ESR spectra of C_{12}-Tempo in PEO–AS solution, PEO concentration 0.5 g/100 ml. *a*, *b*, *c*, *d*, and *e* correspond to the AS concentrations 1.05×10^{-3}, 7×10^{-3}, 1.005×10^{-2}, 1.75×10^{-2} and 2.45×10^{-2} M, respectively

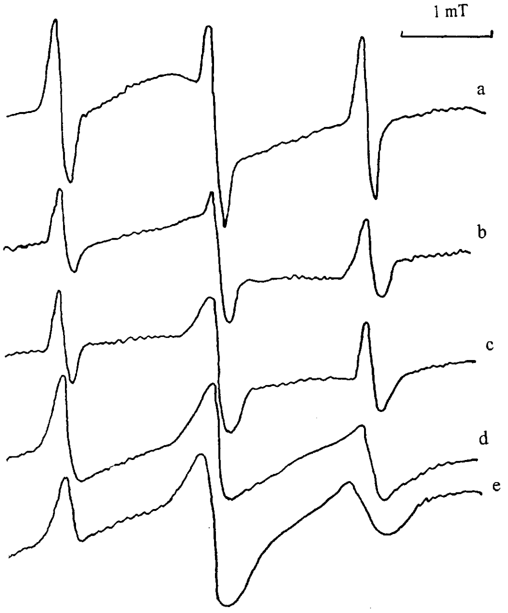


Fig. 5 Representative ESR spectra of C_{12}-Tempo in AS solution, *a*, *b*, *c*, *d* and *e* correspond to the AS concentrations 1.05×10^{-3}, 7×10^{-3}, 1.005×10^{-2}, 1.75×10^{-2}, and 2.45×10^{-2} M, respectively

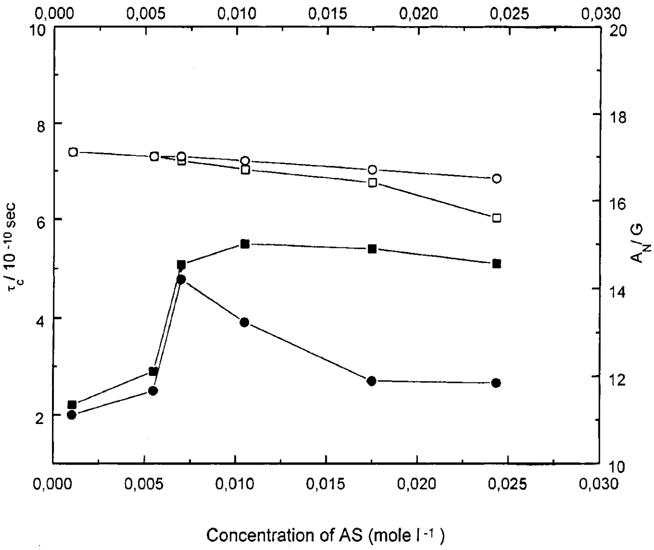
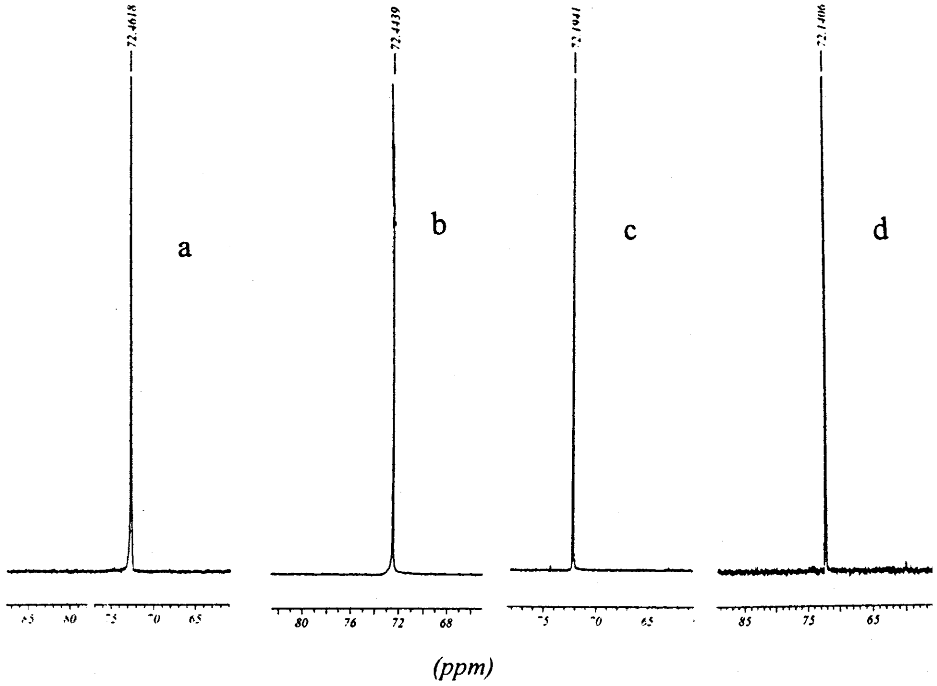


Fig. 7 Variation of rotational correlation time. τ_C, and ■ A_N, of C_{12}-Tempo in AS–PEO solution. The *circles* and *squares* represent AS solution in the presence of PEO in (0.4 g/100 ml) and in the absence of PEO, respectively. *Open circles* and *open squares*: A_N value; *filled circles* and *filled squares*: τ_C values

Fig. 8 The ^{13}C NMR resonance of PEO (0.2 g/100 ml) in the presence of *a* 0, *b* 4×10^{-4}, *c* 4×10^{-3} and *d* 8×10^{-3} M AS



Discussion

In this work, a system with a pure AS micellar solution is compared with a system containing an AS and PEO aqueous solution. When PEO is present all the experimental results indicate that the surfactant starts to interact with the polymer at concentrations (cac) lower than the cmc of AS. When $c_{\mathrm{AS}} = c_2 >$ cmc, this is considered to correspond to polymer saturation by AS. These cac and c_2 values were measured by different methods, and all values are listed in Table 1. According to Gjerde and Nerdal [15], the conductivity and surface-tension methods are sensitive to the surfactant molecules, and the cacs obtained using the two methods are in excellent agreement with each other.

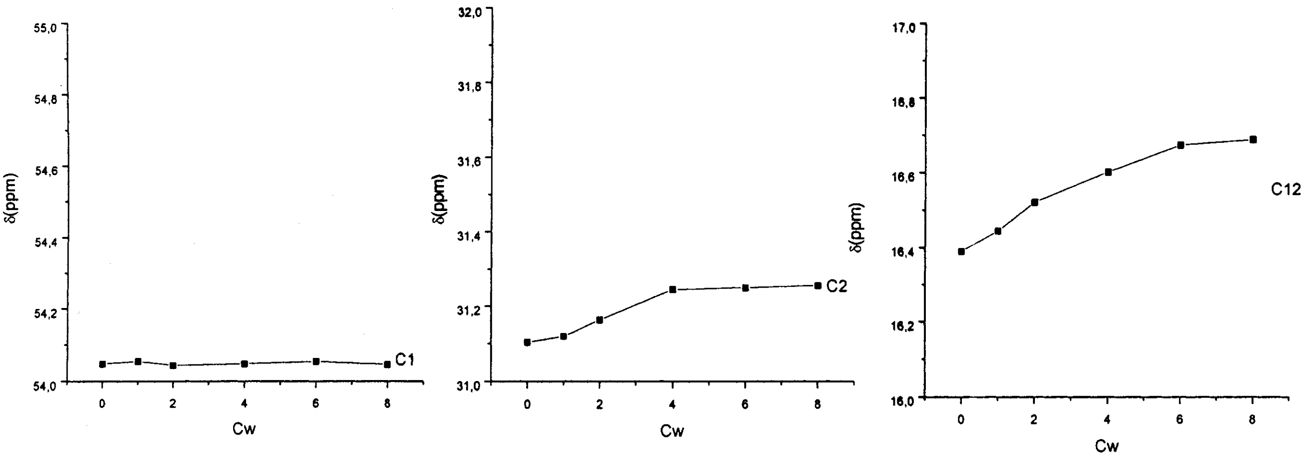
It was observed that the cac is always lower than the cmc of the surfactant. This implies that the surfactant–polymer aggregate is energetically more favorable than the ordinary micelles. To a first approximation, applying the phase-separation model for micelle formation, for the system without polymer the expression for the molar free energy of micellization can be written

$$\Delta G^{\circ}_{\mathrm{in}} = RT(2 - \alpha)\ln \mathrm{cmc} \;, \qquad (1)$$

and the free energy of surfactant for transferring 1 mol of surfactant solution into the complex is given by [22]

$$\Delta G^{\circ}_{\mathrm{b}} = RT[(2 - \alpha_1)\ln \mathrm{cac} + (\ln c_{\mathrm{p})/\mathrm{N}]} \;, \qquad (2)$$

Fig. 9 The ^{13}C resonance of AS (C1, C2, C12) at various concentrations of PEO (g/100 ml), AS concentration: 0.02 M



where N is the aggregate number, being taken to be 54 [17], and c_p is the polymer concentration. If we define $\Delta G^o_{ps} = \Delta G^o_b - \Delta G^o_m$ as the free energy per mole of surfactant for the process free micelle ⇔ polymer-bound micelle this quantity is a convenient measure of the strength of the interaction between the polymer and the surfactant. ΔG^o_{ps} for different PEO concentrations is given in Table 2. It is found that the interaction between polymer and surfactant is enhanced when c_W is increased, up to 0.5 g/100 ml, but addition of more PEO has no significant influence on the strength of the interaction. This implies that at higher c_W in the AS–PEO system, some PEO molecules might be present as a normal structure in water.

If we assume that the free surfactant concentration equals the cmc of the surfactant, the amount of surfactant bound to polymer is given by value of c_2-cmc [23]. For the 0.2 g/100 ml PEO (0.0455 M)/AS system c_2 is determined to be 0.0145 M, corresponding to a binding ratio of 0.107 AS per monomer unit of PEO. The binding ratios for different PEO concentrations have been calculated similarly, and are listed in Table 3. It is shown that the binding ratio does not change when c_W is higher than 0.5 g/100 ml. This reveals that at high polymer concentrations the equilibrium between the polymer–surfactant complex and surfactant micelles has been reached: further addition of PEO does not change this equilibrium. The result is consistent with thermodynamic calculations.

Because the surface tensions of the pure and the AS–PEO complex are identical above the cmc or c_2 (Fig. 1) there obviously will remain no noticeable amount of PEO at the air/water interface. The result displayed in Fig. 2 indicates that the major change in the physical properties occurred over a narrow range of PEO concentrations (0–1.5 g/100 ml). Further addition of PEO does not produce any variation in the properties.

Conductivity can be used to calculate the degree of ionization (α) of the micelle, i.e., the ratio of free counterions in the solution. As a first approximation, the simplest approach is that the degree of ionization is taken as the ratio of the slopes of the conductivity curve above and below the cmc [14]. We have used this method to determine the degree of ionization. For AS in water α is found to be 0.36 (Table 2), which is slightly lower than that for SDS in water [24]. The degree of ionization of the AS–PEO complex (α_1) can also be calculated from the slopes, and it appears to be higher than the degree of ionization for ordinary micelles in a polymer-containing solution (α_2) (0.52 compared to 0.37 at 0.2 g/100 ml PEO concentration). The values in Table 2 shows that the degrees of ionization (α_1 and α_2) increase with increasing c_W and then pass through a maximum value. Further addition of PEO results in a slight decrease in α_1 and α_2. This reveals that at moderate c_W, the polymer strands must somehow penetrate the aggregates inside, affecting the aggregates just like any ordinary solubilized molecules. So the surface charge density, as well as the fraction of associated counterions, would decrease, and consequently the degree of ionization (α_1 and α_2) increases; however, at higher c_W, some PEO molecules located at the aggregate–water interface might loop around surfactant clusters, or exist as normal structures as in water. Dubin and Gruber [25] suggest that PEO may bind Na^+. This physical picture results in the interaction between free Na^+ and the ether groups because of the distance between the two species. This interaction may limit the mobility of Na^+ and lead to a reduction in α_1 and α_2 at higher c_W.

Table 3 Thermodynamic data for ΔG^o_{ps} calculated according to Eqs. (1) and (2)

PEO concentration (c_W, g/100 ml)	0.2	0.4	0.5	1.0
ΔG^o_{ps} (kJ/mol)	−0.30	−0.25	−1.30	−1.25
Binding ratio[a]	0.107	0.172	0.218	0.151

[a] Dodecyl sulfonate ion per monomer unit of PEO

Because of a higher degree of ionic dissociation of AS in the "complex" than that of ordinary surfactant micelles. Therefore, when PEO is added, a slight loss of conductivity at c_{AS} close to CMC corresponds to a decrease in the electrophoretic mobility of the charges due to the fact that the micelles are bound to the polymer of a larger hydrodynamic radius, but not due to a reduction in the average ionization degree (Fig. 4). When the c_{AS} values are higher than the cmc, when micelles are already formed in the bulk before polymer addition, κ increases at low c_W and then passes through a maximum. This implies that at moderate c_W and increasing c_W, the average contribution of an AS molecule to the conductivity increases when it passes from a micelle in the bulk to a micelle located on the macromolecule. The reason why the conductivity increases in this situation is the greater ionization of AS molecules bound to the polymer. At higher c_W, most of the AS free micelles in solution may absorb on the polymer, and the free AS molecules present in solution are in equilibrium with the polymer–surfactant complex. Further addition of polymer results in a reduction in the conductivity due to the lower electrophoretic mobility of the charges which are bound onto the polymer with a larger hydrodynamic radius [7].

In our experiments, the viscosity increases markedly for a dilute solution when c_{AS} is increased and c_W is kept constant. This means that PEO has interacted with the surfactant, and a more extended confirmation of PEO chains occurs as a result of the binding of mutually repulsive charged micelles. The results of viscosity measurements are in agreement with our results.

In order to investigate the surfactant aggregate structure, ESR measurements were performed. Figures 5 and 6 display the ESR spectra of the various systems, and Fig. 7 is obtained from the results in Figs. 5 and 6. From Fig. 7, with increasing c_{AS}, the variations of τ_C or A_N values are compared in the presence of and in the absence of PEO, respectively. The data lead to the conclusion that the spin probes experience a more polar microenvironment and reorient faster in the polymer-absorbed micelles compared to the ordinary free micelles, i.e., the polymer-surfactant complex has a more "open" structure. This is consistent with the studies by Witte and Duplessix [26].

To establish further the mechanism of docking of AS and PEO in the assembly we consider the effect of AS on the ^{13}C NMR spectrum of PEO. The fact that with increasing c_{AS} a significant upfield ^{13}C shift of PEO is observed indicates PEO penetrates into the interior of the polymer–surfactant aggregates (Fig. 8). Further evidence is that the addition of PEO to an AS micelle solution (0.02 M) induces quite small changes in the carbon atoms (C1, C2) of AS, but significant changes in C12 are observed (Fig. 9). This suggests that PEO may penetrate the aggregated micelles, and might then shield the end carbons of AS; this is consistent with studies on the PEO–SDS system by Gjerde and Nerdal [27].

From the discussion above, we may infer that the AS–PEO complex has the structure shown in Fig. 10. This complex allows the PEO stands to penetrate into the AS micelles. Not all PEO segments penetrate into AS aggregates, but from our results at least parts of the PEO segments seem to penetrate into the so-called palisade layer of the micelle between the hydrophilic groups. As already mentioned, the aggregates may have a more "open" structure than that of AS ordinary micelles. It is conceivable that the hydrocarbon groups in the backbone of PEO come in contact with the hydrocarbon portions of the surfactant aggregates. Interaction between the polymeric ether groups and the sulfonate groups is also possible; however, because of the hydration effect of the sulfonate, the latter contribution to the interaction is very small. As previously mentioned, the main driving force for attachment is the hydrophobic effect. This is very similar to the behaviour of the PEO–SDS system [14].

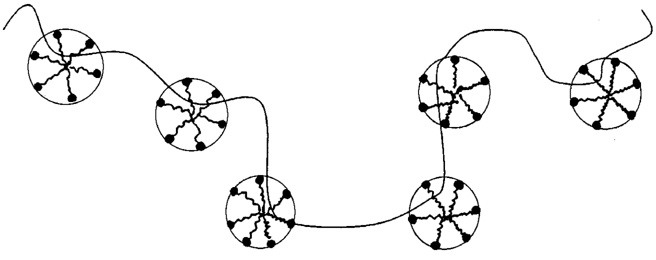


Fig. 10 The physical structure of the AS–PEO complex

Conclusion

All the methods mentioned (surface tension, conductivity, viscosity, ESR and NMR), have been used to confirm the presence of the interaction between PEO and AS. By using different measuring techniques, we determined cac and c_2 values, which were consistent with each other. The ESR and NMR results indicated that the AS–PEO complex may form a more "open" structure than the ordinary micelles, and the PEO strands might penetrate into the aggregates. Hydrophobic interactions were the driving forces for the formation of the AS–PEO complex.

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