Colloid Polym Sci 276:1–10 (1998)

ORIGINAL CONTRIBUTION

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Studies on the interactions between anionic surfactants and polyvinylpyrrolidone: Surface tension measurement, ^{13}C NMR and ESR

Received: 8 May 1996
Accepted: 14 August 1997

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Abstract The interaction between anionic surfactants and polyvinylpyrrolidone (PVP) are investigated using ^{13}C NMR, ESR spectroscopy and surface tension measurements at the air/water interface. The behavior of single-chained surfactant, sodium dodecyl sulphonate (AS), is compared with that of the double-chained surfactant, sodium bis(2-ethylhexyl) phosphate (NaDEHP). The results showed that a surfactant–polymer complex of "necklace and head structure" is formed in AS aqueous solutions in the presence of PVP due to the hydrophobic interaction between PVP and AS. The AS micelles nucleate on the polymer hydrophobic sites, and the mobility of the AS head groups is not affected. But, for NaDEHP surfactant, it was found that PVP is little effective in influencing the monomer–micelle equilibrium and no surfactant–polymer complex formed in the NaDEHP aqueous solution.

Key words Interaction – anionic surfactant – polyvinylpyrrolidone – ESR – NMR

Introduction

The interaction of surfactants with water-soluble polymers has been the subject of active research for many years. Early investigations were mainly concerned with the effect of synthetic detergents on natural proteins [1, 2]. These studies were motivated by observations of biological phenomena involving surfactants and proteins such as the inactivation of bacterial metabolism by synthetic detergents. Recently, attempts at enhanced oil recovery by the chemical flooding process have generated new interest in the nature of interactions occurring between polymers and surfactants injected into ground [3, 4]. Interactions between the surfactant and polymer molecules in these complex chemical systems can lead to phase separation and an alteration in the phase compositions from the originally designed compositions. Consequently, the interfacial tension lowering properties of the surfactant slug and the mobility control characteristics of the polymer buffer, both may adversely be affected. Therefore, in order to develop a viable surfactant–polymer flooding process, chemical systems should be designed in which the unfavorable aspects of the surfactant–polymer interactions are minimized.

In the presence of some polymers, surfactant molecules associate with polymers to form surfactant–polymer aggregates (complexes). For a system containing a polyelectrolyte and a surfactant of opposite charge, electrostatic interactions play an important role in the formation process of surfactant–polymer complex [5, 6]. For the case of neutral polymers and anionic surfactants, several mechanisms for the formation of a surfactant–polymer complex have been proposed, which include: (a) a reduction of the hydrocarbon/water contact area of the alkyl chains of the surfactant [5, 6]. (b) an ion–dipole interaction between the surfactant head group and the polymer [7] and (c) a hydrophobic interaction between the polymer and the

hydrocarbon chain [8, 9]. Recently, many investigators have studied the system of sodium dodecyl sulphate (SDS) and polymers [6, 10–12]. They suggested that the primary mechanism for the formation of the surfactant–polymer complexes in the system of SDS-polyvinylpyrrolidone (PVP) may be a self-assembling of surfactant and polymer molecules driven by the "hydrophobic effect" or by forces similar to those encountered in the formation of surfactant micelles in contrast to the straightforward binding or adsorption of surfactant anion to sites on the polymer. Chari and Lenhart [13] concluded that the polymer (PVP) contacts hydrocarbon groups on the surface of the micelle aggregate to protect these groups from water. A SANS (small angle neutron scattering) study of BSA (bovine serum albumin) [14, 15] with SDS led to the conclusion that the "necklace and head" structure of surfactant–polymer complexes accounted for the scattering behavior of the system.

To our knowledge there are few reports on the interaction between alkylsulphonate and polymers. Alkylsulphonate is a typical kind of anionic surfactant and widely used in Chinese enhanced oil recovery. Sodium dodecyl sulphonate (AS) is very similar to SDS in many physicochemical properties, such as the critical micelle concentration [16, 17] and the micelle aggregation number [18]. But, AS is very different from SDS in the structure. The sulphur atom is directly connected to the terminal carbon atom in the AS molecule. While in the SDS molecule, the sulphur atom is connected to the carbon atom through the oxygen atom. The object of this paper is to determine whether the structure difference between AS and SDS can lead to the different mechanisms for the formation of surfactant–PVP complexes. We compare the behavior of the single-chained surfactant (AS) with that of double-chained surfactant sodium bis(2-ethylhexyl) phosphate (NaDEHP). Besides sodium bis(2-ethylhexyl) sulfosuccinate, NaDEHP has also been studied as another typical double-chained anionic surfactant especially in the formation of reversed micelles [19]. We expect the study will serve as a useful basis for analyzing systems containing surfactants and polymers with more complex chemical structures and guide for Chinese enhanced oil recovery.

Experimental

Materials

Polyvinylpyrrolidone (av. mol. wt. 40 000) was obtained from Sigma Chemical Company. The NMR spectrum (Fig. 1) shows no evidence of impurities. Sodium dodecyl sulphonate (AS) (chemically pure) was recrystallized from ethanol (A.R). NaDEHP was synthesized following the procedure of Yu and Neuman [19]. The plot of surface tension vs log (concentration) of both surfactants does not exhibit any minimum near the critical micellar concentration (cmc). The *P*-dioxane used in NMR experiments and 5-doxylstearic acid were purchased from Aldrich Chemical Company.

Methods

The surface tension was measured using the CBVP-A3 model tensiometer (Kyowakimemkagaku Co.). This method is based on the principle of the Wilhelmy-plate. The ^{13}C NMR spectra were obtained with a Bruker AM-400 NMR spectrometer. All samples in the ^{13}C NMR performance contained 10% W/W deuterium oxide and a trace of P-dioxane. The latter was used as the internal reference. The electron spin resonance (ESR) experiments were performed on a Varian E-115 X-band spectrometer. All samples of the ESR measurements contained 7.0×10^{-4} mol/l of 5-doxylstearic acid and were deoxygenated with nitrogen before performance. All measurements with the solutions containing AS and NaDEHP were conducted at $40.0 \pm 0.1\,^{\circ}$C and room temperature ($25.0 \pm 0.1\,^{\circ}$C) respectively.

Assignments

The ^{13}C NMR spectra of AS, NaDEHP, and PVP in water are shown in Fig. 1. (The numbering of the carbon atoms is given in Table 1.) The assignments were reasonably made according to the spectra of SDS and AOT given by Cabane [20]. The assignment of PVP spectrum has been used by Cheng et al. [21].

Results and discussion

The effect of polyvinylpyrrolidone on the surface tension of sodium dodecyl sulphonate is shown in Fig. 2. Two critical surfactant concentrations T_1 and T_2 are seen in the presence of PVP. From this point, we can see that the association of AS and PVP in the bulk phase begins at T_1. The concentration T_2 represents saturation of the polymer with respect to complex formation with the surfactant. It is expected that at surfactant concentrations just higher than T_1 (Region A), polymer–surfactant aggregates will be in equilibrium with free surfactant molecules and free polymer molecules. When the surfactant concentrations become greater than T_2 (Region B), surfactant–polymer

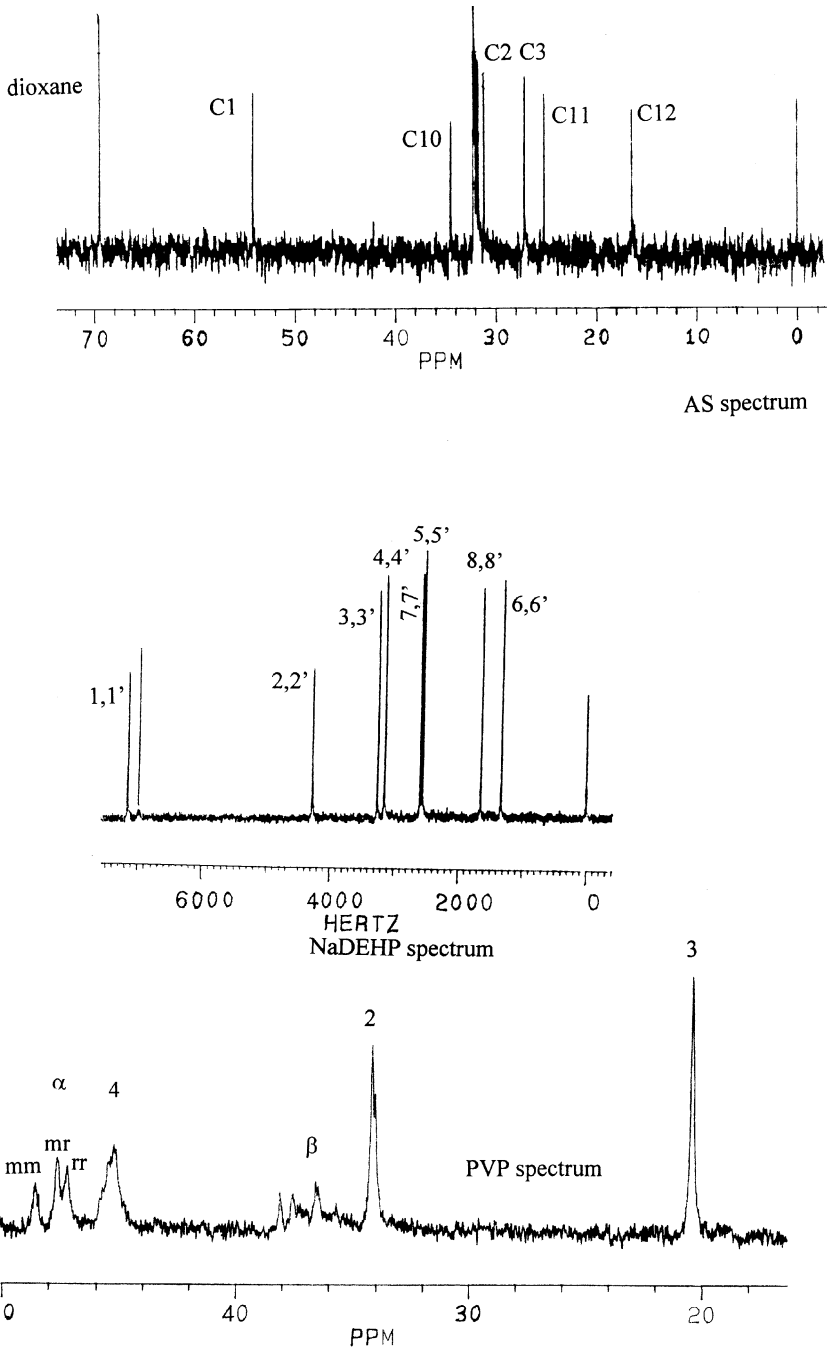

Fig. 1 ^{13}C NMR spectra of (a) 0.02 mol/l AS, (b) 0.02 mol/l NaDEHP and (c) 1.0% PVP in water. In the PVP spectrum three major peaks are seen for the methine (α) carbon, indicating a sensitivity to triads. Five peaks are clearly resolved for the methylene (β) carbon. The numbering of the carbon atoms is given in Table 1

aggregates and regular micelles will coexist, and a larger proportion of surfactant molecules in the aggregated state will be in the form of regular micelles.

The fact that T_1 is lower than the cmc of the surfactant is of particular importance as it implies that the surfactant–polymer aggregate is a more favorable energy state for the surfactant than the regular micelle aggregates. Since the surface tension values of the pure AS and the AS–PVP complex are identical above T_2 there obviously will remain no noticeable amount of PVP at the surface. For the AS–PVP system shown in Fig. 2 the difference in surfactant concentration between the cmc and T_2 is 2.16×10^{-2} mol/l when the concentration of PVP is 0.5%. Knowing the aggregation number of AS regular micelle is 54 [22] and the average molecular weight of PVP is 40 000, we can calculate that about 3.2 AS regular micelles

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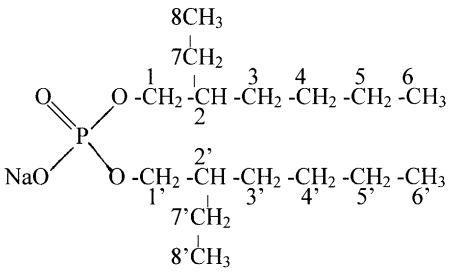
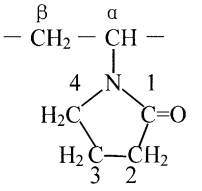
Table 1 Molecular structure of AS, NaDEHP, and PVP

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

will be sufficient to completely remove one PVP molecule from the surface.

The effect of PVP on the surface tension of the solution of NaDEHP is also shown in Fig. 2. The curve in Fig. 2 does not show two transition points in the presence of PVP and the surface tension variation due to the addition of PVP is very small. This means that PVP has negligible influence on the behavior of aqueous solutions of NaDEHP. That is to say surfactant–polymer complexes do not exist in the NaDEHP–PVP system. For the AS–PVP system, before we can provide an explanation for the observation, it is necessary to obtain information about the structure of surfactant–polymer aggregates and the mechanism of docking of surfactant and polymer molecules in the AS–PVP system. In order to obtain this information, analyzing the chemical shifts and line shapes of the NMR signals of the various ^{13}C nuclei of AS and PVP is required. For the NaDEHP–PVP system, in order to make ensure the fact that there is no interaction between NaDEHP and PVP molecules, ^{13}C NMR performance and other experimental methods are also needed.

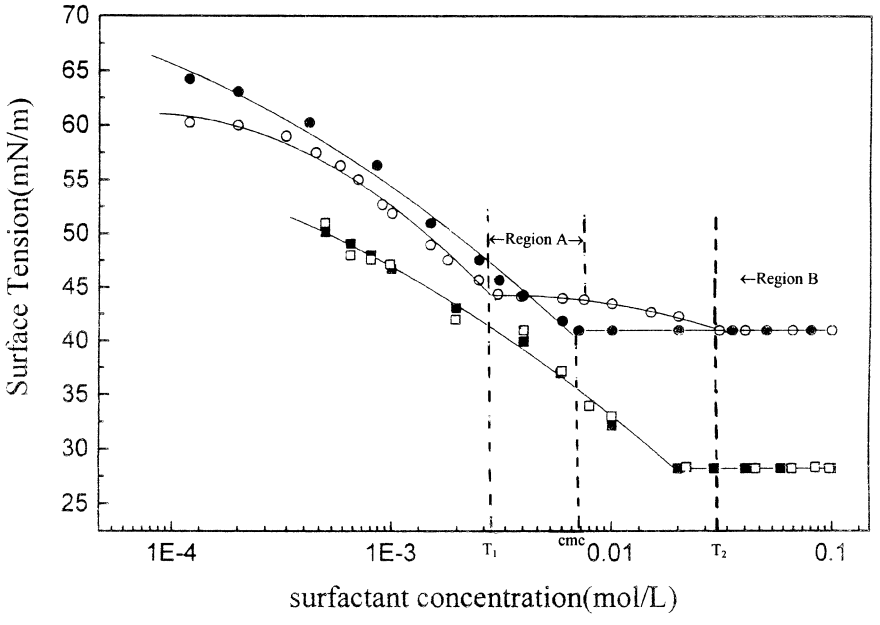


Fig. 2 Effect of PVP on the surface tension of AS and NaDEHP aqueous solution: (●) in the absence of PVP (AS system); (○) in the presence of 0.5 wt% PVP (AS system); (■) in the absence of PVP (NaDEHP system); (□) in the presence of 0.5 wt% PVP (NaDEHP system)

AS–PVP system

The variation of the chemical shifts of the NMR signals of the ^{13}C nuclei of AS with the PVP concentration in AS micellar solution is shown in Fig. 3. Almost no change is observed for the resonance of the C1 carbon or the carbon that is directly attached to the sulphonate head. The signals of the other carbons in the alkyl chain are all shifted downfield in the presence of the polymer. The most significant and regular change is observed for the C12 carbon or the carbon atom of the terminal methyl. At the highest levels of the polymer (4.0%) the C12 resonance occurs at 21 Hz (0.21 ppm) downfield of its position in the absence of the polymer. The carbon atoms in the middle of the chain (C2 to C11) are affected to approximately the same extent. The magnitude of the shifts (15 ± 1 Hz) are all smaller than that observed for C12. The variation in surface tension accompanying the addition of PVP to a micelle solution of AS is shown in Fig. 4. The experimental conditions are identical to those in Fig. 3. From both Figs. 3 and 4 it can be seen that the major change in physical properties occurs over a narrow range in PVP concentration (from 0 to 1.5%). Further addition of PVP does not produce any variation of the properties. The value of the surface tension in the plateau region of the curve in Fig. 4 is very nearly the same as that in Region A of Fig. 2. The addition of PVP to a micellar solution of AS transforms the equilibrium represented by (I) to (II):

free surfactant $\rightleftharpoons$ surfactant in micelle (I)

free surfactant $\rightleftharpoons$ surfactant in PVP–surfactant complex (II)

The region A in Fig. 2 and the plateau regions in Figs. 3 and 4 indicate values of the physical properties corresponding to equilibrium (II). The surface tension decrease associated with the change from (I) to (II) is consistent with a reduction in the concentration of free surfactant. The question to be answered at this stage is whether the chemical shifts in Fig. 3 are caused by portions of the PVP molecule coming in direct contact with the carbon atoms of the AS molecule or whether they simply reflect the fact that the fraction of AS molecules in the aggregated state becomes larger at higher PVP concentrations. To answer this question, we take the same method used by Chari and Lenhar [13] in their studies of the PVP–SDS system, i.e., to examine the changes occurring in the ^{13}C NMR spectrum of surfactant on micellization of the surfactant in the absence of PVP. In order to obtain adequate sensitivity, we take the NMR performance at AS concentrations about two times the cmc. Clearly the observed chemical shift will approach the chemical shift of the AS molecule in the micelle if the

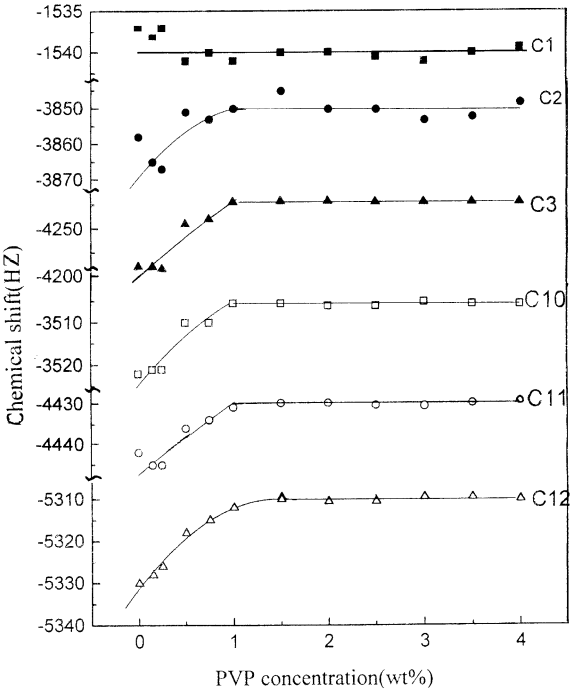


Fig. 3 Variation of chemical shifts of the carbon atom of AS molecules as a function of PVP concentration. The concentration of AS is 0.02 mol/l. The numbering of carbon atoms is given in Table 1

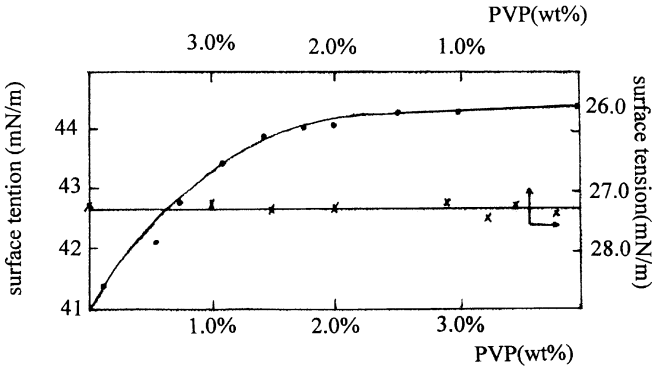


Fig. 4 Variation of surface tension of AS (0.02 mol/l) and NaDEHP (0.03 mol/l) micellar solution vs the concentration of added PVP. (●) AS micellar solution; (×) NaDEHP micellar solution

exchange of surfactant between the aggregated state and free ampliphile state is rapid compared to the time scale of NMR adsorption. Figure 5 shows the chemical shifts of various carbons of AS in a concentration range of 0.02–0.1 mol/l. Micelle formation results in downfield shifts for all carbon atoms of the AS molecule. The downfield shifts of the ^{13}C resonances of the carbons of the surfactant are attributed to an increase in the proportion of *trans* conformations relative to *gauche* conformations in the alkyl chain on micellization

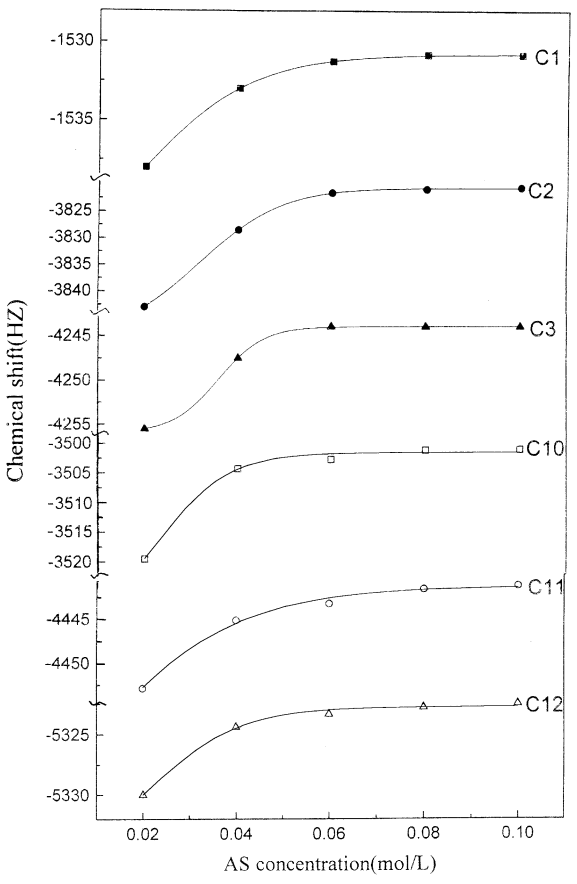


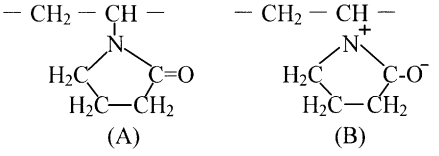
Fig. 5 Variation of chemical shifts of various carbon atoms of AS molecules as a function of AS concentration above its cmc

[23, 24]. The magnitude of the change for the carbons at the ends (C1 and C12) is very small (7 Hz or 0.07 ppm). The magnitude of the change upon micellization for the rest of the carbon atoms (C2, C3, C10 and C11) in the middle of the alkyl chain is 25, 14, 18 and 12 Hz, respectively.

From Figs. 5 and 3, we can see that both the micellization and formation of AS–PVP aggregates can also result in downfield shifts for all the carbon atoms of the surfactant. For the carbons of C1, C2, C3, C10, and C11, the magnitude of the change in Fig. 3 is smaller than or approximately the same as the magnitude of the change upon the micellization in Fig. 5. On the basis of the difference in concentration between the cmc and T_1, we may readily attribute the changes for carbons C1–C11 in Fig. 3 to an increase of the fraction of AS molecules in a "micellar environment" on addition of PVP. Alternatively, we can say that the environment around carbons C1–C11 in the AS–PVP aggregates is similar to that in a regular micelle. However, the same cannot be said about the environment around the C12 carbon of AS in the AS–PVP aggregates. The magnitude of the chemical shift difference is much greater than what we may expect based on the transfer of C12 from the free surfactant state to a "micellar environment". The increased shielding of the C12 carbon of AS may be attributed to the hydrophobic interaction between the polymer and the hydrocarbon chain as a result of the presence of the polymer in the vicinity of the terminal methyl group of the surfactant.

To establish the mechanism of docking of AS and PVP in the assembly we consider the effect of AS on the ^{13}C NMR spectrum of PVP. Adding AS to a solution of PVP has not made significant change in chemical shifts or line shape for the resonance of the carbonyl carbon (C1) or for the resonance of the methylene carbons C2, C3 and C4 in the pyrrolidone ring. However, from Fig. 6 we can see that changes are observed for the resonances of methine (α) and methylene (β) carbons in the backbone. At low surfactant concentrations the stereochemical splitting of the α and β carbon resonances are clearly reserved. On increasing the concentration of AS to 1×10^{-2} mol/l, one observes line-broadening in the β carbon resonances clearly. Continually increasing AS concentration to 2×10^{-2} mol/l results in line broadening in the α carbon resonances. These observations would be consistent with a physical picture of the reduced mobility of the segments in the backbone of PVP (resulting in longer correlation times) caused by the attachment of the backbone to the hydrophobic hydrocarbon chain of AS molecules. Considering the chemical shifts of various carbons in the presence of PVP, we can conclude that the hydrocarbon groups in the backbone of PVP come in contact with the terminal methyl group of the AS molecule, to form an AS–PVP complex. The main driving force for attachment is the hydrophobic interaction between AS and PVP molecules. The mechanism of the formation of the AS–PVP complex is very different from that of the SDS–PVP complex.

Molyneux and Ahmed [25] explained the binding of PVP to anionic solutes on the basis of resonance between structure A and B shown below:



They suggest that an electrostatic attraction should exist between the nitrogen in the ring and the negatively charged head group of the anionic surfactant. This is valid in the SDS–PVP system and Chari and Lenhart [13] concluded that the hydrocarbon groups of the backbone of PVP come in contact with the headgroups of the assembled SDS ions. But, the hydration effect of sulphonate is

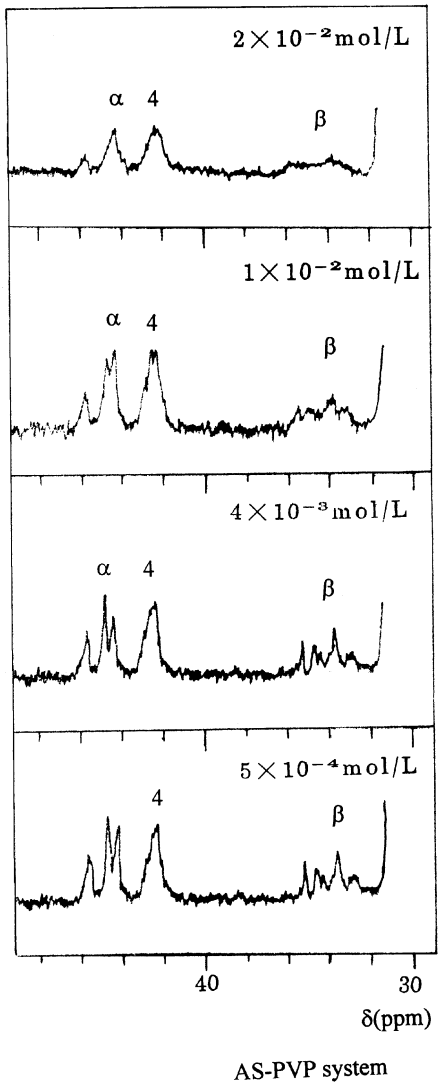


Fig. 6 Variations in the ^{13}C NMR spectrum of PVP as a function of AS concentration. The numbering of the carbon atoms is given in Table 1

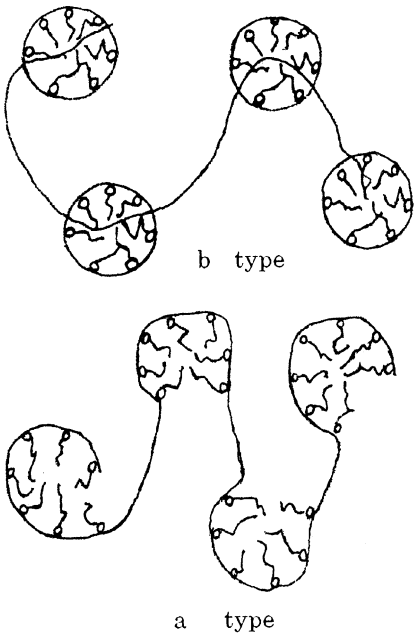


Fig. 7 Two possible "necklace and head structures" of surfactant–polymer complexes

stronger than that of sulphate because of the smaller volume of sulphonate. So the ion–dipole interaction could not exist between AS and PVP. AS could only associate with PVP by the hydrophobic effect between the surfactant alkyl chain and the backbone of PVP. Turro et al. [26] proposed two possible "necklace and head structures" of the surfactant–polymer complex: (a) the polymer wraps around the micelles, and the mobility of the surfactant head group being decreased; (b) the micelles nucleate on the polymer hydrophobic sites, and the mobility of the surfactant head group is not affected (Fig. 7). So we may infer that the SDS–PVP complex is of (a) type and AS–PVP of (b) type. In the SDS–PVP system [13], the difference between the cmc of SDS and T_1 is 5.1×10^{-3} mol/l and the C1 carbon or the carbon that is closest to the head group of SDS molecule occurs 62 Hz upfield of its position in the absence of PVP when PVP reaches 4% concentration. Comparing these with the results in AS–PVP system, we can conclude that the interaction between AS and PVP is not so strong as that between SDS and PVP.

NaDEHP–PVP system

The effect of PVP on the ^{13}C NMR chemical shifts of NaDEHP in micellar solution is shown in Fig. 8. The corresponding change in surface tension can be seen in Fig. 4. In this case, the adding of PVP has almost no influence on the surface tension of NaDEHP micellar solution. This is consistent with the result of Fig. 2 that two transition points (T_1 and T_2) do not occur in the presence of PVP. The NMR results presented in Fig. 8 showed that the resonance signals of C1 and C2 are shifted downfield and the resonance signals of other carbon atoms are all shifted upfield. The magnitudes of the shifts are all less than 16 Hz. Before analyzing these results we also study the effect of micellization (in the absence of PVP) on the chemical shifts of the ^{13}C resonance of NaDEHP like that in AS–PVP system. Figure 9 shows the change occurring in a concentration range above the cmc of NaDEHP.

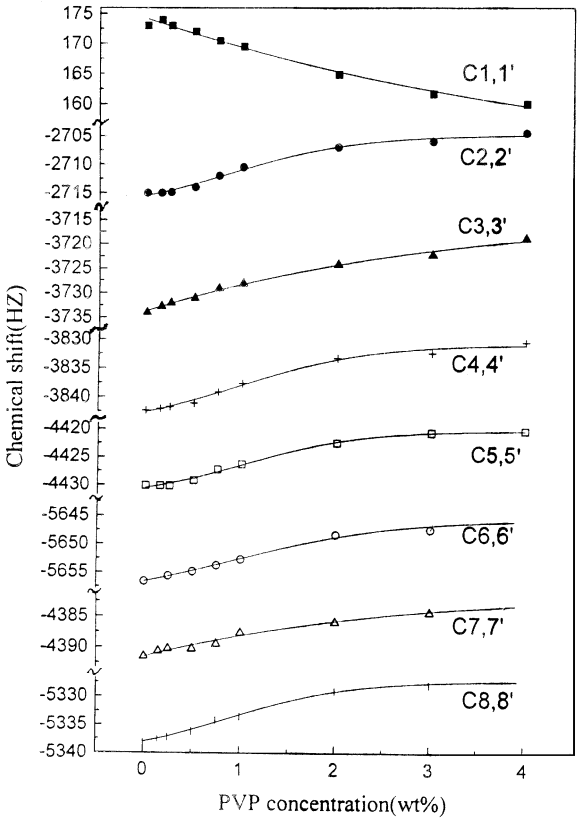


Fig. 8 Variation of chemical shifts of various carbon atoms of NaDEHP as a function of PVP concentration. The numbering of the carbon atoms is given in Table 1

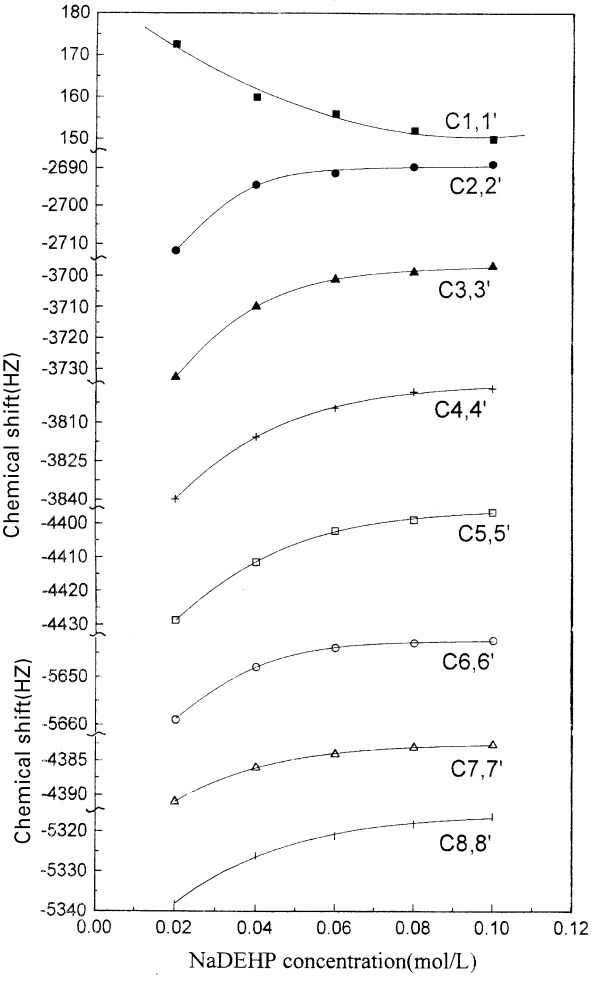


Fig. 9 Variation of chemical shifts of various carbon atoms of NaDEHP as a function of NaDEHP concentration above its cmc

From Figs. 8 and 9 we can see that the magnitude of the chemical shift of every carbon atom associated with the micellization (in Fig. 9) is greater than that of the corresponding carbon atom caused by the effect of PVP concentration (Fig. 8). In other words, the changes for all carbons in Fig. 8 are attributed to an increase in the fraction of NaDEHP molecules in a "micellar environment" on addition of PVP. The effect of NaDEHP on the ^{13}C NMR spectrum of PVP is shown in Fig. 10. No changes are observed in the line shape of the resonances of α, β, C2, C3 and C4 until the concentration of NaDEHP reaches a value as high as 3.0×10^{-2} mol/l. The result also serves as evidence to prove that there is no interaction between PVP and NaDEHP molecule in the PVP–NaDEHP system.

In order to ensure the above result in the PVP–NaDEHP system, we also measured the ESR spectrum of 5-doxylstearic acid in NaDEHP aqueous solution in the absence of PVP (Fig. 11) and in the presence of PVP (Fig. 12). From Fig. 11, we can see that the changes occurring at the cmc (2.2×10^{-2} mol/l, obtained from Fig. 2) are very sharp: below the cmc, the spectra are composed of three narrow lines corresponding to free probe molecules tumbling in solution; at and above cmc, the lines are broader because of a slower motion. This motion is the rotation of the micelles or the diffusion of the probe molecules inside the curved interfacial film of the micelle. The hyperfine splitting constant A_N decreases from 1.575 to 1.525 mT when the NaDEHP concentration reaches the cmc and above cmc. This is a clear indication of a decreased polarity of the environment sensed by the –NO paramagnetic group [27].

In the presence of PVP, below 2.2×10^{-2} mol/l NaDEHP concentration, no ESR resonances of the probe are observed because of the quenching effect of PVP. Only when the surfactant concentration approaches 2.2×10^{-2} mol/l, just equal to the cmc value of NaDEHP, an ESR resonance appears. This is because 5-doxylstearic acid molecules move from the PVP aqueous solution into the micelles and the probe molecules are shielded from the

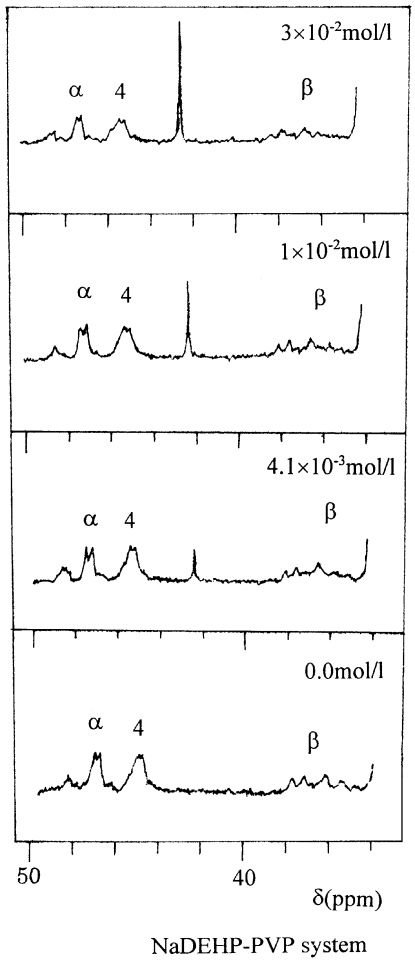


Fig. 10 Variation in the ^{13}C NMR spectrum of PVP as a function of NaDEHP concentration. The numbering of carbon atoms is given in Table 1

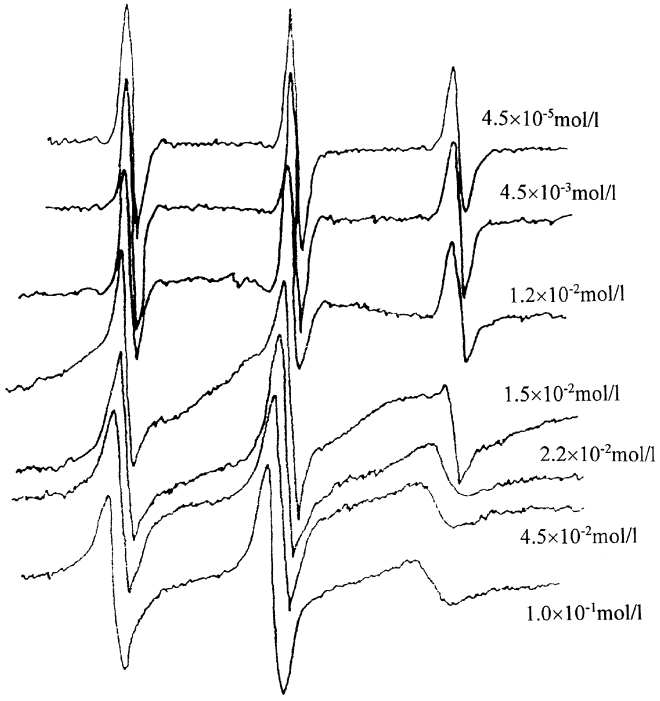


Fig. 11 ESR spectra of 5-doxylstearic acid for increasing NaDEHP concentration without PVP. The concentrations of NaDEHP are listed in the right-hand side of the figure

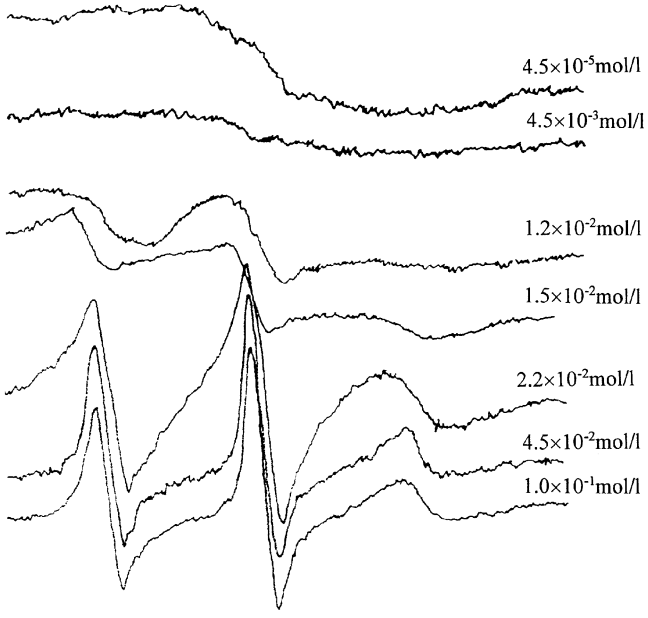


Fig. 12 ESR spectra of the probe for increasing NaDEHP solution in the presence of 4 wt% PVP. The concentrations of NaDEHP are listed in the right-hand side of the figure

PVP molecules. The results show that no NaDEHP molecule cluster is formed in the presence of PVP below cmc, and the formation of NaDEHP micelle is not influenced by the addition of PVP. The hyperfine splitting constant in the presence of PVP is 1.525 mT, equal to that in the absence of PVP, so the probe molecules locate in the same environment both in the presence of PVP, and in the absence of PVP when micelles appear. That is to say, no surfactant–polymer complexes appear and there is no interaction between PVP and NaDEHP molecules. The only difference between the ESR spectra in the presence and in the absence of PVP is that the ESR spectrum in the presence of PVP is slightly broader than that in the absence of PVP. This is because the aqueous PVP solution is more viscous than the micelle aqueous solution without PVP.

All the above-mentioned methods (surface tension, NMR and ESR), lead to the conclusion that there is no interaction between PVP and NaDEHP molecules. This is very different from the result in the AOT–PVP system [13]. Although both AOT and NaDEHP are

doubled-chained anionic surfactants, the two amphiphiles' chemical structures are rather different. Whereas NaDEHP represents an ester with the two ester binds linked to the same hydrophilic head groups (phosphate), AOT does form the ester bridge in α, ω-positions of the succinic acid but the hydrophilic sulfonate group being linked (almost) central to the whole amphiphilic molecule. Thus, the AOT molecule ought to possess a rather broad hydrophilic moiety with the alkyl residues positioned at its brimstone atom whereas in NaDEHP the two hydrophobic branches are linked to the same phosphor atom. Hence NaDEHP's interaction behavior with PVP is so different from that of AOT. The regular micelle aggregate is energetically a more favorable state for NaDEHP than a surfactant–PVP aggregate. In the AOT–PVP system, AOT can form complexes with PVP by the ion–dipole interaction. The electrostatic attraction between surfactant and PVP makes the AOT–PVP complex energetically more favorable than the regular micelle.

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