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Investigation of the Interactions of Polyvinylpyrrolidone with Mixtures of Anionic and Nonionic Surfactants or Anionic and Zwitterionic Surfactants by Pulsed Field Gradient NMR

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Abstract

The interaction of polyvinylpyrrolidone (PVP) with an anionic surfactant (sodium dodecyl sulfate, SDS), a nonionic surfactant (pentaethylene glycol monodecyl ether, $C_{10}E_5$), and a zwitterionic surfactant (lauryl amido propyl betaine, LAPB) has been investigated by means of pulsed gradient spin-echo NMR (FT-PGSE NMR), allowing self-diffusion coefficients to be determined. The results confirm the strong interaction prevailing in the PVP/SDS system, whereas no association has been observed in the PVP/$C_{10}E_5$ and PVP/LAPB systems. Mixing PVP with two surfactants, namely SDS and $C_{10}E_5$ or SDS and LAPB, results in the formation of ternary aggregates between the polymer and the mixed micelles.

Key Words

polymer-surfactant interactions; aggregation; sur fac-tant mixtures; NMR self-diffusion coefficients.

Introduction

Interactions of water-soluble polymers and surfactants in aqueous solution play an increasingly important role in various technological fields, such as detergency, formulation of cosmetics, and paints. Special attention has been paid to associations of uncharged polymers, such as polyvinylpyrrolidone (PVP) and polyethyleneoxide (PEO), with anionic surfactants (usually sodium dodecyl sulfate (SDS)) The necklace model is the most commonly accepted structure for these associations, in which the polymer is the lace and surfactant aggregates form the beads (1-5). A set of experimental techniques have been used to study the polymer/surfactant interactions, including surface tension, fluorescence, ion-specific electrodes, equilibrium dialysis, light scattering, and NMR spectroscopy. Current studies focus on binary polymer/surfactant systems, information being scarce for the structure of ternary systems consisting of one polymer and two surfactants. It is now time to fill this gap since mixtures of at least two surfactants are frequently found in nature and in industrial applications. These mixtures of surfactants, which may have beneficial effects, are the topic of active research, the main purpose being to predict and to measure the composition of the mixed micelles which are formed (6-9) Some mixtures of two surfactants have been studied in the presence of a polyelectroly te (10—14). In these examples, the polymer and one surfactant are oppositely charged, whereas the second surfactant is uncharged Creeth *et al.* (15) have studied the adsorption behavior of a mixture composed of sodium dodecyl sulfate (SDS) and hexaethy-lene glycol monododecyl ether ($C_{12}E_6$) at the water/air interface in the presence of the cationic dimethyldiallylammonium chloride-acrylamide copolymer. Comparison of neutron reflectivity and surface tension data indicates that the polyelectrolyte modifies the surfactant composition at the interface. Neutron reflectivity also proved useful for the analysis of the structure and composition of mixed monolayers of poly(dimethyl silox-ane) and mixtures of bis-2-ethyl-hexyl sodium sulfosuccinate and pentaethylene glycol monododecylether (16). Conductivity measurements have recently been reported (17) for mixtures of poly (ethylene oxide) and two surfactants: sodium dodecyl sulfate and sodium decyl phosphate. These experiments give information on interactions and associations in solution, in contrast to neutron reflectivity, which exclusively probes the liquid/vapor region.

This paper reports on mixtures of an uncharged polymer, polyvinylpyrrolidone (PVP), and two surfactants: the anionic sodium dodecyl sulfate (SDS) combined with either the nonionic pentaethylene glycol monodecyl ether ($C_{10}E_5$) or the zwitteri-onic lauryl amido propyl betaine (LAPB) These aqueous solutions were analyzed by pulsed gradient spin-echo ^{1}H NMR (PGSE ^{1}H NMR) spectroscopy. The PGSE ^{1}H NMR technique has the unique ability to measure the self-diffusion coefficient of the components of the ternary mixture in the aqueous solution, thus to probe how the polymer and the surfactants interact and associate.

Experimental

Materials

Sodium dodecyl sulfate (SDS, MW 288) from BDH Laboratories was used as received. The critical micelle concentration (cmc) of SDS was 8 mM, as determined by surface tension measurements performed at various concentrations. No minimum in the surface tension was observed in the vicinity of the cmc, demonstrating the high purity grade of the SDS sample. Pentaethylene glycol monodecyl ether ($C_{10}E_5$, $C_{20}H_{42}O_5$, MW 378) was used as received from Fluka Bio-Chemika. Lauryl amido propyl betaine (LAPB, MW 400) was provided by Mackam Lmb and used without further purification Polyvinylpyrrolidone (PVP, MW 10,000) from Aldrich was also used as received. All the aqueous solutions were prepared with twice distilled water containing 10% D_2O (Aldrich), unless otherwise stated. Concentrations of the polymer solution will be expressed in moles of constitutive monomer (MW =111) per liter

NMR experiments

Self-diffusion coefficients, D_s, were measured by the pulsed field gradient NMR technique (18, 19) using a Bruker AM 300WB spectrometer operating at the proton Larmor frequency of 300 MHz. The basic sequence (18) was used with pulsed field duration, δ, of 6 ms and a time interval, Δ, between the two gradient pulses of 22 ms. The echo attenuation, *A,* was recorded as a function of the gradient amplitude, *g*, calibrated with octanol, on the assumption that $D_s = 19 \times 10^{-10}$ m^2 s^{-1} at 20°C (20). The field gradient intensity was varied from 1.116 to 3.348 T/m. The signal intensity was found to decrease exponentially, as expected from

$$A = A_0 \exp(-\gamma^2\delta^2 g^2 D_s(\Delta - \delta/3)), \qquad [1]$$

where γ is the proton gyromagnetic ratio. The ^{1}H NMR signal of the alkyl side chain of SDS at 1,3 ppm was selected to follow the intensity decrease as a function of *g*. In the case of $C_{10}E_5$, the signal at 3.7 ppm was followed, which is characteristic of the -CH_2O- protons. The signal at 3.3 ppm, typical of the -CH2-protons in the *a* position of the carbonyl moeity, was selected in the case of LAPB. The proton signal at 2.3 ppm was used to probe PVP, However, the basic pulse sequence, commonly used to determine the self-diffusion coefficients, was not appropriate for PVP, which explains why the longitudinal eddy current delay (LED) pulse sequence was used in this study (21). The field gradient intensity was varied from 0.164 to 0.342 T/m. The field gradient pulse duration, δ, and the diffusion time, *D,* were 6 and 207.1 ms respectively.
Self-diffusion coefficients were calculated on the basis of 13 experimental data by fitting Eq [1]. All the reported values were averages of three independent measurements.

Results

Self-Diffusion Coefficient for Single Surfactant

When aqueous solutions of surfactants are analyzed, an equilibrium between surfactant monomers and micelles has to be considered (19, 22—24). It is therefore reasonable to express the self-diffusion coefficient at concentrations above the cmc as the concentration-weighted average coefficient of the fast diffusing monomers and the slow diffusing micelles, according to

$$D_s^{obs} = p_{mono} D_s^{mono} + p_{mic} D_s^{mic}, \qquad [2]$$

where p_{mono} and P_{mic} are the molar fractions of the monomers and the micelles, respectively. D_s^{obs}

is the experimental self-diffusion coefficient, D_s^{mono} and D_s^{mic} being the values characteristic of the monomers and micelles, respectively D_s^{mono} is measured at a surfactant concentration below the cmc, in contrast to D_s^{mic}, which is measured at concentrations largely exceeding the cmc, thus at which the equilibrium is almost completely shifted toward micelle formation. In some cases, the cmc of the surfactant is too low for D_s^{mono} to be measured accurately. However, according to the relation (24)

$$D_s^{obs} = D_s^{mic} + \frac{cmc}{c_t}(D_s^{mono} - D_s^{mic}), \quad [3]$$

there is a linear relationship between D_s^{obs} and the inverse of the total surfactant concentration, c_t, which allows both the cmc and D_s^{mono} to be determined.

In this study, D_s^{mono} and D_s^{mic} can be determined directly only for SDS, whose cmc is high enough. The cmc of the other surfactants ($C_{10}E_5$ and LAPB) is too low, so that Eq. [3] was used to determine their self-diffusion coefficients (Table 1).

Measurement of self-diffusion coefficients for polymer/ surfactant pairs is a convenient means of analyzing how much surfactant is bound to the water-soluble polymer, by using Eq [4] below, which is a modified version of Eq. [2], The experimental self-diffusion coefficient of the surfactant, D_s^{obs} is the population-weighted average of the self-diffusion coefficients of the surfactant-containing species in solution— surfactant monomer, surfactant micelles, and polymer/surfactant aggregates—whose relative concentration depends on the total concentration of both the surfactant and the polymer. In a well-defined range of surfactant concentration (between C_1 and C_2, which will be defined below), the surfactant may only be associated to the polymer or exist in the monomeric state and thus

$$D_s^{obs} = p_{bound} D_s^{agg} + (1 - P_{bound}) D_s^{free}. \quad [4]$$

Mixtures of sodium dodecyl sulfate (SDS) with hydrophobically modified PEO or (PEO—polypropyleneoxide-PEO) block copolymers, and also cationic surfactants with ethyl hydroxyethyl cellulose, have been studied by this technique (25-29).

We first analyze the interaction of each surfactant (i.e., SDS, $C_{10}E_5$, or LAPB) with PVP, before considering the more complex mixtures of PVP with two surfactants.

TABLE 1 Critical Micellar Concentrations and Self-Diffusion Coefficients for SDS, $C_{10}E_5$, and LAPB at 25°C

	CMC (mM)	D_s (monomer) x 10^{11} (m^2/s)	D_s (micelle) x 10^{11} (m^2/s)
SDS	8.0	48	4.8
$C_{10}E_5$	0 .69	71.8	4.6
LAPB	0.17	190	9.3

Binary Polymer-Surfactant System

PVP/SDS system Interaction of SDS with PVP is well documented in the scientific literature (1-3, 30) As a rule, the surface tension of interacting homopolymer(PVP)/surfactant(SDS) pairs shows two breakpoints (at C_1 and C_2) when the surfactant concentration is increased at constant polymer concentration. *C* is the surfactant concentration at which cooperative binding between the polymer and the surfactant starts to be observed; it is often referred to as the critical association concentration The increase of the surfactant concentration above C_1 results in an increasing surfactant-to-polymer binding ratio. C_2 is most frequently referred to as the surfactant concentration needed to saturate the polymer. Above C_2, polymer/surfactant aggregates coexist with surfactant micelles, Nevertheless, as pointed out by Minatti and Zanette (31) and by Zanette *et al.* (32), polymer/surfactant complexes and regular surfactant micelles may already coexist in an intermediate concentration region slightly below C_2, which suggests that the polymer might be saturated at a surfactant concentration lower than C_2 In this study, the surface tension measured as a function of the SDS concentration in the presence of PVP at a fixed concentration (360 mM) gave C_1 and C_2 as 14 and 104 mM, respectively. However, according to Zanette *et al.* (32), polymer-surfactant associates and regular SDS micelles may coexist at intermediate concentrations, between 84 and 104 mM. Similarly, the self-diffusion coefficient of SDS has been measured as a function of the SDS concentration, by the classical PGSE FT-NMR sequence, the PVP concentration being fixed at 360 mM. The same experiment has been repeated in the absence of PVP (Fig. 1).

The self-diffusion coefficient of SDS expectedly decreases in the presence of PVP as a consequence of the polymer/surfactant aggregation.

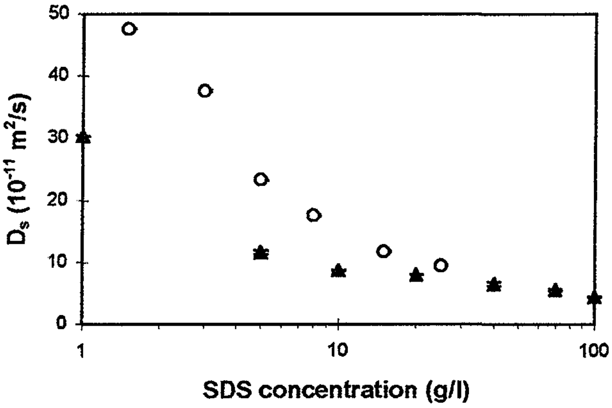

FIG. 1. Self-diffusion coefficients of SDS at various concentrations in the absence (O) and in the presence (▲) of PVP (360 mM)

TABLE 2 Self-Diffusion Coefficients for PVP (360 mM) and SDS (69.4 mM) Mixture

Solvent	Sequence	$D_s^{agg} \times 10^{11}$ (m^2/s)	$D_s^{PVP} \times 10^{11}$(m^2/s)
$H_2O:D_2O$ (90/10)	Classical	7.5 ±0.05	__
D_2O	Classical	5.9 ±0.2	—
D_20	LED	5.1 ±0.1	6.1 ±0 .04

The self-diffusion coefficient of the polymer, saturated by the surfactant (D_s^{agg}), was estimated at a SDS concentration of 69.4 mM (compare to PVP 360 mM), lower than C_2 (104 mM) and also lower than the critical concentration region (84-104 mM). Thus, at 69,4 mM, the existence of free SDS micelles is very unlikely and that of monomers of SDS appears negligible. Therefore, the self-diffusion coefficient obtained for SDS (7.5 x 10^{-11} m^2/s) is a good estimate for D_s^{agg} (Table 2),

This value cannot be cross-checked with the self-diffusion coefficient measured for PVP under the same experimental conditions, since the PVP ^{1}H NMR signal cannot be observed by the classical ^{1}H NMR PGSE sequence. Nevertheless, the experiment has been carried out with the LED sequence, which allows an acceptable ^{1}H PVP signal to be observed. However, the LED sequence is more time consuming and the solutions must be prepared in pure D_2O instead of in the 90/10 H_2O: D_2O mixture, in order to prevent the peaks for PVP and water from overlapping at the lowest field gradients required by this sequence. The D_s values measured for SDS and PVP using the LED sequence, were 5.1 x 10^{-11} and 6.1 x 10^{-11} m^2/s, respectively, thus close enough to each other to be characteristic of a unique species, namely the PVP/SDS complex (Fig. 2a). For the sake of comparison, D_s for PVP at 360 mM in D_20 was 11.5 x 10^{-11} m^2/s in the absence of SDS (Table 2), highlighting the strong effect of surfactant on the polymer mobility as result of complex formation. It must be noted that the self-diffusion coefficients measured in D_20 by both the classical and the LED sequences are in agreement, within the limits of experimental error However, replacement of the 90/10 $H_2O:D_2O$ mixture with pure D_2O significantly decreases the mobility of the species in the PVP/SDS mixture *PVP/$C_{10}E_5$ system.*

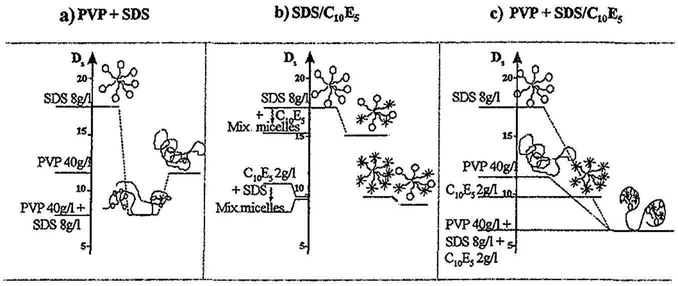

FIG. 2. Schematic representation of (a) PVP/SDS aggregates, (b) SDS/ $C_{10}E_5$ mixed micelles, and (c) PVP/SDS/$C_{10}E_5$ associations

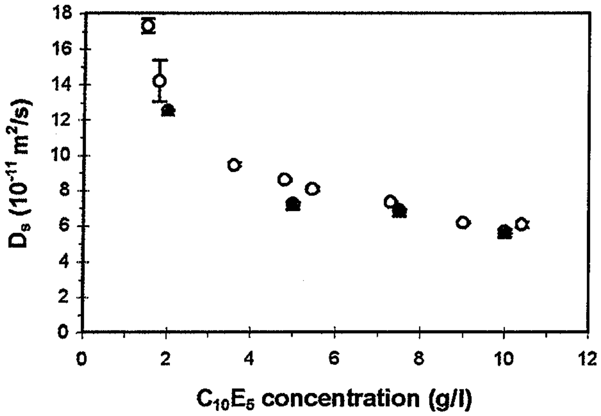

FIG. 3. Self-diffusion coefficients of $C_{10}E_5$ at various concentrations in the absence (O) and in the presence (▲) of PVP (360 mM)

Figure 3 shows that PVP (360 mM) has no influence on the concentration dependance of the self-diffusion coefficient of the $C_{10}E_5$ surfactant, which indicates the absence of interaction between the polymer and the non-ionic surfactant. This observation is in complete agreement with the surface tension data classically used to assess for polymer/surfactant interaction. PVP addition does not affect the surface tension of $C_{10}E_5$ solutions of different concentration, except for a slight increase in the cmc

PVPILAPB system. The zwitterionic surfactant, LAPB, similarly to the nonionic surfactant, does not interact with PVP, as supported by both the surface tension and the self-diffusion coefficient of the surfactant, which are insensitive to the presence of PVP (Fig, 4).

Ternary Polymer-Two Surfactants Systems

This section deals with the behavior of one polymer mixed with two surfactants; SDS and $C_{10}E_5$, or SDS and LAPB. In the absence of PVP, both the surfactant pairs lead to the formation of mixed micelles.

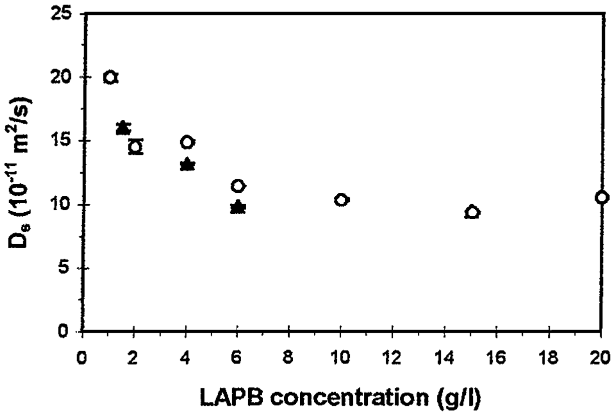

FIG. 4. Self-diffusion coefficients of LAPB at various concentrations in the absence (O) and in the presence (▲) of PVP (360 mM).

Indeed, the mutual interaction of the head-groups of the surfactants results in nonideal mixture behavior (6) On the basis of the regular solution theory developed by Rub-ingh (7, 8), a set of relationships can be drawn between the cmc of the mixed micelles, their composition, the monomer concentration, and an interaction parameter, *β,* which actually depends on the molecular interactions in the mixed micelles. The stronger these interactions are, the more negative is *β.* Based on regular solution theory and self-diffusion coefficients valid for binary surfactant mixtures, the interaction strength between SDS and $C_{10}E_5$ has been ranked as weak to medium (33). In contrast SDS and LAPB strongly interact as a result of electrostatic attraction of the negative headgroup of SDS by the strong dipole of the zwitterionic surfactant When a mixture of surfactants is added to an aqueous solution of PVP, new supramolecular structures can be formed, as a result of the relative strength of the interactions between the three constituents in water, Measurement of the self-diffusion coefficients of the two surfactants in the presence of PVP can give information on this architecture. The self-diffusion coefficient of $C_{10}E_5$ can easily be determined in the presence of SDS and PVP, since the nonionic surfactant $-CH_2-O-$ signal at 3.7 ppm is not obscured by resonances of other protons in the system. However, determination of the self-diffusion coefficient of SDS for the same $C_{10}E_5$/SDS/PVP ternary system is less straigthtforward since the signals of the $-CH_2-$ protons of SDS at 1.3 ppm and of the alkyl chain protons of the nonionic surfactant overlap This problem can be solved when the contribution of the individual surfactants to the experimental self-diffusion coefficient is very uneven, The echo attenuation is then a biexponential function that allows the individual self-diffusion coefficients to be determined. Unfortunately, this data treatment is not applicable to the $C_{10}E_5$-/SDS pair because a monoexponential decay is observed as result of comparable self-diffusion coefficients. Therefore, the self-diffusion coefficient of SDS has been extracted from the signal at 1,3 ppm, on the hypothesis that the experimental D_S is the weight average of the individual D_S^{SDS} and D_S^{C10E5} values, according to

$$D_s = X_{C_{10}E_5} D_s^{C_{10}E_5} + X_{SDS} D_s^{SDS}, \qquad [5]$$

where $XC_{10}E_5$ ar>d X_{SDS} are the molar fractions of the nonionic and the anionic surfactants, respectively

Tables 3 and 4 list the self-diffusion coefficients calculated for the surfactant pair in the SDS/$C_{10}E_5$/PVP and in the SDS/LAPB/PVP ternary mixtures. Concentrations of PVP and SDS have been selected in order to favor the formation of mixed aggregates in the absence of either $C_{10}E_5$ or LAPB; thus SDS concentrations are chosen slightly lower than those of C_2. The addition of the second surfactant to the PVP/SDS binary system may then be viewed as a perturbation for the aggregation process which can be investigated by FT-PGSE NMR. The self-diffusion coefficients accordingly measured for the two surfactants in the ternary systems are compared to those ones measured for the constitutive binary systems—polymer/surfactant and surfactant/surfactant pairs—and for the individual surfactants at the same concentration.

TABLE 3 Self-Diffusion Coefficients for Single Surfactants and Binary and Ternary Systems of SDS (27.8 mM), $C_{10}E_5$ (5.3 mM), and PVP (360 mM) in 90/10 $H_2$0:$D_2$0 by the Classical PGSE FT-NMR Sequence

Composition	Self-diffusion coefficient for SDS x 10^{11} (m^2/s)	Self-diffusion coefficient for $C_{10}E_5$ x 10^{11} (m^2/s)
$C_{10}E_5$	—	9.8 ±0.2
SDS	17.5 ± 0.2	—
SDS/$C_{10}E_5$	15.4 ±0.5	9.3 ±0.4
PVP/$C_{10}E_5$	—	11.4 ±0.3
PVP/SDS	7.8 ± 0.2	—
PVP/SDS/$C_{10}E_5$	7.6 ±0.1	6.6 ± 0.05

It has already been noted that the classical PGSE FT-NMR sequence which was used in this case does not allow the self-diffusion coefficient of PVP to be calculated.

D_S measured for each surfactant at concentrations given in Tables 3 and 4 fall between D_S for the parent monomer and the micelles, respectively (Table 1), although they are closer to the D_S for the micelles since the concentrations exceed the cmc. As pointed out in the previous paragraph, binding of SDS to PVP results in a substantial decrease of the self-diffusion coefficient for SDS, whereas no significant modification is reported in the case of LAPB and $C_{10}E_5$, which confirms the absence of interaction. When SDS is mixed with either $C_{10}E_5$ or LAPB, mixed micelles are formed and the self-diffusion coefficients measured for each surfactant of the binary system are controlled by the equilibrium between the monomers and the micelles that exists at the composition of the surfactant mixture In the case of the SDS(27,8 mM)/$C_{10}E_5$(5.3 mM) mixture, D_S for SDS is decreased from 17.5 x 10^{-11} to 15 4 x 10^{-11} m^2/s, whereas D_S for the nonionic surfactant is only slightly decreased from 9 8 x $10^{-11}$to 9.3 x 10^{-11} m^2/s,, Figure 2b helps to visualize the changes in the self-diffusion coefficient of each surfactant upon mixed micellization. The same general trend can be observed for the SDS/LAPB system, altough the decrease in the self-diffusion coefficients for each surfactant is greater than that for the SDS/$C_{10}E_5$ pair.

Finally, when PVP is added to the binary surfactant mixture, the self-diffusion coefficients of each surfactant are further decreased, to the point where they tend to the same "low" value.

TABLE 4 Self-Diffusion Coefficients for Single Surfactants and Binary and Ternary Systems of SDS (27.8 mM), LAPB (5 mM), and PVP (360 mM) in 90/10 $H_2$0:$D_2$0 by the Classical PGSE FT-NMR Sequence

Composition	Self-diffusion coefficient for SDS x 10^{11} (m^2/s)	Self-diffusion coefficient for LAPB x 10^{11} (m^2/s)
LAPB	—	12.2 ±0.4
SDS	17 .5 ± 0.2	—
SDS/LAPB	12.9 ± 0.4	8.6 ±02
PVP/LAPB	—	12.0 ±03
PVP/SDS	7.8 ±0.2	—
PVP/SDS/LAPB	8.3 ±0.1	7 .1 ± 0.1

PVP/SDS/$C_{10}E_5$ *system.*

Two hypotheses may be proposed to explain the experimental observations. First, the aggregation of the mixed micelles to the polymer is consistent with quite comparable low self-diffusion coefficients measured for SDS and $C_{10}E_5$ when they are mixed with PVP The slight difference between the self-diffusion coefficients for SDS (7.6 x 10^{-11} m^2/s) and $C_{10}E_5$ (6.6 x 10^{-11} m^2/s) could result from the higher number of SDS momomers than of $C_{10}E_5$ monomers, in equilibrium with aggregates of polymer/mixed micelles.

An alternative explanation might be the perturbation of the mixed micelle composition by PVP. It might be argued that the selective interaction of PVP with SDS leads to the formation of PVP/SDS aggregates that would be in equilibrium with monomers and mixed micelles of possibly changed composition This hypothesis is, however, questionable since D_S^{SDS}, observed for the ternary system (7 2 x 10^{-11} m^2/s), is very close to the value reported for the binary PVP/SDS system (7 8 x 10^{-11} m^2/s), which means that the whole amount of SDS should be associated to PVP and that the micelles left in solution would be $C_{10}E_5$ micelles. This conclusion is not consistent with D_S reported for $C_{10}E_5$ in the ternary system (6.6 x 10^{-11} m^2/s), which is far below D_S measured for $C_{10}E_5$ (9.8 x 10^{-11} m^2/s) at the same concentration.

The first hypothesis—mixed micelles of the two surfactants that interact with the polymer—has been further confirmed by the measurement of the self-diffusion coefficient of PVP in the presence of the two surfactants, which requires the use of the more time-consuming LED sequence (Table 5).

As already pointed out, substitution of D_2O for H_2O slightly decreases the surfactant self-diffusion coefficients. Nevertheless the important observation is that the self-diffusion coefficient of PVP is comparable to the values observed for the two surfactants, consistent with the formation of ternary aggregates, as suggested in Fig. 2c. The self-diffusion coefficient of neat PVP at 360mM(11.5 x 10^{-11} m^2/s) is decreased to 7.4 x 10^{-11} m^2/s in the presence of the two surfactants, as a consequence of interaction with them, As a whole, the experimental data strongly suggest that PVP interacts with SDS/$C_{10}E_5$ mixed micelles of composition more likely comparable to that observed in the absence of PVP.

TABLE 5 Self-Diffusion Coefficients for Ternary Systems Containing SDS (27.8 mM), $C_{10}E_5$ (5.3 mM), and PVP (360 mM); Effect of D_2O

Solvent	Sequence	D_s^{SDS} x 10^{11} (m^2/s)	D_s^{C10E5} x 10^{11} (m^2/s)	D_s^{pvp} x 10^{11} (m^2/s)
H_2O:D_2O (90/10)	Classical	7.6 ±0.1	6.6 ±0.05	—
D_2O	Classical	6.4 ±0.2	5.0 ±0.1	—
D_2O	LED	6.4 ±0.2	5.5 ±015	7.4 ±0,2

TABLE 6 Self-Diffusion Coefficients for Ternary Systems Containing SDS (27,8 mM), LAPB (5 mM), and PVP (360 mM); Effect of D_20

Solvent	Sequence	D_s^{SDS} x 10^{11} (m^2/s)	D_s^{LAPB} x 10^{11} (m^2/s)	D_s^{PVP} x 10^{11} (m^2/s)
H_2O: D_2O (90/10)	Classical	8.0 ±0.3	7 .0 ± 0.2	—
D_2O	Classical	6.5 ± 0,2	6.2 ± 0 1	—
D_2O	LED	6.4 ± 0.3	6.8 ±0.2	7.4 ±03

PVP/SDS/LAPB

According to Table 4, the conclusions drawn for the previous PVP/SDS/$C_{10}E_5$ ternary system are still valid when LAPB is substituted for $C_{10}E_5$, Formation of mixed micelles is supported by the decrease of D_S of each surfactant upon mixing: from 17.5 x 10^{-11} to 12.9 x 10^{-11} m^2/s for SDS and from 12 2 x 10^{-11} to 8.6 x 10^{-11} m^2/s for LAPB. These D_S values for the mixture of surfactants reflect the actual composition of monomers and micelles at the concentrations used in the experiments. When PVP is added to the SDS/LAPB mixture, the self-diffusion coefficients of the two surfactants are further decreased to 8 3 x 10^{-11} m^2/s (SDS) and 7 1 x 10^{-11} m^2/s (LAPB) Once again, comparable D_S values for SDS and LAPB in the presence of PVP agree with the aggregation of mixed micelles with the polymer (Fig. 2c). Table 6 confirms this general behavior since the self-diffusion coefficient of PVP as measured by the LED sequence (7.4 x 10^{-11} m^2/s) is close to D_S measured for SDS and LAPB. As previously pointed out, substitution of D_2O for the 90/10 H_2O: D_2O mixture decreases the observed self-diffusion coefficients.

Conclusion

The analysis of the PVP/SDS/$C_{10}E_5$ and PVP/SDS/LAPB ternary mixtures by PGSE FT-NMR has shown that, at least in the concentration range used in this study, the PVP/SDS aggregates formed in the absence of a second surfactant remain stable when $C_{10}E_5$ or LAPB is added, so that mixed micelles of the surfactants are not formed that would coexist with PVP/SDS aggregates. The experimental observations are consistent with the formation of ternary aggregates that might be viewed as aggregates of PVP with mixed micelles of the surfactants. This conclusion is in line with observations by Creeth *et al* (1.5) on aqueous solutions of the cationic dimethyldiallylarnmonium chloride-acrylamide copolymer in the presence of SDS/$C_{12}E_6$ mixtures Their neutron reflectivity data are consistent with the formation of bound micellar-like aggregates at the liquid/air interface. Creeth *et al* suggest that SDS bound to the polymer creates hydrophobic sites favorable to the formation of mixed micelles. The main difference in the ternary systems studied by Creeth *et al.* and by us is the water-soluble polymer, which is cationic (Creeth *et al.)* instead of being uncharged in this study Finally, Lima *et al. (17)* have analyzed mixtures of poly(ethylene oxide) with sodium dodecyl sulfate and sodium decyl phosphate They also conclude that polymer-mixed surfactant complexes are formed.

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References

[1]. Goddard, ED, and Ananthapadmanabhan, K. P., "Interactions of Surfactants with Polymers and Proteins " CRC Press, Boca Raton, FL, 1993
[2] Goddard, E. D, *Colloids Surf* 19, 255 (1986).
[3]. Goddard, E. D,,,,.J. *Am Oil Chem Soc* 71,1(1994).
[4]. Hansson, P., *Curr. Opin Colloid Interface Sci* 1, 604 (1996).
[5]. Kamenka, N, Burgaud, I.., Treiner, C, and Zana, R.., *Langmuir* 10, 3455 (1994)
[6]. Rosen, M,,, *in* "Surfactants and Interfacial Phenomena" (M Rosen, Ed.) Wiley, New York, 1989.
[7]. Rubingh, D N , *in* "Solution Chemistry of Surfactants" (K L. Mittal, Ed.), p. 337. Plenum, New York, 1979.
[8] Holland, P M, and Rubingh, P, *in* "Mixed Surfactant Systems: An Overview, Mixed Surfactant Systems" (P. M. Holland and D. N. Rubingh, Eds.) American Chemical Society, Washington, DC, 1996
[9]. Scamehom, J. F, *in* "Mixed Surfactant Systems; ACS Symposium Series" (J. F. Scamehom, Ed..), p 3.31. Am. Chem. Soc, Washington, DC, 1996
[10]. Dubin, P, Rigsby, R,,, and McQuigg, D W,,, J.. *Colloid Interface Sci* 105, 509 (1985).
[11]. Dubin, P. L , and Oten, R, J *Colloid Interface Sci.* 95, 453 (1983),
[12]. Tones M. N , Gilhooly, E, M.., and Nicholas, A. R ,.J.. *Chem Soc , Faraday Trans* 88,2733(1992).
[13]. Dubin, P. L,,, and Oteri, R ,./ *Colloid Interface Sci.* 1.3, 113 (1985).
[14]. Semchyshyn, D. J., Carbone, M A.., and Macdonald, P. M., *Langmuir* 12, 253(1996).
[15]. Creeth, A, Staples, E, Thompson, L., Tucker, I, and Penfold, J.., J.. *Chem Soc ., Faraday Tram* 92, 589 (1996)
[16] Lee, L T, Mann, E. K.., Cruselin, D, Langevin, D., Farnoux, B., and Penfold, J., *Macromolecules 26,* 7041 (1993) [17], Lima. C. F,,, Nome, E, and Zanette, D,,,.J *Colloid Interface Sci.* 189, 174
(1997). [18] Stejskal, E. 0,,, and Tanner, J. E , / *Chem Phyy.* 42, 288 (1965).
[19]. Stilbs, P., *Prog. NMR Spectrosc* 19, 1 (1987).
[20]. Herden, H,,, Karger, J.., Pfeifer, H., Kube, C, and Schollner, R, J.. *Colloid Interface Sci.* 152,281(1992).
[21]. Gibbs, S J.., and Johnson, C. S,,, *J. Magn Reson.* 93, 391 (1991).
[22]. Stilbs, P., *in* "Solubility in Surfactant Aggregates" (D. Christian and J. F. Scamehom, Eds.), Surfactant Science Series, p. 367 Dekker, New York, 1995.
[23]. Söderman, O., and Stilbs, P., *Progr. NMR Spectrosc.* 26,445 (1994)
[24]. Lindman, B , Olsson, U,, and Söderman, O., *in* "Dynamic of Solutions and Fluid Mixtures by NMR" (J. T. Delpuech, Ed), p. 321 Wiley, New York, 1995.
[25] Almgren, A-., van Stam, J.., Lindblad, C,., Li, P., Stilbs, P., and Bahadur, P., .J. *Phys. Chem..* 95,5677 (1991).
[26] Carlsson A.., Karlstiom, G, and Lindman, B.., J *Phys. Chem* 93, 3673 (1989).
[27]. Zana, R.., Binana-Limpbele, W.., Kamenka, N , and Lindman, B..,.J.. *Phys. Chem.* 96,5461 (1992),. [28] Zhang, K, Jonstrδmei, M.,, and Lindman, B.., J *Phys. Chem* 98, 2459
(1994).
[29]. Abrahamsen-Alami, S.., and Stilbs, P.,.J.. *Phys. Chem* 98,6359 (1994)..
[30]. Sesta, B.., D'Apiano, A., Segre, A. L,,, and Pioietti, N,,, *Langmuir* 1.3,6612 (1997).
[31]. Minatti, E,, and Zanette, D, *Colloids Surf* 113,237 (1996)
[32]. Zanette, D.., Ruzza, A. A.., Fioehnei, S.. J., and Minatti, E., *Colloids Surf.* 108,91(1996)
[33] Misselyn-Bauduin, A. M., Thibaut, A., Giandjean, J,., Bioze, G, and Jerome, R., *Langmuir* 16,4430 (2000).