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ESR Study of Sodium Dodecyl Sulfate and Dodecyltrimethylammonium Bromide Micellar Solutions. Effect of Urea

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Electron spin resonance spectroscopy of cationic ((4-(trimethylammonio)-2,2,6,6-tetramethylpiperidinyl)-1-oxy iodide, Temp-TMA$^+$) and nonionic spin probes ((4-octanoyl-2,2,6,6-tetramethylpiperidinyl)-1-oxy, C_8-TEMPO, and x-doxylstearic acid with the nitroxide group in position x = 5, 12, and 16, along the stearic acid chain, 5-DSA, 12-DSA, and 16-DSA) has been studied in sodium dodecyl sulfate and in dodecyltrimethylammonium bromide solutions as a function of surfactant and urea concentration. The analysis of the nitrogen hyperfine coupling constant, $\langle A_N \rangle$, and of the correlation time for the probe motion, τ, indicates that urea interacts with the surfactant polar headgroups of the micelle and penetrates below them. Urea slightly decreases the polarity and strongly increases (from 20% to 100% depending on the surfactant and on the urea concentration) the microviscosity of the micelle interface. These results support recent molecular dynamics and Monte Carlo experiments and are in agreement with a direct mechanism of action in which urea replaces some water molecules that solvate the hydrophobic chain and the polar headgroups of the amphiphile.

Introduction

The properties of micellar solutions, such as critical micellar concentration (cmc), aggregation number, micelle size and shape, etc., depend on the balance between "hydrophobic" and "hydrophilic" interactions.[1] For ionic surfactants this balance can be modified in several ways, i.e., salt addition, counterion complexation, addition of alcohols or other substances that can be solubilized into the micelle, change of the solvent, or change of the "structure" of the solvent itself. Several studies have been performed in the past using urea as an additive to check the effect of this additive on the properties of micellar solutions[2-4] and on the denaturation of proteins.[4,5] Two different mechanisms for urea action have been proposed:[6-8] (i) urea changes the "structure" of water to facilitate the solvation of a hydrocarbon chain; (ii) urea replaces some water molecules that solvate the hydrophobic chain and the polar headgroup of the amphiphile.

The first mechanism is the most widely accepted, and many experimental results seem to support the hypothesis that urea acts as a "water structure breaker".[9-17] In particular the addition of urea to micellar solutions leads to an increase of the cmc value. This effect is attributed to the breaking of the water structure favoring the dissolution of hydrophobic solutes, and urea is considered not to penetrate the micellar surface.[3,4,18] However some recent molecular dynamic and Monte Carlo[19-23] experiments suggest that very small differences are present between the properties of water molecules in the solvation region of urea and the bulk, and these differences can be assigned to direct urea-water interactions with no substantial perturbation of water-water interactions. These results have also been confirmed by the calculation of energy minimization of urea clusters consisting of one or two solute molecules surrounded by up to 19 water molecules.[24] Furthermore, it is found that urea in the solvation region of an apolar sphere weakens the water-water interactions, displacing several water molecules from the apolar solvation shell.[20] These experiments seem to support the second mechanism of urea action.

This paper reports the effects of urea addition to dodecyltrimethylammonium bromide (DTAB) and sodium dodecyl sulfate (SDS) micellar solutions studied by using ESR of nitroxide spin probes. This technique has been successfully used to investigate the local polarity and microviscosity of the micellar interface and of polymeric latexes[25-28] interface, through the analysis of the nitrogen coupling constant, $\langle A_N \rangle$, and the analysis of the correlation time for probe motion, τ, respectively. Three different ESR spin probes have been used: (i) positively charged (4-(trimethylammonio)-2,2,6,6-tetramethylpiperidinyl)-1-oxy iodide (Temp-TMA$^+$); (ii and iii) the nonionic spin probes (4-octanoyl-2,2,6,6-tetramethylpiperidinyl-1-oxy (C_8-TEMPO) and x-doxylstearic acid with the nitroxide group in position x = 5, 12, and 16, along the stearic acid chain (5-DSA, 12-DSA, and 16-DSA). The results are analyzed in terms of polarity and microviscosity of the SDS and DTAB micellar interface. We show that urea addition to micellar solutions of SDS and DTAB leads to an increase of the microviscosity and to a variation of the local polarity of the micelle surface, indicating that urea directly interacts with the surfactant headgroups, replacing some water molecules in the surface region.

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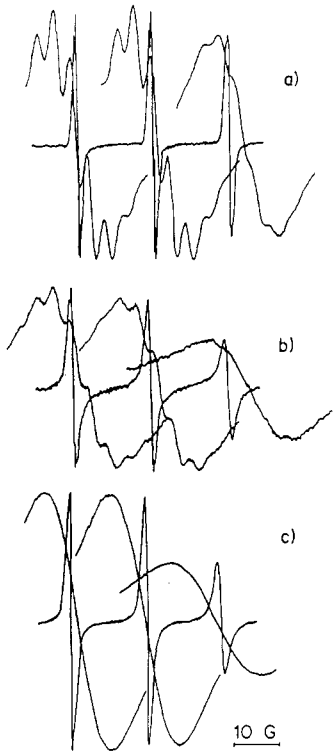

Figure 1. ESR spectra for the C_8-TEMPO/SDS/6 M urea system as a function of SDS concentration: (a) below the cmc of SDS; (b) at SDS cmc; (c) with 0.05 M SDS.

Experimental Section

Sodium dodecyl sulfate (SDS) was obtained from Carlo Erba, Milan, Italy. It was recrystallized three times from ethanol, washed with ethyl ether, and dried at 40 °C under moderate vacuum. Dodecyltrimethylammonium bromide (DTAB) was obtained from Eastman Kodak; it was recrystallized three times from acetone and dried under moderate vacuum. Urea was obtained from Aldrich and used without further purification. x-Doxylstearic acid spin probes (x-DSA) with x = 5, 12, and 16, (4-(trimethylammonio)-2,2,6,6-tetramethylpiperidinyl)-1-oxy iodide (Temp-TMA$^+$) and (4-octanoyl-2,2,6,6-tetramethylpiperidinyl)-1-oxy (C_8-TEMPO) were obtained from Molecular Probes, Eugene, OR, and used as received. Stock solutions of x-DSA, Temp-TMA$^+$ and C_8-TEMPO were prepared in chloroform. Stock solutions of 0.1 M surfactant were prepared in triply distilled water purified by a Milli-Q water system (Millipore) and deoxygenated by nitrogen bubbling. Films of the probes generated in vials by evaporating the chloroform were dissolved in the surfactant solution in a nitrogen atmosphere. The final probe concentration was 1×10^{-4} M. ESR measurements were performed with a Bruker 200D spectrometer operating in the X-band, equipped with an Aspect 2000 EPR handling system and an ST100/700 temperature controller. All the measurements were made at 25 °C. The mean error was ±0.02 G for the nitrogen hyperfine coupling constant, $\langle A_N \rangle$, and about 10% for the rotational correlation time, τ.

Results

Figure 1 shows the ESR spectra obtained by using the C_8-TEMPO probe in urea–SDS solutions (a) below the SDS cmc, (b) at the SDS cmc, and (c) above the SDS cmc (0.05 M). Similar spectra have been obtained with DTAB. The spectrum below the cmc of the surfactant shows a well-resolved superhyperfine structure due to the coupling of the unpaired electron of the probe with the hydrogen nuclei of the methyl groups and of the piperidine ring. Near the cmc of the surfactant the ESR spectrum is rather complex and consists of at least two different absorptions due to the probe in the micellar "phase" and to the probe in the solvent "phase". Because of the complexity of the spectra obtained in this range of surfactant concentration, accurate correlation time values can be obtained only via extensive computer simulation of the ESR spectra. This is beyond the aim of this paper. In the ESR spectra where a superhyperfine structure was present, the correlation times for the probe motion have been computed following a procedure similar to that reported in previous works.[25-28] The Temp-TMA$^+$ and C_8-TEMPO probes exhibit isotropic Brownian motion, $\tau_B \approx \tau_c = \tau$. The spectra obtained with x-DSA probes do not show superhyperfine structure. For these probes the correlation time has been computed by using the approximate equations proposed by Cannon et al.[29] In Table I are reported the $\langle A_N \rangle$ and τ_c parameters. Figures 2, 4, and 6 show the nitrogen hyperfine coupling constant as a function of surfactant and urea concentration for Temp-TMA$^+$/SDS, C_8-TEMPO/SDS, and C_8-TEMPO/DTAB systems. Finally Figures 3, 5, and 7 show

TABLE I: Nitrogen Coupling Constant, $\langle A_N \rangle$, and Correlation Time, τ_c, for 5-, 12-, and 16-DSA Probes in 0.1 M SDS and DTAB as a Function of Urea Concentration

	$\langle A_N \rangle$, G			τ_c, ns		
[urea], M	5DSA	12DSA	16DSA	5DSA	12DSA	16DSA
			SDS			
0	15.3	15.3	15.3	1.1	0.82	0.43
2	15.3	15.3	15.4	1.2	0.83	0.44
6	15.3	15.3	15.4	1.4	1.0	0.46
			DTAB			
0	15.0	15.0	15.0	1.0	0.80	0.43
2	15.0	15.0	15.0	1.3	0.82	0.45
6	15.0	15.0	15.0	1.4	0.87	0.47

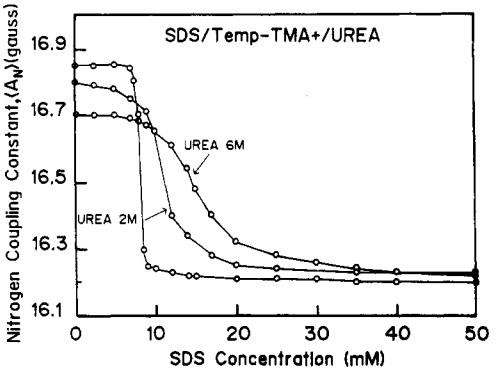

Figure 2. Nitrogen coupling constant, $\langle A_N \rangle$, for the probe Temp-TMA$^+$ as a function of SDS and urea concentration.

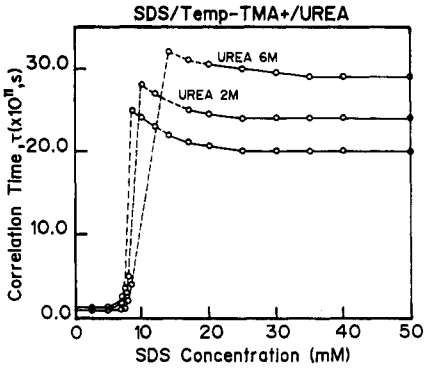

Figure 3. Correlation time, τ_c, for the Temp-TMA$^+$ probe as a function of SDS and urea concentration.

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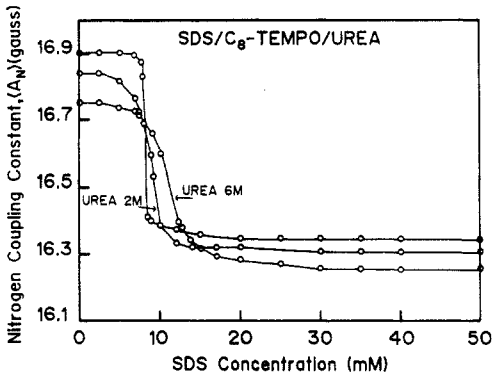

Figure 4. Nitrogen coupling constant, $\langle A_N \rangle$, for the probe C_8-TEMPO as a function of SDS and urea concentration.

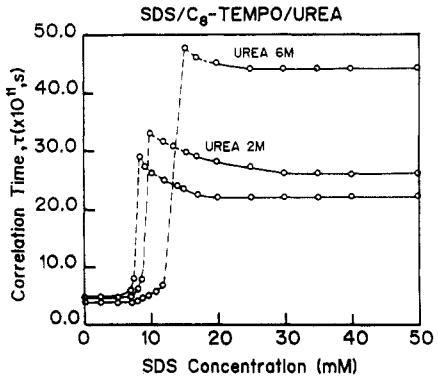

Figure 5. Correlation time, τ_c, for the C_8-TEMPO probe as a function of SDS and urea concentration.

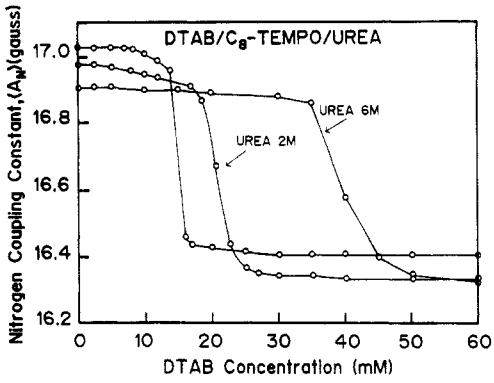

Figure 6. Nitrogen coupling constant, $\langle A_N \rangle$, for the probe C_8-TEMPO as a function of DTAB and urea concentration.

the correlation time as a function of surfactant and urea concentration for Temp-TMA$^+$/SDS, C_8-TEMPO/SDS, and C_8-TEMPO/DTAB systems.

Discussion

In previous studies it has been shown that the location of a nitroxide spin probe in a micelle is dependent on the interactions that the probe experiences with the micelle.[25-28] Therefore probes that can interact in different ways with the micelle can be used to investigate physicochemical properties of different regions of the micellar interface and to investigate the possible site of interaction of a solubilized molecule.

It has been demonstrated that the cationic Temp-TMA$^+$ probe interacts mainly electrostatically with the SDS negatively charged micelle surface, and it is located in the solvation layers of the micelle.[25] Because of the unfavorable electrostatic interaction between the Temp-TMA$^+$ probe and the cationic DTAB micelles, no information can be obtained for the system DTAB/UREA/Temp-TMA$^+$ from the analysis of the ESR spectra. C_8-TEMPO and x-DSA probes are surfactant-like molecules and solubilize in the SDS or DTAB micelles.[30] It has been shown that the

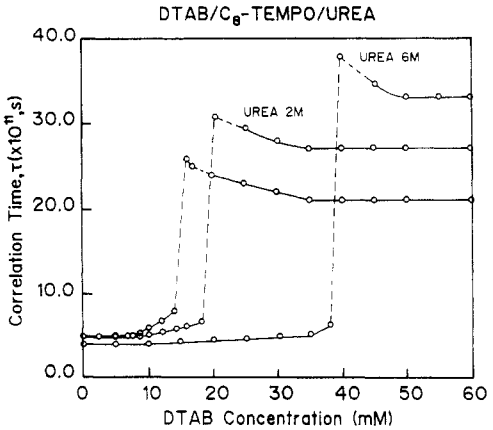

Figure 7. Correlation time, τ_c, for the C_8-TEMPO probe as a function of DTAB and urea concentration.

carboxyl and nitroxide groups of the x-DSA probe are located in the Stern layer close to the micelle polar headgroups in anionic and cationic micelles,[31-33] while they are located in the poly(ethylene oxide) mantle in nonionic alkylpoly(ethylene oxide) micelles.[34] An average distribution of the x-DSA probe in anionic, cationic, and nonionic micelles has also been reported.[31-34] The location of the C_8-TEMPO probe has been found to be similar to x-DSA probe in SDS and DTAB micelles.[26] However the higher deuterium modulation depth values obtained with C_8-TEMPO probe show that this probe is more exposed to water contacts[35] than x-DSA.

The nitrogen hyperfine coupling constant, $\langle A_N \rangle$, in liquid solutions is sensitive to the local polarity.[30,36-40] A sharp decrease of $\langle A_N \rangle$ is usually present at the surfactant cmc and corresponds to the transfer of the probe from the continuous phase to the less polar surface of the micelle. From the analysis of the $\langle A_N \rangle$ trend as a function of surfactant concentration, it is possible to determine the critical micellar concentration and the local polarity of the micelle interface. In particular the cmc is obtained from the inflection point in the $\langle A_N \rangle$–surfactant concentration curve, which is related to the interaction that the probe experiences with the micelle. It follows that if this interaction is hindered, the cmc deduced by using the above method will be higher than the "true" cmc. This can be used to detect the effect of additives to micellar solutions.

Since the probe Temp-TMA$^+$ mainly interacts via electrostatic interactions, a disagreement in the cmc values obtained through the $\langle A_N \rangle$ analysis and the "true" cmc value (obtained with techniques that can detect the monomers aggregation) is expected in the presence of additives that screen the micelle electrostatic charge and decrease the probe–micelle interaction strength. This has been reported with the Temp-TMA$^+$/SDS system in the presence of sodium chloride,[41] which screens the surface charge of the micelle. It was found that the disagreement between the cmc computed from the $\langle A_N \rangle$ trend as a function of SDS concentration and the "true" cmc is a function of the sodium chloride

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concentration.[41] Therefore, if urea changes the micellar charge density, a disagreement between the cmc values obtained from the $\langle A_N \rangle$ analysis and the "true" cmc values should occur; in particular, as reported above, the presence of a screening of the surface charge should produce a shift to higher values of cmc obtained by the Temp-TMA$^+$ probe.[41]

Figure 2 reports the $\langle A_N \rangle$ trend for the probe Temp-TMA$^+$ as a function of SDS and urea concentration. Two main results can be deduced from the analysis of the figure: (1) The cmc value computed from $\langle A_N \rangle$ for SDS micellar solutions without added urea (8.2×10^{-3} M) is in good agreement with the literature data.[42] In the presence of 2 and 6 M urea the cmc is 1.1×10^{-2} and 1.7×10^{-2} M. These values are greater than the values reported in the literature[2,3] and those obtained with the C_8-TEMPO probe (see below), i.e., 9.2×10^{-3} and 1.2×10^{-2} in the presence of 2 and 6 M urea, respectively. (2) The addition of urea produces a lowering of the $\langle A_N \rangle$ value in the $(0-8) \times 10^{-3}$ M SDS concentration range (i.e., below the SDS cmc) that depends on the urea concentration. This last result supports the hypothesis of a direct interaction between urea and probe molecules below the cmc of SDS. This probably occurs by replacing some water molecules from the probe hydration shell and/or by forming clusters.[43] Above the SDS cmc the $\langle A_N \rangle$ parameter stabilizes to a value of about 16.20 G without urea and 16.24 G with 2 and 6 M urea. The higher $\langle A_N \rangle$ value found in presence of urea can be explained in two different ways: (a) urea increases the water penetration at the micelle surface, or (b) urea increases the mean distance of the probe from the micelle surface with resultant increases of the water–probe interactions and therefore of the polarity sensed by the probe. This last effect can be due to the solvation by urea molecules of the surfactant polar headgroups of the micelle and/or of the probe itself.

In fact, in both cases urea molecules would hinder the electrostatic interactions between the probe and the surfactants polar headgroups. Simply from the analysis of the $\langle A_N \rangle$ trend it is not possible to discriminate between the above hypotheses. However, analysis of the correlation time for the probe motion (see below) and analysis of the electron spin echo modulation results reported in a previous paper[35] show that urea does interact with the micellar surface and it does not increase the water penetration at the micelle surface. Figure 3 reports the correlation times for the Temp-TMA$^+$ probe motion as a function of SDS and urea concentration. Below the critical micellar concentration of SDS, the addition of urea produces a decrease of the correlation time, indicating that the probe "sees" a less viscous environment. On the contrary, above the cmc of SDS a strong increase of the correlation time is observed. In particular, the correlation time increase is about 20% and 45% for SDS micellar solutions containing 2 and 6 M urea, respectively, showing that urea addition to SDS micellar solutions increases the microviscosity of the micellar interface.

A similar result has been obtained from fluorescence measurements.[45,46] It is reported that the microviscosity of *N,N,N',N'*-tetramethyldiaminodiphenyl ketoimine solubilized in SDS micellar solutions is 60% greater in 5 M urea than in the micellar system without urea.[45]

The increase of the microviscosity sensed by the Temp-TMA$^+$ probe for SDS micellar solutions containing urea supports the hypothesis of a direct interaction of urea with SDS micelle. In fact in the absence of this interaction the microviscosity sensed by the probe should decrease, as found in the premicellar region of the system studied, or should be insensitive to urea addition. It follows that the higher cmc and $\langle A_N \rangle$ plateau values found for the Temp-TMA$^+$/SDS/urea systems can be attributed to a screening of the micellar surface charge due to a direct interaction of urea at the micellar surface, which increases the mean probe–micellar surface distance. It might be stressed that a possible change of the aggregation number of the SDS micelle upon urea addition could affect the ESR line shape. However, Almgren and Swarup reported[47] that the aggregation number changes very little (about 10%) upon urea addition to SDS micellar solutions. This variation is too weak to affect the ESR line shape. Furthermore the ESR signal is little affected by the collective properties of micellar systems.

Figures 4 and 5 show the nitrogen coupling constant and the correlation time behavior as a function of urea and SDS concentration for C_8-TEMPO probe. As reported above, this probe mainly interacts with the micelle via hydrophobic interactions and is solubilized in the SDS or DTAB micelle with the nitroxide group located at the micellar surface. Therefore, unlike Temp-TMA$^+$, C_8-TEMPO is almost insensitive to a screening of the micelle surface charge[41] by urea molecules. Considering that the probe solubilizes into the micelle with the active ESR group at the micelle surface, changes in the ESR spectra are expected only if urea molecules interact at the micelle surface or penetrate into the micelle. Figure 4 shows that below the cmc of SDS the $\langle A_N \rangle$ value decreases as the urea concentration increases, demonstrating that urea molecules interact with C_8-TEMPO by replacing water molecules, in agreement with the results obtained with Temp-TMA$^+$. Above the cmc of SDS the $\langle A_N \rangle$ parameter stabilizes to a value that depends on the urea concentration, and in particular this value decreases as urea concentration increases, supporting the view that urea interacts with the SDS micelle by replacing some water molecules that solvate the polar headgroups and the hydrophobic chain of the amphiphile. Furthermore the cmc computed from the $\langle A_N \rangle$ trend as a function of urea and SDS concentrations (8.2×10^{-3} M without urea, 9.2×10^{-3} M with 2 M urea and 1.2×10^{-2} M with 6 M urea, in good agreement with the results reported in the literature by using different experimental methods[2,3]) shows that urea addition does not affect the C_8-TEMPO probe solubilization in the SDS micelle. The analysis of the correlation time (Figure 5) strongly supports the above findings. Below the SDS cmc the interaction of urea with C_8-TEMPO leads to a slight decrease of the microviscosity sensed by the probe, while above the cmc urea produces an increase of the microviscosity of the micellar interface of about 20% and 100% in presence of 2 and 6 M urea. As previously reported, this increase can be explained by considering that urea molecules interact with the surfactant polar headgroups at the micelle surface. Similar results are obtained with C_8-TEMPO in the DTAB/urea system.

The cmc computed from the $\langle A_N \rangle$ trend as a function of DTAB concentration are 1.48×10^{-2} and 2.09×10^{-2} M for 0 and 2 M urea concentrations, in good agreement with data reported by Burning and Holtzer.[3,48] The value obtained for 6 M urea (4.0×10^{-2} M) deviates from the value reported in ref 48 by about 15%. A possible explanation can be the different experimental method used. In this work the cmc is deduced from $\langle A_N \rangle$ and the ESR line shape change that occurs when the probe is solubilized in the micelle. ESR and ESEM as well as fluorescence give information at short range from the probe and therefore are little affected by the "collective" properties of the system. Burning and Holtzer used conductivity to measure the cmc. Since this technique integrates the signal over the whole micellar particle, including the particle interface, the cmc value can be overestimated in the presence of the high urea concentration that can alter the micellar interface.

The correlation time and the nitrogen coupling constant present a trend very similar to the C_8-TEMPO/SDS/UREA system. In particular, the microviscosity of the DTAB micellar interface increases about 25% and 60% upon addition of 2 and 6 M urea. These results suggest, in agreement with the results obtained for

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the Temp-TMA$^+$/SDS and C_8-TEMPO/SDS systems, that urea solubilizes at the micellar surface. Further evidence comes from the results obtained with x-DSA spin probes. Table I shows that the $\langle A_N \rangle$ parameter of x-DSA probes is almost insensitive to urea addition while the correlation time increases from 20% to 30% depending on the surfactant and urea concentration. Doxylstearic acids spin probes are located deeper inside the micelle with respect to C_8-TEMPO.[35] In fact the deuterium modulation depth, as measured by using the electron spin echo modulation technique, is greater for C_8-TEMPO than for x-DSA for both SDS/D_2O and DTAB/D_2O micellar solutions, showing that this probe is more exposed to water.[35] In particular x-DSA probes are located below the surfactant polar headgroups. The above results suggest that urea penetrates below the surfactant polar headgroups. This is in agreement with structural investigations of the micellar interface by ESEM.[35]

Conclusions

The use of nitroxide spin probes that due to the different kind of interactions (electrostatic or hydrophobic) with SDS or DTAB micelles are located in different regions of the micellar interface allows one investigation of the site of the interaction of the urea molecule with the micelle. It is shown that the addition of urea to premicellar solutions of SDS and DTAB leads to a decrease of the microviscosity and of the polarity sensed by the nitroxide spin probes, supporting the formation of a clathrate structure around the probe itself. The analysis of the ESR parameters shows that the addition of urea to micellar solutions produces a decrease of the polarity and a strong increase of the microviscosity of the micellar interface. These effects are dependent on the urea concentration. The above results suggest that urea solubilizes at the micellar surface and penetrates below the surfactant polar headgroups by replacing some water molecules that solvate the hydrophobic chain and the polar headgroup of the amphiphile. These results provide information at a molecular level of the mechanism of action of urea and are in agreement with molecular dynamics and Monte Carlo calculations and with a recent Raman study on the water/acetone/urea ternary system in which it is postulated that the main mechanism of the urea action is a direct interaction with the organic molecule.[49]

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Charge-Carrier Dynamics in TiO_2 Powders

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Contactless transient photoconductivity measurements in TiO_2 powder are presented. Large differences between the modifications anatase and rutile are observed with anatase exhibiting higher yields and longer lifetimes of photoinduced excess charge carriers. It is shown that surface modification drastically changes the electron decay kinetics, where adsorption of 2-propanol and of tetranitromethane leads to a lower and a higher decay rate, respectively. Platinization opens an additional fast decay channel. The results are discussed in view of their relevance for photocatalysis.

1. Introduction

Titanium dioxide powder has two important applications, as white pigment[1] and as photocatalyst.[2] The most important modifications of TiO_2 are rutile and anatase.[1] Anatase, which is metastable and transforms into rutile at higher temperatures,[1] is produced by precipitation of Ti^{4+} compounds.[1] The structures consist of slightly distorted octahedrons of oxygen atoms around a titanium atom, where the modifications differ in the connection of the octahedrons.[1]

The two applications as pigment and as photocatalyst are complementary, and the kinetics of the light-induced excess charge carriers is of fundamental importance for both applications. In the first case fast recombination of the excess charge carriers and inhibition of the charge transfer from the powder to possible reactants are required to prevent the photocatalytic degradation of the polymeric binder, which leads to "chalking" of the paint.[3] In the second case slow recombination of the excess charge carriers and an efficient charge transfer of these carriers from the powder to the reactants are necessary for a high photocatalytic activity of the powder. In general, it is found that rutile is photocatalytically less active than anatase.[4]

In this work transient photoconductivity measurements are chosen as a tool for the investigation of excess charge carrier kinetics in titanium dioxide powder. A contactless transient photoconductivity method, the time-resolved microwave conductivity (TRMC) method, is used to avoid contact problems.[5] This method was already successfully applied to a number of semiconductor powders.[6-8] The kinetics of mobile charger carriers in powders is a relatively new field of research, and the interpretation of the decay of the photoconductivity is complicated. Therefore, it is convenient to study the influence of a small structure perturbation of the powders on the decay of the photoconductivity. This approach has the advantage that these treatments lead to changes of the decay behavior, which in general can be interpreted more easily. As photocatalysis implies, the reactions between photoinduced charge carriers and molecules adsorbed occur at the surface, and the most interesting way to modify the structure of the particles is to change their surface

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