Influence of Alcohol on the Behavior of Sodium Dodecylsulfate Micelles

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The effect of medium chain alcohol molecules on the size and shape of sodium dodecylsulfate micelles, and on the self-diffusion coefficient of the surfactant and alcohol, has been investigated by means of small angle neutron scattering (SANS), and Fourier transform pulsed field gradient spin echo (FT-PGSE) nuclear magnetic resonance measurements. All measurements were done in D₂O containing a sodium chloride concentration of 0.4 mol/kg, and a surfactant concentration of 0.04 mol/kg. The alcohols used were 1-propanol, 1-butanol, and 1-pentanol. The data obtained from the different techniques agrees qualitatively. The results show that propanol successively breaks down the micelles while pentanol brings about a structural change toward large wormlike aggregates. Butanol shows a highly complex behavior on the structure of the micelles and can decrease and increase the size of the aggregates, depending on the added alcohol concentration range. All analyzed solutions show a distribution of the alcohol between the aqueous bulk solution and the palisade layer of the micelles, resulting in an increased "hydration" of D₂O in the micellar surface. Moreover, the structural changes of the micelles indicate that butanol and pentanol solubilize in the micellar core in the high molality range, near the end of the solubility limit. Propanol is apparently too hydrophilic to do so. © 1998 Academic Press

Key Words: micelles; surfactants; sodium dodecylsulfate; alcohol; small angle neutron scattering; SANS; NMR self-diffusion.

INTRODUCTION

The hydrophobic and electrostatic forces among ionic surfactant molecules play an essential role for the self-association and formation of micelles. One of the most interesting aspects of these heterogeneous micelles is their ability to accommodate organic molecules (1-3). The ability to solubilize a large amount of otherwise insoluble or sparingly soluble molecules forms the basic functionalities of soap solutions and microemulsions (4-7). An increased flexibility of the micellar membrane and thereby an improved ability to solubilize hydrophobic molecules can be achieved by adding neutral salt and a medium chain alcohol (7, 8). Therefore, these elements make the basic components in most microemulsions. However, the intricate behavior of these mixed micellar aggregates makes it difficult to predict any variation in the system upon variation in the composition of the solution. This problem is caused by a delicate balance of attractive and repulsive forces among the amphiphilic molecules in the micelles.

The size and shape of micelle aggregates containing commonly used surfactants and co-surfactants have been thoroughly investigated during the past decades (9, 10). The commonly used sodium dodecylsufate (SDS) micelles form spherically aggregates consisting of about 60 monomers in aqueous solutions at cmc (11, 12). Addition of NaCl increases the micellar size and promotes a shape transition into prolate ellipsoids and flexible rods (13-15). Addition of alcohol can strongly influence the behavior of the micelles and increase or decrease the micellar size depending on the hydrophilic/hydrophobic character of the alcohol (16, 17). Whereas the hydrophilic alcohols (methanol to propanol) mainly solubilize in the aqueous solution and affect the micellization process by modifying the solvent (18), the more hydrophobic alcohol molecules (pentanol and higher homologues) take part in the micellization process and become unique components of the micelle aggregates (19). The micelle has two regions of differing polarity for solubilization, the outer hydrophilic region (palisade layer) and the hydrophobic core. Compounds with polar groups such as alcohol molecules can be expected to solubilize in the hydrophilic regions. The degree of solubilization into this shell region depends on the amphiphilic character of the alcohol molecules (17, 18). However, the roles of the amphiphilic alcohol molecules as co-surfactants are still unclear and a matter of discussion. This is especially true for the medium chain length alcohol molecules which are the most commonly used co-surfactants in microemulsions. Even though the influence of *n*-alcohols on the structure of SDS micelles has been extensively investigated, several conflicting results have been reported. Attwood et al. (20) indicates that SDS

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micelles decrease progressively in size upon addition of butanol in aqueous salt solutions. Similar result was shown by Boström *et al.* (21) and Rubio *et al.* (12) in micellar SDS solutions without salt. On the other hand, McGreevy and Schechter (22) indicate that the size of the SDS micelles is not influenced upon addition of 1-butanol. Stilbs (23) indicates that SDS micelles grow upon addition of small amounts of butanol and progressively break down upon addition of butanol in the high concentration range. In a previous work, Førland *et al.* (17) showed that butanol influences SDS micelles by either increasing or decreasing the size of the micelles depending on the concentration range of the alcohol.

In order to elucidate some of the problems concerning the effect of intermediate alcohols on the behavior of SDS micelles, this paper reports a study of the size, shape, and self-diffusion of SDS micelles in the presence of various amounts of propanol, butanol, and pentanol. Small angle neutron scattering (SANS) was used in the study of micellar size and shape, while Fourier transform pulsed field gradient spin echo (FT-PGSE) nuclear magnetic resonance measurements were used for determining the self-diffusion coefficients of the surfactant and alcohol. All measurements were done in D_2O instead of water, and in solutions containing 0.4 mol/kg NaCl.

MATERIALS AND METHODS

Materials

The sodium chloride was obtained from Merck and was of "pro analysis" reagent grade. It was dried at 120°C before use. The sodium dodecylsulfate (SDS) obtained from BDH "specially pure" was dried in an evacuated desiccator at 50°C before use. The alcohols, 1-propanol, 1-butanol and 1pentanol, were obtained from Riedel de Haën, "purified grade more than 99.5%." All measurements were used with D_2O instead of water and carried out at 30°C, which is well above the Krafft temperature.

SANS Measurements and Analysis

The small angle neutron scattering experiments were carried out at Risø National Laboratory, Denmark. The neutron wavelength was 3 and 6 Å and the sample-to-detector distance was 2 and 3 m, which corresponds to a *q*-range from 0.01 to 0.3 Å⁻¹. The scattering from the cuvette and the instrumental background was subtracted from the data. Finally, the data were normalized relative to water and radially integrated.

The dependence of the neutron scattering cross-section $(d\Sigma(Q)/d\Omega)$ on the magnitude of the scattering vector (Q) can be expressed as a function of the micellar particle structure factor P(Q) and the interparticle structure factor S'(Q). In the simple case, where spherical monodisperse micelles

are present, the neutron scattering cross-section can be written as

$$d\Sigma(Q)/d\Omega = n_{\rm p}P(Q)S'(Q), \qquad [1]$$

where $n_{\rm p}$ is the number density of micelles, which can be calculated from

$$n_{\rm p} = (C - C_{\rm cmc}) \text{Na}/1000n.$$
 [2]

C and $C_{\rm cmc}$ are the total and critical surfactant concentrations in molarity, Na is Avogadro's number, and *n* is the number of surfactant molecules in the micelles. For the solutions studied in this work, where the concentration of the surfactant is low and the presence of neutral salt (0.4 molal) effectively screens the electrostatic repulsion between the micelles, the electrostatic interaction among the micelles was neglected and S(Q) was taken to unity. For all the normalized and integrated data sets, the S(Q) was set to unity throughout the observed *Q*-range and the intensity data were fitted to the intraparticle structure factor for various geometric models including spheres, rods, prolate ellipsoids, and oblate ellipsoids (9, 24).

NMR Self-Diffusion Measurement and Analysis

The ¹H self-diffusion measurements were carried out at 400.13 MHz on a Bruker DMX-400. The field gradients were generated by the Bruker BGU II with a Bruker BGPA10 amplifier. Eddy current effects were reduced by the use of a Z-shielded 5-mm probehead, and a Bruker B-VT 2000 temperature-control unit kept the temperature within ± 0.5 K.

The self-diffusion coefficients (*D*-values) were determined by the use of a pulsed field gradient spin echo method (25, 26) in the improved Fourier transformed mode (27, 28) (FT-PGSE). The pulse sequence employed is similar to that originally described by Stilbs and Moseley (29, 30). The magnitude of the gradient pulse (*G*) was calibrated against a solution of 6% H₂O in D₂O (31). The self-diffusion coefficient (*D*) for the given species was determined from the intensity of the NMR signal (*A*) of the species according to the equation

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

where A/A_0 is the ratio of echo amplitudes in presence (A) and in absence (A₀) of the gradient, γ is the gyromagnetic ratio, δ is the duration of each gradient pulse, and Δ is the time delay between the two gradient pulses.

RESULTS

Sodium dodecylsulfate (SDS) forms spherical or slightly ellipsoidal micelles with a minor radius (as measured by



FIG. 1. The minor radius (R_{\min}) and the major to minor axial ratios (major/minor) of the prolate SDS micelles plotted against the molality of NaCl.

SANS) of about 18 Å in dilute aqueous solutions. The polydispersity in size is about 30% (32), and it probably increases upon addition of NaCl and alcohols (17). Figure 1 shows the minor radius and the major to minor axial ratios of SDS micelles against the molality of NaCl. The SANS data fit a model for prolate ellipsoids with varying ratios of the major to minor axes. The result shows that the size increment of the micelles is not a monotonic function of the ionic strength in the solution. The minor radius remains fairly constant and the major to minor axial ratio increases slowly up to about 0.4 molal NaCl. Above this salt concentration, the major axis increases rapidly, producing large wormlike micelles. This behavior agrees with previous findings for SDS micelles in NaCl solutions (10, 14).

The intermicellar interaction in aqueous SDS solutions are strongly repulsive and long-ranged even in the vicinity of the cmc. In order to effectively screen the electrostatic interactions, but at the same time take care of the small ellipsoidal micelles, we used solutions containing 0.4 mol/kg NaCl subsequent to the addition of alcohol. At this salt content, the micelles have a major to minor axial ratio of about 2.3 and the reported Krafft temperature is about 24°C (14).

The experimental SANS intensity distributions for mixed solutions of SDS and alcohols are shown in Fig. 2. The labels a, b, and c represent the data obtained for the solutions containing propanol, butanol, and pentanol, respectively. The solid lines through the experimental data points represent fitted theoretical functions for spheres, ellipsoids, and rods. In all models used for fitting the data, the instrumental resolution function was included. The measured data and the theoretically calculated result agree well for the samples investigated. The results comprising the alcohol concentrations, the fitted models, the axis values, and the χ^2 -values are presented in Table 1.

The minor radius and the major to minor axial ratio of the micelles against the molality of added alcohol is presented in Fig. 3. The structure parameter profiles observed depends on the alcohol used. Addition of propanol (Fig. 3a) decreases the axial ratio and the minor radius and transform the micelles into small spherical aggregates at alcohol concentrations above 1.5 mol/kg. The best fit at low alcohol concentration was obtained with the model for ellipsoids. At higher propanol concentrations, above 1.2 mol/kg, the model for spherical structures was the best fit. Addition of butanol affects the micelles in a more complex manner. For butanol concentrations up to about 0.1 mol/kg, the axial ratio doubles its value from 2.3 up to 4.5, indicating that the micelles grow into longer aggregates. At 0.1 mol/kg, the axial ratio goes through a maximum value. The rapidly decreasing axial ratio above this concentration indicates that the large micelles break down and form small spherical aggregates. However, as the butanol concentration exceeds 0.5 mol/kg, the micelles start to grow again. This surprising result shows that the micelles can increase or decrease in size, depending



FIG. 2. The normalized neutron scattering cross-section $(d\Sigma(Q)/d\Omega)$ plotted against the scattering vector Q. The solid line corresponds to a fit using the local form factor of a sphere (a), an ellipsoid (b), and a rod (c) for propanol, butanol, and pentanol, respectively.

TABLE 1 Alcohol Molalities, χ -Values, and Minor Radii (R_{min}) and Major Radius (R_{mai}) of Micelles

Molality (mol/kg)	Model	Molality (mol/kg)	Minor radius (Å)	Major radius (Å)	χ^2 -values	Major/minor
Propanol						
0	ellipsoid	0	17.7	40	5.6	2.3
0.2	ellipsoid	0.2	17.2	35	14.7	2.0
0.4	ellipsoid	0.4	17.2	28.2	5.0	1.6
0.8	ellipsoid	0.8	16.8	22.7	12.5	1.2
1.2	sphere	1.2	17.4		13.5	1
1.6	sphere	1.6	16.3		13.1	1
2.0	sphere	2.0	15.1		9.7	1
2.4	sphere	2.4	14.4		8.4	1
2.8	sphere	2.8	13.7		4.0	1
4.4	sphere	4.4	13.3		2.0	1
Butanol						
0.033	ellipsoid	0.033	16.5	68.9	42.4	3.1 ± 0.1
0.066	ellipsoid	0.066	16.3	72.8	44.2	4.2 ± 0.1
0.1	ellipsoid	0.1	16.0	69.0	48.6	4.5 ± 0.2
0.15	ellipsoid	0.15	16.9	51.8	12.7	4.3 ± 0.1
0.2	ellipsoid	0.2	15.6	38.4	21.5	3.0 ± 0.1
0.3	ellipsoid	0.3	15.7	36.8	20.2	2.5 ± 0.1
0.4	ellipsoid	0.4	15.7	28.2	2.3	1.8
0.5	ellipsoid	0.5	15.1	27.9	1.3	1.8
0.6	ellipsoid	0.6	14.5	28.3	1.8	2.0
0.8	ellipsoid	0.8	13.0	37.5	6.7	2.9
0.9	ellipsoid	0.9	13.3	54.3	3.7	4.1
Pentanol						
0.005	ellipsoid	0.005	16.3	78.5	9.0	3.0
0.01	ellipsoid	0.01	15.9	112.5	17	4.2
0.02	ellipsoid	0.02	15.9	178.0	11.9	5.5
0.03	rod	0.03	15.7	263.0	10.1	7.6
0.06	rod	0.06	15.4	370.9	7.7	11.3
0.10	rod	0.10	15.0	350.9	6.9	10.7
0.13	rod	0.13	14.8	371.8	5.1	11.4
0.16	rod	0.16	14.6	554.0	3.0	17.9

on the concentration range of added butanol. For all data, the best fitted model was for ellipsoids, but for the solutions containing butanol molalities in vicinity of 0.1 mol/kg, the model for rods gave approximately equal fitting values. The effect of pentanol is shown in Fig. 3c. Addition of pentanol increases the axial ratio of the micelles. A micellar transition from ellipsoidal to wormlike aggregates appears. The model for ellipsoids gave the best fit at low alcohol concentrations up to 0.02 mol/kg, whereas the model for rods gave the best fit at higher alcohol concentrations.

The data on self-diffusion shows that addition of propanol increases the self-diffusion coefficient of SDS and decreases the self-diffusion coefficient of propanol molecules with increasing alcohol molality, up to 3 mol/kg. A minor increase of the self-diffusion coefficient of SDS can be seen in the molality range up to about 1.5 mol/kg. This concentration

range of added propanol corresponds to the range where the micelles change from ellipsoidal to small spherical aggregates as observed in the SANS data. A rapid increase in the self-diffusion coefficient was observed in the high molality range, indicating a progressive breakdown of the micellar structures. Addition of butanol (Fig. 4b) is more complex concerning the self-diffusion data of the surfactant. In the low molality range ($C_4OH < 0.1 \text{ mol/kg}$), where the micelles apparently change their structure from ellipsoidal to wormlike, the self-diffusion coefficient of SDS decreases successively. Above 0.1 mol/kg, where the micelles change from rods and back to small, nearly spherical aggregates, the self-diffusion coefficient of SDS increases rapidly. Moreover, in the high molality range where the butanol approaches the solubility limit, the self-diffusion coefficient of the surfactant again starts to decrease. This high concentra-



FIG. 3. The minor radius (R_{\min}) and the major to minor axial ratios (major/minor) plotted against the molality of alcohol. (a) Propanol, (b) butanol, and (c) pentanol.

tion region corresponds to the region where the SANS data show an increase in the micelle size. Thus, the results obtained from the SANS measurements and the FT-PGSE measurements agree qualitatively with what happens with the micelles when butanol is added. The self-diffusion of SDS and pentanol shows a lowering of the self-diffusion coefficient in the concentration range up to about 0.06 mol/kg. Above this molality, the self-diffusion coefficient flattens and starts to increase slowly near the solubility limit of the alcohol. The corresponding coefficient of the pentanol molecules shows the same trend as the coefficient of the surfactant, indicating that a large portion of the added pentanol is solubilized in the micelles.

DISCUSSION

The interpretation of the SANS data builds on the assumption that the electrostatic interaction between the micelles is negligible in aqueous solutions containing 0.4 mol/kg NaCl, i.e., the interparticle structure factor is equal to unity. This is supported by the work of Corti and Degiorgio (15), who demonstrate that the electrostatic interaction between SDS micelles becomes negligible at NaCl concentrations higher than 0.4 M. At this salt content, the micelles form prolate ellipsoids with an axial ratio of about 2.3.

The highly water-soluble alcohols such as methanol, ethanol, and propanol dissolve mainly in the aqueous bulk solution (33), and not in any substantial amount in the palisade layer of the micellar pseudophase. Previously reported results show that these alcohol solutions thermodynamically and kinetically destabilize the micelles and contribute toward breaking down the aggregates (18). Stilbs (23) suggests that the medium chain alcohol molecules preferentially solubilize in the palisade layer of the micelles and remove the barriers for structural deformation by decreasing the surface



FIG. 4. The self-diffusion coefficients of SDS (D_{SDS}) and the major to minor axial ratios of the micelles (major/minor) plotted against the alcohol to surfactant mole ratio in the micelles. (a) Propanol, (b) butanol, and (c) pentanol.

energy at this polar-apolar interface. The decreasing minor radius of the micelles and the increasing self-diffusion coefficient of the surfactant upon addition of propanol indicate that a successive breakdown of the micelle aggregates takes place. Totally different results have been reported for micellar solutions containing hydrophobic alcohol molecules (34, 35). A considerable number of these alcohol molecules solubilize in the palisade layer of the micelle aggregates. This solubilization leads to a decreasing electrostatic interaction between the surfactant headgroups, and makes the surfactant molecules more energetically favorable for being a part of the micelles. It also alters the surfactant packing condition in the micelles and promotes a shape transition toward large anisotropical aggregates. This tendency toward building large wormlike micelles was observed when pentanol was added to the solution. The more complex behavior observed upon addition of butanol indicates that this alcohol may behave both as a hydrophilic and as a hydrophobic alcohol depending on the concentration range of added butanol.

In general, the alcohol may be distributed among three energetically different sites. It can be dispersed in the aqueous bulk solution, oriented in the micellar surface, and located in the hydrocarbon core of the aggregates. Thermodynamic measurements indicate that solubilization of medium chain alcohols in micelles occur to a large extent in the palisade layer (36). McManus and co-workers (37) showed that the position of the solubilized alcohol depends on the alkyl chain length. The more hydrophobic alcohols seem to penetrate deeper into the hydrocarbon interior of the micelles than the hydrophilic ones. Moreover, the alcohols for which the hydrophobic contributions predominate over the hydrophilic ones also solubilize in the hydrocarbon core of the micelles (36).

Analysis of the SANS data shows an apparent decrease of the minor radius upon increasing alcohol concentration. However, this effect could be ascribed to a variation in the neutron scattering contrast between the D_2O and the hydrocarbon environment caused by an increased solvation of D_2O in the surface region of the micelles (9). The alcohol molecules penetrate the surfactant headgroup region and bring along an increased penetration of deuterated water molecules. Not surprisingly, this solvation effect seems to be most pronounced for the solutions containing propanol.

In order to quantify the solubilization or association of alcohol in the micelles, the fraction (p) of the alcohol which is present in the micellar pseudophase was determined from the measured self-diffusion coefficients by using (30)

$$D_{\rm A} = (1 - p)D_{\rm A}^{\rm free} + pD_{\rm A}^{\rm mic},$$
 [4]

where D_A is the measured self-diffusion coefficient of the alcohol, D_A^{free} is the self-diffusion coefficient of the free alcohol molecules, and D_A^{mic} is the self-diffusion coefficient

of the alcohol molecules bound in the micelles. In solutions where the cmc is low and the concentration of surfactant is large compared to the cmc, the $D_A^{\rm mic}$ is considered equal to the measured self-diffusion coefficient of the surfactant. $D_A^{\rm free}$ is determined from the self-diffusion coefficient of alcohol measured in solutions without surfactant.

In the high concentration range of added propanol, the viscosity of the solution varies in a complex manner because of the rapid breakdown of micelles and increases of free surfactant monomers in the aqueous bulk solution. Based on the assumptions mentioned earlier, this leads to erroneous D_A^{free} and D_A^{mic} values, and thus to erroneous α values. Hence, the α values obtained for propanol were determined from the solutions containing alcohol concentrations up to 1 mol/kg. The calculated *p* values for all solutions, independent of the type of alcohol used, vary slightly with the total concentration of alcohol in the solutions. The values obtained for propanol were all lower than 0.08. The values obtained for butanol varied between 0.15 and 0.20, while the corresponding values obtained for pentanol varied between 0.35 and 0.40.

Figure 4 shows a graphic presentation of the surfactant self-diffusion coefficient (D_s) and the major to minor axial ratio as a function of the determined alcohol to surfactant mole ratio of the micelles. The plots show a sudden change in the analyzed properties of the micelles at alcohol to surfactant mole fractions between 0.5 and 1. The sudden change in the data occurs at approximately the same mole fraction independent of the alcohol chain length for all the analyzed systems. The observed transitions in the micellar properties at this alcohol-to-surfactant mole fraction correspond well to a transition in the apparent partition constant of hexanol and heptanol observed by Abuin and Lissi (38). They showed that a sharp decrease in the apparent partition constant (K_A) occurs when the alcohol mole fraction in the micellar pseudophase exceeds 0.5. Moreover, they suggest that this break was related to a "saturation" of the micellar surface. Considering this interpretation, the sudden change in the micellar behavior seen in Fig. 4 may be related to an increase in the activity coefficient of the alcohol in the micellar palisade layer. Thus, further addition of alcohol will mainly be distributed between the aqueous bulk and the hydrocarbon core of the micelles.

Whereas pentanol has shown to solubilize in the palisade layer as well as in the hydrocarbon core of ionic micelles (39, 40), propanol is thought to solubilize only in the palisade layer of the micelles (41). Butanol has shown to act as an intermediate alcohol and can decrease or increase the size of the micelles depending on the concentration of alcohol present. The molecular distribution coefficient between the micellar and aqueous phases shows that the major part of the butanol will be dissolved in the aqueous phase. This seems to be sufficient to start the process seen for the lower alcohol homologues, a tendency toward breaking down the micelles. Moreover, as the butanol concentration approaches the solubility limit, a new transition of the micellar shape toward larger aggregates can be observed. This might be due to an increased solubility in the micellar core producing butanol-swollen aggregates. This corresponds well with some results obtained in cationic micellar solutions (40), suggesting that butanol might affect the micelle hydrophobic core, whereas propanol is too short to do so.

CONCLUSION

The results obtained from the SANS and the FT-PGSE measurements agree qualitatively with regard to what happens as alcohol is added to the micellar solution. The SANS measurements show that a successive change from ellipsoidal to small spherical micelles occurs when propanol is added up to 1.5 molal. Further addition of propanol decreases the minor radius of the micelles and rapidly increases the selfdiffusion coefficient of SDS, indicating a progressive micellar breakdown. In contrast, addition of pentanol increases the micellar size, producing large wormlike aggregates. The axial ratio of the micelles increases from 2.3 in solutions without pentanol to about 18 in the solutions where pentanol approaches the alcohol solubility limit. Addition of butanol shows a more complex effect on the behavior of the micelles. As butanol is added, the axial ratio of the micelles and the self-diffusion coefficient of the SDS either increase or decrease depending on the added alcohol concentration range. Butanol contents up to 0.1 mol/kg produces large micelles with an axial ratio of about 4.5. Addition of butanol beyond this molality seems to decrease the size of the micelles. However, at about 0.5 mol/kg of added butanol, the micelles reach a minimum in size and start to grow again. The calculated degree of alcohol solubilization in the micelles shows that a change in the micellar properties occurs at an alcoholto-surfactant mole ratio in the micellar pseudophase between 0.5 and 1. We suggest that this sudden change in the properties of the micelles is caused by a "saturation" of alcohol in the palisade layer of the aggregates. Butanol and pentanol might also be solubilized in the micellar core in the high molality range, near the end of the solubility limit. Propanol is apparently too hydrophilic to do so.

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