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ORIGINAL CONTRIBUTION

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The size of sodium dodecyl sulfate micelles in the presence of *n*-alcohols as determined by fluorescence quenching measurements

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Abstract The steady-state fluorescence quenching technique was used to investigate the effect of the presence of a series of alcohol homologues of mid-sized straight chain on the size of mixed micelles of sodium dodecyl sulfate (SDS). We used pyrene at concentration of ca. 10^{-6} M, where only its monomer exhibits any fluorescence, as fluorescent probe, and cetylpiridinium chloride at concentrations in the range $(1-9)\times 10^{-5}$ M as quencher. This technique allows one to determine the micellar aggregation number. The number of alcohol molecules per micelle was calculated from reported values for the micelle-water partition coefficient. On the assumption of spherical micelles, their hydrophobic radii was then calculated. The hypothesis that micelle size is determined by the available surface area per charged headgroup is discussed in the light of the results obtained.

Key words Micelles – micelle size – fluorescence – polar additives

Introduction

A wide variety of alcohols is seemingly able to partition between an aqueous solution and a micellar phase; however, the micellar composition under such conditions [1, 2] has scarcely been studied so far owing to the lack of straightforward, convenient methods for determining micelle size and the partition coefficient for the dissolved additive.

Turro and Yekta [3] developed the first available method for determining the micellar aggregation number for anionic micelles, based on the quenching effect of micelle-dissolved 9-methylanthracene on $Ru(bpy)_3^{2+}$ ions.

In this work we used pyrene as the fluorescent probe and cetylpiridinium chloride as the quencher. The shortcomings of this method have been discussed by several authors [3–6]. In any case, the reliability of the results it provides depends on some of its characteristics. Thus, the method essentially entails assuming that micelles only exhibit fluorescence in the absence of a quencher, which is usually true.

The fluorescence observed is proportional to the number of quencher-free micelles. Provided the quencher concentration is known and quenchers are assumed to adopt a random distribution in the micellar phase (i.e., a Poisson distribution), the number of micelles and their mean size can be calculated fairly readily. The problems arising from polydispersity in micelle size have also been discussed [5]. Thus, an average aggregation number can be calculated under conditions of low polydispersity (e.g. with small, spherical micelles).

Atik et al. [7] developed a new method based on the formation of intramicellar pyrene excimers and the subsequent analysis of fluorescence decay curves. This method is widely used for the determination of aggegation numbers of new surfactant systems, and for studying the way such numbers are affected by the presence of additives (alcohols, electrolytes, etc.)

This paper discusses the effect of addition of alcohols on the size of sodium dodecyl sulfate (SDS) micelles on the basis of steady-state fluorescence quenching measurements.

Experimental

Apparatus

Steady-state fluorescence quenching measurements were carried out on a Kontron SFM-23 spectrofluorimeter at $\lambda_{ex} = 336$ nm and $\lambda_{em} = 395$ nm (the maximum fluorescence wavelength for micellized pyrene).

Reagents

The surfactant sodium dodecyl sulfate (SDS) and the fluorescence probe (pyrene) were both purchased from Sigma, and the quencher, cetylpyridinium chloride, was supplied by Aldrich. All three were used as supplied by the manufacturers. The alcohols were obtained from Merck.

Procedure

Experimental solutions were prepared as follows: an appropriate volume of an ethanol solution of pyrene was pipetted into a volumetric flask and the alcohol was evaporated by passing a nitrogen stream in order to leave a pyrene residue. The flask was then made to the mark with a previously made aqueous solution of SDS at an appropriate concentration. The solution was stirred for about 12 h with gentle heating in order to completely micellize the pyrene. Then, aliquots of this solution were transferred to 5-ml volumetric flasks and supplied with increasing volumes of an aqueous solution of cetylpyridinium chloride at an appropriate concentration, followed by dilution to the mark and stirring for ca. 1 h. In this way, a series of solutions containing the same concentrations of SDS (0.02 M) and pyrene (10^{-6} M), but different concentrations of the quencher over the range $(1 - 9) \times 10^{-5}$ M, is obtained.

Additive solutions were similarly prepared, but the SDS solution was supplied with a preset volume of alcohol and stirred for 12 h as well in order to ensure uniform partitioning between the micellar and aqueous phase.

Calculations

For a static quenching with fully micellized quencher, we have [8]:

$$\frac{I}{I_0} = \exp\left(-\frac{Q \cdot N_S}{\mathrm{SDS} - \mathrm{SDS}_F}\right), \tag{1}$$

where I and I_0 denote the fluorescence intensity in the presence and absence of quencher, respectively, Q the total concentration of quencher, N_S the micellar aggregation number, SDS the total concentration of surfactant, and SDS_F that of unmicellized surfactant on the provision that total SDS should exceed the critical micelle concentration (CMC).

The amount of pyrene that is dissolved by the micelles does not alter the calculated micelle aggregation number since, over the concentration range tested, each micelle contains one pyrene molecule at the most; however, the majority (over 99%) contain no pyrene. If Eq. (1) holds, then a plot of $\ln(I_0/I)$ *vs* Q should be linear, as was indeed the case in all of our experiments provided the pyrene concentration used was not so high as to allow the formation of excimers and the total amount of quencher did not result in saturation.

A plot of $\ln(I_0/I)$ against Q at a constant SDS will thus be a straight line of slope $(\mathrm{SDS} - \mathrm{SDS}_F)/N_S$. Figure 1 shows two typical plots obtained at as many different SDS concentrations in the absence of alcoholic additives.

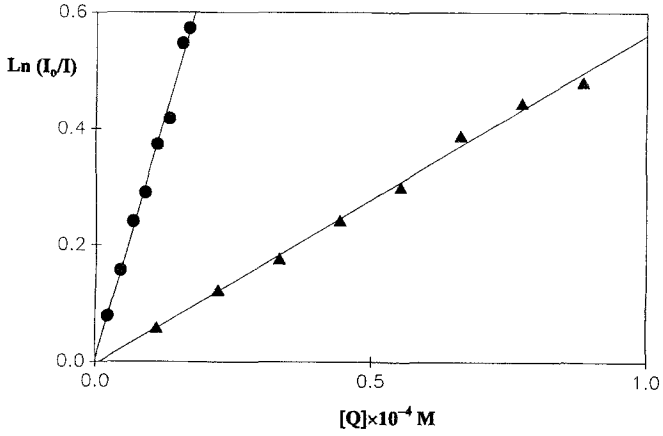
The aggregation number for the additive, N_A, can be calculated from:

$$N_A = \frac{A - A_F}{\mathrm{MIC}}, \tag{2}$$

where A is the total additive concentration, A_F is the additive concentration in the non-micellar phase, and MIC the micellar concentration, which is given by:

$$\mathrm{MIC} = \frac{\mathrm{SDS} - \mathrm{SDS}_F}{N_S}. \tag{3}$$

Fig. 1 Plots of $\ln(I_0/I)$ *vs* Q obtained at an SDS concentration of ● 0.01019 and ▲ 0.02038 M



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In order to calculate SDS_F, its decrease above the CMC is estimated from reported values for aqueous SDS [9–12]. The error made in calculating N_S will be directly proportional to that in SDS_F. The total surfactant concentration employed is usually quite high (ca. 0.1 M) in order to ensure full micellization of the fluorescent probe. The problem lies in the fact that the assumption $SDS_F \approx CMC$ does not hold at high SDS concentrations. The Gunnarsson model [11] accounts for this decreasing trend and can thus be used to calculate SDS_F. However, the model may not be accurate at high surfactant concentrations and thus would provide spurious SDS_F values. These shortcomings can be circumvented by using low SDS concentrations and an appropriate ratio between the probe and quencher concentrations. In this work, we used a surfactant concentration of ca. 0.02 M, which resulted in $SDS_F \approx 6.5 \times 10^{-3}$ M. There are no available similar data for calculating SDS_F in the presence of alcohols; however, because these are non-ionic species, they should reasonably conform to the Gunnarsson model. The concentration of free surfactant monomers can be calculated on the assumption of a similar decreasing trend from the CMC in the absence of additives. Also, the free additive concentration, A_F, can be calculated from data reported by Stilbs [14] on the assumption that partitioning of the alcoholic additive between the aqueous and micellar phase conforms to the following equation:

$$K = \frac{A_M}{A_F \cdot SDS_M}, \tag{4}$$

where A_M and SDS_M are the micellized alcohol and surfactant concentrations, respectively, and K the partition coefficient.

Equation (4) and similar expressions have been experimentally checked to hold at low additive concentrations [14, 15], but not at high concentrations, which may result in considerable errors in the estimation of the number of alcohol molecules per micelle. Provided N_S, N_A and the volume of the hydrocarbon tail of the alcohol are known, the hydrophobic volume of the micelles can readily be calculated.

Micelle size is usually expressed by the hydrophobic radius, R; this is calculated on the assumption of a spherical micelle geometry, which is also adopted in calculating the surface area per headgroup. This assumption gives rise to negligible errors with small micelles.

After the average micellar composition (i.e. the number of surfactant and additive molecules per micelle) has been determined, the volume of the hydrocarbon core can be calculated as the summation of the contributions of all the groups involved (viz. 49 Å^3 per CH_3 and 28 Å^3 per CH_2 group [16, 17]). On the assumption of a spherical geometry for the micelles, the radius and surface area of the surfactant monomers can thus be calculated.

Results and discussion

The aggregation number obtained for SDS in the absence of an alcoholic additive was 69.0, which is consistent with reported values for other fluorescent probes and quenchers. This aggregation number led to a calculated micelle radius of 18 Å.

Table 1 summarizes the results obtained in the presence of various alcoholic additives. The micellar aggregation number decreased with increasing additive concentration for the three alcohols tested. Also, the number of micellized molecules of additive increased with increase in the alcohol concentration.

The micellar composition is seemingly determined by a partitioning equilibrium between micelles and the aqueous phase, even though the particulars of such an equilibrium (e.g., the dependence of the partition coefficient on the composition of the *pseudo*-phases involved) are still obscure.

The micellar composition can be characterized by X_A, the mole fraction of the additive in the micellar phase, which is given by:

$$X_A = \frac{A_M}{A_M + SDS_M} \tag{5}$$

or, alternatively:

$$X_A = \frac{N_A}{N_A + N_S}. \tag{6}$$

If every polar group lies at the micelle surface – which is most often the case provided the core volume is not too large relative to the interfacial region-, the size of ionic micelles for a given composition is seemingly determined by the surface area per surfactant monomer, or, in other words, the surface charge density:

$$\frac{\sigma}{e} = \frac{N_S}{A}. \tag{7}$$

Almgren and Swarup [18] found the charge density to be always very similar for a given interfacial composition X_A. The aggregation number and micelle size will thus be determined by the contributions of the alcohol and surfactant volumes, provided micelles are spherically shaped. The overall volume of the hydrophobic core will thus be given by:

$$V = N_S \cdot V_S + N_A \cdot V_A, \tag{8}$$

where V_S and V_A are the volume of a surfactant and additive molecule, respectively.

Table 1 Size and composition of SDS micelles in the presence of butanol, pentanol and hexanol

[A](M)	N_S	A_M (mM)	N_A	R(Å)	N_S/A(Å^{-2})	X_A
n-Butanol						
0.0903	52.1	3.96	15.3	17.0	0.0143	0.227
0.1325	48.3	5.81	20.8	16.8	0.0136	0.301
0.2283	36.2	10.00	26.9	15.8	0.0116	0.426
0.3775	32.7	16.60	40.1	16.0	0.0102	0.551
0.4712	27.8	20.70	42.6	15.5	0.0092	0.605
0.6783	22.5	29.80	49.6	15.2	0.0078	0.688
0.9849	22.1	43.20	70.8	16.0	0.0068	0.762
n-Pentanol						
0.0154	63.5	2.54	11.9	18.0	0.0155	0.158
0.0327	53.9	5.38	21.5	17.6	0.0139	0.335
0.0778	35.8	12.8	34.0	16.3	0.0107	0.487
0.1014	34.0	16.7	42.0	16.5	0.0099	0.553
0.1895	31.4	31.2	72.6	17.6	0.0081	0.698
0.2714	30.1	44.7	99.6	18.6	0.0070	0.768
n-Hexanol						
0.0067	64.7	2.70	12.9	18.3	0.0154	0.167
0.0086	59.9	3.47	15.4	18.0	0.0148	0.204
0.0134	53.4	5.40	21.4	17.7	0.0136	0.286
0.0202	47.3	8.14	28.5	17.5	0.0124	0.376
0.0246	43.7	9.91	32.1	17.3	0.0116	0.423
0.0338	40.3	13.6	40.7	17.4	0.0106	0.502
0.0474	36.0	19.1	50.9	17.5	0.0093	0.586

From Eq. (6) it follows that:

$$N_A = \frac{N_S \cdot X_A}{1 - X_A} . \tag{9}$$

Substitution of Eq. (9) into Eq. (8) gives the overall volume of the hydrophobic core:

$$V = N_S \cdot \left\{ V_S + \frac{X_A}{1 - X_A} V_A \right\} . \tag{10}$$

Figure 2 shows a plot of N_S/A against X_A for the three alcohols studied. Data fitting provided the following regression equation:

$$\frac{N_S}{A} = 0.0177(\text{Å}^{-2}) - 0.0141(\text{Å}^{-2}) \cdot X_A . \tag{11}$$

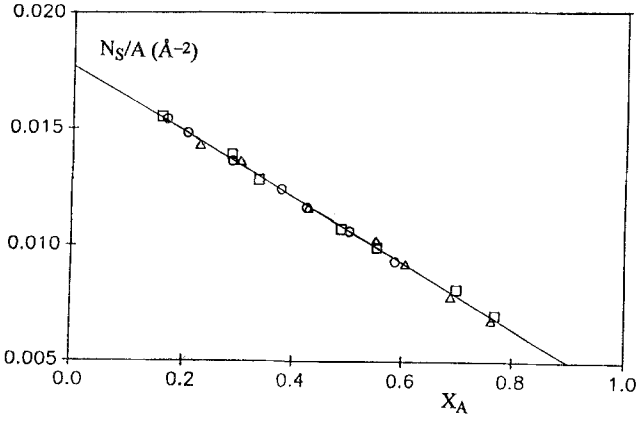
On the assumption that Eq. (11) is an adequate expression for the relationship between N_S/A and X_A, the hydrophobic radius for a spherical micelle in terms of X_A will be given by:

$$R = \frac{3 \cdot V}{A} = 3 \cdot \left(V_S + \frac{X_A}{1 - X_A} V_A \right) \cdot \frac{N_S}{A} . \tag{12}$$

Figure 3 shows a plot of experimentally calculated radii against X_A for each alcohol studied. The curves represent the theoretical values of the radii obtained from Eqs. (11) and (12). As can be seen, the three curves have a minimum that is markedly sensitive to small changes in the slope and intercept of the straight line defined by Eq. (11), as is the curve shape. Within the experimental error range for this alcohol series and the concentration range considered, the surface charge density can be assumed to be the limiting factor for the volume of the mixed micelles.

The micelle structure is essentially the result of the equilibrium of the repulsive forces between charged heads, which tend to increase the interfacial area per monomer (A/N_S) and the attractive forces of the hydrocarbon core, which tend to decrease it. Introduction of a polar additive (e.g., an alcohol with a mid- to long-sized chain) alters both forces.

Fig. 2 Plots of N_S/A *vs* X_A obtained in the presence of ○ *n*-hexanol, □ *n*-pentanol and △ *n*-butanol



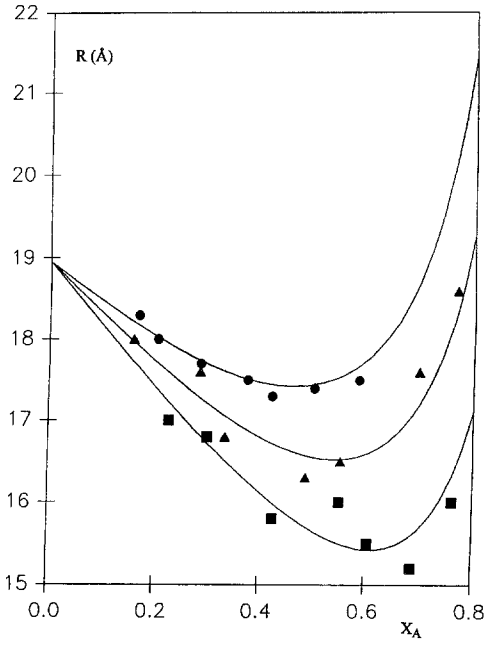


Fig. 3 Plots of R (Å) *vs* X_A obtained in the presence of ● *n*-hexanol, ▲ *n*-pentanol and ■ *n*-butanol. The lines represent the theoretical curves ensuing from Eqs. (11) and (12)

Based on the model of Jönsson and Wennerström [17], the free energy of formation of micellar aggregates consists of five different contributions, of which those from the electrostatic and surface free energy are the most significant. The model relies on the following relation:

$$2 \cdot E_{el} = \gamma \cdot A \,, \tag{13}$$

where E_{el} is the electrostatic energy, A the micelle area, and γ the interfacial free energy G_S per unit area:

$$\gamma = G_S/A \,. \tag{14}$$

Jönsson and Wennerström found γ for medium- to long-chain alcohols to be the sum of the contributions of the surfactant and alcohol:

$$\gamma = \gamma_S \cdot X_S + \gamma_A \cdot X_A \,, \tag{15}$$

where γ_S and γ_A are the interfacial free energy per unit area for the surfactant and alcohol, respectively; γ_S is of the order of 20–50 mJ/m^2, while γ_A is somewhat smaller and does not depend on the alcohol chain size. Since N_S/A is proportional to E_{el}/A, from Eqs. (13)–(15) it follows that:

$$N_S/A = a - b \cdot X_A \,, \tag{16}$$

where a and b are two constants.

This does not hold with shorter alcohols [18]. Seemingly, short-chain alcohols modify micellar parameters by altering the solvent properties. Rather than changing the structure of the micelle hydrophobic core, they appear to act on the interfacial region, probably as a result of the short length of the hydrocarbon chain.

Some authors [19–21] suggest that the first few methylene groups in the surfactant tail lying close to the head may be in contact with the water. Hence, water may somehow penetrate into the hydrocarbon core of micelles. In this way, the surrounding ion atmosphere would overlap with the first methylene group in the alkyl chain. Short-chain alcohols would accompany water to this position, thereby altering the electrical properties of this region [22]. On the other hand, long-chain alcohols can interact hydrophobically with the surfactant tail and penetrate into the hydrophobic micelle core with their non-polar chain [23].

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