FLUORESCENCE PROBING IN MICELLAR SOLUTIONS: ORGANIC ADDITIVES IN MICELLES OF SODIUM DODECYLSULPHATE

ANGELOS MALLIARIS

N.R.C. "Demokritos", Athens 153 10 (Greece)

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Summary

The changes induced in the structure of micelles of sodium dodecylsulphate when alkanes, alcohols and ketones are solubilized were studied by steady state fluorescence probing methods. Important information concerning micellar properties, such as size, micropolarity, interfacial charge density etc., obtained from fluorescence measurements are presented and some general trends are discussed.

1. Introduction

One of the most important properties of aqueous micelles is their ability to solubilize water-insoluble organic compounds [1]. Solubilization has been widely employed, either to modify deliberately the micellar entity or to probe the environment at the site of solubilization, thus providing valuable information concerning the structure and properties of micellar systems [2]. Physicochemical parameters of the additive compound, such as the polarity, molar volume, chain length, branching, planarity, substitution etc., have been found to be important in determining the degree of solubilization [3]. The effect of organic additives on micellization and micellar properties has been investigated in many systems [4]. However, most attention has been focused on medium-chain-length alcohols because of their wide use as cosurfactants in microemulsions. Thus, parameters such as the critical micelle concentration (CMC) [5], the degree α of micellar ionization [5, 6], the counterion binding constant [7], the mean micelle aggregation number N_S [8, 9], the number N_A of micelle-bound additive molecules [8, 9] and other properties of micellar solutions [10, 11] have been determined with respect to the nature and the concentration of the additive as well as the surfactant. Although some approximate generalizations have been proposed, the complexity of these systems has been recognized [12].

This article contains the results of our study on the effect of *n*-alkanes, 1-alkanols and aliphatic ketones (containing six to ten carbon atoms) on the micellization of sodium dodecylsulphate (SDS). Linear additive molecules

were chosen since they are expected to disturb the micellar structure less than other bulkier solubilizates. As far as ketones are concerned, we mention that they have not been systematically employed as micellar additives [13 - 15] although they have physical and chemical properties suitable for this purpose, while the fact that their chemistry is well understood allows the prediction of possible surfactant—solubilizate specific interactions, which are known to produce confusing results [16].

2. Experimental details

SDS and pyrene were the same samples used in previous studies [17, 18]. Hexadecylpyridinium chloride (HPC, Serva) used as quencher of the fluorescence of micelle-bound pyrene was recrystallized from acetone and ethyl acetate. The alkanes (Aldrich, Gold Label) were used as received, whereas alcohols (Aldrich) and aliphatic ketones (Aldrich) were purified by vacuum distillation.

Fluorescence spectra were obtained using an instrument described previously [19]. The CMC values in the presence or the absence of the additives were determined by electrical conductivity measurements. Alkane additives did not induce measurable changes in the CMC of SDS over the concentration range employed. Deionized and triply distilled water was used and had an electrical conductivity of $2 - 3 \ \mu S \ cm^{-1}$.

For the determination of N_S the steady state fluorescence quenching method [20 - 22] was used in the simplified version described by the equation

$$\ln\left(\frac{F_0}{F}\right) = \frac{[Q]}{[M]} \tag{1}$$

F and F_0 are the fluorescence intensities with and without the quencher, $[Q]$ is the analytical concentration of the quencher and $[M]$ is the micellar concentration. Finally, N_S was calculated from the equation

$$N_S = \frac{C_S - [S]}{[M]} \tag{2}$$

where $[S]$ stands for the concentration of the non-micellized surfactant, and is usually set equal to CMC [23]. In the presence of additives the CMC itself changes in a way dependent on both C_S and C_A [23, 24]. Concerning the number N_A of additive molecules per micelle, we note that since all the additives used here have very low water solubility [25], N_A can be estimated by using the equation

$$N_A = \frac{[C_A]_T}{[M]} \tag{3}$$

where $[C_A]_T$ is the total additive concentration.

It should be mentioned here that the method of steady state fluorescence quenching has been criticized for leading to underestimation of N_S

[21]. However, this underestimation can be made negligible, to within the experimental error of other more sophisticated methods, under the appropriate conditions. The most important of these conditions are that (i) the micellar size should be small, (ii) there should be no probe and/or quencher specific interaction with the surfactant and (iii) that there should be an effective fluorophore–quencher pair. In the present case all the above conditions are fulfilled, and more specifically the SDS micelles are quite small at the low [SDS] used here, there is no interaction between SDS and quencher or fluorophore (such interactions are known to take place between pyrene and quaternary ammonium salts [15]) and, finally, the pyrene–HPC pair has a very good quenching efficiency, for which we have measured $k_q = 6.5 \times 10^9$ s^{-1} in homogeneous media.

3. Results and discussion

It is immediately evident from Tables 1 - 3 and Fig. 1 that the effect which the additive has on N_S definitely depends on its polarity. Thus, N_S decreases on addition of polar additives while it increases when the additive is
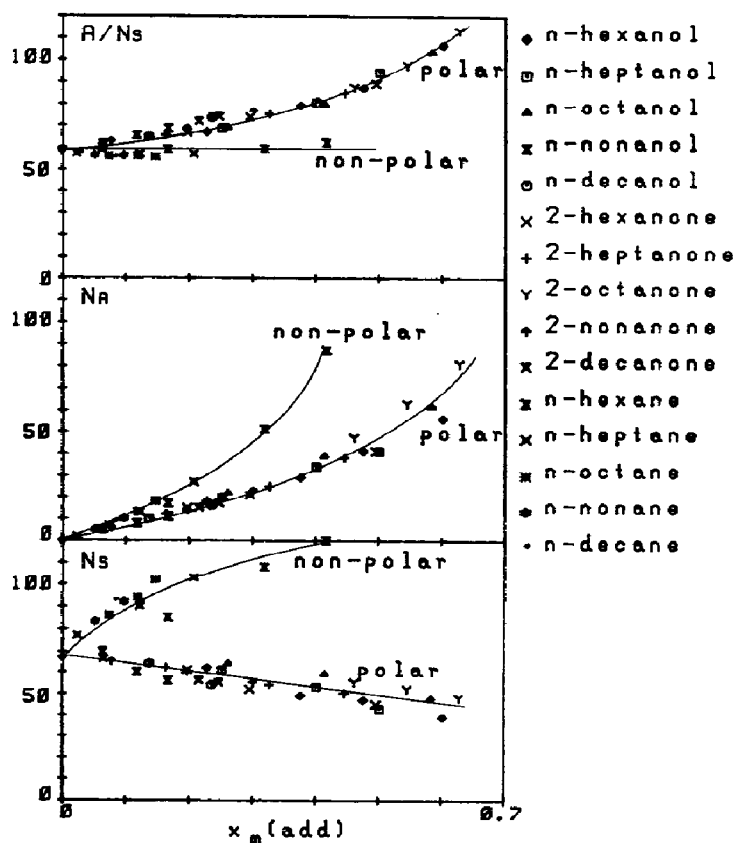

Fig. 1. Plots of χ_m(add.) vs. N_S, N_A and A/N_S. χ_m(add.) = $C_A/([SDS] + C_A)$.

TABLE 1

Parameters of the SDS–alcohol mixed micelle

C_A ($\times 10^{-2}$ M)	N_S	N_A	A/N_S (Å^2 per ion)	CMC (M)
No additive				
0	67	0	58.7	0.008
C_6H_{13}—OH				
1.18	62	18	67.1	0.0067
2.42	49	29	79.4	0.0059
3.63	47	41	87.5	0.0054
6.05	39	56	106.7	0.0049
C_7H_{15}—OH				
1.35	61	20	68.9	0.0065
2.69	53	34	81.1	0.0058
4.03	43	41	94.6	0.0053
C_8H_{17}—OH				
1.41	64	22	69.3	0.0065
2.84	59	39	80.1	0.0057
5.62	48	62	103.6	0.005
C_9H_{19}—OH				
0.274	70	5	60.1	0.0076
0.54	60	8	65.6	0.0073
0.813	56	11	68.7	0.0070
$C_{10}H_{21}$—OH				
0.64	64	10	65	0.0072
1.24	54	16	73.7	0.0066

[SDS] = 0.04 M.

non-polar. The polar additives, which solubilize in the palisade region, lower the charge density on the micellar surface and counterions are released from the Stern layer into the aqueous phase, thus increasing the micellar ionization and therefore destabilizing the aggregate. Formation of smaller micelles partially compensates for the excess coulombic energy and restabilizes the system. However, when [M] becomes sufficiently large, at low N_S, inter-micellar repulsions due to close approach of highly ionized micelles oppose any further increase in [M], and consequently the decrease in N_S is stopped. Therefore the system reaches equilibrium, but with an N_S value lower than in the absence of the additive. It should be mentioned that at high SDS and alcohol concentrations there is a reversal in the behaviour of N_S and it increases as C_A increases [25]. Totally different behaviour is exhibited by N_S when the additive is an alkane. Thus, increasing C_A at constant C_S always induces an increase in N_S (Table 3, Fig. 1).

The number N_A of additive molecules per micelle systematically increases as the additive concentration of either polar or non-polar molecules

TABLE 2

Parameters of the SDS–ketone mixed micelle

C_A ($\times 10^{-2}$ M)	N_S	N_A	A/N_S (Å^2 per ion)	CMC (M)
C_6H_{12}—C=O				
0.99	61	15	66.7	0.007
1.69	52	21	74	0.0068
3.95	45	41	89.4	0.0057
C_7H_{14}—C=O				
0.79	62	12	65.6	0.007
1.95	54	25	75.3	0.0065
3.23	50	38	85	0.0059
C_8H_{16}—C=O				
3.43	55	47	87.7	0.006
4.81	52	63	97.6	0.0058
6.78	48	81	113.21	0.0055
C_9H_{18}—C=O				
0.34	65	6	62.6	0.0076
0.99	60	14	68.6	0.0072
1.73	55	23	76.5	0.007
$C_{10}H_{20}$—C=O				
0.28	66	5	61.6	0.0078
1.11	56	15	71.8	0.0072
1.32	55	17	74	0.007

[SDS] = 0.04 M.

increases (Tables 1 - 3, Fig. 1). It is interesting to note, however, that N_A is higher for non-polar additives than for polar additives, at the same additive mole fraction χ_m(add.), although the maximum additive concentration MAC is higher for polar solubilizates than for non-polar solubilizates [26]. This difference in behaviour at low and high additive concentrations arises from the fact that in the former case geometrical considerations dictate that N_A is larger for non-polar additives than for polar additives, while in the latter it is the surface tension of the additive against the water which determines the value of MAC [3]. The surface tension of alcohols and ketones is about three times lower than that of alkanes [27], and therefore polar molecules solubilize in greater numbers than non-polar molecules in micellar media [3]. Note, however, that at high alcohol concentration the system becomes quite complicated since the highly dynamical nature of surfactant–alcohol mixed micelles [18, 28] introduces considerable ambiguity in the values of N_S and N_A obtained from time-dependent fluorescence quenching measurements, and therefore many published results should be treated with great caution [28].

TABLE 3

Parameters of the SDS–alkane micelle

C_A (× 10^{-2} M)	N_S	N_A	A/N_S (Å² per ion)	CMC (M)
C_6H_{14}				
0.81	85	17	59.1	0.008
1.88	108	51	59.4	0.008
2.88	120	87	62.3	0.008
C_7H_{16}				
0.1	77	2	57	0.008
0.57	90	13	56.9	0.008
1.06	103	27	56.9	0.008
C_8H_{18}				
0.32	86	7	56.1	0.008
0.55	94	13	56.1	0.008
0.7	102	18	55.8	0.008
C_9H_{20}				
0.22	83	5	56.3	0.008
0.44	92	10	56.2	0.008
$C_{10}H_{22}$				
0.12	77	2	57	0.008
0.37	93	9	55.6	0.008

[SDS] = 0.04 M.

The interfacial area per surfactant ion, A/N_S (Å² per ion), which is related to the coulombic energy of the interface, is another important micellar parameter. Here A stands for the total water–micelle interfacial area. It is characteristic that when χ_m(add.) increases the parameter A/N_S increases in the case of polar additives but remains nearly constant in the case of non-polar additives (Tables 1 - 3, Fig. 1). More interestingly, if one takes into account the accuracy of these measurements it appears that A/N_S increases in the same way for all polar additives on increasing χ_m(add.), while it remains constant (about 58 - 59 Å² per ion) in the pure SDS micelle when the additive compound is an alkane. The importance of this parameter has been pointed out by other workers [9] and its dependence on χ_m(add.) and the nature of the additive is consistent with the dependence of the degree α of micellar ionization on these factors. Thus, values of α close to unity have been found for alkyltrimethylammonium bromide micelles in water–alcohol media [29]. Such a high value of α has been interpreted in terms of the formation of surfactant–alcohol mixed micelles, built from only a few detergent ions and a large number of alcohol molecules. Figure 1 shows clearly the effect of alcoholic additives, i.e. when χ_m(add.) increases N_S decreases while N_A increases. Under these conditions the interfacial area per ion becomes large. In contrast, solubilization of alkanes does not

significantly affect the ionization of the micelles and α remains nearly constant. In the surfactant–alkane mixed micelle the additive molecules aggregate away from the surface, while the detergent ions arrange themselves in such a way as to optimize the interfacial energy. This results in the constancy of A/N_S on increasing χ_m(add.).

The results of the present study lead to the following conclusions concerning the effect of solubilizates on the properties and the structure of SDS micelles. The polarity of the additive is one of the main factors determining the behaviour of the surfactant–additive mixed micelle. The micelle aggregation number decreases with polar additives while it increases with non-polar ones. The number of additive molecules per micelle always increases with increasing additive concentration of either polar or non-polar solubilizates. The surface charge density increases with increasing concentration of polar additives, while with non-polar additives it remains independent of the additive concentration.

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