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ORIGINAL CONTRIBUTION

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The aggregation of the sodium dodecyl sulfate – *n*-octanol–water system at low concentration

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Abstract Micelle formation in sodium dodecyl sulfate (SDS)–*n*-octanol mixtures was studied by several techniques and the results were interpreted using regular solution theory for mixed-micelle formation. Octanol was considered as a nonionic surfactant. The composition of micelles at the critical micelle concentration (cmc) was computed together with the interaction parameter and the activity coefficient of the components of the micelles. The fluorescence quenching technique with pyrene was employed to obtain the SDS and octanol aggregation numbers at the cmc. The results were in agreement with similar studies on other alcohol–SDS systems. At the cmc spherical, almost fully ionized micelles formed, while at a higher concentration there was a transition to anisometric (probably rodlike) micelles which pushed sodium counterions into their Stern double layer. Mixed anisometric micelles were more ionized than pure SDS micelles. When the octanol:SDS total ratio exceeded 0.85:1, an emulsion of octanol appeared in equilibrium with the micelles.

Key words Mixed micelles · Octanol · Sodium dodecyl sulfate · Surfactants

Introduction

An important property of micellar solutions is their ability to solubilize compounds that are otherwise sparingly soluble in water: this is a familiar phenomenon in our daily lives. Micellar solubilization is important for many technical applications such as in pharmaceuticals, polymerization processes, detergency, foods and enhanced oil recovery [1]. The solubilization of aliphatic alcohols in micelles is one of the aspects of this phenomenon which has been studied by means of various techniques, such as vapour pressure [2], total solubility [3], NMR paramagnetic relaxation [4], decrease of the critical micelle concentration (cmc) [5], Krafft point depression [6], fluorescence [7], and calorimetry [6].

Addition of alcohols to aqueous solutions of surfactants has allowed the investigation of the effect of hydrophobic interactions on the micellar structure [8], and research on alcohol–surfactant interactions is very active nowadays [9–11]; however, the micellar composition of aqueous surfactant–alcohol systems has scarcely been studied [12]. Moreover, the measured changes in the micellar size or structure upon addition of medium; chain-length alcohols are not entirely consistent, suggesting that to a certain extent the conclusions depend upon the measuring technique used [13, 14]. As an example, partition coefficients in micelles have been reported to vary up to a factor of about 5 depending on the method employed [15]. On the other hand, the data from the various workers are difficult to compare directly due to the many variables of the system. The results refer to different surfactant systems at different concentrations and with different additives.

The solubilization process can be treated with the phase-separation model, in which micelles are considered as a pseudomicrophase, and solubilization can be treated as a distribution equilibrium between two phases: micelles and intermicellar solution.

It may be possible to consider the alcohol as one kind of nonionic surfactant [16], and thus theories about mixed-micelle formation may be used in surfactant–long-chain alcohol systems. Solubilized alcohols are thought to be oriented in the same way as the surfactant molecules in micelles [17]. The regular solution approach has been used by Treiner et al. [18] to analyze 1-pentanol–binary surfactant solution mixed micelles; however, they did not consider alcohols as a third surfactant component, but as a solubilizate. Long-chain alcohols produce the same effect on ionic surfactant micelles as the addition of nonionic surfactants, i.e., a decrease in the cmc and an increase in the degree of ionization of the micelles [3, 19, 20]. We have used regular solution theory on the aqueous sodium dodecyl sulfate (SDS)-octanol system, considering the alcohol as a nonionic surfactant, to obtain information about micelle composition and the interaction between micellized components.

Experimental

SDS (Aldrich), *n*-octanol (Merck) and cetylpyridinium chloride (CPC, Merck) were used as received. Pyrene (Aldrich) was recrystallized from ethanol Solutions were prepared with double-distilled water.

Fluorescene measurements were carried out with an Aminco Bowman series 2 luminiscence spectrofluorometer. The concentration of pyrene was 10^{-6} M.

The aggregation number of SDS in mixed micelles was estimated from the fluorescence intensity changes of pyrene at 395 nm on addition of CPC ($1-14 \times 10^{-5}$ M). Solutions were prepared by adding an appropriate volume of an ethanol solution of pyrene into a volumetric flask. Then the alcohol was evaporated in order to leave a pyrene residue. The flask was then filled to a mark with the SDS-octanol aqueous solution and was sonicated with gentle heating for about 6 hours in order to completely micellize the pyrene. Then, aliquots of this solution were transferred to 5-ml volumetric flasks and the appropriate amount of CPC solution was added, followed by dilution to the mark and sonication for about 1 hour.

Surface-tension measurements were carried out with a Du Noüy ring tensiometer (Krüss). Na determinations were carried out with an Orion ion-selective electrode and a millivoltmeter. Conductivity measurements were performed with an immersion cell and an automatic conductimeter, namely an Antares II (Instrumentalia). Dye solubilization measurements were performed in sealed tubes with Sudan III and surfactant mixture solutions of different concentrations, which were left for 1 week in a constant temperature bath with periodic stirring. Then the solutions were centrifuged and the supernatant's absorbance was measured with a Hewlett–Packard HP84 52A diode array spectrophotometer at 488 nm.

Changes in the color and the flourescence of Rhodamine 6G [21] were detected by the naked eye after adding a drop of dilute Rhodamine 6G solution to surfactant–octanol mixtures at different concentrations.

All measurements were performed at 25.0 °C.

Theory

The commonly used model to describe mixed-micelle formation is the pseudophase separation model [22] which considers the micelles as a thermodynamic phase in equilibrium with the monomer. According to the pseudophase model for micellization, octanol is considered as a nonionic surfactant the cmc of which is equal to its water solubility (0.0038 M) [23]. The separation of a macrophase instead of micelles at this concentration is a consequence of the small volume of the hydrophilic head group, according to the theory of the steric fitting of the micelle size [24]. The cmc of SDS was 0.008 M, in good agreement with literature values [9, 25]. The spherical-to-rodlike micelle transition of SDS was taken from the literature: 0.065–0.07 M [26].

In the case of micelles of mixed dissimilar surfactants (ionic–nonionic), the cmc is less than that predicted by ideal solution theory [27–29]. This indicates that mixed-micelle formation between these dissimilar surfactants is enhanced, relative to that between surfactants of similar structure.

Regular solution theory has been very widely used to model the thermodynamic nonidealities of mixed micelles; it has been shown to accurately model cmc values [30] and monomer–micelle equilibrium compositions [31] in surfactant systems exhibiting negative deviations from ideality.

The most important mechanistic reason for the nonideality of the ionic–nonionic micelles is believed to be the reduction in the repulsion between the ionic head groups due to insertion of the nonionic hydrophilic groups between the charged groups [32].

A mixture of two different surfactants, 1 and 2, forms micelles with composition X_1 and X_2, in equilibrium with solution monomers of composition α_1 and α_2. These mole fractions are on a surfactant-only basis, so

$$X_1 + X_2 = 1 \tag{1}$$

$$\alpha_1 + \alpha_2 = 1 \tag{2}$$

At the cmc [33]:

$$\alpha_1 \gamma_{1,\mathrm{m}}\, \mathrm{cmc}_1 = X_1 \gamma_{1,\mathrm{M}}\, \mathrm{cmc}_\mathrm{M} \tag{3}$$

$$\alpha_2 \gamma_{2,\mathrm{m}}\, \mathrm{cmc}_2 = X_2 \gamma_{2,\mathrm{M}}\, \mathrm{cmc}_\mathrm{M} \tag{4}$$

where $\gamma_{i,\mathrm{m}}$ and $\gamma_{i,\mathrm{M}}$ are the activity coefficients of surfactant i in the intermicellar solution and in micelles, cmc_1, cmc_2, and cmc_M are the cmcs of pure surfactant 1 and 2, and the mixture. Each surfactant monomeric form is assumed to be dilute enough to obey Henry's law, i.e., based on the infinite dilution standard state, surfactant monomer activity coefficients are unity [34]. In applying regular solution theory to mixed micelles, the micellar activity coefficients are given by [35]

$$\gamma_{1,\mathrm{M}} = \exp(\beta X_2^2) \tag{5}$$

$$\gamma_{2,\mathrm{M}} = \exp(\beta X_1^2) \ , \tag{6}$$

where β is the regular solution theory interaction parameter (in units of kT), k is the Boltzmann constant and T the absolute temperature. Theoretically, β is independent of both temperature and the composition of the micelle; however, in practice β is temperature-dependent [36] and often depends on the micelle composition [37], so an average value is commonly used [34].

The nature and the strength of the interaction between two surfactants are measured by the value of the β parameter, which is a measure of the degree of nonideality of the interaction in a mixed micelle. The larger the negative value of β, the stronger the attractive interaction between the two different surfactant molecules, and the greater the synergism between them [38]. Repulsive interactions yield a positive β value and the possibility of antagonism, whereas $\beta = 0$ indicates an ideal mixture. Positive β values occur in mixtures of fluorocarbon–hydrocarbon surfactants [39, 40].

Typical values of β are $+2.2$ for lithium dodecyl sulfate–lithium perfluorooctanesulfonate [41], -2.6 for SDS–poly(oxyethylene)(23)dodecyl ether [42], -3.9 for SDS–poly(oxyethylene)(4)dodecyl ether [31] and -13.2 for sodium decyl sulfate–decyl trimethylammonium bromide [29].

The parameter β is related to the molecular interactions in the mixed micelle by [31]

$$\beta = N_A(W_{11} + W_{22} - 2W_{12}) \ , \tag{7}$$

where W_{11} and W_{22} are the energies of interaction between molecules in the pure micelle and W_{12} is the interaction between the two species in the mixed micelle. N_A is Avogadros's number.

The parameter β reflects the two main contributions to the Gibbs free energy of mixed micellization. These are a free-energy contribution associated with interactions between the hydrophobic groups of surfactants 1 and 2 in the micelle core, β_{core}, and an electrostatic contribution, β_{elec}, associated with electrostatic interactions between the charged hydrophilic groups of surfactants 1 and 2 [43]:

$$\beta = \beta_{\text{core}} + \beta_{\text{elec}} \ . \tag{8}$$

It is noteworthy that β_{core} is typically zero for mixtures of two hydrocarbon–based (or fluorocarbon-based) surfactants [44], but is larger than zero for a binary mixture of hydrocarbon and fluorocarbon surfactants due to the repulsive interactions in the micellar core [45].

It can be demonstrated within regular solution theory that the free energy of mixing is given by

$$\Delta\mu_{\text{mix}}^{\text{excess}} = \beta RTX_1X_2 \ . \tag{9}$$

Negative values of $\Delta\mu_{\text{mix}}^{\text{excess}}$ indicate attraction between the two components in the micelles, most of which may result from a decrease in the electrostatic energy of the micelles. $\Delta\mu_{\text{mix}}^{\text{excess}}$ is the difference between the partial molar free energy of the mixed micelles and that calculated according to the ideal behavior, as a function of the mixture composition. This energy is expected to depend more on the surface charge density of micelles and the ionic strength, and less on the size and shape of the micelles [28]. The $\Delta\mu_{\text{mix}}^{\text{excess}}$ value does not take into account the change in the degree of association of the counterion upon surfactant mixing [36].

The value of the parameter β for interactions in a mixed micelle was calculated from the equations [31]

$$F = \frac{(X_1)^2 \ln(\alpha_1\,\text{cmc}_\text{M}/X_1\,\text{cmc}_1)}{(1-X_1)^2 \ln[(1-\alpha_1)\,\text{cmc}_\text{M}/(1-X_1)\,\text{cmc}_2]} - 1 = 0 \tag{10}$$

$$\beta = \frac{\ln(\alpha_1\,\text{cmc}_\text{M}/X_1\text{cmc}_1)}{(1-X_1)^2} \ . \tag{11}$$

Equation (10) is solved for X_1, which is then used in Eq. (11) to obtain β. Hoffmann and Pössnecker [40] have demonstrated by error expansion of Eq. (11) that the minimum error for β in a single determination is nearly $0.1\,kT$. The error increases greatly which one component in the micelle dominates.

Fluorescence measurements and interpretation were performed according to the method of Turro [46]. A detailed explanation is given in Ref. [12]. Briefly, for static quenching with a fully micellized quencher, the following equation holds [47]:

$$I/I_0 = \exp\{-Qn_\text{s}/([S] - \text{cmc})\} \ , \tag{12}$$

where I and I_0 denote the fluorescence intensity in the presence and absence of quencher, respectively, Q is the total concentration of quencher, n_s is the micellar aggregation number of surfactant, and [S] is the total concentration of surfactant.

With the value of n_s and the surfactant mole fraction in the micelles, X_{SDS}, the aggregation number of octanol n_{oct} can be computed.

Conductivity plots were used to determine the degree of counterion association, α, by the Evans [48] method.

Results

A typical specific conductivity (κ) versus total concentration (c) plot, showing two breaks which correspond to two different aggregation steps, is shown in Fig. 1. Two typical surface tension versus $\log c$ plots are shown in Fig. 2. At high total composition Y_{SDS}, these plots show a minimum. (Y_{SDS} is the total mole fraction of SDS in the mixture, on a surfactant-only basis, including the monomeric and micellized molecules). This was due to the octanol which acted as a highly surface active

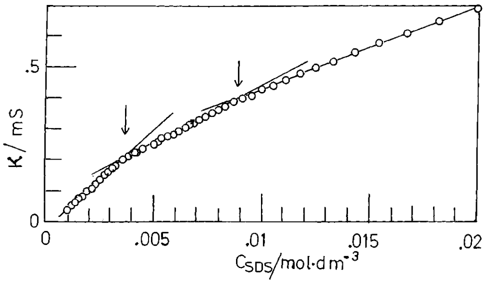

Fig. 1 Specific conductivity versus sodium dodecyl sulfate (*SDS*) concentration. The total mole fraction of SDS in the surfactant mixture (Y_{SDS}) was 0.936. *Arrows* indicate the two transitions

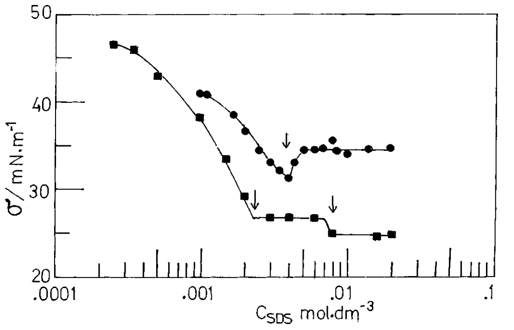

Fig. 2 Typical surface tension–log SDS concentration plots. ●: $Y_{SDS} = 0.881$; ■: $Y_{SDS} = 0.541$. *Arrows* indicate the two transitions

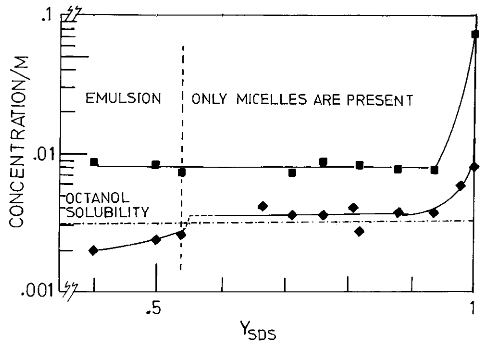

Fig. 3 The two transition concentrations as functions of Y_{SDS}. ■: isometric to anisometric micelle transition; ◆: critical micelle concentration (*cmc*)

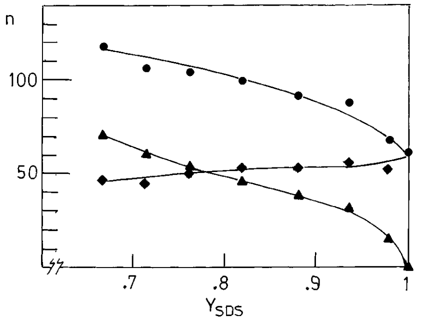

Fig. 4 Micellar aggregation numbers as functions of Y_{SDS}. ◆: n_{SDS}; ▲: n_{oct}; ●: n_{tot}

impurity in SDS. At Y_{SDS} values lower than about 0.54, this minimum disappeared. Using neutron reflection techniques on aqueous dodecanol–SDS systems, Lu et al. [10] found that the amount of dodecanol adsorbed at the air–solution interface dropped sharply at the cmc, although not to zero. This alcohol was solubilized by SDS even below the cmc, and the concentration may be up to 4 times the pure water solubility of the alcohol. Dodecanol formed a 1:1 complex with SDS, which was adsorbed at the surface as a single compound. It may be thought that once Y_{SDS} became less than 0.5, all SDS molecules were in the complex form, which acted as an impurity which is less surface-active than the main surfactant, octanol. Two transitions might also be seen in the surface-tension plots.

The concentration at which the two changes in aggregation occurred are plotted versus Y_{SDS} in Fig. 3. At the lower-concentration transition aggregates dissolved Sudan III and changed the color and fluorescence of Rhodamine 6G. At the higher-concentration transition, Na$^+$ counterions joined the micellar surface, and the solution viscosity increased, denoting the formation of anisometric micelles.

Figure 4 shows the association number of SDS in micelles at the lower-concentration transition, n_{SDS}, together with the octanol association number n_{oct} and the total aggregation number n_{tot}. The aggregation number of SDS micelles was 62, in agreement with values in the literature [49]. At $Y_{SDS} < 0.54$, micelles are accompanied by emulsified octanol.

Discussion

The true cmc value is that of the lower-concentration transition, because the aggregates dissolved the hydrophobic dye and changed the optical properties of Rhodamine 6G. At this transition the micelles are spherical, in accordance with viscosity measurements, and the n_{tot} values are compatible with a spherical micelle shape [24]. Moreover, micelles are fully (or almost fully) ionized, because the aggregation of counterions was only noticeable at the higher-concentration transition, as demonstrated by the Na$^+$-ion-selective electrode. This higher-concentration transition is related to a shape change from spherical to anisometric (probably rodlike) micelles. This transition from small spherical micelles to large rodlike ones has also been observed in SDS–alcohol systems, in which the alcohol was hexanol or heptanol [50], and pentanol or hexanol [51]. It is known that polar solubilizates may induce changes from small spherical to large rodlike micelles [52].

The micelle composition at the cmc was computed with Eqs. (10) and (11) and is plotted in Fig. 5 versus Y_{SDS}. It may be seen that the micelles were always richer in octanol, i.e., $X_{SDS} < Y_{SDS}$ at compositions in which no emulsion occurred; however, when emulsion appeared, $X_{SDS} \rightarrow Y_{SDS}$ as Y_{SDS} decreased, and $X_{SDS} = Y_{SDS}$ at $Y_{SDS} < 0.4$. It is known that addition of medium-to-long-chain alcohols increases the aggregation number, thus producing larger alcohol–surfactant mixed micelles [53–55].

The behavior of the aggregation numbers of SDS and octanol in micelles as a function of the alcohol content is in agreement with that found by Suárez Varela et al. [12] in SDS–butanol, SDS–pentanol and SDS–hexanol systems, and that found by Almgen and Swarup [13] in the SDS–octanol system using the steady-state fluorescence-quenching method.

The β parameter was negative but was not constant: its value increased as Y_{SDS} decreased, becoming zero at $Y_{SDS} = 0.54$ ($n_{octanol}/n_{SDS} = 0.85$), the composition at which emulsified octanol appeared. (Fig. 6). This can be compared SDS–dodecanol systems, in which turbidity appeared at $Y_{SDS} = 0.95$ ($n_{dodecanol}/n_{SDS} = 0.053$) [56], owing to the lower solubility of dodecanol than octanol. Since β is essentially β_{elec}, this situation may be interpreted as the gradual separation of the sulfate headgroups at the micelle surface, thus reducing their mutual interaction. At lower Y_{SDS} values β became negative again, and its (negative) value increased as Y_{SDS} decreased; however, it is doubtful whether regular solution theory can be used properly to describe situations when an emulsion is present. The value $\beta = 0$ corresponds to ideal mixing. It may be interpreted as the appearance of octanol micelles, with some very dilute solubilized SDS molecules. Since octanol micelles do not exist, this situation corresponds to the separation of octanol as a macroscopic phase, which was emulsified by the SDS molecules. Accordingly to Høiland and Blokhus [50] the separating phase is almost pure alcohol.

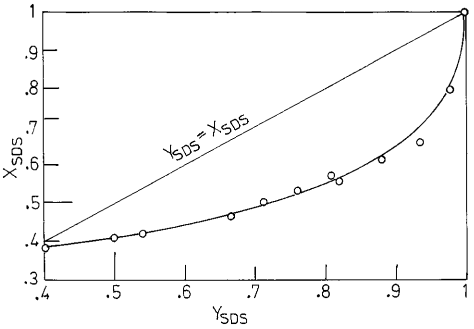

Fig. 5 Micellar composition (X_{SDS}) at the cmc versus Y_{SDS}

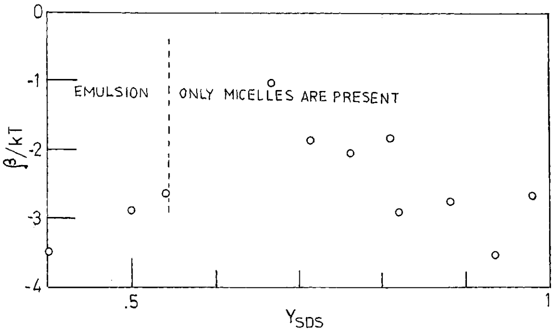

Fig. 6 The interaction parameter β as a function of Y_{SDS}

At high alcohol contents it has been proposed that the medium-chain-length alcohols are solubilized in the micellar interior as well as in the palisade layer, thus producing large swollen alcohol aggregates [13, 53, 54, 57].

Lianos and Zana [58] have calculated that only about 2.5 alcohol molecules per surfactant molecule can be accomodated in micelles with the polar group at the surface. If the solubilization ratio for primary alcohols is larger than 2.5, it seems necessary that the excess must be located in the micelle core. Since the octanol–SDS system did not surpass this limiting value, it seems that all alcohol hydroxyl groups were at the micelle surface.

According to several authors [53, 59], the hydrocarbon chain of the alcohol should penetrate the micellar interior, while the polar groups should remain at the micelle surface. The alcohol polar groups, present at the micelle surface, would lead to a reduction in the effect due to repulsion of the surfactant head groups. This seems to be the appropriate picture for the SDS–octanol mixed micelles.

The logarithm of the activity coefficients of both components in micelles, $\gamma_{SDS,M}$ and $\gamma_{oct,M}$, versus the square root of the concentration of SDS in micelles, X_{SDS}, is shown in Fig. 7. It may be seen that at first $\gamma_{SDS,M}$ decreased as X_{SDS} decreased, as may be expected from theory; however, it passed through a minimum at $\sqrt{X_{SDS}} \approx 0.82$ ($X_{SDS} \approx 0.67$) and through a maximum at

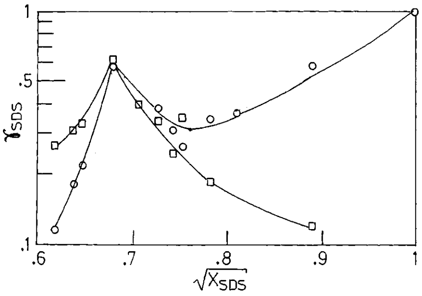

Fig. 7 Activity coefficients in micelles versus the square root of the mole fraction of SDS in micelles, X_{SDS}. ○: γ_{SDS}; □: γ_{oct}

$\sqrt{X_{\mathrm{SDS}}} \approx 0.69$ ($X_{\mathrm{SDS}} \approx 0.476$), with a subsequent decrease. The micellized octanol activity coefficient also had a maximum at the same position, but the increase to $\gamma_{\mathrm{oct,M}} = 1$ at $X_{\mathrm{SDS}} = 0$ might not be reached because of the formation of emulsified octanol and the subsequent phase separation in two layers. The large negative deviations from ideality in binary ionic–nonionic surfactant mixtures are mainly due to the reduced repulsion between ionic head groups in the micelle upon addition of nonionic molecules [27]. This situation also occurred in this system.

The total aggregation number of micelles is compatible with spherical or low-eccentricity elipsoidal shape [24], and justifies the use of a spherical model to compute the surface potential.

The volume of the micelle core was computed with

$$V_{\mathrm{core}} = V_{\mathrm{C8H17}} \cdot n_{\mathrm{oct}} + V_{\mathrm{C12H25}} \cdot n_{\mathrm{SDS}} \ , \tag{13}$$

where V_{C8H17} and V_{C12H25} are the volumes of the octyl and dodecyl radicals. These volumes were computed with [59, 60]

$$V_{\mathrm{CH3}}(\mathrm{nm}^3) = 0.05108 + 0.000131t \tag{14}$$

$$V_{\mathrm{CH2}}(\mathrm{nm}^3) = 0.02669 + 0.0000143t \ , \tag{15}$$

where t is temperature is Celsius. Since the spherical micelles were fully ionized (except that of pure SDS) the surface potential ψ_0 was computed with the radius of a micelle whose volume was V_{core} and whose charge was n_{SDS}. The ψ_0 value for a fully ionized (hypothetical) SDS micelle was also computed, and the data were plotted in Fig. 8. According to current theories on electrical double-layer formation in colloids [21], the high value of ψ_0 at the pure SDS micelle surface causes the immediate "condensation" of counterions giving rise to the formation of the Stern double layer; however, our results indicated that the dilution of the sulfate groups by the hydroxyl groups at the mixed-micelle surface reduced ψ_0 to a value in which no counterion "condensation" occurred. This situation is enhanced by the reduced ionic strength resulting from the reduction of the cmc in mixed systems.

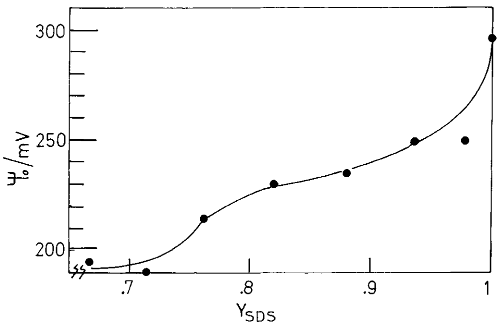

Fig. 8 Potential at the spherical micelle surface versus Y_{SDS}

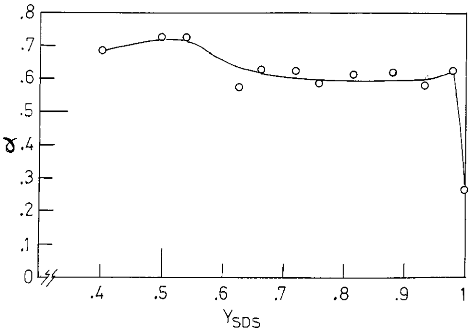

Fig. 9 The ionization degree of anisometric micelles versus Y_{SDS}

When the concentrations was increased, the combination of increasing ionic strength and the change in shape from spheres to rods (which approached the ionic head groups among them and increased ψ_0) produced the ion "condensation" on the micelle surface, as the Na^+-ion-selective electrode measurements demonstrated; however, the surface dilution of the ionic head groups was still high and produced a micelle ionization degree (α) higher than that of the pure SDS micelles, as can be seen in Fig. 9. The degree of counterion association has been reported [61] to increase when rodlike micelles are formed, confirming the conclusions reached from viscosity measurements.

Conclusions

1. Regular solution theory for mixed ionic–nonionic micelles can be applied to surfactant–long-chain-alcohol systems giving results which are in general agreement with those obtained using other approaches.
2. The aqueous octanol–SDS system has two aggregation steps. The lower–concentration transition is the cmc, giving isometric (spherical or elipsoidal), almost fully ionized micelles. The higher–concentration transition corresponds to the transition to anisometric (probably rodlike) micelles, accompanied by micellization of counterions.
3. At low octanol content, this substance acts as a more tensioactive impurity in SDS giving a minimum in the surface tension versus concentration plot, whereas once the octanol–SDS molar ratio is almost unity, the minimum disappears. This may be due to the formation of a 1:1 complex between alcohol and surfactant, acting as a less tensioactive impurity in octanol.

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References

1. (a) McBain MEL, Hutchinson E (1955) Solubilization and related phenomena. Academic Press, New York; (b) Elworthy PH, Florence AT, McFarlane CB (1968) Solubilization by surface active agents. Chapman & Hall, London; (c) Wennerstrom H, Lindman B (1979) Phys Rev 52:1; (d) Mukerjee P (1979) In: Mittal KL (ed) Solution chemistry of surfactants, vol 1. Plenum, New York, pp 153–174; (e) Mittal KL, Mukerjee P (1977) In: Mittal KL (ed) Micellization, solubilization, and microemulsions, vol 1. Plenum, New York, pp 1–21
2. (a) Eda Y, Takisawa N, Shirahama K (1993) Prog Anesth Mech 1:27; (b) Hayase K, Hayano S, Tsubota H (1984) J Colloid Interface Sci 101:336; (c) Morgan ME, Uchiyama H, Christian SD, Tucker EE, Scamehorn JF (1994) Langmuir 10:2170; (d) Wan-Badhi W, Bloor DM, Wyn-Jones E (1994) Langmuir 10:2219; (e) Treiner C, Khodja A, Fromon M, Chevalet J (1989) J Solution Chem 18:217
3. Lianos P, Zana R (1984) J Colloid Interface Sci 101:587
4. (a) Marangoni DG, Kwak JCT (1991) Langmuir 7:2083; (b) Gao Z, Wasylishen RE, Kwak CT (1991) J Chem Soc Faraday Trans 87:947; (c) Gan Z, Wasylishen RE, Kwak JCT (1989) J Phys Chem 93:2190
5. (a) Shirahama K, Kashiwabara T (1971) J Colloid Interface Sci 36:65; (b) Rao IV, Ruckenstein E (1986) J Colloid Interface Sci 113:375
6. Kaneshina S, Kamaya H, Ueda I (1986) J Colloid Interface Sci 113:375
7. Abuin EB, Lissi EA (1983) J Colloid Interface Sci 95:189
8. (a) Baglioni P, Kevan L (1987) J Phys Chem 91:1516; (b) Baglioni P, Kevan L (1987) J Phys Chem 91:2106
9. Benito I, Garcia MA, Monge C, Saz JM, Marina ML (1997) Colloids Surf A 125:221
10. Lu JR, Purcell IP, Lee EM, Simister EA, Thomas RK, Rennie AR, Penfold J (1995) J Colloid Interface Sci 174:441
11. (a) Caponetti E, Chillura Martino D, Floriano MA, Triolo R (1997) Langmuir 13:53; (b) Kunieda H, Nakamura K (1991) J Phys Chem 95:1425; (c) Karukstis KK, D'Angelo ND, Loftus CT (1997) J Phys Chem 101:1968; (d) Hoffmann H, Thunig C, Valiente M (1992) Colloids Surf 67:223
12. Suárez Varela A, Sánchez Macho MI, Gil González A (1995) Colloid Polym Sci 273:876
13. Almgren M, Swarup S (1983) J Colloid Interface Sci 91:256
14. (a) Backlund S, Rundt K, Birdi KS, Dalsager S (1981) Colloid Polym Sci 259:1105; (b) Høiland H, Blokhus AM, Kvammen OJ, Backlund S (1985) J Colloid Interface Sci 107:576; (c) McGreevy RJ, Schechter RS (1989) J Colloid Interface Sci 127:209; (d) Attwood D, Mosquera V, Pérez-Villar V (1989) J Colloid Interface Sci 127:532
15. Marangoni JF, Kwak JCT (1995) In: Christian SD, Scamehorn JF (eds) Solubilization. Surfactant Science Series No. 55. Dekker, New York, p 165
16. Hayase K, Hayano S (1978) J Colloid Interface Sci 63:446
17. Mukerjee P, Cardinal JR (1978) J Phys Chem 82:1620
18. Treiner C, Amar Khodja A, Fromon M (1987) Langmuir 3:729
19. Castedo A, del Castillo JL, Suérez-Filloy MJ, Rodr JR (1997) J Colloid Interface Sci 196:148, and references therein
20. Zana R, Yiv S, Strazielle C, Liaos P (1981) J Colloid Interface Sci 80:208
21. Schukin ED, Pertsov AV, Amélina EA (1988) Química colloidal. MIR, Moscow
22. Shinoda K (1963) In: Shinoda K, Tamamushi B, Nakagawa T, Isemura T (eds) Colloidal surfactants. Academic Press, New York, p 25
23. Shinoda K (1978) Principles of solution and solubility. Dekker, Basel, p 86
24. (a) Schulz PC (1991) Colloid Polym Sci 269:612; (b) Schulz PC (1991) J Colloid Interface Sci 152:333
25. Esposito C, Colicchio P, Facchiano A, Ragone R (1998) J Colloid Interface Sci 200:310
26. (a) Miura M, Kodama M (1972) Bull Chem Soc Jpn 45:428; (b) Kodama M, Miura M (1972) Bull Chem Soc Jpn 45:2265; (c) Nakagaki M, Inagari H (1965) Hikari Sanran Zikken Hou Nankodo, Tokyo, p 108; (d) Kodama M, Kubota Y, Miura M (1972) Bull Chem Soc Jpn 45:2953
27. Rathman JF, Scamehorn JF (1986) Langmuir 2:354
28. (a) Lange H, Beck KH (1973) Kolloid Z Z Polym 251:424; (b) Funasaki N, Hada S (1979) J Phys Chem 83:2471
29. Holland PM, Rubingh DN (1983) J Phys Chem 87:1984
30. Osborne-Lee IW, Schechter RS (1985) J Colloid Interface Sci 108:60; (b) Hua XY, Rosen MJ (1982) J Colloid Interface Sci 90:212; (c) Rosen MJ, Zhu By (1984) J Colloid Interface Sci 99:427; (d) Zhu BY, Rosen MJ (1984) J Colloid Interface Sci 99:435; (e) Kamrath RF, Franses EI (1983) Ind Eng Chem Fundam 22:230
31. Rubingh DN (1979) In: Mittal KL (ed) Solution chemistry of surfactants, vol 1. Plenum, New York, p 337
32. (a) Moroi Y, Nishikido N, Saito M, Matuura R (1975) J Colloid Interface Sci 52:356; (b) Rathman JF, Scamehorn JF (1984) J Phys Chem 88:5807
33. Scamehorn JF, Schechter RS, Wade WH (1982) J Dispersion Sci Technol 3:261
34. Minardi RM, Schulz PC, Vuano B (1996) Colloid Polym Sci 274:669
35. Balzhiser RE, Samuels MR, Eliassen JD (1972) Chemical engineering thermodynamics. Prentice Hall, Englewood Cliffs, New York, p 173
36. (a) Crisantino R, De Lisi R, Miloto S (1994) J Solution Chem 23:639; (b) Hey MJ, Mac Taggart JW (1985) J Chem Soc Faraday Trans 1 81:207; (c) Rosen MJ, Zhac F (1983) J Colloid Interface Sci 95:443
37. Treiner C, Amar Khodja A, Fromon M (1987) Langmuir 3:729
38. Rosen MJ, Gao T, Nakatsuji Y, Masuyama A (1994) Colloids Surf A 88:1
39. Mukerjee P, Yang A (1976) J Phys Chem 89:1388
40. Hoffmann H, Pössnecker G (1994) Langmuir 10:381
41. Miyagishi JH, Ishibai Y, Asakawa T, Nishida M (1985) J Colloid Interface Sci 103:164
42. Treiner C, Vaution C, Miralles E, Puiseux F (1985) Colloids Surf 14:285
43. Sarmoria C, Puvvada S, Blankschtein D (1992) Langmuir 8:2690
44. Scamehorn JF (1986) In: Scamehorn JF (ed) Phenomena in mixed surfactant systems. ACS Symposium Series 311. American Chemical Society, Washington, pp
45. (a) Mukerjee P, Handa T (1981) J Phys Chem 85:2298; (b) Handa T, Mukerjee P (1981) J Phys Chem 85:3916; (c) Clapperton RM, Ottewill RH, Ingram BT (1994) Langmuir 10:51; (d) Burkitt SJ, Ingram BT, Ottewill RH (1988) Prog Colloid Polym Sci 76:247
46. Turro MJ, Yekta AJ (1978) J Am Chem Soc 10:951
47. Kalyanasundaram K (1987) In: Kalyanasundaram K Photochemistry in microheterogeneous systems. Academic Press, New York, pp 56–57
48. Evans HC (1956) J Chem Soc Perkin Trans 1:579
49. Mysels KJ, Princen LH (1959) J Phys Chem 63:1696
50. Høiland H, Blokhus AM (1990) In: Bloor DM, Wyn-Jones E (eds) The structure, dynamics and equilibrium properties of colloidal systems. Kluwer Academic Publishers, Boston, pp 39–48

51. Frland GM, Samset J, Høiland H, Mortensen K (1994) J Colloid Interface Sci 164:163
52. (a) Larsen JW, Magid LJ, Payton V (1973) Tetrahedron Lett 29:2663; (b) Tominaga T, Sten TB, Evans DF (1980) Bull Chem Soc Jpn 53:795; (c) Lindblom G, Lindaman B, Mandell LJ (1971) J Colloid Interface Sci 35:519
53. Blokhus AM, Høiland H, Backlund S (1986) J Colloid Interface Sci 114:9
54. (a) Backlund S, Bakken J, Blokhus AM, Høiland H, Vikholm I (1986) Acta Chem Scand 440:241; (b) Vikholm I, Douheret G, Backlund S, Høiland H (1987) J Colloid Interface Sci 116:582
55. Vikholm I, Backlund S, Høiland H, Veggenland K (1988) Mater Sci Forum 25–26:339
56. Fang JP, Joos P (1992) Colloids Surf 65:121
57. (a) Hirch E, Candau S, Zana R (1984) J Colloid Interface Sci 97:318; (b) Backlund S, Høiland H, Kvammen OJ, Ljosland E (1982) Acta Chem Scand A 36:697; (c) Blokhus AM, Høiland H, Gilger H, Backlund S (1988) J Colloid Interface Sci 124:125; (d) Høiland H, Blokhus AM, Kvammen OJ, Backlund S (1985) J Colloid Interface Sci 107:576
58. Lianos P, Zana R (1984) J Colloid Interface Sci 101:58
59. (a) Guveli DE, Kayes JB, Davis SS (1979) J Colloid Interface Sci 72:130; (b) Eda Y, Takisawa N, Shirahama K (1996) Langmuir 12:325
60. Gruen DW (1986) J Phys Chem 89:146
61. Kamenka N, Fabre H, Chorro M, Lindman B (1977) J Chim Phys 74:510