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ORIGINAL CONTRIBUTION

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Photophysical characterization of mixed micelles of *n*-butanol/SDS and *n*-hexanol/SDS. A study at low alcohol concentrations

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Abstract The effect of the addition of *n*-butanol (BuOH) and *n*-hexanol (HexOH) on the micellization of sodium dodecylsulfate (SDS) has been investigated using fluorescence quenching methods. The binding constants were calculated using an expression which relates the total concentration of alcohols and the micelle concentration. The values of K were 4.67 and 17.6 M^{-1} for BuOH/SDS and HexOH/SDS, similar to values obtained by other methods. The cmc of SDS decreases on addition of alcohols and goes through a minimum for the BuOH/SDS system. Micellar aggregation numbers (N) were determined from linear plots of Ln (I^0/I) against [Quencher] at low alcohol concentrations. For 15 mM SDS, in the presence of BuOH the N values decrease on addition of alcohol up to 0.2 M. For HexOH, N can be assumed to be constant up to 4.8 mM, after which N decreases. The polarity of the micellar core containing alcohol was evaluated from the I_1/I_3 ratio of monomeric pyrene. The effect of addition of the alcohol causes a decrease in the I_1/I_3, which corresponds to a decrease in the polarity of the pyrene solubilization site.

Key words Mixed micelles – alcohol/surfactant interactions – cmc – aggregation numbers

Introduction

In most of their applications, surfactants are used in the presence of additives in order to improve their properties. Among the very large number of additives revealed by a literature survey, alcohols hold a special place, being by far the most frequently used. This has been especially so in recent years because alcohols are the most common cosurfactants which are added to surfactant–oil systems to generate microemulsions [1]. The oil crisis and the suggested use of microemulsions in tertiary oil recovery [2] to improve the yield of oil fields has greatly stimulated research on every possible aspects of the physical–chemistry of surfactant–alcohol systems: partition of alcohols between the micellar pseudo-phase and the intermicellar phase, surface tension of mixed solutions, critical micellization concentration (cmc), micelle ionization degree, micelle aggregation numbers and micelle dynamics in the presence of alcohols, etc.

Fluorescence probes are very useful for analysing the micropolarity and microviscosity of the probe environment in micelles and for determining micelle aggregation number [3–7]. In this study, the polarity of the core of the micelles containing alcohol was evaluated from the ratio between the intensities of the first and third vibronic peaks of the emission spectra of monomeric pyrene, I_1/I_3.

Solubilization of alcohols in surfactant micelles has been extensively investigated [3–14] and the partition coefficients of alcohols between the intermicellar phase

and the micellar pseudophase have been determined by various methods. Hayase and Hayano [9] determined the partition coefficients of alcohols using vapour pressure measurements. Gettins et al. [10] determined the partition coefficients using solubility measurements. Abuin and Lissi [11] also determined the partition coefficients using the fluorescence quenching method. Recently, Eda et al. [12] determined the solubilization of alcohols in ionic micelles using piezoelectric gas sensors. All these studies discussed the partition of hydrocarbon compounds between the aqueous phase and hydrocarbon surfactant micelles. It has been reported that the cmc of aqueous solutions of surfactants containing alcohol decreases with the addition of alcohols [3, 4, 11], as found also in this study.

In this paper we present results on the cmc, micelle aggregation numbers and binding constants of alcohol/SDS systems at concentrations below those usually reported in the literature [4–7]. Typical results are presented supporting the new method employed for the determination of binding constants.

Experimental details

Sodium dodecylsulfate (SDS, Aldrich), *n*-butanol (Merck), *n*-hexanol (Reagent), and cetylpyridinium chloride (CPC, Aldrich) were employed as received. Pyrene (Py, Aldrich), was recrystallized twice from ethanol. Solutions were prepared in Milli-Q purified water.

Fluorescence measurements were carried out with a CD-900, Edinburgh Instruments Spectrofluorimeter. The concentration of pyrene was 10^{-6} M and the concentration of the surfactant was kept constant at 15 mM. The solutions were used 24 h after preparation.

Aggregation numbers of SDS were estimated from the changes of the fluorescence intensity of pyrene at 373 nm on addition of CPC ($1.0–14.0 \times 10^{-5}$ M) according to the method of Turro [15]. All measurements were carried out at 25°C.

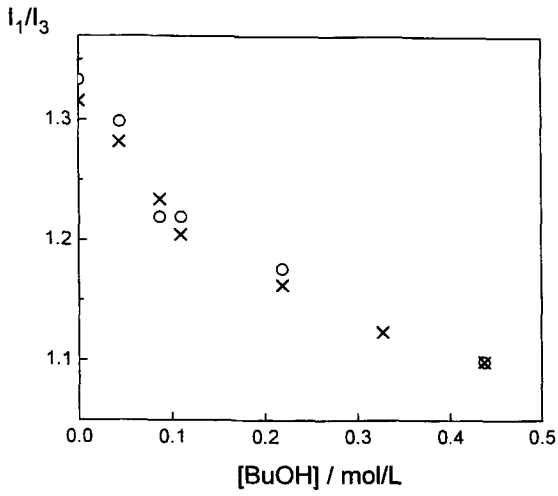

Fig. 1 Dependence of the I_1/I_3 ratio of pyrene in SDS in the presence of butanol. Aereated (×) and deaereated (○) solutions. [SDS] = 15 mM; [Py] = 10^{-6} M

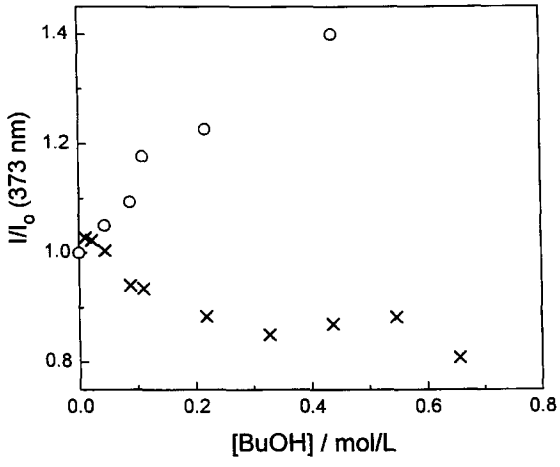

Fig. 2 Fluorescence of pyrene in aereated (×) and deaereated (○) solutions of SDS in the presence of butanol. [SDS] = 15 mM; [Py] = 10^{-6} M

Results and discussion

Steady-state fluorescence of pyrene

The changes of the I_1/I_3 ratio of pyrene on adding *n*-butanol to SDS micelles are shown in Fig. 1, which also shows these effects in deaereated solutions. The observed decrease in I_1/I_3 corresponds to a decrease in the polarity at the pyrene solubilization sites, because of the expulsion of water molecules from the micellar core [4, 6]. The values obtained of the I_1/I_3 ratio in the absence and presence of oxygen are practically identical, showing that the increased local concentration of oxygen solubilized in the micelles, due to the alcohol incorporation, does not affect the polarity of the solubilization sites of pyrene.

Figure 2 shows plots of I/I^0 against [*n*-butanol] in aereated and deaereated solutions, where I and I^0 are the fluorescence intensities of pyrene in the presence and absence of *n*-butanol, respectively, measured at 373 nm. The results indicate that quenching by oxygen is more efficient in the presence of alcohol, as expected from the higher solubility of oxygen when alcohol is added to the micelles.

These results show that the concentration of oxygen in micelles can be monitored better by the emission intensity of the probe than by the I_1/I_3 ratio. Abuin and Lissi [8] developed a method for determining the partition constants of alcohols in micellar solutions using this property of the system.

Critical micellar concentration

The cmc's were determined utilizing pyrene as a probe and the results obtained agree with the literature values [4, 9]. The dependence of the cmc of SDS with the concentrations of butanol and hexanol is shown in Fig. 3. A logarithmic representation of cmc/cmc^0 against the concentration of added alcohol is used in order to be able to compare the results for surfactant–alcohol systems over a large range of cmc values. In this plot cmc^0 stands for the cmc of the surfactant in the absence of added alcohol. At low alcohol concentrations, the cmc decreases linearly with increasing alcohol concentrations, in agreement with earlier reports [4, 11]. For the BuOH/SDS system the decrease of the cmc starts at higher alcohol concentrations and seems to go through a minimum. It has been assumed that at higher concentrations the micelles are almost saturated by alcohol, and can be considered rather like a cosolvent influencing the micellization process by modifying the properties of the water [3]. As alcohol–water mixtures are better solvents for the surfactants than pure water, the micelles will start being formed again at higher concentrations. In this range the system can be considered alternatively as consisting of droplets of alcohol stabilized by the surfactant (like inverse micelles) [16]. It must be noted that at high alcohol concentrations the cmc's are more difficult to determine by stationary fluorescence methods [3, 7]. Therefore, larger errors may effect the points at the higher butanol concentrations in Fig. 3.

The emission spectra of pyrene in the range of surfactant concentrations around the cmc in the presence of alcohol, where the probe begins to change its environment, are shown in Fig. 4. An increasing amount of excimer emission can be observed up to a maximum, which is coincident with the change of the probe environment, as evidenced by the change in the I_1/I_3 ratio (Figs. 5 and 6). These results indicate that prior to the formation of micelles, the probe will migrate from the bulk of the solution to a more hydrophobic environment formed by the aggregation of surfactant molecules, which did not reach, at this stage, a micellar structure. As the concentration of these pre-micelles will be initially low, more than one probe molecule may be present in each aggregate, giving rise to excimer emission. The addition of larger

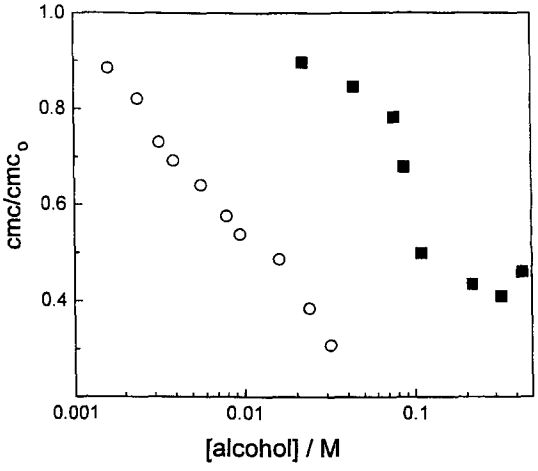

Fig. 3 Dependence of the cmc of SDS with alcohol concentration at 25°C. (○) HexOH and (■) BuOH

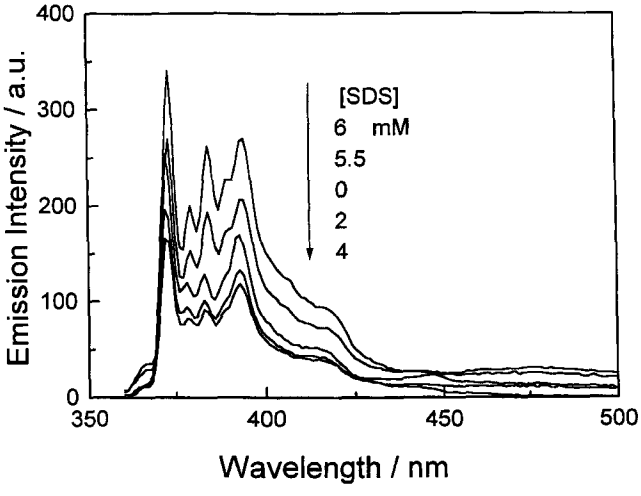

Fig. 4 Emission spectra of pyrene at various concentrations of SDS in the presence of HexOH 3.9 mM

amounts of surfactant will increase the concentration of the pre-aggregates and their aggregation number, up to the formation of real micelles, allowing the probe molecules to be redistributed, to one or less molecules per micelle. The presence of alcohol molecules in the pre-aggregates or the micelles, does not alter this picture. Furthermore, it proves that the alcohol molecules will be already present in the pre-aggregates, as the final I_1/I_3 corresponds to that of the mixed micelle. Previous studies with surfactants in the presence of polyelectrolytes show a similar behaviour due to the presence of premicellar aggregates [17].

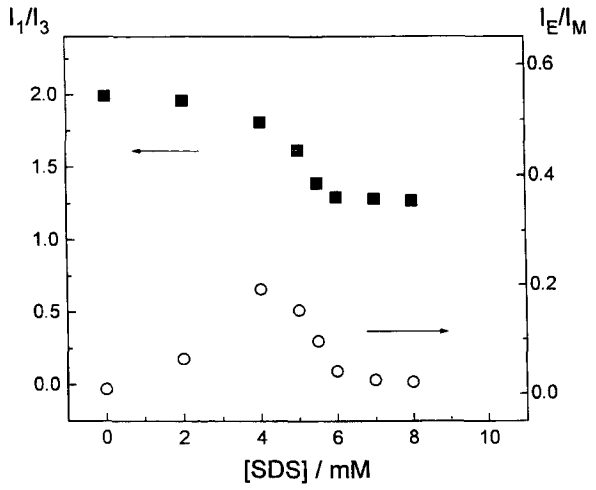

Fig. 5 Dependence of the I_1/I_3 and I_E/I_M ratios of pyrene with SDS concentration in the presence of HexOH 3.9 mM

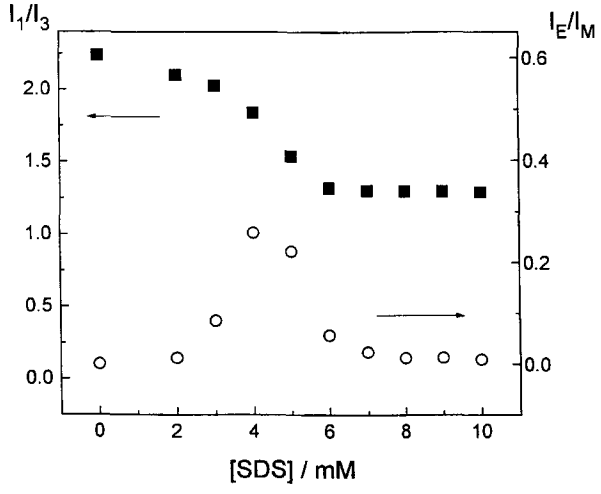

Fig. 6 Dependence of the I_1/I_3 and I_E/I_M ratios of pyrene with SDS concentration in the presence of BuOH 44 mM

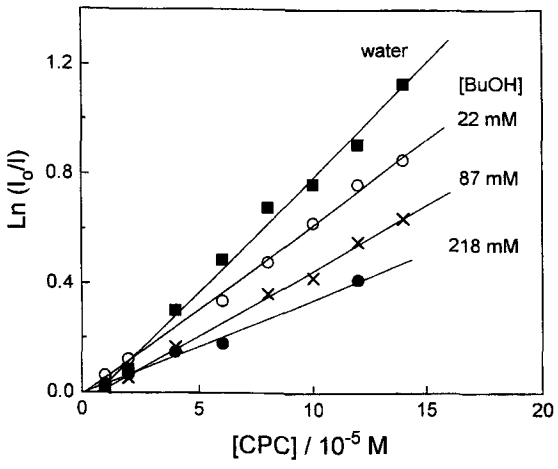

Fig. 7 Fluorescence quenching of pyrene by CPC in micelles of SDS at several BuOH concentrations. [SDS] = 15 mM; [Py] = 10^{-6} M

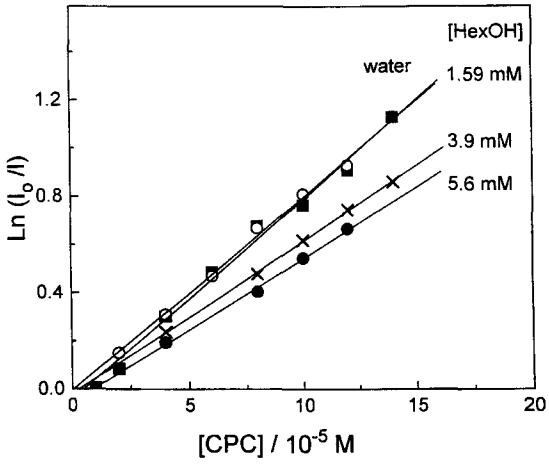

Fig. 8 Fluorescence quenching of pyrene by CPC in micelles of SDS at several HexOH concentrations. [SDS] = 15 mM; [Py] = 10^{-6} M

Aggregation micellar number

The method of Turro and Yekta [15] was used to determine the aggregation number of the micelles. Plots of $\mathrm{Ln}(I^0/I)$ against [CPC] were linear at low alcohol concentrations. Throughout all the quenching experiments the I_1/I_3 ratio remained constant, showing that the presence of quencher in the micelle does not affect the solubilization site of the pyrene. The average aggregation number N of the surfactant was determined using [3–7]

$$N = (C - \mathrm{cmc})/M, \quad (1)$$

where C is the total concentration of surfactant, M is the micelle concentration and cmc is the critical micellar concentration.

Figures 7 and 8 show representative plots for the quenching of the pyrene fluorescence in SDS micelles by CPC in the presence of *n*-butanol and *n*-hexanol, respectively. The aggregation numbers for the surfactants (N) in the micelles were calculated using Eq. (1), and are shown in Tables 1 and 2 as a function of the alcohol concentrations. These values are similar, but slightly lower, than those determined by Nome et al. [4] with 0.05 M SDS at 25°C. According to Almgren and Swarup [7], the aggregation

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Table 1 Parameters for the BuOH/SDS system. [SDS] = 15 mM

[BuOH], [mol/L]	0	0.022	0.044	0.076	0.087	0.109	0.218
[M] [10^{-4} mol/L]	1.18	1.62	1.70	1.77	2.08	2.52	2.91
cmc [10^{-3} mol/L]	7.8	7.0	6.7	6.3	5.4	3.9	3.4
N	61	49	49	49	46	44	40
a	—	115	219	364	355	367	635

Table 2 Parameters for the HexOH/SDS system. [SDS] = 15 mM

[HexOH], [10^{-3} mol/L]	0	1.6	2.4	3.9	4.8	5.6	7.9
[M] [10^{-4} mol/L]	1.18	1.25	1.32	1.39	1.44	1.68	2.00
cmc [10^{-3} mol/L]	7.8	7.0	6.4	5.8	5.3	5.1	4.6
N	61	64	65	66	67	59	52
a	—	12	17	26	32	32	37

numbers determined in this way will have errors of about 10%.

In previous investigations [4, 7] it was found the N values decrease with increasing alcohol concentration. During these works the concentration of alcohol did not go as low as in the research presented here. At the lowest concentrations of alcohol (up to ~80 mM for BuOH/SDS and up to ~5 mM for HexOH/SDS), the aggregation numbers remain constant. At higher concentrations N begins to decrease as described previously. In both systems the micelle concentrations increase progressively with the addition of alcohol.

The aggregates of the BuOH/SDS system consist of a smaller number of surfactant molecules over the whole range of concentrations. This decrease is due to the expulsion of water molecules, which results in surfactant molecules leaving the aggregate because of electrostatic repulsion between the head groups [3–5, 15]. For the HexOH/SDS system the aggregation number can be assumed to remain constant up to 5 mM/L. In this case, the amount of alcohol solubilized in the micelle is quite smaller and is not sufficient to affect significantly the penetration of water in the micelle.

Micellar incorporation of alcohols

The partition constants and aggregation numbers of alcohols and surfactants in micelles can be calculated by fluorescence quenching methods. The method developed in this study uses an expression which relates the total concentration of alcohols and the micelle concentration. For this, a simultaneous partition of surfactants and alcohol molecules between the mixed micelles and the intermicellar aqueous phase is assumed. After its addition, the alcohol associates with the surfactants to form the mixed micelles. The process can be represented qualitatively by

$$A_w + S_w \rightleftharpoons M \,, \tag{2}$$

where A_w and S_w signify alcohol and surfactant in water, respectively. After the association (in the equilibrium), the concentration of free alcohol will be $(A_o - A_m)$, where A_o and A_m are the total and micellized alcohol concentrations, respectively. The relationship between A_m and the concentration of mixed micelles is

$$A_m = a \times M \,, \tag{3}$$

where a is the average aggregation number of alcohol in the mixed micelles. On the other hand, after the association of alcohol, the concentration of free surfactant changes by $(N_oM_o - NM)$, where N_oM_o and NM are the micellized surfactant concentrations before and after alcohol addition.

The partition constant or solubilization constant for this system can be represented by

$$K = M/(A_o - A_m)(N_oM_o - NM) \,, \tag{4}$$

where M_o and M are the micelle concentrations, and N_o and N are the aggregation numbers of surfactant in the absence and presence of alcohol, respectively. This constant is related to the distribution of alcohol and surfactant molecules between the intermicellar phase an the micellar pseudophase, i.e., with the process of formation of mixed micelles.

Substituting Eq. (3) in Eq. (4)

$$A_o \times (N_oM_o - NM)/M = K^{-1} + a \times (N_oM_o - NM) \,, \tag{5}$$

A plot of $A_o \times (N_oM_o - NM)/M$ against $(N_oM_o - NM)$ should yield a straight line, where the inclination is the average number of alcohol molecules per micelle in the

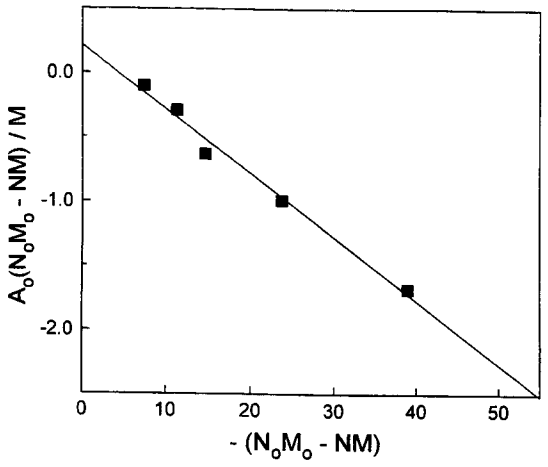

Fig. 9 Determination of the binding constant for the BuOH/SDS system

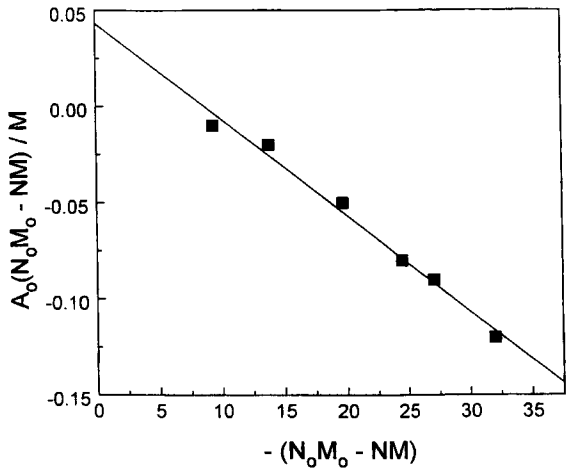

Fig. 10 Determination of the binding constant for the HexOH/SDS system

Table 3 Values of K for BuOH/SDS systems

	K/M^{-1}	[SDS]/mM	A_o/[Surf.]	Methods
This work	4.7	15	1.4–14	Fluorescence quenching
Ref. 5	1.8	—	—	Calculated
Ref. 4	1.0	50	1.1–20	Solubility
Ref. 7	5.4	40	—	Vapor pressure
Ref. 10	1.0	10–100	33–100	Solubility[a]
Ref. 14	3.9	90	0.4	Ultrafiltration[b]
Ref. 7	3.4	30	3.2–28	Fluorescence quenching[c]

[a] CTAB micelles; [b] CTAB + NaBr. 0.16 M.
[c] The concentration of free additives was calculated from Stilbs P (1982) J Colloid Interface Sci 87:385.

range of used concentrations and the extrapolation to zero is the reciprocal of the partition constant.

The partition constants, K, were determined graphically from the plots according to Eq. (5) (Figs. 9 and 10). The results obtained together with the data reported in the literature are shown in Tables 3 and 4 for BuOH/SDS and HexOH/SDS, respectively. There is a good coincidence of the data reported here with that obtained using other methodologies, giving support to the method. The present way to perform these calculations uses quantities that are easily measured and a simple equilibrium model, yielding reasonable values for K in the range of concentration where a linear relationship is observed for Turro's method. As seen from the tables, some of the reported partition coefficients K differ by a factor of about 5 depending on the method employed [10]. These differences can be ascribed to the dependence of K with the composition of the system [3–5, 11].

The inclination of the straight line Figs. 9 and 10 yields the average number of alcohol molecules per micelle a, in the range of concentration used. An approximation was made to estimate the number of alcohol molecules per micelle for each composition of system. The distribution of alcohol molecules between the bulk of the solution and the micelle may be represented by

$$K_p = A_m/A_w \, . \tag{6}$$

The subscripts m and w denote micellar and aqueous pseudophases, respectively. An expression for a is obtained substituting Eq. (6) into Eq. (3), and rearranging terms

$$a = (A_o/M) \times [K_p/(1 + K_p)] \, . \tag{7}$$

Equation (7) shows the dependence of a with the A_o/M ratio and permits the calculation of the micellar aggregation number of alcohol molecules per micelle for each composition of system. The values of a, assuming $K_p = 55.5 \times K$ [13], are shown in Tables 1 and 2 for the systems studied. These figures are slightly higher than those reported by Almgren and Swarup [7]. In the range of concentrations studied they indicate a large growth of

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Table 4 Values of K for HexOH/SDS systems

	K/M^{-1}	[SDS]/mM	A_0/[Surf.]	Methods
This work	17.6	15	0.1–0.5	Fluorescence quenching
Ref. 5	13.6	—	—	Calculated
Ref. 8	14.3	—	—	Solubility
Ref. 11	22.6	50	0.2–1.2	Fluorescence quenching
Ref. 9	40.4	40	—	Vapor pressure
Ref. 10	10.2	10–100	4–12	Solubility[a]
Ref. 7	50	30	0.5–2.3	Fluorescence quenching
Ref. 14	17.8	90		Dialysis equilibrium[b]

[a] and [b] Same meaning as in Table 3.

the micelle size for the BuOH/SDS system (Table 1), which agrees with the observation by Gamboa et al. [14] using viscosity measurements. This behaviour shows that rather than having a mixed micelle of surfactant and alcohol, the system behaves more like an inverse micelle of butanol, stabilized by the surfactant.

Conclusions

The results obtained in this study show that the incorporation of alcohols to micelles promotes the aggregation of surfactant molecules at low concentrations. This is attributed to the co-micellization of alcohol with the surfactant forming mixed micelles. On the other hand, the formation of the smaller aggregates at pre-micelle concentrations, which are evidenced by the formation of pyrene excimers, show that hidrophobic interactions are effective below the cmc.

The method employed in the present work is able to provide partition constants between water and micelles of surfactant over a range of alcohols concentrations where a linear relationship is observed for Turro's method. This method, although based on fluorescence measurements can be used to determine the partition of additives that form mixed micelles with surfactant.

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