

## Time-Resolved Fluorescence Quenching Studies of Sodium Lauryl Ether Sulfate Micelles

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Números de agregação ( $N_{Ag}$ ) de micelas do detergente aniônico lauril éter sulfato de sódio (SLES), com duas subunidades de óxido de etileno, foram determinados a 30 e 40 °C por supressão de fluorescência resolvida no tempo, utilizando pireno como sonda fluorescente e o íon *N*-hexadecilpiridíneo como o supressor. O crescimento das micelas de SLES induzido por sal ( $\gamma = 0,11-0,15$ , sendo  $\gamma$  a inclinação de um gráfico do log do número de agregação vs.  $\log [Y_{aq}]$  e  $[Y_{aq}]$  a concentração de contraíons sódio livres na fase aquosa intermicellar) é significativamente menor do que o de micelas de alquilsulfato de sódio ( $\gamma$  ca. 0,25), uma diferença atribuída ao tamanho maior do grupo polar de SLES. A razão de intensidades vibrônicas  $I_1/I_3$  e a constante de velocidade para a supressão intramicelar do pireno demonstram que a polaridade do microambiente de solubilização e a viscosidade intramicelar são insensíveis ao tamanho da micela ou à presença de sal.

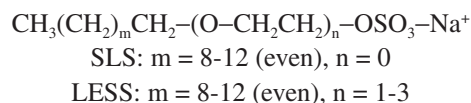
Aggregation numbers ( $N_{Ag}$ ) of micelles of the commercial anionic detergent sodium lauryl ether sulfate (SLES), with an average of two ethylene oxide subunits, were determined at 30 and 40 °C by the time-resolved fluorescence quenching method with pyrene as the fluorescent probe and the *N*-hexadecylpyridinium ion as the quencher. The added-salt dependent growth of SLES micelles ( $\gamma = 0.11-0.15$ , where  $\gamma$  is the slope of a plot of log aggregation number vs.  $\log [Y_{aq}]$  and  $[Y_{aq}]$  is the sodium counterion concentration free in the intermicellar aqueous phase) is found to be significantly lower than that of sodium alkyl sulfate micelles ( $\gamma$  ca. 0.25), a difference attributed to the larger headgroup size of SLES. The  $I_1/I_3$  vibronic intensity ratio and the rate constant for intramicellar quenching of pyrene show that the pyrene solubilization microenvironment and the intramicellar microviscosity are insensitive to micelle size or the presence of added salt.

**Keywords:** time-resolved fluorescence, micelles, detergents, aggregation number

### Introduction

The worldwide consumption of detergents is dominated by anionic surfactants<sup>1</sup> and, among these, alkylbenzenesulfonates (LABS) predominate, followed by alkyl ether sulfates (LESS, Scheme 1) and linear alkyl sulfates (LAS, Scheme 1) such as sodium dodecylsulfate (SDS). Although they are more expensive to produce than either LABS or LAS, LESS have several unique properties that enhance their utility in higher added-value personal care products and dishwashing formulations. In addition, unlike LABS, which are derived from petroleum-based precursors, both LAS and LESS can be produced from

straight-chain fatty alcohols, a renewable feedstock, and are biodegradable.<sup>1</sup>



**Scheme 1.** Generic structures of linear alkyl sulfate (LAS) and linear alkyl ether sulfate (LESS) detergents.

The presence of one or more ethylene oxide units between the alkyl chain and the sulfate group in LESS results in properties that are quite distinct from those of the corresponding LAS with the same alkyl chain.<sup>1,2</sup> Thus, the critical micelle concentration (CMC) is lower than that of the corresponding LAS and decreases with increasing

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number of ethylene oxide subunits. This suggests that the extent of hydration of the ethylene oxide subunits is lower in LESS than in a typical alkyl poly(oxyethylene) nonionic detergent. Moreover, the Krafft point, or the temperature below which it precipitates from aqueous solution, is much lower than that of the corresponding LAS, particularly in the presence of divalent cations such as  $\text{Ca}^{2+}$  that are present in hard water. Thus, consumer products that use LESS can be formulated without the addition of chelating agents.<sup>2</sup> Compared to LAS, LESS adsorbs more strongly at the air-water interface<sup>1-3</sup> and produces a more agreeable sensation of mildness in contact with the skin.<sup>1</sup> Finally, the tensoactive and cleaning properties of LAS are enhanced by admixture with LESS, the maximum synergy being observed at about 20 mol% LESS.<sup>2</sup> Compared to SDS, however, there are relatively few studies of the properties of the micelles formed by LESS and even fewer studies of the effect of LESS on reaction rates or equilibria.

The present work examines the [detergent]- and [salt]-induced growth of an important commercial LESS surfactant sodium dodecyl ether sulfate (SLES), which has an average of two ethylene oxide subunits in the ether bridge. Micelles of simple ionic detergents are typically spherical or roughly spherical in aqueous solution at low to moderate detergent concentrations in the absence of added salt.<sup>4-7</sup> At higher detergent and/or added salt concentrations, many ionic detergents, including SLES,<sup>8</sup> undergo a relatively abrupt change from a spherical to a rod-like shape, with a marked increase in the micellar aggregation number. However, in the concentration region prior to the sphere-to-rod transition, i.e., in which the micelles are still roughly spherical or globular in shape, they also grow somewhat in size upon addition of common counterion salt or upon increasing the detergent concentration.<sup>9,10</sup> The determination of the aggregation numbers of SLES micelles over a wide concentration range of detergent and added NaCl by the time-resolved fluorescence quenching method<sup>7,10-12</sup> shows that SLES micelles are somewhat larger than those of SDS but are markedly less sensitive to salt-induced growth. The fluorescence results provide additional information on the micellar properties and the microenvironment in SLES micelles.

## Experimental

### Materials

Pyrene (Aldrich), acetonitrile (spectroscopic grade, Merck), acetone (Aldrich), *N*-hexadecylpyridinium chloride monohydrate (Aldrich) and sodium chloride (Merck) were used as received. The pyrene stock solution was

prepared in acetonitrile. All other solutions were prepared in ultrapure water (Millipore Milli-Q). A commercial solution of sodium lauryl ether sulfate (SLES; Alkapon N, kindly provided by Oxiteno do Brasil, Mauá-SP, Brazil) was lyophilized and the solid obtained recrystallized from acetone. The purified SLES was characterized by <sup>1</sup>H nuclear magnetic resonance (NMR), which confirmed the presence of an average of 2 oxyethylene units.

### Methods

CMCs were determined from measurements of the surface tension as a function of log [SLES], performed on a du Nouÿ tensiometer equipped with a platinum ring. Micellar aggregation numbers were determined by the fluorescence quenching method,<sup>7,10-12</sup> analyzing the fluorescence decay curves of pyrene in the presence of variable concentrations of the micelle-bound quencher *N*-hexadecylpyridinium chloride (HPCl).<sup>10</sup> Aliquots of an aqueous solution of the quencher were added to a solution of pyrene ( $5 \times 10^{-6}$  mol L<sup>-1</sup>) in micellar SLES (25-100 mmol L<sup>-1</sup>) at constant temperature, maintained by a thermostatic bath. Steady-state fluorescence measurements were performed with an Edinburgh Analytical Instruments Model FS-920 Fluorimeter. Pyrene fluorescence decay curves were collected by the single photon counting technique using an Edinburgh Analytical Instruments Model FL-920 Fluorescence Lifetime Spectrometer (pulsed diode laser excitation at 335.6 nm; 390 nm emission). Fluorescence decay curves in the absence of quencher were analyzed utilizing the standard single-exponential decay software of the FL-920. The micelle-quenching module of the Edinburgh Instruments Level 2 analysis software was employed to fit the corresponding decay curves in the presence of quencher. In all cases, the observed fits were consistent with the Infelta-Tachiya equation<sup>7,10-12</sup> for a non-mobile probe-quencher pair. The criteria used for the goodness-of-fit were the chi squared values (< 1.06) and the absence of any trend in the weighted residuals.

## Results and Discussion

The critical micelle concentration of our commercial SLES in water, determined from plots of surface tension vs. log [SLES], were 0.53 and 0.74 mmol L<sup>-1</sup> at 30 and 40 °C, respectively. As expected, in the presence of 0.10 mol L<sup>-1</sup> NaCl, these values decreased to 0.16 and 0.12 mmol L<sup>-1</sup> at 30 and 40 °C, respectively. The values in water are in reasonable agreement with literature values of ca. 0.8 mmol L<sup>-1</sup> in water for commercial samples of SLES,<sup>13,14</sup> but lower than CMC of synthetically pure

SLES,<sup>3,13</sup> which is ca. 3 mmol L<sup>-1</sup>. This reflects primarily the fact that the commercial surfactant is a mixture of homologs, particularly in the ethylene oxide portion of the headgroup. Moreover, because it is commercial SLES and not the pure homolog (LESS-2) that it is of importance in consumer products, studies of its micellar properties are much more relevant to its behavior in practical industrial applications of SLES.

The ratio of the intensities of the first and third vibronic bands ( $I_1/I_3$ ) in the fluorescence spectrum of pyrene provides an indication of the nature of the microenvironment in which pyrene is solubilized.<sup>14</sup> For pyrene ( $5 \times 10^{-6}$  mol L<sup>-1</sup>) solubilized in 0.10 mol L<sup>-1</sup> SLES at 30 °C, the  $I_1/I_3$  ratio was  $1.17 \pm 0.01$  in water and  $1.19 \pm 0.01$  in the presence of 0.10 mol L<sup>-1</sup> NaCl, indicating little or no change in the probe microenvironment with added salt. These values are similar to the corresponding ratio in ethanol and in SDS micelles (1.14-1.21), but much smaller than the ratio in micelles of typical cationic (ca. 1.3-1.4) or non-ionic detergents (also ca. 1.3-1.4).<sup>14,15</sup>

The aggregation numbers of SLES micelles (25-100 mmol L<sup>-1</sup> SLES) were determined from time-resolved fluorescence quenching data with pyrene ( $5 \times 10^{-6}$  mol L<sup>-1</sup>) as the fluorescence probe and the *N*-hexadecylpyridinium cation ([HPCl] = 0 to 1.0 mmol L<sup>-1</sup>) as the quencher in the absence and presence of added NaCl (0-100 mmol L<sup>-1</sup>). In all cases, the quenching behavior conformed to the Infelta-Tachiya equation (equation 1)<sup>11</sup> for the case of a completely micelle-associated probe-quencher pair, both of which remain in the micelle on the time scale of the quenching experiment ( $> 2 \mu\text{s}$ ).

$$F(t) = F(0) \exp[-t/\tau^0 - \langle n \rangle \{1 - \exp(-k_q t)\}] \quad (1)$$

In this equation,  $F(0)$  is the initial pyrene fluorescence intensity at time  $t=0$  and  $\tau^0$  is the pyrene fluorescence lifetime in the absence of quencher. The two important parameters derived from the fit of the fluorescence decay curves to this equation are  $\langle n \rangle$  and  $k_q$ . Since the number of quenchers *per* micellized detergent is known ( $[HPCl]/C_D$ ) and  $\langle n \rangle$  is the corresponding average number of quenchers *per* micelle, the value of the micellar aggregation number ( $N_{Ag}$ ) can be calculated from the relationship:

$$N_{Ag} = (\langle n \rangle C_D) / [HPCl] \quad (2)$$

where  $C_D$  is the analytical concentration of micellized surfactant (the total detergent concentration minus CMC) and  $[HPCl]$  is the total concentration of added quencher. The other parameter,  $k_q$ , corresponds to the first-order rate constant for quenching of pyrene by the

*N*-hexadecylpyridinium ion in a SLES micelle containing pyrene and a single quencher molecule,<sup>10,11</sup> which is related to the size and effective viscosity of the micelle.

The aggregation numbers determined in this work for SLES as a function of the detergent concentration and added NaCl at two temperatures are collected in Table 1. Literature values of the aggregation numbers of SLES, most of which were determined at or around 25 °C, are listed in Table 2 for comparison. Several of these studies<sup>16-18</sup> report unreasonably small aggregation numbers, in the range of 19-50. The value of Barry and Wilson,<sup>16</sup> determined by static light scattering, is clearly incorrect. The value of 42 reported by Aoudia *et al.*<sup>17</sup> was determined from static fluorescence quenching data. Unlike the time-resolved quenching method employed in the present work, the static fluorescence methods are based on the assumption that a single quencher is capable of completely quenching the fluorescence of the probe.<sup>19</sup> Consequently, when there is residual probe emission from quencher-containing micelles, the static fluorescence quenching method underestimates the aggregation number, sometimes substantially. Indeed, our  $k_q$  values (Table 1), which correspond to probe-quencher encounter times of the order of 30 ns, indicate that there will necessarily be residual probe emission in SLES micelles containing a single quencher. The aggregation number determined by sedimentation<sup>20</sup> in the presence of high added salt also appears to be low. Clancy *et al.*<sup>8,9</sup> reported aggregation numbers determined by static light scattering as a function of temperature and two sets of aggregation numbers have been determined by small-angle neutron scattering.<sup>21,22</sup> These latter are in much better agreement with our values.

**Table 1.** Aggregation numbers ( $N_{Ag}$ ) of SLES micelles at 30 and 40 °C

T / °C	[SLES] / (mmol L <sup>-1</sup> )	[NaCl] / (mmol L <sup>-1</sup> )	$k_q \times 10^{-9} / \text{s}^{-1}$	$N_{Ag}^a$
30	25	0	0.025	109
	50	0	0.023	115
	100	0	0.023	120
	25	25	0.021	126
	50	50	0.019	136
	100	100	0.018	149
40	25	0	0.032	112
	50	0	0.031	116
	100	0	0.028	117
	25	25	0.027	131
	50	50	0.026	148
	100	100	0.024	152

<sup>a</sup>  $\pm 5\%$ .

**Table 2.** Compendium of literature values for the aggregation numbers of SLES micelles

T / °C	[SLES] / (mmol L <sup>-1</sup> )	[NaCl] / (mmol L <sup>-1</sup> )	N <sub>Ag</sub>	Reference
25	3	0	19	16
23	2.5	0	42	17
27	CMC	0	45	18
25	0.73	100	71.5	20
25	1	0	71	9
25	1	15	75	9
25	5	100	207	9
30	5	100	173	9
35	5	100	152	9
45	5	100	123	9
25	20	0	90	21
25	20	18	109	21
25	20	36	120	21
25	20	54	127	21
25	20	72	132	21
25	20	144	153	21
25	22	0	71	22
25	42	0	80	22
25	58	0	85	22
25	81	0	89	22
25	105	0	92	22
25	115	0	97	22
25	80	20	98	22
25	78	39	103	22
25	77	101	113	22
25	75	191	132	22

Below the sphere-to-rod transition, it has been shown for many detergents that the micellar aggregation numbers (N<sub>Ag</sub>) increase with added common-counterion salt concentration ([salt]) according to:<sup>23</sup>

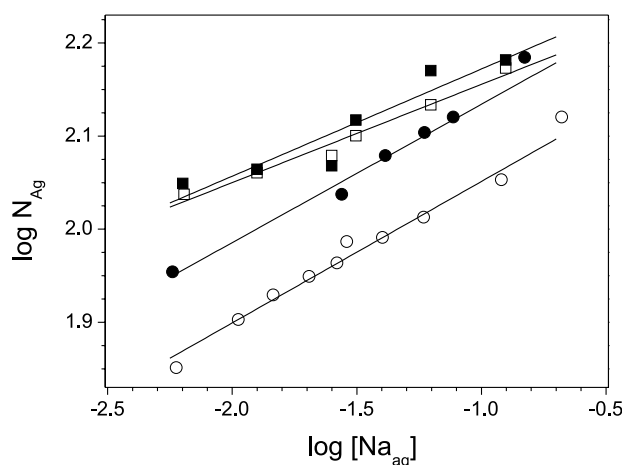
$$\log N_{Ag} = \log N_{Ag}^0 + \gamma \log [Y_{aq}] \quad (3)$$

where [Y<sub>aq</sub>] is the concentration of counterions free in the intermicellar aqueous phase and  $\gamma$  an empirical constant that indicates the sensitivity of the aggregation number to changes in the free counterion concentration. For a monovalent common-counterion salt, [Y<sub>aq</sub>] can be expressed as:

$$[Y_{ad}] = \alpha C_D + CMC + [salt] \quad (4)$$

where  $\alpha$  is the degree of counterion dissociation from the micelle and C<sub>D</sub> is the concentration of micellized detergent.

The applicability of equation 3 to SLES is indicated in Figure 1, in which our data at 30 and 40 °C are compared to those of Petkov *et al.*<sup>21</sup> and Caponetti *et al.*<sup>22</sup> at 25 °C, using the value of  $\alpha = 0.25$  determined by Petkov *et al.*<sup>21</sup> In all cases, there is a good linear correlation with values of  $\gamma$  in the range of 0.11-0.15. The fact that the values of  $\gamma$  are significantly smaller than those of SDS and its alkyl chain homologs is consistent with a larger headgroup size of SLES, indicated, for example, by its larger area *per* molecule at the air-water interface compared to SDS.<sup>2,13</sup>



**Figure 1.** Variation of the micellar aggregation numbers of SLES with the common-counterion concentration in the intermicellar aqueous phase, according to equation 3: (a) open squares (this work), 30 °C ( $\gamma = 0.11$ , correlation coefficient  $R = 0.988$ ); (b) filled squares, this work, 40 °C, ( $\gamma = 0.12$ ,  $R = 0.939$ ); (c) filled circles, Petkov *et al.*,<sup>21</sup> 25 °C, ( $\gamma = 0.15$ ,  $R = 0.994$ ); (d) open circles, Caponetti *et al.*,<sup>22</sup> 25 °C, ( $\gamma = 0.15$ ,  $R = 0.989$ ).

Although a clear theoretical justification for the magnitude of  $\gamma$  is still lacking, the experimental data obtained thus far indicate that the magnitude of  $\gamma$  is rather insensitive to the alkyl chain length of the detergent or the value of  $\alpha$  of the micelle. Thus, experimental studies with sodium dodecylsulfate (SDS)<sup>23</sup> and a homologous series of sodium alkylsulfates (octyl, nonyl, decyl, undecyl and tetradecyl) confirmed that growth of the spherical micelles of these anionic detergents obeys equation 1 with  $\gamma$  values in the range 0.20-0.25 in all cases.<sup>24</sup> Cationic detergents such as hexadecyltrimethylammonium chloride (CTACl) or acetate (CTAOAc) also obey equation 1,<sup>10</sup> but with substantially smaller values of  $\gamma$ , in the range of 0.1. However, for cationic detergents, there does appear to be a dependence on the size of the headgroup, the value of  $\gamma$  increasing as the headgroup size decreases from tetramethylammonium to ammonium.<sup>10</sup> Likewise, for anionic dodecylsulfate detergents, the value of  $\gamma$  decreases as the counterion size increases, particularly for very large tetraalkylammonium counterions.<sup>25</sup>

Finally, it is considered the values of  $k_q$  and their relationship to the micellar aggregation number. Since  $k_q$  is the first-order rate constant for excited probe quencher encounters in the confined volume of the micelle and the micellar volume is proportional to the aggregation number, an increase in aggregation number should be accompanied by a decrease in  $k_q$ . Indeed, the product  $k_q N_{Ag}$  is relatively constant, with a value of  $(3.6 \pm 0.3) \times 10^9 \text{ s}^{-1}$  at 40 °C and  $(2.7 \pm 0.2) \times 10^9 \text{ s}^{-1}$  at 30 °C. The relative constancy of the product  $k_q N_{Ag}$  at each temperature provides a convenient check on the quality of the parameters derived from the time-resolved fluorescence quenching data and indicates that, like the pyrene  $I_1/I_3$  ratio, the micellar microviscosity and relative probe-quencher mobilities are insensitive to the presence of added salt or detergent concentration. The temperature dependence of the value of  $k_q N_{Ag}$  is predominantly due to the values of  $k_q$  and reflects the faster rate of probe-quencher migration (decreased micellar viscosity) at the higher temperature.

## Conclusions

In the present work, it was shown that the anionic micelles of the commercial detergent SLES grow with both detergent concentration and added NaCl. Although the micelles are larger than those of SDS, the corresponding detergent without the two additional ethylene oxide subunits, the rate of growth, as measured by  $\gamma$  in equation 3, is smaller. Fluorescence data for pyrene, including the  $I_1/I_3$  vibronic intensity ratio and the rate constant for intramicellar quenching, show that micellar properties such as the effective polarity of the solubilization microenvironment and the intramicellar microviscosity are insensitive to micelle size or the presence of added salt.

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