

Time-Resolved Fluorescence Quenching Measurements of the Aggregation Numbers of Normal Sodium Alkyl Sulfate Micelles Well above the Critical Micelle Concentrations

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The aggregation numbers, N_A , of normal sodium alkyl sulfate micelles were measured by time-resolved fluorescence quenching in order to test two aspects of a recent proposal by Quina et al. (*J. Phys. Chem.* **1995**, *99*, 17028) that these micelles grow as a power law of the total counterion concentration, $[Na^+]_{aq}$, in the aqueous phase according to $N_A = \kappa_2([Na^+]_{aq})^\gamma$, where κ_2 and γ are constants for a given detergent. Both the surfactant and any added salt contribute to $[Na^+]_{aq}$; thus the power law predicts that different combinations of surfactant and salt concentrations leading to the same value of $[Na^+]_{aq}$ should yield the same value of N_A . This was confirmed, and the values of κ_2 were determined.

Introduction

For the series of normal sodium alkyl sulfates (SNS, where N denotes the number of carbon atoms in the normal alkyl chain) from $N = 8$ to 12, Huisman¹ found an empirical relationship between the aggregation number, N_A , and the critical micelle concentration (cmc) that was independent of both N and the concentration of added common counterion. Incorporating the results due to Sasaki et al.,² Quina et al.³ made the suggestion that this empirical relationship¹ could be extended to surfactant concentrations above the cmc and derived the result that

$$N_A = \kappa_2([Na^+]_{aq})^\gamma \quad (1)$$

where $[Na^+]_{aq}$ is the molar concentration of sodium ions in the aqueous phase which is provided by both the SNS and added salt. The quantities κ_2 and γ are constants that depend on N . If eq 1 can be shown to be accurate for all members of the SNS family above the cmc, then it would be of valuable practical utility, because most of the interesting uses of micelles occur at finite micelle concentrations.

For sodium dodecyl sulfate, S12S, Quina et al.³ went on to show that experimental results from a wide variety of techniques, even at surfactant concentrations well above the cmc, fit an equation of the form of eq 1 quite well if $[Na^+]$ is computed from the conventional ion exchange mass balance relationship:³ that is

$$[Na^+]_{aq} = \alpha([SNS] - [SNS]_{free}) + [SNS]_{free} + [Na^+]_{ad} = \alpha[SNS] + \beta[SNS]_{free} + [NaCl] \quad (2)$$

where the brackets indicate molar concentrations, α is the apparent degree of counterion dissociation, $\beta = 1 - \alpha$, and $[SNS]_{free}$ is the concentration of monomeric SNS. In eq 2, $[Na^+]_{ad}$ denotes the molar concentration of added sodium ion and $[Na^+]_{ad} = [NaCl]$ in our experiments. The values of $[SNS]_{free}$ may be found from an iterative solution to eq 5 of ref

3. We undertook the present work to begin to test eq 1 above the cmc for other members of the SNS family.

Combining eqs 1 and 2 yields

$$N_A = \kappa_2(\alpha[SNS] + \beta[SNS]_{free} + [NaCl])^\gamma \quad (3)$$

We are not aware of any theoretical justification of eq 3; however, Bezzobotnov et al.⁴ have offered a qualitative thermodynamic argument that SDS micelles ought to grow as $[SDS]^{1/4}$. Thus, in the absence of salt, an equation of the form of eq 3, with $\gamma = 1/4$ and the term $[SDS]_{free}$ being neglected has been advanced. The constants in eq 3 are given by (eqs 10 and 11 of ref 3)

$$\gamma = K_1\beta \quad (4)$$

and

$$\kappa_2 = (1/MW)10^{(K_1K_3 + K_2)} \quad (5)$$

where

$$K_3 = -(1 + \beta) \log(\text{cmc}_0) \quad (6)$$

In eqs 4–6, MW denotes the molecular weight of the surfactant, cmc_0 is the cmc of the detergent alone when no added salts are present, and K_1 and K_2 are constants. The numerical values of 0.336 for K_1 and 3.465 for K_2 were derived by Huisman¹ from the linear empirical relation he found between $\log(N_A)$ and $\log(\text{cmc})$ for all SNS with $N = 8–12$ at $T = 21$ °C.

Provided reliable values of β and cmc_0 are available, eq 3 may be used to predict the growth of the micelles of all members of the SNS family from $N = 8–12$ under conditions of increasing either $[SNS]$ or $[NaCl]$. Since β is dependent upon the experimental method employed (see for example ref 5 and references therein), we use the operational definition² of β as being the slope of the linear curve resulting from a plot of $\log(\text{cmc})$ vs $\log(\text{cmc} + [Na^+]_{ad})$, thus using a consistent method throughout the series.

The purpose of the present work is to test the concept that N_A depends only on the value of $[Na^+]_{aq}$ and not on the

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TABLE 1: Relevant Parameters for SNS

SNS	cmc ₀ (M)	β	γ^c
S8S	0.134 ^a	0.655 ^a	0.22
S9S	0.0646 ^a	0.574 ^a	0.19
S10S	0.030 ^a	0.638 ^a	0.21
S11S	0.0141 ^a	0.567 ^a	0.19
S12S	0.00814 ^a	0.678 ^a	0.23
S14S	0.002 ^b	0.81 ^b	0.27

^a Data taken from ref 1. ^b Data taken from ref 6. ^c Calculated from eq 4.

particular combination of [SNS] and [NaCl]. We do this by measuring the aggregation numbers of SNS micelles for two different combinations of [SNS] and [NaCl] that yield the same values of [Na⁺]_{aq}. We refer to such a pair as a conjugate pair. Note that this test is independent of the values of cmc₀ or γ but does depend weakly on the choice of β .

We have chosen the well established and convenient method of time-resolved fluorescence quenching to determine N_A .

A second purpose of the work is to establish tentative experimental values of κ_2 by applying eq 3 to our measurements of N_A by employing the values of γ estimated from eq 4. The values of κ_2 are tentative because eq 4 estimates γ from a global fit of Huisman's data (at the cmc) to all members of the SMS family. Refined values of κ_2 can be recomputed when better estimates of γ become available by measurements above the cmc.

Table 1 shows the values of the constants that are used in this work. The data in Table 1 refer to measurements made at cmc at $T = 21$ °C with variations in [Na⁺]_{aq} being provided predominantly by added salt. Sodium tetradecyl sulfate, S14S, was not studied by Huisman,¹ and so it is not certain if eqs 3–5 hold for S14S; nevertheless, we include this surfactant in our study.⁶

Experimental Section

Samples. The various SNS, $N = 8$ –12, and 14 (99%), were obtained from Lancaster Synthesis, Inc., and were used without further purification. The fluorescence probe pyrene (optical grade, 99%), the quencher dimethyl benzophenone (DMBP, 99%), and the added salt sodium chloride (99+%) were all obtained from Aldrich Chemicals and used as received. A 25 mM stock solution of pyrene in ethanol was prepared and stored in the freezer until needed. The pyrene concentration in the samples prepared for TRFQ experiments was kept at about one hundredth the concentration of micelles. This ensures that the fraction of micelles with two or more pyrenes is negligible. The appropriate amount of the pyrene/ethanol stock solution was weighed into a vial, and the ethanol was evaporated by a gentle stream of dry nitrogen. The required amounts of the surfactant, NaCl, and fresh doubly distilled water were added to this vial and stirred for 12 h. DMBP was weighed into a vial, and a portion of the pyrene/micelle solution was added to approximately two quenchers per micelle and allowed to mix for 12 h. Other quencher concentrations were obtained by mixing proportional amounts of the solutions with and without DMBP. For each SNS, the conjugate pair of combinations of SNS and NaCl selected was such that the SNS concentrations differed by about a factor of 2. Thus 12 samples were studied as detailed in Table 2. The first column identifies the sample by chain length and through the final digit the member of the conjugate pair. The second and third columns give the SNS and NaCl concentrations, respectively. Also listed are the values of the monomer concentration, [SNS]_{free}, calculated by an iterative solution of eq 5 of ref 3 in column 4 of Table 2.

Method. Time-resolved fluorescence quenching measurements were performed using an FL900 lifetime measurement spectrometer of Edinburgh Analytical Instruments. Excitation pulses of width 1.5 ns were provided by a nanosecond flashlamp containing hydrogen gas as the medium, at a pressure of 0.38 bar. The pulse repetition rate was 40 kHz. The fluorescence was excited at 335 nm and detected at 393 nm with a fast photomultiplier tube. The fluorescence photon counts were accumulated using the technique of time correlated single photon counting. The slit width and the excitation level were maintained at a value such that the count rate did not exceed 800 cps in order to prevent pulse pile up. A water circulating temperature bath was used to maintain the sample temperature at 25 °C for all measurements except for those on sodium tetradecyl sulfate for which the measurement temperature was 40 °C.

The time-dependent fluorescence decay curves were fitted to the Infelta–Tachiya equation^{7,8} given by

$$F(t) = F(0) \exp\{-A_2 t + A_3[\exp(-A_4 t) - 1]\} \quad (7)$$

The quantity $F(0)$ denotes the initial fluorescence intensity, and

$$A_2 = k_0 + k_q k_- <N_q> / (k_q + k_-)$$

$$A_3 = <N_q> k_q^2 / (k_q + k_-)^2$$

$$A_4 = k_q + k_-$$

where k_0 is the decay rate of excited pyrene in a micelle when no quenchers are present, k_q is the rate constant for quenching of pyrene fluorescence by a single quencher, k_- is the exit rate constant of a quencher from a micelle, and $<N_q>$ is the average number of quenchers per micelle and is equal to $[Q]/[\text{micelles}]$, where $[Q]$ is the quencher concentration and $[\text{micelles}]$ is the concentration of micelles. If the quenchers do not migrate from one micelle to another during the lifetime of the probe, then k_- is zero. In this case, $A_3 = <N_q>$ and $A_4 = k_q$ and the quantity A_2 becomes the unquenched decay rate of pyrene. The derivation of eq 7 assumes that the micelles are monodisperse and the probes and quenchers are distributed according to Poisson statistics.^{7–9} The procedure is standard in TRFQ experiments. The fits yield the values for A_2 , A_3 , and A_4 from which the aggregation number may be calculated. If $k_- = 0$, then

$$N_A = A_3([SNS] - [SNS]_{\text{free}})/[Q] \quad (8)$$

Measurements were performed for $[Q] = 0$ and four other quencher concentrations in each case. For each of the quencher concentrations, the measurement was repeated three or four times, and thus, for each sample N_A was determined as the average of 12–16 values.

Results and Discussion

As an example, fluorescence decay curves are displayed on a logarithmic scale in Figure 1 for the S10S 2 sample. The decay curves in the absence of quencher were fit satisfactorily to pure exponential functions; thus small effects due to lifetime broadening of the type reported to occur in SDS micelles by Siemiarzuk and Ware¹⁰ were not considered. Such lifetime broadening is not expected to affect the evaluation of the aggregation numbers significantly. The long time decays for the different quencher concentrations are parallel to each other and indicate that there is no diffusional quenching due to

TABLE 2: Details of Samples, Aggregation Numbers, and Quenching Rate Constants of SNS Micelles for Conjugate Pairs of Combinations of Detergent and Salt Concentrations

sample ^a	[SNS] (M)	[NaCl] (M)	[SNS] _{free} (mM)	[Na ⁺] _{aq} (M)	N _A	10 ⁻⁸ k _q (s ⁻¹)
S8S 1 ^b	0.146	0.352	61.3	0.443	46	1.25 ± 0.10
S8S 2 ^b	0.278	0.316	60.5	0.452	49	1.39 ± 0.16
S9S 1 ^b	0.100	0.459	19.7	0.513	54	1.24 ± 0.55
S9S 2 ^b	0.200	0.421	19.6	0.517	56	1.21 ± 0.63
S10S 1 ^b	0.100	0.198	7.98	0.239	64	0.76 ± 0.20
S10S 2 ^b	0.210	0.156	8.02	0.237	66	0.75 ± 0.16
S11S 1 ^b	0.099	0.159	3.49	0.204	80	0.47 ± 0.15
S11S 2 ^b	0.199	0.093	3.32	0.181	80	0.46 ± 0.10
S12S 1 ^b	0.100	0.034	1.93	0.068	92	0.34 ± 0.16
S12S 2 ^b	0.200	0	1.97	0.066	92	0.35 ± 0.06
S14S 1 ^c	0.048	0.015	0.03	0.024	119	0.34 ± 0.24
S14S 2 ^c	0.095	0	0.03	0.018	110	0.25 ± 0.29

^a Final digit denotes member of conjugate pair. ^b T = 25 °C. ^c T = 40 °C.

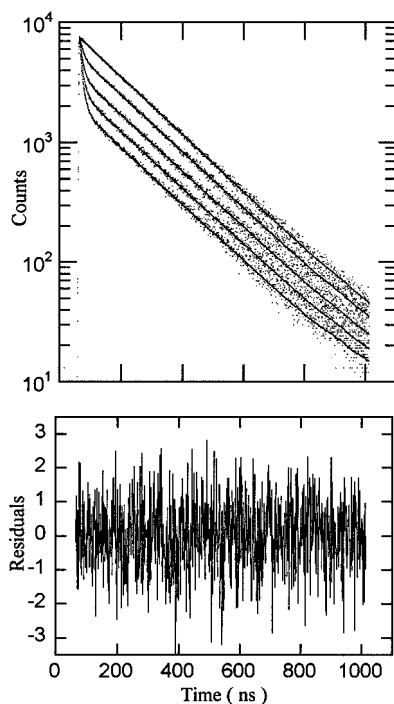


Figure 1. Fluorescence decay data of sample S10S 2 at 25 °C. The five curves are the data together with their least-squares fits to the Infelta–Tachiya model (eq 7), for various concentrations of the quencher DMBP. The values of the DMBP concentrations from the uppermost to the lowest curves are 0, 0.63, 1.18, 1.80, and 2.37 mM. The residuals for [DMBP] = 1.18 mM, typical of fits in this study, are shown in the lower trace.

quencher migration between micelles. The fits of eq 7 to the decay data yield $k_- = 0$, and therefore, $A_2 = k_0$ for all quencher concentrations. A graph of the aggregation number vs the number of quenchers per micelle for each of the SNS 1 samples is presented in Figure 2. The results of the experiments and calculations are tabulated in Table 2. The aggregation numbers are given in column 6. Values of the rate constant k_q are tabulated in the final column of Table 2. The values obtained for the aggregation numbers show clearly that keeping $[\text{Na}^+]_{\text{aq}}$ constant to within about 20% for S8S, 8% for S9S, S10S, and S11S and 3% for S12S produces about the same aggregation number. Thus conjugate pairs of SNS lead to a value of N_A that is the same within the measurable accuracy. From eq 1, it may be determined that $(\Delta N_A/N_A) = \gamma(\Delta[\text{Na}^+]_{\text{aq}}/[\text{Na}^+]_{\text{aq}})$, where ΔN_A and $\Delta[\text{Na}^+]_{\text{aq}}$ are variations respectively in N_A and $[\text{Na}^+]_{\text{aq}}$. If the accuracy in N_A is taken as 2, then the conjugate pairs may be defined to only within 20% (for S8S) to 10% (for S12S) variation in $[\text{Na}^+]_{\text{aq}}$ in the range of aggregation numbers

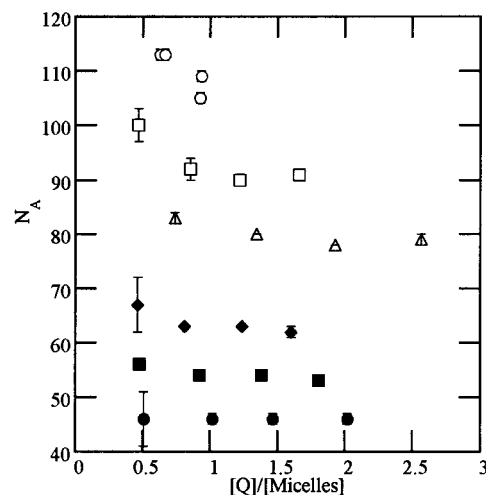


Figure 2. Aggregation number determined according to eq 8 as a function of the average number of quenchers per micelle for the SNS 1 samples: S8S 1 (●); S9S 1 (■); S10S 1 (◆); S11S 1 (△); S12S 1 (□); S14S 1 (○).

TABLE 3: Values of κ_2

SNS	κ_2 (M ^{-γ})	κ_2 (M ^{-γ}) ^b
S8S	57 ± 3 ^a	39 ± 8
S9S	62 ± 3 ^a	51 ± 10
S10S	86 ± 4 ^a	77 ± 16
S11S	112 ± 6 ^a	100 ± 20
S12S	176 ± 9 ^a	153 ± 31
S14S	325 ± 16 ^c	404 ± 80

^a This work, above the cmc, T = 25 °C. ^b Computed from eq 5 using data¹ at T = 21 °C, estimated uncertainties (see text). ^c T = 40 °C.

studied. This is because the value of γ , being a fraction, leads to a weak dependence of N_A on $[\text{Na}^+]_{\text{aq}}$. The precision available in the present day techniques of measuring N_A directly combined with the nature of the dependence of N_A on $[\text{Na}^+]_{\text{aq}}$ poses limits on the severity with which eq 3 may be tested; however our results are in accord with eq 3 within experimental error and may be used to obtain tentative values of κ_2 .

The value of κ_2 for each member of the conjugate pair was calculated from the measured N_A using eq 3 with the value of γ given in Table 1. The average of the two values of κ_2 for each of the SNS is presented in Table 3. Also shown in Table 3 are the values estimated from eq 5. The uncertainty in each of our values and in the estimated values were calculated by assuming an uncertainty of 10% in β and 3–5% in K_1 , K_2 , and cmc₀. The constant κ_2 in this work is given by the expression $N_A/[\text{Na}^+]^\gamma$, and the resulting uncertainty in our values is typically less than 5%. Values of κ_2 estimated from eq 5 have a much

larger uncertainty of 20%. The percent values of uncertainty used in our analysis are based on available data.⁵ From fits to Huisman's original data¹ we have determined a standard deviation of 3% in K_1 and 5% in K_2 when N varies from 8 to 12. Furthermore the values of β found in the literature show large variations of even greater than 10%. Viewed in the light of these uncertainties, the agreement of the values of κ_2 determined from our experiments above the cmc with the values estimated from eq 5 at the cmc support the validity of generalizations involved in deriving eq 3 for all concentrations. The implication of eq 3 is that the aggregation number could be kept the same over variations of orders of magnitude in the detergent concentration (from cmc to well above the cmc) provided the counterion concentration in the aqueous phase is held constant by adding salt appropriately. The significance of this statement is that intermicellar interactions do not affect N_A over a wide range of concentrations. It would be of interest to determine if there is a limit of [SNS] above which eq 3 is no longer valid.

The quenching constants k_q (Table 2) show the expected trend if they are controlled by the bimolecular collision rate, since the larger the micelle the smaller k_q . Nevertheless, no quantitative conclusions can be drawn as yet, since the relative viscosities of the SNS micelle surfaces are not yet known.

Conclusions

For a given sodium alkyl sulfate, the same aggregation number results if the total counterion concentration in the aqueous phase is kept constant. The present measurements show

this to be true for conjugate pairs of combinations of detergent and salt concentrations upon doubling the surfactant concentration. The general agreement between the values of κ_2 found in this work with those previously found at the cmc shows that it is also true if the surfactant concentration is varied over about 2 orders of magnitude.

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