# Surfactant- and Salt-Induced Growth of Normal Sodium Alkyl Sulfate Micelles Well above Their Critical Micelle Concentrations

### Radha Ranganathan,* Linh Tran, and Barney L. Bales

*Department of Physics, California State University Northridge, Northridge, California 91330*

*Received: November 5, 1999; In Final Form: January 6, 2000*

Time-resolved fluorescence quenching measurements were performed on normal sodium alkyl sulfate micelles, well above their critical micelle concentrations, to determine the functional dependence of the aggregation number on the detergent and added common counterion concentrations. Six members of the sodium alkyl sulfate family with different alkyl chain lengths including octyl, nonyl, decyl, undecyl, dodecyl, and tetradecyl were studied. In all cases, the growth of the aggregates with added salt and surfactant concentrations was found to obey the power law proposed by Quina et al. (*J. Phys. Chem.* **1995,** *99,* 17028) namely, $N_A = \kappa_2 ([Na^+_{aq}])^\gamma$, where $N_A$ is the aggregation number and $[Na^+_{aq}]$ is the total counterion concentration in the aqueous phase (supplied by the surfactant and the added salt). The constants $\kappa_2$ and $\gamma$ were determined for each of the sodium alkyl sulfates.

## Introduction

For the series of normal sodium alkyl sulfates, S*N*S, where *N* denotes the number of carbon atoms in the normal alkyl chain from $N = 8$ to 12, Huisman[1] 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 counterions. Incorporating the results due to Sasaki et al.,[2] Quina et al.[3] made the suggestion that this empirical relationship due to Huisman[1] could be extended to surfactant concentrations above the cmc and derived the result that

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

where $\kappa_2$ and $\gamma$ are constants that depend on *N*. The quantity $[Na^+_{aq}]$ is the molar concentration of sodium ions in the aqueous phase which is provided by both the S*N*S and added salt of the common counterion. The concentration $[Na^+_{aq}]$ may be computed from the conventional ion exchange mass balance relationship;[3] that is,

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

where the brackets indicate molar concentrations, $\alpha$ is the apparent degree of counterion dissociation, $\beta = 1 - \alpha$, and $[SNS_{free}]$ is the concentration of monomeric S*N*S. In eq 2, $[Na^+_{ad}]$ denotes the molar concentration of added sodium ions and $[Na^+_{ad}] = [NaCl]$ in our experiments. Substituting eq 2 in eq 1 yields

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

According to eq 1, for a given S*N*S, different combinations of [S*N*S] and [NaCl] that yield the same $[Na^+_{aq}]$ should yield the same $N_A$, regardless of the values of $\gamma$ or $\kappa_2$. This concept was

successfully tested[4] for two combinations (conjugate pairs) for the series of S*N*S, with $N = 8−12$ and 14. The growth law, namely eq 1, itself however has not been investigated experimentally for the S*N*S series, for surfactant concentrations well above the cmc. If eq 1 can be shown to be accurate for all members of the S*N*S 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. The purpose of the present work is to investigate if a power law above the cmc may describe micellar growth for other members of the S*N*S family and determine the values of $\gamma$ in each case. In the experiments described here, the aggregation numbers were measured using time-resolved fluorescence quenching (TRFQ) methods for the various members of the sodium alkyl sulfate family. These include the various S*N*S with $N = 8, 9, 10, 11, 12,$ and 14. For each of the S*N*S, the aggregation numbers were measured for various concentrations of added sodium chloride, with the goal of studying the dependence of $N_A$ on $[Na^+_{aq}]$. The monomer concentration, $[SNS_{free}]$, was calculated by a self-consistent iterative solution of eq 5 of ref 3. These calculations of $[SNS_{free}]$ involve the values of the cmc in the absence of added counterions (cmc$_0$) and $\beta$. The values of $\beta$ were approximated by employing the well-known result, $\log[cmc] = - K_3 - K_4 \log([cmc] + [M^+])$, where $[M^+]$ is the concentration of the added counterion and $K_3$ and $K_4$ are constants. Mass action theory predicts $\beta \approx K_4$ in the limit of large $N_A$, and the excellent linearity in the plots of this equation is generally taken as evidence that $\beta$ is constant. The values of $\beta$ and cmc$_0$ used in this work are those available in the literature and found from a variation of cmc with counterion concentration.[1,2,5]

## Experimental Section

**Samples.** Sodium alkyl sulfates of different chain lengths (octyl, nonyl, decyl, undecyl, dodecyl, and tetradecyl) were obtained from Lancaster Synthesis, Inc (purity of 99%). The

---

* Corresponding author. E-mail: radha.ranganathan@csun.edu.

materials were not further purified for most of the measurements and the others were carried out on surfactants purified by repeated recrystallizations from ethanol. Pyrene was used as the fluorescence probe and dimethyl benzophenone (DMBP) as the quencher. Pyrene, DMBP, and the sodium chloride, were all obtained from Aldrich and used as received. A 25 mM stock solution of pyrene in ethanol was prepared. The pyrene concentration in the samples prepared for TRFQ experiments was kept at about 1/100 times the concentration of micelles. This ensures that the fraction of micelles with two or more pyrene is negligible. The calculated amount of pyrene/ethanol from the 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 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 prepare a sample with approximately two quenchers per micelle, which was then stirred gently for 12 h. Other quencher concentrations were obtained by mixing proportional amounts of the solutions with and without DMBP. A particular detergent/quencher mixture was selected and salt was added in steps from a 3.00 M stock solution of NaCl in water to prepare various combinations of detergent and salt concentrations.

**Method.** The fluorescence decay curves of pyrene were obtained using an FL900 lifetime measurement spectrometer of Edinburgh Analytical Instruments. A nanosecond flashlamp in hydrogen gas at a pressure of 0.38 bar provided the fluorescence excitation pulses. 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 fluorescence photon counts were accumulated using the technique of time-correlated single photon counting. All decay curves were corrected for by a deconvolution with the instrument response function obtained using a scattering solution. The profile of the instrument response pulse had a width of 1.5 ns. The S8S surfactants are the most rapidly quenched of the systems studied. The shortest of the inverse of the quenching rates for the systems studied is ~7 ns. The time-dependent fluorescence decay curves were fitted to the Infelta–Tachiya equation given by.[6-8]

$$F(t) = F(0) \exp\{-A_2 t + A_3 [\exp(-A_4 t) - 1]\} \quad (4)$$

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

$$A_2 = k_0 + k_q k_- \langle N_q \rangle / (k_q + k_-)$$
$$A_3 = \langle N_q \rangle k_q^2 / (k_q + k_-)^2$$
$$A_4 = k_q + k_-$$

where $k_0$ is the decay rate of excited pyrene in a micelle when no quenchers are present and $k_q$ 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 $\langle N_q \rangle$ is the average number of quenchers per micelle and is equal to [Q]/[micelles], where [Q] is the quencher concentration in the micelles and [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 negligible. This is the case for the quencher, DMBP, used in the present experiments. Under these conditions, $A_3 = \langle N_q \rangle$, $A_4 = k_q$, and $A_2 = k_0$, independent of quencher concentration. The derivation of eq 4 assumes that the micelles are monodisperse, and the probes and quenchers

**TABLE 1: Values of Parameters Used in the Calculations of the Monomer and Aqueous Ion Concentrations**

| sodium alkyl sulfate | cmc$_0$ mM | $\beta$ |
|---|---|---|
| S8S | 134[a] | 0.655[b] |
| S9S | 64.6[a] | 0.574[b] |
| S10S | 30.0[a] | 0.638[b] |
| S11S | 14.1[a] | 0.567[b] |
| S12S | 8.14[a] | 0.678[b] |
| S12S | 8.30[c] | 0.73[c] |
| S14S | 2.00[d] | 0.81[d] |

[a] Data from refractive index and surface tension measurements.[1] [b] Approximated as the slope $(-\beta)$ of the linear fit to log cmc vs log [Na$^+_{aq}$].[1,3] [c] From activity and surface tension measurements.[2] [d] From activity and surface tension measurements.[5]

are distributed according to Poisson statistics.[6-8] The fits yield the values for $A_2$, $A_3$, and $A_4$ from which the aggregation number may be calculated. If $k_-$ is set to 0, then

$$N_A = A_3([S\textit{N}S] - [S\textit{N}S_{free}])/[Q] \quad (5)$$

For the quencher DMBP, [Q] is approximated by the total quencher concentration. Solubility measurements, at 25 °C, in the case of 100 mM sodium dodecyl sulfate show that 99.6% of DMBP is dissolved in the micelles.[9,10] Measurements were performed for [Q] = 0 and four other quencher concentrations in each case, that is for each of the combinations of detergent and NaCl studied. The four nonzero quencher concentrations were such that the average micelle occupation number ranged between 0.5 and 2 quenchers per micelle. The values of [S*N*S$_{free}$] were calculated as described in the introductory section. The values for the parameters, $\beta$ and cmc$_0$, used in the calculations of [S*N*S$_{free}$] and [Na$^+_{aq}$] are shown in Table 1.

**Results and Discussion**

The aggregation numbers were determined from the fits of eq 4 to the fluorescence decay curves and using eq 5 as described in the previous section (the decay curves are quite typical of those observed in TRFQ and representations may be seen in our previous publication[4]). The resulting values of $N_A$, reported in sections a through f of Table 2, are those for a concentration of about two quenchers per micelle. For each of the quencher concentrations, the measurement was repeated on the same sample three times and thus the $N_A$ appearing in column 5 of Table 2 was determined as the average of three values. Measurements on a given salt/surfactant concentration using different quencher concentrations show a variation of about ±5% in the aggregation numbers. Our experience with S12S in several investigations over recent years shows that the variations from sample to sample are about ±5% as well. Therefore, the error in the measured values of $N_A$ is set to be ±5%. Sections a–f of Table 2 are representative of the data sets, and similar tables were obtained for all the other quencher concentrations. Logarithmic plots of $N_A$ vs [Na$^+_{aq}$] are shown in Figure 1 for all of the S*N*S. These plots are for the data of Table 2. The power law of eq 3 was then fit to the data points for each of the S*N*S. The fits appear as straight lines on a logarithmic scale and yield the values of the exponent $\gamma$ and the prefactor $\kappa_2$. The linear least-squares fitting routine was performed for each of the other quencher concentrations. The final values of $\gamma$ and $\kappa_2$ are obtained as averages of four values and are reported in Table 3. The average values and the uncertainties in Table 3 are weighted with the errors in the numbers obtained in the fitting routine. Also shown by the open symbols in Figure 1 are the aggregation numbers at the cmc

**TABLE 2: Aggregation Numbers of Micelles**

(a) S8S Micelles, $T = 25\ °C$

| [S8S] mM | [NaCl] mM | [S8S]$_{free}$ mM | [Na$^+_{aq}$] mM | $N_A$ |
|---|---|---|---|---|
| 275 | 0 | 110 | 170 | 41 |
| 265 | 108 | 88 | 256 | 46 |
| 256 | 198 | 74 | 334 | 49 |
| 247 | 289 | 64 | 416 | 52 |
| 240 | 361 | 58 | 482 | 53 |
| 232 | 453 | 52 | 568 | 55 |
| 225 | 520 | 49 | 629 | 56 |

(b) S9S Micelles, $T = 25\ °C$

| [S9S] mM | [NaCl] mM | [S9S]$_{free}$ mM | [Na$^+_{aq}$] mM | $N_A$ |
|---|---|---|---|---|
| 183 | 0 | 49 | 106 | 40 |
| 176 | 115 | 33 | 209 | 47 |
| 170 | 220 | 26 | 308 | 51 |
| 162 | 346 | 22 | 427 | 58 |
| 156 | 429 | 20 | 507 | 59 |
| 150 | 530 | 12 | 601 | 64 |
| 144 | 620 | 17 | 691 | 63 |
| 139 | 710 | 16 | 778 | 65 |

(c) S10S Micelles, $T = 25\ °C$

| [S10S] mM | [NaCl] mM | [S10S]$_{free}$ mM | [Na$^+_{aq}$] mM | $N_A$ |
|---|---|---|---|---|
| 100 | 0 | 22 | 50 | 49 |
| 99 | 25 | 17 | 71 | 54 |
| 97 | 73 | 13 | 117 | 58 |
| 96 | 122 | 10 | 163 | 63 |
| 94 | 167 | 9 | 207 | 66 |
| 93 | 208 | 8 | 247 | 68 |
| 91 | 251 | 7 | 289 | 70 |
| 90 | 294 | 6 | 331 | 71 |

(d) S11S Micelles, $T = 25\ °C$

| [S11S] mM | [NaCl] mM | [S11S]$_{free}$ mM | [Na$^+_{aq}$] mM | $N_A$ |
|---|---|---|---|---|
| 103 | 0 | 7 | 48 | 63 |
| 102 | 17 | 6 | 65 | 68 |
| 101 | 34 | 5 | 81 | 71 |
| 101 | 51 | 8 | 97 | 73 |
| 100 | 68 | 4 | 113 | 75 |
| 100 | 84 | 4 | 130 | 77 |
| 99 | 100 | 4 | 145 | 79 |
| 99 | 116 | 4 | 161 | 81 |
| 98 | 132 | 3 | 117.0 | 83 |
| 98 | 148 | 3 | 192 | 84 |

(e) S12S Micelles, $T = 25\ °C$; $\beta = 0.678$

| [S12S] mM | [NaCl] mM | [S12S]$_{free}$ mM | [Na$^+_{aq}$] mM | $N_A$ |
|---|---|---|---|---|
| 100 | 0 | 3 | 34 | 76 |
| 96 | 107 | 1 | 138 | 103 |
| 93 | 186 | 0.9 | 217 | 116 |
| 92 | 210 | 0.8 | 240 | 116 |
| 92 | 229 | 0.8 | 259 | 118 |
| 91 | 254 | 0.7 | 284 | 120 |
| 90 | 278 | 0.7 | 308 | 128 |
| 89 | 301 | 0.66 | 330 | 133 |
| 88 | 341 | 0.6 | 369 | 137 |

(f) S14S Micelles, $T = 40\ °C$

| [S14S] mM | [NaCl] mM | [S14S]$_{free}$ mM | [Na$^+_{aq}$] mM | $N_A$ |
|---|---|---|---|---|
| 96 | 0 | 0.33 | 18 | 107 |
| 93 | 23 | 0.20 | 34 | 120 |
| 90 | 56 | 0.15 | 49 | 127 |
| 85 | 110 | 0.12 | 63 | 132 |
| 80 | 157 | 0.10 | 80 | 141 |
| 77 | 199 | 0.09 | 94 | 147 |
| 73 | 237 | 0.075 | 109 | 153 |
| 69 | 273 | 0.07 | 124 | 158 |

measured by Huisman using the technique of light scattering.[1] The values of $\gamma$ and $\kappa_2$ obtained from fits to Huisman's data are provided in Table 3. A comparison shows excellent



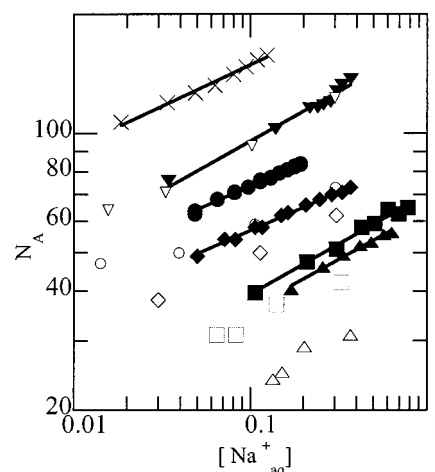**Figure 1.** Logarithmic plots of aggregation number, $N_A$, vs [Na$^+_{aq}$] for sodium alkyl sulfate micelles determined by (filled symbols) TRFQ and (open symbols) light scattering: (▲,△) S8S; (■,□) S9S; (◆,◇) S10S; (●,○) S11S; (▼,▽) S12S; (×) S14S. The TRFQ data shown were obtained for a quencher concentration of about two quenchers per micelle and the errors in the numbers are ±5%. Other quencher concentrations yield similar lines.

**TABLE 3: Values of the Constants of the Power Law, $\kappa_2$ and $\gamma$, Describing the Growth of Sodium Alkyl Sulfate Micelles**

| S$N$S | $\kappa_2$ | $\kappa_2{}^a$ | $\gamma$ | $\gamma^a$ |
|---|---|---|---|---|
| S8S$^d$ | 63 ± 1 | 47 ± 2 | 0.25 ± 0.01 | 0.33 ± 0.03 |
| S9S$^d$ | 68 ± 1 | 53 ± 3 | 0.24 ± 0.01 | 0.20 ± 0.03 |
| S10S$^d$ | 89 ± 1 | 79 ± 5 | 0.20 ± 0.01 | 0.21 ± 0.01 |
| S11S$^d$ | 116 ± 1 | 91 ± 2 | 0.21 ± 0.01 | 0.19 ± 0.01 |
| S12S$^{b,d}$ | 170 ± 5 | 161 ± 6 | 0.25 ± 0.01 | 0.22 ± 0.01 |
| S12S$^{c,d}$ | 168 ± 5 | | 0.24 ± 0.02 | |
| S14S$^e$ | 247 ± 3 | | 0.20 ± 0.01 | |

$^a$ From fits to the data (light scattering), at $T = 21\ °C$[1] of $N_A$ vs [Na$^+_{aq}$] at cmc. $^b$ [Na$^+_{aq}$] calculated with $\beta = 0.678$. $^c$ [Na$^+_{aq}$] calculated with $\beta = 0.73$. $^d$ $T = 25\ °C$. $^e$ $T = 40\ °C$.

agreement for $\gamma$ between the values at the cmc and at finite surfactant concentrations well above cmc for $N = 9-12$. This result shows that a power law may describe micelle growth with the same exponent over orders of magnitude variation in surfactant and salt concentrations. On the other hand, there are clearly discrepancies in the values of $\kappa_2$. The quantity $\kappa_2$ may also be interpreted as the aggregation number at [Na$^+_{aq}$] = 1 M. Another physical quantity that is interesting as well as useful for comparison is the aggregation number $N_A{}^0$, at the cmc in the absence of NaCl. This is measured by light scattering and may also be obtained by extrapolation of the TRFQ data using the power law. At the cmc, [Na$^+_{aq}$] = cmc and in the absence of salt this is cmc$_0$. Therefore,

$$N_A{}^0 = \kappa_2[\text{cmc}_0]^\gamma \qquad (6)$$

In Figure 2, the values of $N_A{}^0$ calculated using eq 6 are compared with those measured by Huisman.[1] The numbers are provided in Table 4. The error in $N_A{}^0$ is also ±5%, the same as that for $N_A$. The plot in Figure 2 illustrates that extrapolated values of $N_A{}^0$ are in excellent agreement with Huisman's values. This is despite the fact that extrapolations to cmc$_0$ ought to be viewed with caution. For surfactants with small values of cmc$_0$, there is very little buffering from the available monomers and small changes in surfactant or salt concentrations can give rise to measurable effects. The disagreement in $\kappa_2$, that is the aggregation number at [Na$^+_{aq}$] = 1 M, is due to differences in the
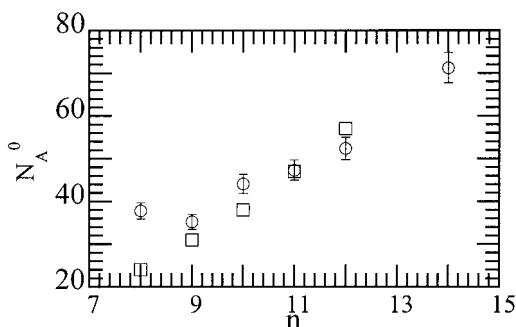
**Figure 2.** Dependence of the aggregation number, $N_A^0$, at the $cmc_0$ on the number of carbon atoms in the hydrocarbon chain as determined by (○) extrapolation down to the cmc using eq 1, of aggregation numbers derived from TRFQ at concentrations above the cmc, and (□) light scattering.[1]

**TABLE 4: The Aggregation Number, $N_A^0$, at the cmc in the Absence of Added Salt ($cmc_0$) Obtained by the Application of Eq 1 to the TRFQ Data above the cmc and Extrapolation to $[Na^+_{Aq}] = cmc_0$ with the Values of $N_A^0$ Obtained from Light Scattering[1] Provided for Comparison**

| sodium alkyl sulfate | $N_A^0$ (TRFQ; this work) | $N_A^0$ (ref 1) |
|---|---|---|
| S8S | 38 | 24 |
| S9S | 35 | 31 |
| S10S | 44 | 38 |
| S11S | 47 | 47 |
| S12S | 52 | 57 |
| S14S | 71 | |

average values of $\gamma$ as well as the differences in the absolute values of $N_A$. At the present time, there is no available method or model that allows the use of TRFQ to determine the aggregation numbers at the cmc directly by a measurement at or near the cmc itself. The power law (eq 1) is purely empirical and is found to fit the TRFQ data above the cmc. Furthermore, in the TRFQ method, basically one counts the number of micelles. So the questions of a proper accounting of electrostatics and micelle interactions do not pose a problem in the determination of $N_A$ from TRFQ by direct measurements above cmc or by extrapolation at cmc. However, these are perennial problems in the interpretation of light scattering. The value of $N_A^0$ obtained by extrapolation of the power law may at best be viewed as an empirical number. A comparison with available values of $N_A^0$ and the agreement found show the wide range of application for this power law. The aggregation numbers determined by light scattering are in general smaller than those determined by TRFQ (Figure 1), which leads to the systematically larger values of $\kappa_2$ for the data of TRFQ. One possible source for such a systematic disagreement in the absolute values of $N_A$ could be the techniques themselves. A comparison of the data available in the literature on the aggregation numbers for sodium dodecyl sulfate[3] at varying concentrations of added sodium chloride, shows that in general the absolute values are in disagreement. Fits show that the values of $\kappa_2$ vary by about 18%, while the values of $\gamma$ are in excellent agreement. In the Infelta model used for interpreting the TRFQ decay, micelle occupation by the additives (probes and quenchers) are assumed to follow Poisson statistics and the micelles are required to be monodisperse. Micelle polydispersity is reported to be negligibly small for the S*N*S micelles in the concentration range studied by us.[11,12] Poisson statistics apply if the probability of micelle occupation is equal, there is no limit to the number of molecules solubilized per micelle, and the molecules are noninteracting. This is known to hold well for classic ionic surfactants with pyrene probes and DMBP quenchers.[4,13] For the case of interacting quenchers, it has been argued that the measured

aggregation numbers would depend on the quencher concentration.[14,15] In our experiments, we found $N_A$ to be independent of the quencher concentrations used. In the procedure employed in the present experiments, $\kappa_2$ and $\gamma$ were determined for $N_A$ vs $[Na^+_{aq}]$ curves for four different quencher concentrations. The four values for each of $\kappa_2$ and $\gamma$ agree to within 3%. The assumptions of the Infelta model are therefore valid for S*N*S micelles with pyrene probes and DMBP quenchers. In the conventional light scattering technique, measurements are performed in the vicinity of the cmc. The aggregation number is then determined by an extrapolation to zero micelle concentration.[1] In this extrapolation, the monomer concentration and the micelle size are assumed to be independent of the detergent concentration. Micelles are known to grow with detergent concentration along with a decrease in the monomer concentration.[3,16] The errors due to these changes are however expected to be insignificant. More important perhaps are the electrostatic interactions and the nonideality of the solvent.[1,17–19] The approach outlined by Vrij and Overbeek[20] has been used by Huisman[1] in treating the contributions to scattering by small ions. Interpretation of light scattering data, in general, relies heavily on modeling the scattering contributions from the solvent consisting of detergent monomers, $Na^+$ and $Cl^-$ ions and the electrostatic interactions between the charged micelles. The charge of the micelle is not a well-defined quantity because the counterion distribution profile is ill defined. At low electrolyte and high micelle concentrations, the validity of the linear relation for the dependence of the structure factor on the micelle concentration is doubtful.[17–19] A neglect of the co-ion and counterion contributions to scattering and in general an underestimation of the strength of the electrostatic interactions lead to aggregation numbers that could be as much as 15% smaller.[19,21] In view of the limitations of model-dependent interpretations, it is difficult to compare the absolute values of the aggregation numbers obtained by different techniques. A critical evaluation of the various techniques is necessary before a comparison between the values of $\gamma$ and $\kappa_2$ can be made. The emphasis in the present work is on testing the power law and the determination of $\gamma$.

Another source of discrepancy could be the purity of the samples. However, the value of $\gamma$ is not affected by the sample purity. This was verified by TRFQ measurements on S12S and S10S purified by recrystallizations from ethanol. Additional evidence that small amounts of impurities contained in the commercially obtained S8S do not affect the values of $N_A$ was found using electron paramagnetic resonance (EPR). Recent work[22] showed that relative values of $N_A$ could be determined to a precision of one molecule from measurements of the hyperfine coupling constant of a nitroxide spin probe dissolved into the micelles. The sodium octyl sulfate was purified by repeated recrystallizations from ethanol. Two identical series of samples with varying salt concentration were prepared from the commercial and the purified surfactant. The hyperfine coupling constants in the two series were the same, within experimental error, showing that their aggregation numbers are the same.

## Conclusions

The power law for the growth of micelles with added salt proposed by Quina et al. is verified for sodium alkyl sulfate micelles at concentrations well above the cmc. The present TRFQ results considered together with those of light scattering show this law to apply over a wide range of concentrations, from the cmc to well above the cmc. The significance of this

observation is that the relative strengths of interactions that promote or limit the growth of micelles do not change over a wide range of concentrations.

## References and Notes

(1) Huisman, H. F. *Proc. Kon. Ned. Akad. Wetensch.* **1964**, *B67*, 367, 376, 388, 407.

(2) Sasaki, T.; Hattori, M.; Sasaki, J.; Nukina, K. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1397−1403.

(3) Quina, F. H.; Nassar, P. M.; Bonilha, J. B. S.; Bales, B. L. *J. Phys. Chem.* **1995**, *99*, 17028−17031.

(4) Ranganathan, R.; Peric, M.; Bales, B. L. *J. Phys. Chem.* **1998**, *102*, 8436−39.

(5) Koshinuma, M.; Sasaki, T. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2755−2759.

(6) Infelta, P. P.; Grätzel, M.; Thomas, J. K. *J. Phys. Chem.* **1974**, *78*, 190.

(7) Tachiya, M. *Chem. Phys. Lett.* **1975**, *33*, 289.

(8) Gehlen, M. H.; De Schryver, F. C. *Chem. Rev.* **1993**, *93*, 199.

(9) Almgren, M.; Alsins, J. *Prog. Colloid Polym. Sci.* **1987**, *74*, 55−63.

(10) Alsins, J.

(11) Dutt, G. B.; van Stam, J.; De Schryver, F. C. *Langmuir* **1997**, *13*, 1957−1963.

(12) Siemiarczuk, A.; Ware, W. R.; Liu, Y. S. *J. Phys. Chem.* **1993**, *97*, 8082−8091.

(13) Lianos, P.; Zana, R. *J. Phys. Chem.* **1980**, *84*, 3339.

(14) Almgren, M.; Hansson, P.; Wang, K. *Langmuir* **1996**, *12*, 3858.

(15) Bales, B. L.; Almgren, M. *J. Phys. Chem.* **1995**, *99*, 15153−15162.

(16) Mukerjee, P. *J. Phys. Chem.* **1972**, *76*, 565.

(17) Corti, M.; Degiorgio, V. *J. Phys. Chem.* **1981**, *85*, 711.

(18) Schurtenberger, P. *Light Scattering: Principles and development*; Oxford: Clarendon Press: New York, 1996.

(19) Mazer, N. A.; Benedek, G. B.; Carey, M. C. *J. Phys. Chem.* **1976**, *80*, 1075.

(20) Vrij, A.; Overbeek, J. T. G. *J. Colloid Sci.* **1962**, *17*, 570.

(21) Ikeda, S. *Colloid Polym. Sci.* **1991**, *269*, 49.

(22) Bales, B. L.; Messina, L.; Vidal, A.; Peric, M.; Nascimento, O. R. *J. Phys. Chem.* **1998**, *102*, 10347−10358.