

## Growth of Sodium Dodecyl Sulfate Micelles with Detergent Concentration

Frank H. Quina

Instituto de Química, Universidade de São Paulo, CP 26.077, 05599-970 São Paulo, Brazil

Patricia M. Nassar and João B. S. Bonilha

Departamento de Química, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, Universidade de São Paulo, CEP 14040-901 Ribeirão Preto, Brazil

Barney L. Bales\*,†

Instituto de Física de São Carlos, Universidade de São Paulo, CEP 13560-970 São Carlos, Brazil

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Sodium alkyl sulfate micelles are predicted to grow as a power law of the total counterion salt concentration,  $Y_{\text{aq}}$ , in the aqueous phase as follows:  $N_A = \kappa_2(Y_{\text{aq}})^\gamma$ , where  $N_A$  is the micelle aggregation number and  $\kappa_2$  and  $\gamma$  are constants which are estimated from the critical micelle concentration and the apparent degree of counterion attachment. For sodium dodecyl sulfate,  $N_A = 162(Y_{\text{aq}})^{1/4}$  is predicted and is shown to be in good agreement with aggregation numbers measured by a number of techniques over a wide range of  $Y_{\text{aq}}$  whether this quantity is varied by changing the concentrations of the detergent, the added counterion salt, or both. Values of  $\kappa_2$  and  $\gamma$  are estimated for six members of the sodium alkyl sulfate family.

### Introduction

It has been known for some time<sup>1</sup> that sodium dodecyl sulfate (SDS) micelles grow slowly as a function of the detergent concentration. This growth has been observed by steady-state and time-resolved fluorescence quenching (TRFQ),<sup>1</sup> stopped-flow experiments,<sup>2</sup> and small-angle neutron scattering (SANS).<sup>3</sup> Similar growth has been observed in potassium octanoate and potassium dodecanoate by EPR and fluorescence quenching.<sup>4</sup> A few years ago, SANS experiments<sup>3</sup> suggested that, in the absence of added electrolyte, SDS micelles grow as  $[\text{SDS}]^{1/4}$ , where  $[\text{SDS}]$  is the total molar concentration of SDS. Denoting the total detergent concentration by  $C_T$ , the SANS results may be expressed as

$$N_A = \kappa'_2(C_T)^\gamma \quad (1)$$

where  $N_A$  is the aggregation number and  $\kappa'_2$  is a constant. In the case of SDS, the SANS results<sup>3</sup> yielded  $\gamma \approx 1/4$  and  $\kappa'_2 \approx 200$  molecules/M<sup>1/4</sup>, with a squared coefficient of correlation  $r^2 = 0.991$ . The absolute magnitude of  $\kappa'_2$  is uncertain because absolute values of  $N_A$  derived from small-angle neutron diffraction measurements are dependent upon the model used and upon the normalization of the scattering intensity data. The value of  $\kappa'_2$  quoted above was determined using the Guinier and Porod approximations,<sup>3</sup> which do not take into account the interparticle structure function  $S(Q)$ . Taking this factor into account by a mean spheres approximation reduces  $N_A$  by about one-half.<sup>3</sup>

EPR experiments on SDS in the concentration range  $[\text{SDS}] = 25\text{--}200$  mM showed that the average polarity sensed by a hydrophobic spin probe varied as  $(C_T)^{1/4}$  with  $r^2 = 0.997^5$  and  $r^2 = 0.998^6$  in two separate experiments. The quantity measured in the EPR experiments is the nitrogen hyperfine coupling

constant, which can be measured with a relative precision equivalent to a change of  $\pm 0.003$  in  $(C_T)^{1/4}$ , corresponding to an average change in  $N_A$  of less than one molecule per micelle according to eq 1.

Recently, careful TRFQ measurements<sup>7</sup> showed that the relative aggregation numbers of SDS micelles grew linearly with  $[\text{SDS}]^{1/4}$  in the concentration range  $[\text{SDS}] = 25\text{--}200$  mM, the fit of the data to eq 1 with  $\gamma = 1/4$  and  $\kappa'_2 \approx 134$  molecules/M<sup>1/4</sup>, yielding  $r^2 = 0.922$ . The absolute values of the aggregation numbers derived from TRFQ measurements depend somewhat upon the distribution of the quenchers among micelles; the above values were derived assuming a Poisson distribution in a series of measurements in which  $[\text{SDS}]$  was varied while maintaining a constant detergent/quencher ratio, thereby minimizing the effect of the quencher distribution on the relative aggregation numbers. Absolute determination of micelle sizes with the TRFQ technique depends somewhat upon the data reduction method,<sup>8</sup> so  $\kappa'_2$  could be in error by as much as 10–15%.

Each of these various techniques can be criticized for various reasons, but taken together they form a compelling description of the size dependence of SDS micelles as given by eq 1 with  $\gamma = 1/4$ . Although Bezzobotov et al.<sup>3</sup> have offered a heuristic derivation, there is as yet no theoretical reason to expect SDS micelles to grow as  $[\text{SDS}]^{1/4}$ . In the present work, we develop an explicit expression for the growth of sodium alkyl sulfate micelles which predicts that the controlling factor for such growth is the counterion concentration in the intermicellar aqueous phase. For the particular case of SDS in the absence of added salt, this expression simplifies to the observed  $[\text{SDS}]^{1/4}$  dependent growth only at high  $[\text{SDS}]$ .

### Empirical Expression for Micelle Size

In his classic light scattering experiments on a series of sodium alkyl sulfates, Huisman<sup>9</sup> found an empirical relationship between the molecular weight of a micelle and the critical micelle concentration (cmc, in mol L<sup>-1</sup>) independent of the

\* On leave from the Department of Physics and Astronomy and The Center for Cancer and Developmental Biology, California State University at Northridge, Northridge, CA 91330. bbales@huey.csun.edu.

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length of the alkyl chain and independent of the concentration of added univalent salts. Rewriting Huisman's equation<sup>10</sup> in terms of the molecular weight, MW, of the detergent monomer yields the following relationship:

$$\log(N_A) = -K_1 \log(\text{cmc}) - \log(\text{MW}) + K_2 \quad (2)$$

where  $K_1$  and  $K_2$  are constants. Fitting data at 21 °C for sodium dodecyl, undecyl, decyl, nonyl, and octyl sulfates yielded  $K_1 = 0.336$  and  $K_2 = 3.465$ . It has been known for many years (see, for example, ref 11 and references therein) that the cmc in turn is related to the counterion concentration by

$$\log(\text{cmc}) = -K_3 - K_4 \log(\text{cmc} + Y_{\text{ad}}) \quad (3)$$

where  $K_3$  and  $K_4$  are constants, and  $Y_{\text{ad}}$  is the concentration in mol L<sup>-1</sup> of added common counterion. Sasaki et al.<sup>12</sup> and Hall<sup>11</sup> showed that an equation of the form of eq 3 is valid above the cmc and identified  $K_4$  as the degree of counterion attachment,  $\beta$ , based upon activity measurements. For SDS at 25 °C, Sasaki et al.<sup>12</sup> found  $\beta = 0.73$  in the range [SDS] = cmc to 80 mM. Fixing  $\beta$ , the constant  $K_3$  may be found from eq 3 as follows:

$$K_3 = -(1 + \beta) \log(\text{cmc}_0) \quad (4)$$

where  $\text{cmc}_0$  is the value of the cmc in the absence of added salt,  $Y_{\text{ad}} = 0$ .

Generalizing eq 3 to above the cmc by replacing cmc with the free monomer concentration,  $m_f$ , and replacing the total counterion concentration at the cmc ( $\text{cmc} + Y_{\text{ad}}$ ) with the counterion concentration in the aqueous phase above the cmc,  $Y_{\text{aq}}$ , yields

$$\log(m_f) = -K_3 - \beta \log(Y_{\text{aq}}) \quad (5)$$

Using the conventional pseudophase ion exchange mass balance relationship<sup>13-15</sup>

$$Y_{\text{aq}} = \alpha(C_T - m_f) + m_f + Y_{\text{ad}} \quad (6)$$

where  $\alpha = 1 - \beta$  is the apparent degree of counterion dissociation, yields upon substituting into eq 5

$$\log(m_f) = -K_3 - \beta \log\{\alpha(C_T - m_f) + m_f + Y_{\text{ad}}\} \quad (7)$$

Combining eq 7 with eq 2 (generalized to above the cmc by replacing cmc with  $m_f$ ) yields

$$\log(N_A) = -K_1\{-K_3 - \beta \log[\alpha(C_T - m_f) + m_f + Y_{\text{ad}}]\} - \log(\text{MW}) + K_2 \quad (8)$$

Equation 8 may be written as

$$N_A = \kappa_2(\alpha C_T + \beta m_f + Y_{\text{ad}})^\gamma \quad (9)$$

with

$$\gamma = K_1\beta \quad (10)$$

and

$$\kappa_2 = (1/\text{MW}) \times 10^{(K_1 K_1 + K_2)} \quad (11)$$

For a given value of  $C_T$ ,  $m_f$  may be calculated iteratively from eq 7. In the absence of added salt ( $Y_{\text{ad}} = 0$ ) at high detergent concentrations ( $\alpha C_T \gg \beta m_f$ ), eq 9 is the same as eq

1 with  $\kappa'_2 = \kappa_2 \alpha^\gamma$ :

$$N_A = \kappa_2(\alpha C_T)^\gamma \quad (1)$$

At lower detergent concentrations, the functional dependence of  $N_A$  upon the concentration is different in eqs 1 and 9.

## Experimental Section

**Materials.** SDS (Merck, for biochemical use) was purified by recrystallization from absolute ethanol. Purity was checked by surface tensiometric determination of the critical micelle concentration (cmc) in the usual manner. Tris(bipyridine)-ruthenium(II) chloride ( $\text{Ru}(\text{bpy})_3^{2+}$ ; Aldrich) and analytical reagent grade NaCl (Merck) were used as received; 9-methylanthracene (Aldrich) was purified by sublimation. All solutions were prepared in distilled, freshly deionized water.

**Methods.** All measurements were performed at 30 °C. Apparent surface tensions were determined with a DeNoüy tensiometer equipped with a Pt ring. Emission measurements were performed with a Perkin-Elmer LS-5B fluorescence spectrometer on air-equilibrated solutions contained in Teflon-stoppered 1 cm path length fluorescence cuvettes (Hellma). Aggregation numbers were determined by the method of Turro and Yekta.<sup>16</sup> Successive aliquots of a concentrated (0.2 M) stock solution of 9-methylanthracene in spectroquality acetonitrile were added to aqueous solutions containing the emissive probe  $\text{Ru}(\text{bpy})_3^{2+}$  ( $7 \times 10^{-5}$  M), NaCl, and SDS, and the emission intensity (excitation/emission 450/627 nm) was recorded following each addition. Aggregation numbers were obtained from the slopes of linear plots of  $\ln(I_0/I)$  versus [9-methylanthracene] as described,<sup>16</sup> where  $I_0$  and  $I$  are the corresponding probe emission intensities in the absence and presence of 9-methylanthracene.

## Results

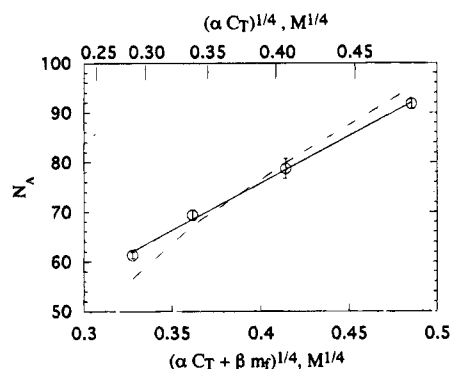
In the case of SDS, MW = 288. Taking  $K_1 = 0.336$ ,  $K_2 = 3.465$  from Huisman's<sup>9</sup> results and  $\beta = 0.73$  ( $\alpha = 0.27$ ) from Sasaki's<sup>12</sup> yields the exponent  $\gamma = 0.25$ . Taking  $\text{cmc}_0 = 8.3$  mM yields  $K_3 = 3.6$  and the coefficient  $\kappa_2 = 164$ . Thus, for SDS in the absence of added salt ( $Y_{\text{ad}} = 0$ ), eq 9 gives

$$N_A = 164(0.27C_T + 0.73m_f)^{1/4} \text{ (SDS)} \quad (12)$$

Thus, both eqs 12 and 1 predict that the growth of sodium dodecyl sulfate micelles is governed by a power law with  $\gamma = 1/4$ , however with the argument  $\alpha C_T + \beta m_f$  in eq 12 rather than the argument  $\alpha C_T$  in eq 1. Figure 1 shows results from TRFQ measurements taken from Figure 7 of ref 7 plotted as a function of the arguments of eq 9 (lower scale) and eq 1 (upper scale). Note that the lower scale is linear, while the upper is not. The solid line is the linear least-squares fit of the data to eq 12, and the dashed line is the linear fit to eq 1. The fit to eq 12, with a squared correlation coefficient of  $r^2 = 0.997$ , is a significant improvement over the fit to eq 1 ( $r^2 = 0.922$ ) and has removed the previous<sup>7</sup> need, ad hoc, to add a constant term to eq 1 to improve the fit.

Equation 9 describes TRFQ results upon varying [SDS] very well, and its derivation shows that it ought to describe the results of adding common counterion as well. Thus, eq 9 predicts that sodium alkyl sulfate micelles ought to grow as the  $\gamma$ th power of  $Y_{\text{aq}}$  whether  $Y_{\text{aq}}$  is varied with detergent or the added common counterion or both. In particular, for SDS micelles, we have

$$N_A = 164(0.27C_T + 0.73m_f + Y_{\text{ad}})^{1/4} \text{ (SDS)} \quad (13)$$



**Figure 1.** Aggregation numbers of SDS micelles at 25 °C derived from time-resolved fluorescence quenching of pyrene by  $\text{Cu}^{2+}$  plotted versus  $(\alpha C_T + \beta m_f)^{1/4}$  (lower scale) and versus  $(\alpha C_T)^{1/4}$  (upper scale). Data taken from Figure 7 of ref 7. The solid line is a linear least-squares fit to eq 12 referred to the lower scale, and the dashed line is a linear least-squares fit to eq 1 referred to the upper scale. The upper scale is not linear, so the dashed line is curved. The error bars are standard deviations in measurements using three sources of SDS. The units of  $C_T$  and  $m_f$  are  $\text{mol L}^{-1}$ .

**TABLE 1: Aggregation Numbers of SDS Micelles ( $T = 30$  °C)**

[SDS] <sub>T</sub> , mM	[NaCl], mM	[SDS] <sub>f</sub> , mM <sup>a</sup>	$Y_{\text{aq}}$ , mM	$N_A$
50	20	2.9	35.6	71
50	50	1.9	64.9	87
50	75	1.5	89.6	91
50	100	1.2	114.	92
50	250	0.7	264.	104
50	325	0.6	339.	111
50	400	0.5	414.	117
20	0	7.0	10.5	55
30	0	6.1	12.6	59
40	0	5.5	14.8	64
50	0	4.9	17.1	64
60	0	4.5	19.5	68
70	0	4.1	21.9	68
80	0	3.8	24.4	71

<sup>a</sup> Computed from an iterative solution of eq 5 with  $\alpha = 0.27$ .

Table 1 shows the results of experiments in which both [SDS] and  $Y_{\text{ad}}$  have been varied. Table 2 shows the results of least-squares fits to eq 9 (by varying  $\gamma$  and  $\kappa_2$ ) of the data in Table 1 plus literature data.

SDS micelles become polydisperse at higher concentrations of salt: for example, Siemiarz, Ware, and Liu<sup>8</sup> quote a size dispersion of  $\sigma \approx 20$  at  $Y_{\text{ad}} = 0.4$  M and  $\sigma \approx 140$  at  $Y_{\text{ad}} = 0.5$  M. Furthermore, at the latter concentration, the size distribution becomes bimodal.<sup>8</sup> Thus, it would seem prudent to consider only literature data up to, say,  $Y_{\text{ad}} \approx 0.3$ ; however, doing so would eliminate two of the light scattering data sets.<sup>17,18</sup> Remarkably, for these two sets, the fit of eq 9 is excellent up to  $Y_{\text{ad}} \approx 0.5$  M, so all three data points in each set were retained. For the rest of the data, fits were limited to values of  $Y_{\text{ad}} < 0.5$  M. The literature data encompass a number of techniques as listed in the first column of Table 2. The values of  $\gamma$  for all of the techniques are remarkably near  $\gamma = 0.25$  predicted by eq 9 despite the fact eq 9 was derived on the basis of the constancy of  $\beta$  in eq 5, which was only demonstrated<sup>12</sup> up to [SDS] = 80 mM ( $Y_{\text{aq}} = 24.4$  mM). The unweighted average and standard deviation of all of the values of  $\gamma$  gives  $\gamma = 0.24 \pm 0.05$ , although the significance of this average is difficult to assess in the absence of criteria to weight the data.

The values of  $\kappa_2$  are scattered for reasons discussed above. Further,  $\kappa_2$  depends upon temperature,<sup>3,19</sup> so the data from various experiments in Table 2 would be altered somewhat when adjusted to a common temperature. Taking the average of TRFQ<sup>19</sup> and SANS<sup>3</sup> results, adjustment to 25 °C would amount

**TABLE 2: Least-Squares Fits to Eq 9 Varying  $\gamma$  and  $\kappa_2$  ( $N_A = \kappa_2(Y_{\text{aq}})^\gamma$ ,  $T = 25 \pm 5$  °C)**

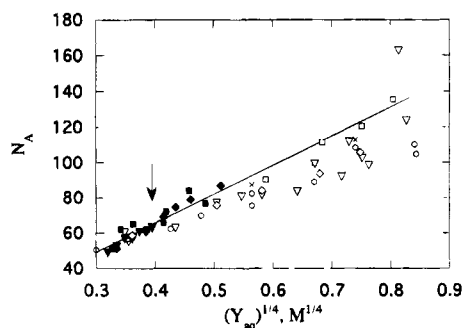
technique <sup>a</sup> (no. points)	ref	vary	$Y_{\text{aq}}$ , M	$\kappa_2$	$\gamma$	$\Omega^c$
eq 13			8.3–24.4 <sup>d</sup>	164 <sup>e</sup>	0.25 <sup>e</sup>	
L.S. (3)	17 <sup>f</sup>	NaCl	1–500	160	0.185	0.989
L.S. (3)	18 <sup>f</sup>	NaCl	52–510	140	0.179	1.000
L.S. (5)	9	NaCl	8–300	150	0.212	0.993
E.U. (3)	27	NaCl	100–300	160	0.232	0.991
SSFQ (7)	16 <sup>f</sup>	NaCl	160–470	150	0.238	0.926
SSFQ (2)	28 <sup>f</sup>	NaCl	17–280	150	0.237	1.00
SSFQ (8)	this	NaCl	17–410	140	0.185	0.989
		work				
SSFQ (7)	this	SDS	11–24	200	0.288	0.977
		work				
TRFQ (4)	26 <sup>g</sup>	SDS	14–44	180	0.247	0.978
TRFQ (4)	7 <sup>h</sup>	SDS	12–56	190	0.252	0.998
TRFQ (5)	29 <sup>f</sup>	NaCl	22–420	160	0.259	0.995
SANS (6)	30	NaCl	17–410	130	0.215	0.987
SANS (6)	3	SDS	13–69	340	0.319	0.994

<sup>a</sup> L.S., light scattering; E.U., equilibrium ultracentrifugation; SSFQ, steady-state fluorescence quenching; TRFQ, time-resolved fluorescence quenching; SANS, small-angle neutron scattering. <sup>b</sup> Correlation coefficient. <sup>c</sup> Multiplicative factor normalizing aggregation numbers at  $Y_{\text{aq}} = 17.1$  mM, used to prepare Figure 2. <sup>d</sup> Range of validity of eq 5.<sup>12</sup> <sup>e</sup> Equations 10 and 11 with  $K_3 = 3.60$  (eq 4  $\text{cmc}_0 = 8.3$  mM,  $\beta = 0.73^{12}$ ),  $K_1 = 0.336$ , and  $K_2 = 3.465$ .<sup>9</sup> <sup>f</sup> As cited in ref 20. <sup>g</sup> After recalculating the aggregation numbers using  $m_f$  rather than  $\text{cmc}_0$  to calculate the concentration of micellized SDS. <sup>h</sup> Using a Poisson distribution of the quencher,  $\text{Cu}^{2+}$ .

to a decrease in  $\kappa_2$  of about 3% for Husiman's data<sup>9</sup> and an increase in  $\kappa_2$  of about 4% for the data of Table 1. The data taken from ref 20 are quoted to be at  $T = 25 \pm 5$  °C, so there would be comparable small corrections to those data. There are probably other minor difficulties in the determination of  $\kappa_2$  as well.<sup>20</sup> To focus attention on the functional dependence of SDS micelle size versus  $Y_{\text{aq}}$ , we have maintained the original aggregation numbers and have calculated a normalizing factor,  $\Omega$ , such that  $\Omega N_A$  is the same for all techniques at one value of  $Y_{\text{aq}}$ ; 50 mM SDS in the absence of added salt was chosen as the common point because it falls within the range of all of the experiments. At  $C_T = 50$  mM, an iterative solution of eq 5 with  $\alpha = 1 - \beta = 0.27$  yields  $m_f = 4.9$  mM. Substituting these values into eq 13 gives  $Y_{\text{aq}} = 17.1$  mM and  $N_A = 59.3$ . For each technique,  $N_A$  at  $Y_{\text{aq}} = 17.1$  mM was calculated from the best fit to eq 9 and  $\Omega N_A$  was set equal to 59.3. The renormalization factors  $\Omega$  appear in the final column of Table 2, and except for the last row, referring to the SANS results<sup>3</sup> already discussed in the Introduction, these factors are remarkably near unity considering the various uncertainties in the differing methods. Figure 2 shows a plot of  $\Omega N_A$  versus  $(Y_{\text{aq}})^{1/4}$ . Experiments varying [SDS] are shown as solid symbols; those varying  $Y_{\text{ad}}$ , as open symbols. For clarity, all results from a given technique are plotted with the same symbol. The solid line is the behavior predicted by eq 13, and the vertical arrow marks the limit of the demonstrated<sup>12</sup> validity of eq 5 with constant  $\beta$ . The solid line coincides well with the data even somewhat above the arrow but deviates somewhat at higher values of  $Y_{\text{aq}}$ . This is reflected in our work, in which  $\gamma = 0.185$  when derived from data extending to  $Y_{\text{aq}} = 410$  mM and  $\gamma = 0.288$  for data extending to  $Y_{\text{aq}} = 24$  mM (Table 2).

## Discussion

As shown in Figure 2, eq 13 is a remarkably accurate description of the growth of SDS micelles as a function of total aqueous counterion concentration,  $Y_{\text{aq}}$ , over a very wide range of  $Y_{\text{aq}}$ , despite the fact that  $\beta$  was assumed to be constant. Thus, the growth of SDS micelles with [SDS] can be understood solely



**Figure 2.** Aggregation numbers from Table 1 ( $\nabla$ ,  $\blacktriangledown$ ) and from the literature versus  $(Y_{aq})^{1/4}$ . The sources of the literature data are given in Table 2. For clarity, the data are grouped together as follows: light scattering<sup>9,17,18</sup> ( $\circ$ ); equilibrium ultracentrifugation<sup>27</sup> ( $\times$ ); steady-state fluorescence quenching<sup>16,28</sup> ( $\nabla$ ,  $\blacktriangledown$ ); time-resolved fluorescence quenching<sup>7,26,29</sup> ( $\square$ ,  $\blacksquare$ ); small-angle neutron scattering ( $\diamond$ ,  $\blacklozenge$ ). Filled symbols represent data obtained by varying [SDS]; others, by varying [NaCl]. The line is eq 13.

**TABLE 3: Approximate Evaluation of Parameters of Eq 9 Describing the Growth of Sodium Alkyl Sulfate Micelles**

sodium alkyl sulfate	cmc <sub>0</sub> , mM	$\beta$	$K_4^c$	$\gamma^d$	$\kappa_2^e$
octyl	134 <sup>a</sup>	0.655 <sup>a,b</sup>	1.44	0.22	38.5
nonyl	64.6 <sup>a</sup>	0.574 <sup>a,b</sup>	1.87	0.19	50.5
decyl	30.0 <sup>a</sup>	0.638 <sup>a,b</sup>	2.49	0.21	77.3
undecyl	14.1 <sup>a</sup>	0.567 <sup>a,b</sup>	2.90	0.19	100.
dodecyl	8.14 <sup>a</sup>	0.678 <sup>a,b</sup>	3.51	0.23	153
dodecyl (eq 9)	8.30 <sup>f</sup>	0.73 <sup>f,g</sup>	3.60	0.25	164
tetradecyl	2.00 <sup>h</sup>	0.81 <sup>h</sup>	4.89	0.27	404

<sup>a</sup> Data from ref 10. <sup>b</sup>  $\beta$  approximated by  $K_4$ , eq 3. <sup>c</sup> Equation 4. <sup>d</sup> Equation 10. <sup>e</sup> Equation 11 with  $K_1 = 0.336$  and  $K_2 = 3.465$ .<sup>10</sup> <sup>f</sup> Assumed in the derivation of eq 9. <sup>g</sup> Reference 12. <sup>h</sup> Reference 22.

in terms of increasing  $Y_{aq}$  since the same growth is observed when [SDS] is held constant and  $Y_{ad}$  is increased.

Provided reliable values of cmc<sub>0</sub> and  $\beta$  are available, eqs 4 and 9–11 should also provide a description of the growth of micelles of any of the sodium alkyl sulfates from octyl through dodecyl. For SDS, we have chosen to use  $\beta$  obtained from EMF measurements in a concentration cell with an ion-exchange membrane because the measurements are almost free of assumptions and approximations.<sup>12</sup> An approximate value of  $\beta$  may be obtained from measurements of dependence of the cmc on the concentration of added common counterion salt through eq 3 because mass action theory predicts that  $K_4 \approx \beta$  in the limit of large aggregation numbers.<sup>11,12</sup> For example, from Huisman's<sup>9</sup> measurements on SDS,  $K_4 = 0.678$ , which compares well with the result,  $K_4 = 0.679$ , found in earlier measurements.<sup>21</sup> By using Huisman's<sup>9</sup> values of  $K_4$  as approximations for  $\beta$  and his values for cmc<sub>0</sub>, we can estimate values of  $\gamma$  and  $\kappa_2$  in eqs 9–11 for various sodium alkyl sulfates. These are given in Table 3 together with the result for sodium tetradecyl sulfate calculated with reliable values<sup>22</sup> of cmc<sub>0</sub> and  $\beta$  by assuming that eq 2 may be extrapolated to this longer chain surfactant. Comparison of the exponent  $\gamma = 0.23$ , evaluated on the basis of  $\beta = 0.678$ <sup>9</sup> and cmc<sub>0</sub> = 8.14 mM, with the value  $\gamma = 0.25$  obtained by using  $\beta = 0.73$ <sup>12</sup> and cmc<sub>0</sub> = 8.3 mM, gives an idea of the uncertainties involved in the calculations. A similar comparison of  $\kappa_2$  in the final column of Table 3 shows a variation of about 7%.

The size variation predicted by eq 9 gives a systematic basis upon which to interpret other data. For example, the rate constant for intramicellar quenching of pyrene fluorescence by a variety of quenchers is known to decrease with SDS concentration.<sup>23</sup> With a size dependence given by eq 9, a framework is available for testing the micelle size variation of the first-order quenching rate constant,  $k_q$ , which has been suggested to be proportional to the surface area of the micelle<sup>24,25</sup> or, alternatively, to the volume of the micelle.<sup>23</sup> Over the range

of sizes in which the micelles may be approximated as spheres, plots of  $k_q$  versus  $(0.27C_T + 0.73m_f)^{-1/6}$  or  $(0.27C_T + 0.73m_f)^{-1/4}$  would then be appropriate for testing the surface area versus the volume hypothesis. Other examples include the variations with micelle size of microviscosity sensed by a nitroxide free radical;<sup>6</sup> the polarity sensed by pyrene or a nitroxide probe;<sup>5</sup> the small but measurable<sup>6</sup> increase in microviscosity induced by addition of divalent cations; and the Stokes–Einstein contribution to the translational or rotational diffusion coefficient of the micelles.<sup>4</sup>

## Conclusions

An equation predicting the sizes of sodium alkyl sulfate micelles as a function of either detergent or added counterion salt concentrations has been derived. When applied to SDS, the micelles are predicted to vary as the one-fourth power of the total common counterion concentration in the aqueous phase, in excellent agreement with recent TRFQ measurements<sup>7,26</sup> and good agreement with measurements using a wide range of techniques. The behavior of sizes of other sodium alkyl sulfates is predicted.

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