A Definition of the Degree of Ionization of a Micelle Based on Its Aggregation Number

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The "degree of ionization" of a micelle or the "apparent degree of counterion dissociation", α, is defined by asserting that the aggregation number, N, is dependent only on the concentration, C_{aq}, of counterions in the aqueous pseudophase. Using different combinations of surfactant and added salt concentrations yielding the same value of C_{aq} leads to a straightforward definition of α. Any experimental method able to precisely distinguish values of N may be used and should give the same values of α. The value of N is not needed in the method; the experiment needs only ensure that the value of N is the same for two samples. For systems in which N is a known function of C_{aq}, α may be determined as a function of N. The method is demonstrated with sodium dodecyl sulfate (SDS) using an electron paramagnetic resonance method. For SDS, the method yields a constant value of $\alpha = 0.272 \pm 0.017$ for values of the aggregation number less than about $N \approx 110$, which corresponds to combinations of surfactant and salt concentrations from [SDS] = 600 mM and [NaCl] = 0 to [SDS] = 25 mM and [NaCl] = 155 mM. This value of α is in excellent agreement with literature values based on activity measurements, micelle mobility measurements, and radioisotope mobility measurements of the Na^+ ion but in poor agreement with measurements employing light scattering. The constancy of α is in accord with theoretical arguments based on the Poisson−Boltzmann equation.

Introduction

It has been accepted for almost 65 years[1] that a fraction, α, of an ionic surfactant's counterions are dissociated from the micelles, leaving the micelles charged.[2,3] A quantitative measure of the value of α is crucial in order to understand many aspects of the behavior of micelles. For example, reaction rates between organic substrates and hydrophilic ions that can "bind" to the micelle depend critically on the value of α.[4,5] The value of α is an important element in micelle stability in general[4] and in the growth of spherical micelles into rodlike structures,[5] which can lead to viscoelastic behavior.[6] As a practical matter, the charge of a micelle is important in many applications that exploit the micelle as a charged interface, for example, DNA transport.[7] Further, it is clear that a complete thermodynamic or structural theory of micelles must be able to predict values of and changes in α;[4,8−10] thus, accurate experimental values are needed.

The fundamental importance of α accounts for the vast number of papers dedicated entirely or in part to its measurement, using a wide array of experimental techniques.[4] Nevertheless, there is not a satisfactory consensus as to the value of α for any surfactant, not even the often studied surfactant sodium dodecyl sulfate (SDS). To illustrate, Table 1 of Romsted's review[4] compiles 30 determinations of α for SDS near the cmc. These values vary from a low of $\alpha = 0.14$ to a high of $\alpha = 0.70$. Romsted[4] noted that the variability in the values of α using a particular technique was less than the variability from technique to technique. That a particular technique would lead to distinct values of α is not surprising in view of the fact that each technique is likely to measure a different definition of what is meant by "dissociated" counterions.

It would clearly be an important step forward to define α in a way that is independent of any particular experimental method. The purpose of this paper is to propose such a definition and to illustrate the measurement of α on the basis of this definition.

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Theory

We employ the language of the pseudophase ion exchange model,[2] in which the micelles act as a separate phase from water. This language is for clarity of the discussion only; we do not find it necessary to assume that the micelles are indeed a separate phase in the thermodynamic sense. Thus, we assert that a fraction, $1 - \alpha$, of an ionic surfactant's counterions are associated with the micelles. If S_m is the concentration of surfactant forming the micelles, then the concentration of counterions associated with the micelles is $(1 - \alpha)S_m$. The total surfactant concentration is given by $S_t = S_m + S_f$, where S_f is the concentration in monomeric form. The entire sample contains counterions contributed by the surfactant, in concentration S_t, plus any additional counterions added as salt, in concentration C_{ad}. Thus, the total counterion concentration of counterions is $S_t + C_{ad}$. Subtracting from this total concentration, the concentration associated with the micelles, $(1 - \alpha)S_m$, yields the concentration in the aqueous phase $C^*_{aq} = S_t + C_{ad} - (1 - \alpha)S_m$, which gives $C^*_{aq} = \alpha S_t + (1 - \alpha)S_f + C_{ad}$, employing $S_t = S_m + S_f$. The concentrations S_t, S_m, S_f, and C_{ad} are all given in units of moles per liter of solution. Therefore, C^*_{aq} would be the concentration of counterions in the aqueous phase if that phase occupied the entire sample. At low surfactant concentrations, the volume of the aqueous phase is nearly equal to the volume of the sample; however, at higher surfactant concentrations, the excluded volume effect becomes important.[5] Following Soldi et al.,[5] we correct for this excluded volume effect by including the factor $F(S_t)$ and write the concentration of counterions in the aqueous phase as

$$C_{aq} = F(S_t)\{\alpha S_t + (1 - \alpha)S_f + C_{ad}\} \quad (1)$$

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The excluded volume factor is given by[5]

$$F(S_t) = \frac{1}{1 - VS_t} \quad (2)$$

where V is the molar volume of the anhydrous surfactant in moles per liter, assuming that the density of the surfactants is approximately 1.0 g/mL.[5] Equation 1, with $F(S_t) = 1.0$, which results in $C_{aq}^* \approx C_{aq}$, is the conventional pseudophase ion exchange mass balance relationship.[2,11] For typical surfactants with molecular weights of 200−400, $F(S_t)$ amounts to a 5% correction when S_t reaches 125−250 mM. In this work, where we extend S_t to values as high as 600 mM, the factor is needed.

A Definition of α. The definition is embodied in eq 1, which separates formally counterions associated with the micelles and those which are not and is completed by the hypothesis that, at a constant temperature, the aggregation number is a function of the concentration C_{aq} only; i.e.

$$N = N(C_{aq}) \quad (3)$$

where N is the aggregation number and $N(C_{aq})$ is a monotonic function of C_{aq}. We simplify the notation by suppressing the dependence of N on temperature.

There is a locus of points on the $S_t - C_{ad}$ surface that give the same value of C_{aq} and thus the same value of N. Let S_t and C_{ad} denote one such point and S_t' and C'_{ad} another. For these two points, using eqs 1 and 3

$$F(S_t)\{\alpha S_t + [1 - \alpha]S_f + C_{ad}\} = F(S_t')\{\alpha S_t' + [1 - \alpha]S_f' + C'_{ad}\} \quad (4)$$

The use of the same value of α on both sides of eq 4 implies a second hypothesis; the value of α depends only on the aggregation number. The free monomer concentration may be computed using eq 5 of ref 12 derived from the work of Sasaki et al.[13] and Hall[8]

$$\log(S_f) = (2 - \alpha)\log(\mathrm{cmc}_0) - (1 - \alpha)\log(C_{aq}) \quad (5)$$

where cmc_0 is the critical micelle concentration at $C_{ad} = 0$. See ref 12 and references therein for a discussion of the assumptions leading to eq 5. The value of S_f given by eq 5 is sensitive to the value of cmc_0 at low values of C_{aq} but is rather insensitive to the value of α. For our purpose, it is sufficient to note that for equal values of C_{aq}, $S_f = S_f'$. Now, $F(S_t) \approx F(S_t')$ for values of S_t, $S_t' < \approx 100-200$ mM, and above these concentrations, S_f is small compared with S_t. In either case, the terms involving S_f and S_f' cancel in eq 4. Solving eq 4 for α yields

$$\alpha = \frac{F(S_t)C_{ad} - F(S_t')C'_{ad}}{F(S_t')S_t' - F(S_t)S_t} \quad (6)$$

To summarize, for any two combinations of S_t and C_{ad} yielding the same value of the aggregation number, eq 6 yields a value of α. The resulting values should be independent of the measurement method as long as the method faithfully reports that the two values of N are the same. By varying the combinations of S_t and C_{ad} that yield the same value of C_{aq}, one may check the consistency of the definition. By varying C_{aq}, one may determine the dependence of α on C_{aq}.

As a practical matter, defining α by eq 6 might not seem to be useful because most techniques to determine N are tedious, often requiring involved analysis relying on models. The value of N derived from the data can be severely model dependent.[14] However, it is important to note that the value of N corresponding to the value of C_{aq} is not needed; one only needs to ensure that two aggregation numbers are the same. Thus, it is the relative precision in determining the values of N that is important in eq 6. In most experiments, relative values tend to be considerably more precise than absolute values.

If knowledge of the variation of N with C_{aq} is available, then values of α may be transformed into values of α(N).

Demonstration of the Measurement of α. In this paper, we demonstrate the use of eqs 1−6 with sodium dodecyl sulfate (SDS) employing an indirect but precise method to determine whether two aggregation numbers are equal. The method rests upon the fact that the hydration of the polar shell of SDS micelles varies monotonically with N for aggregation numbers smaller than about $N = 130$, above which the sphere-to-rod transition occurs.[15] The surface hydration is detected by a spin probe residing in the Stern layer using an electron paramagnetic resonance (EPR) technique detailed in recent papers.[15−17] The method utilizes the difference in resonance fields of the low- and central-field line of a nitroxide spin probe, denoted by A_+. Thus, the value of A_+ is a monotonic function of N for $N <$ 130

$$A_+ = A_+(N) \text{ only} \quad (7)$$

For SDS micelles, the aggregation number shows a power law dependence on C_{aq} as follows:[12]

$$N = \kappa_2 C_{aq}^{\ \gamma} \quad (8)$$

where the constants $\kappa_2 = 164$ molecules $M^{-0.25}$ and $\gamma = 0.25$ fit the results of a wide variety of experimental techniques.[12]

Experimental Section

SDS was purchased from Serva and recrystallized three times from ethanol and dried in a vacuum oven. A solution of the spin probe 5-doxylstearic acid methyl ester (5DSE) (Aldrich, as received) in ethanol was distributed to vials by weight, dried with dry filtered air, capped, and stored in the freezer until needed. After a vial was warmed to room temperature, Milli-Q water (18 MΩ) and SDS were added by weight to prepare mother samples with surfactant concentrations in the range of approximately $S_t = 0.5-0.6$ M. In each case, the spin probe:SDS molar ratio was 1:500. Corrections on the order of 1% were made to convert gravimetric measurements into molarities employing known values of the densities of SDS solutions.[18] All other samples were derived from these mother samples in a manner that preserved the spin probe:SDS molar ratio. Thus, small corrections to the hyperfine spacing, due to micelles housing more than a single spin probe, amounting to about 4 mG (see the appendix to ref 15), would be the same for all samples and would cancel when applying eq 6. Three types of sample series were prepared by weight as follows:

(1) "zero salt": The concentration of SDS in the absence of salt was varied by diluting a mother sample with distilled water.

(2) "reference": The concentration of NaCl was varied while holding the concentration of SDS at a low, constant value, by mixing the two solutions; one at the maximum desired salt concentration and one without salt.

(3) "constant C_{aq}": The concentrations of SDS and NaCl were varied such that C_{aq} was maintained approximately constant by mixing the mother solution without salt and a reference solution at a salt concentration computed from eq 4. This series must be prepared by assuming some preliminary value of α.

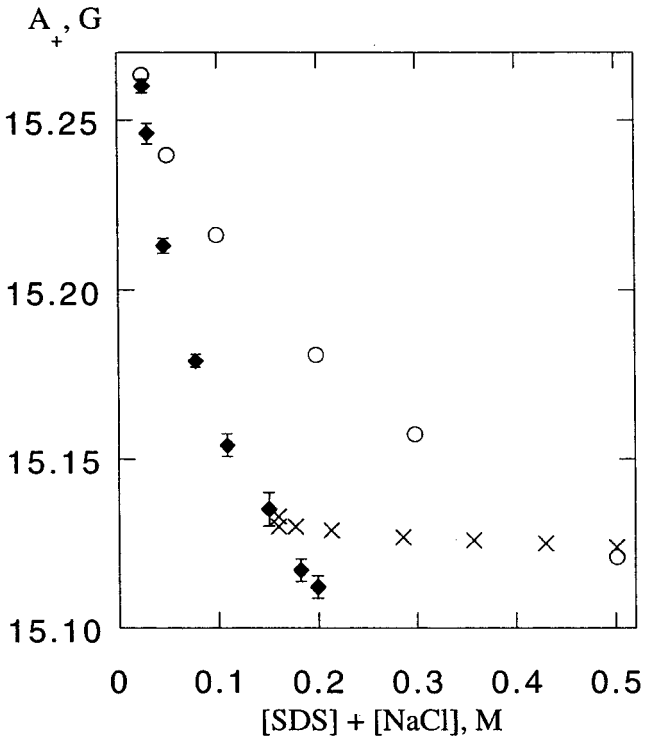

Figure 1. Hyperfine spacing A_+ vs [SDS] + [NaCl] for a "zero salt" series (○), a "reference" series (◆), and a "constant C_{aq}" series prepared with a trial value of $\alpha = 0.243$ (×). The error bars shown are standard deviations in five measurements of the same sample; others are smaller than the symbols.

The molarities of these series were derived from the known densities of SDS[18] and NaCl[19] solutions. We refer to these three types of series as "zero salt", "reference", and "constant C_{aq}", respectively. For SDS, the molar volume in eq 2 is $V = 0.288$ L mol^{-1}.

Results

Three-line narrow EPR spectra of 5DSE in SDS micelles typical of nitroxide free radicals undergoing approximately isotropic motion in the motional narrowing region were observed for all samples. See Figure 1a of ref 15. The difference in resonance fields between the center and low-field lines, A_+, has been shown[15,17] to be monotonic (in fact, very nearly linear) with the value of N, provided that C_{aq} is less than approximately 0.4 M. Above this value of C_{aq}, the sphere−rod transition renders EPR ineffective because A_+ no longer varies with N. A measurement of the value of A_+ alone cannot yield the value of N; however, the equivalence of two values of N may be determined with high precision, as discussed below.

Figure 1 shows the variation of A_+ with $S_t + C_{ad} =$ [SDS] + [NaCl] for one each of "zero salt" (open circles), "reference" (filled diamonds), and "constant C_{aq}" (crosses) series. Each point is the mean value of measurements from five spectra. The error bars on the "reference" data are the standard deviations from the five measurements; the standard deviations for the other two series are smaller than the size of the symbols. The values of A_+ for the "zero salt" series in Figure 1 and one additional "zero salt" series are given in Table 1.

The error bars for the "reference" series are larger than those for the other two series because the signal decreases as [SDS] is reduced. The choice of the value of [SDS] for a reference series is a compromise between obtaining a good signal-to-noise ratio and the desire to explore the value of α to as low a value of [SDS] as possible.

TABLE 1: Apparent Degree of Counterion Dissociation for SDS Zero Salt at $T = 25$ °C

[SDS], M	$[SDS]_f$, M[a]	A_+[b], G	$\alpha(C_{aq})$[c]	N[d]
0.0493[e]	0.0049	15.242 ± 0.0016	0.260 ± 0.037	58.9± 0.5
0.0987[e]	0.0033	15.215 ± 0.0009	0.272 ± 0.018	68.3 ± 0.0
0.198[e]	0.0021	15.181 ± 0.0007	0.261 ± 0.017	80.0 ± 0.8
0.298[e]	0.0016	15.158 ± 0.0005	0.278 ± 0.017	90.3 ± 0.4
0.501[e]	0.0011	15.121 ± 0.0016	0.279 ± 0.009	104.4 ± 0.5
0.197[f]	0.0021	15.184 ± 0.0006	0.239 ± 0.028	78.1 ± 1.6
0.252[f]	0.0018	15.169 ± 0.0007	0.248 ± 0.021	84.0 ± 0.9
0.305[f]	0.0016	15.158 ± 0.0004	0.244 ± 0.012	88.0 ± 1.9
0.352[f]	0.0014	15.149 ± 0.0002	0.248 ± 0.011	91.8 ± 0.7
0.455[f]	0.0012	15.131 ± 0.0009	0.252 ± 0.015	99.0 ± 0.8
0.610[f]	0.0009	15.106 ± 0.0010	0.273 ± 0.023	110.0 ± 0.3

[a] Equation 5. [b] Mean value and standard deviation in 5 (run 1) or 10 (run 2) spectra. [c] Equation 6; mean values and standard deviations using 5 or 10 matched pairs of A_+ from the "zero salt" and "reference" series, respectively. [d] Equations 1, 2, and 8, where $\alpha(C_{aq})$ is given in the penultimate column of this table. The uncertainties in the values of N correspond to the extremes of the values using the uncertainties in the values of α. [e] Run 1. [f] Run 2.

TABLE 2: Apparent Degree of Counterion Dissociation[a] for "Constant C_{aq}" with Trial $\alpha = 0.243$[a]

[SDS], M	[NaCl], M	A_+, G[b]	$\alpha(C_{aq})$[c]
0.0245	0.1355	15.130 ± 0.0014	reference
0.0495	0.128	15.130 ± 0.0009	0.267 ± 0.080
0.0997	0.114	15.129 ± 0.0010	0.302 ± 0.030
0.200	0.0856	15.127 ± 0.0006	0.289 ± 0.008
0.300	0.0572	15.126 ± 0.0005	0.274 ± 0.004
0.401	0.0285	15.125 ± 0.0003	0.271 ± 0.002
0.501	0	15.124 ± 0.0004	0.268 ± 0.002
		mean[d]	0.271 ± 0.001

[a] $T = 25$ °C. $[SDS]_f = 0.0010$ for all samples. [b] Mean value and standard deviation in five measurements of the same sample, one after another. [c] Equation 6; mean values and standard deviations using five matched pairs of A_+ from the "constant C_{aq}" and the reference sample, respectively. [d] Mean value of all values weighted inversely by their variance (pp 69−70 of ref 20); the error is the uncertainty of the mean.

An approximately "constant C_{aq}" series may be prepared by mixing two samples of differing values of [SDS] but similar values of A_+. The data in Figure 1 denoted by crosses were derived by mixing a sample of composition [SDS] = 0.501 M and [NaCl] = 0 with one of [SDS]′ = 0.0245 M and [NaCl]′ = 0.1355. Inserting these values into eq 4 yield a trial value $\alpha = 0.243$ for these two samples. Details of these mixtures are given in Table 2, together with the results of the EPR measurements. Because of small density variations and the factor $F(S_t)$ in eq 4, the trial value of α increases slightly as the value of [SDS] decreases. If the series were truly at constant values of C_{aq}, then all of the values of A_+ in Table 2 would be identical, but this is not observed. A second "constant C_{aq}" series was prepared and studied using a trial value of $\alpha = 0.284$; these data are presented in Table 3. The data for both series are plotted in Figure 2. The fact that A_+ decreases with [SDS] + [NaCl] for the series using a trial value of $\alpha = 0.243$ shows that the actual value of α is larger than 0.243; conversely, the increase in A_+ for the other series shows that α is smaller than 0.284.

We now turn to the computation of α. In the remainder of this paper, we denote $S_t =$ [SDS], $S_f = [SDS]_f$, and $C_{ad} =$ [NaCl]. We first apply eq 6 to members of the "zero salt" series of Figure 1, matched with members of the "reference" series of Figure 1 in which [SDS]′ = 0.0246 M and [NaCl]′ is varied. Equal values of N in the two series are indicated by equal values of A_+. For a perfect match of $A'_+ = A_+$, eq 4 gives the value of α directly. For values of A'_+ near values of A_+, a nearby

TABLE 3: Apparent Degree of Counterion Dissociation[a] for "Constant C_{aq}" with Trial α = 0.284[a]

[SDS], M	[NaCl], M	A_+, G[b]	α(C_{aq})[c]
0.0249	0.158	15.118 ± 0.003	reference
0.0719	0.142	15.117 ± 0.002	0.311 ± 0.184
0.120	0.126	15.118 ± 0.001	0.293 ± 0.078
0.214	0.0949	15.118 ± 0.0004	0.284 ± 0.035
0.311[d]	0.0631	15.118 ± 0.0006	0.274 ± 0.027
0.311[e]	0.0631	15.119 ± 0.0006	0.285 ± 0.022
0.311[f]	0.0631	15.119 ± 0.001	0.280 ± 0.024
0.406	0.0315	15.120 ± 0.002	0.276 ± 0.025
0.501[d]	0	15.120 ± 0.0005	0.274 ± 0.015
0.501[e]	0	15.120 ± 0.001	0.278 ± 0.012
0.501[f]	0	15.120 ± 0.001	0.277 ± 0.015
		mean[h]	0.277 ± 0.007

[a] T = 25 °C. $[SDS]_f$ = 0.0010 for all samples. [b] Mean value and standard deviation in five measurements of the same sample, one after another. [c] Equation 8; mean values and standard deviations using five matched pairs of A_+ from the "constant C_{aq}" and the reference sample, respectively. Different values of α(C_{aq}) can occur for identical mean values of A_+ because the averaging over five samples is different. [d] First sample of a duplicate pair. [e] Second sample of a duplicate pair. [f] First sample of a duplicate pair measured 1 day later. [h] Mean value of all values weighted inversely by their variance (pp 69−70 of ref 20); the error is the uncertainty of the mean.

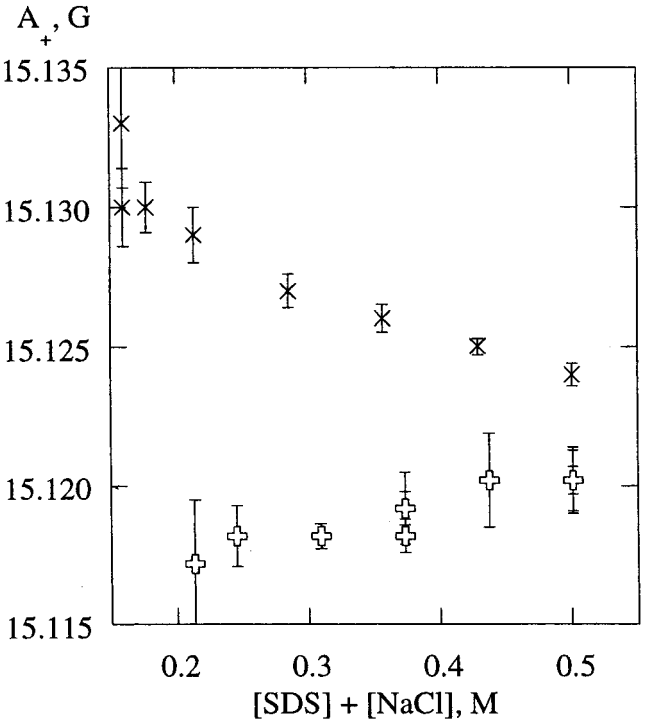

Figure 2. Hyperfine spacing A_+ vs [SDS] + [NaCl] for two "constant C_{aq}" series prepared with a trial values of α = 0.243 (×) and 0.284 (open cross). The error bars shown are standard deviations in five measurements of the same sample. The two points at [SDS] + [NaCl] = 0.501 M are due to two samples, identically prepared; thus, the discrepancy in sample preparation is larger than the uncertainty in measuring A_+. This discrepancy is due to a ±0.7 molecule difference in the value of N for the two samples. Decreasing values of A_+ indicate that the trial value of α is too low, and increasing values indicate the opposite.

interpolated value of [NaCl]′ is found. For each sample, 5 spectra were taken. By pairing 5 values of A'_+ for a sample in the reference series with 5 of A_+ for a sample in the "zero salt" series, we computed five values of α. The mean values and standard deviations of these 5 values of α are given in column 4 of Table 1. Uncertainties in the values of both A_+ and A'_+ contribute to the uncertainties in the values of α; however, the latter tend to dominate.

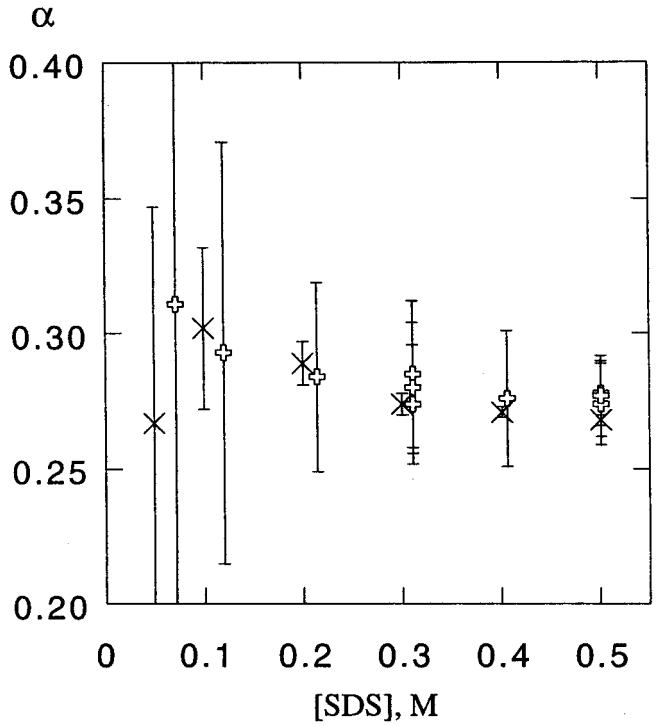

Figure 3. Values of the degree of ionization for SDS micelles, α, for the two "constant C_{aq}" series. The symbols have the same meaning as those in Figure 2.

Another set of "zero salt" and "reference" series were prepared and run, this time collecting 10 spectra of each. These results are given in the final six rows of Table 1.

The same procedure was then applied to the two "constant C_{aq}" series. The results for series prepared with trial values of α = 0.243 and 0.284 are given in Tables 2 and 3, respectively. Duplicate samples and a few spectra repeated the next day (Table 3) show that the results are well reproduced. The resulting values of α for the two "constant C_{aq}" series are plotted versus [SDS] in Figure 3, showing that α is constant within experimental error. Note that choosing an incorrect trial value of α still results in finding the correct value if the trial value does not differ radically from the correct one. The mean value of all values in Figure 3 weighted inversely by their variance (pp 69−70 of ref 20) is 0.271 ± 0.001 (trial value α = 0.243) and 0.277 ± 0.007 (trial value α = 0.284), where the errors are the uncertainties of the means.[20]

The values of α given in Tables 1−3 did not require on any knowledge of the values of N. For SDS, we may transform values of C_{aq} into values of N using eqs 1, 2, and 8. These are given in Table 1. Thus, α is given as a function of N. We reemphasize[12,15] that eq 8 yields values of N with an accuracy no better than that of the various experiments from which it was derived, perhaps 5−10%, but it does give relative values to high precision. Figure 4 shows the values of α versus N, including the average values of the results from the two "constant C_{aq}" series. The error bars in Figure 4 reflect the uncertainty in the measurements of A_+, and the spread in the individual values of α reflect sample preparation errors.

Discussion

The value of α is constant, within experimental uncertainty, for all values of N investigated. The unweighted mean of all

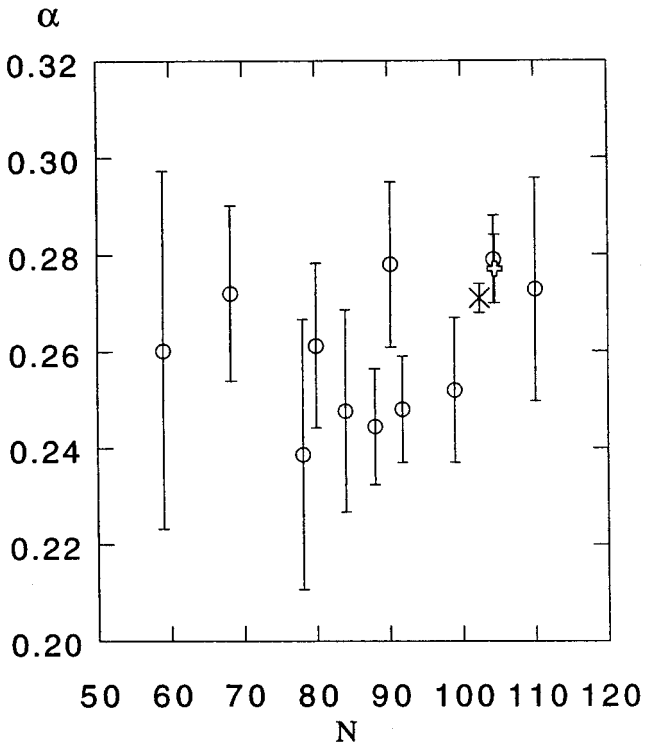

Figure 4. Values of α (eq 6) vs the aggregation number N (eqs 1, 2, and 8). Pairing of "reference" and "zero salt" (○) and pairing of "reference" and the two "constant C_{aq}" series (× and open cross).

values of α in Tables 1−3 yields $\alpha = 0.272 \pm 0.017$. From the numerous data available in the literature, we have used in previous work[12,15,17] the value $\alpha = 0.27$ obtain by Sasaki and co-workers[13] from EMF measurements in a concentration cell with an ion-exchange membrane because the measurements are almost free of assumptions and approximations.[13] Approximate values of α may be obtained from measurements of dependence of the cmc on the concentration of added common counterion salt.[8,13] From Huisman's[21] measurements on SDS, $\alpha = 0.322$, which compares well with the result, $\alpha = 0.321$, found in earlier measurements.[22] Light-scattering techniques lead to values of α that are consistent with one another but lower than those derived from other measurements. For example, from Table 1 of Romsted[4,] five determinations of α from light scattering yielded $\alpha = 0.17 \pm 0.02$, where the uncertainty is the standard deviation in the five measurements. For the other 25 determinations in the same table, using various techniques yields $\alpha = 0.23 \pm 0.05$,[4] which is within experimental error of the present determination.

We now turn to the question of the constancy of the value of α in the literature. Experimentally, the effect of increasing surfactant concentration is presented in Table 3 and increasing salt concentration in Table 4 of Romsted.[4] All of the data taken as a whole forced Romsted to conclude[4] that α seemed to be constant in both of these cases. Sasaki et al.,[13] using activity measurements, concluded that α was constant at $\alpha = 0.27$ up to [SDS] = 80 mM. Mysels and Dulin,[23] combining mobility and tracer electrophoresis measurements, came to the same conclusion up to about 80 mM. Of course, the present work makes no distinction between adding salt or surfactant and pushes the limit of constant α up to about $N \approx 110$, which corresponds to combinations of surfactant and salt concentrations from [SDS] = 600 mM and [NaCl] = 0 to [SDS] = 25 mM and [NaCl] = 155 mM.

Our results are in accord with the recent general assertion by Jönsson et al.[3] that the value of α is constant over orders of magnitude of micelle concentration as well as under variations of salt concentration and temperature. They[3] further assert that this phenomenon, termed counterion condensation, is common to all systems of high charge densities, including polyelectrolyes and charged surfaces. Jönsson et al.[3] show that counterion condensation is a plausible phenomenon by applying the Poisson−Boltzmann equation to two charged plates in one dimension under which conditions the equation has an analytical solution. See chapter 7 of ref 3.

It is useful to return to the original data for a different perspective on the question of the constancy of α. Figure 5 shows A_+ versus N computed from eqs 1, 2, and 8 holding α constant at $\alpha = 0.27$ for all the data in Tables 1−3, together with one of the "reference" series. If α is, in fact, constant at $\alpha = 0.27$, a universal curve would result for all data in the "zero salt", "reference", and "constant C_{aq}" series. Inspection of Figure 5 shows this to be so all the way up to near $N = 110$. Figure 5b is a blowup of the data in the vicinity of $N = 103$.

Thus, from the direct calculations using eq 6 shown in Figure 4 and from the graphical presentation in Figure 5, α is found to be constant.

Precision of the EPR Method. The slope of the line in Figure 5 is approximately $\partial A_+/\partial N \approx 0.0029$ G/molecule; thus, a precision in the value of A_+ of ± 0.001 G, typical of results for [SDS] > 100 mM, leads to a precision of ±0.3 molecules in the value of N. For the reference series in which the uncertainty in A_+ is typically ±0.003 G, the uncertainty in the value of N increases to about one molecule.

Referring to Figure 2, the difference in the two values at [SDS] + [NaCl] = 0.501 M, both prepared with [SDS] = 501 mM and [NaCl] = 0, is indicative of the reproducibility from one mother sample preparation to the next. The difference in the two measurements 15.124 G − 15.120 G = 0.004 G corresponds to an error in N of ±0.7 molecules. Clearly, the reproducibility in measuring A_+ in a mother sample is superior to the reproducibility in its preparation, so small differences in samples leading to discrepancies of one molecule or less are detectable. The data in Table 3 show that the uncertainties in the measurement of A_+ on duplicate samples and on samples measured 1 day later are negligible.

A determination of the value of α for a given value of C_{aq} using just two samples tends to be noisy (see the individual points in Figure 4). This is especially so if we wish the reference value of S_t' to be small because the signal-to-noise decreases with S_t'. The precision of both measurements, at S_t and S_t', are relevant; however, the latter usually dominates the uncertainty. The accuracy increases in a "constant C_{aq}" experiment because of the increase in statistics, but this requires the preparation of several samples.

High precision in the measurement of A_+ is a result of advances in the equipment and data processing techniques developed over the past 10 years. Modern magnet power supplies and controllers provide extraordinary reproducibility and linearity in magnetic field sweeps. Typically, over a 2 h run, a 50-G field sweep is reproduced to within ±2 mG, so the field sweep only accounts for about ±0.0006 G in the uncertainty in A_+. With improved understanding of spectral line shapes of nitroxides[24] and the resulting ability to employ spectral fitting techniques,[25,26] we have found that A_+ may be reproduced within a few mG even on rather noisy spectra.[15] When the signal-to-noise is especially favorable and when several spectra are averaged to increase the statistics, the reproducibility

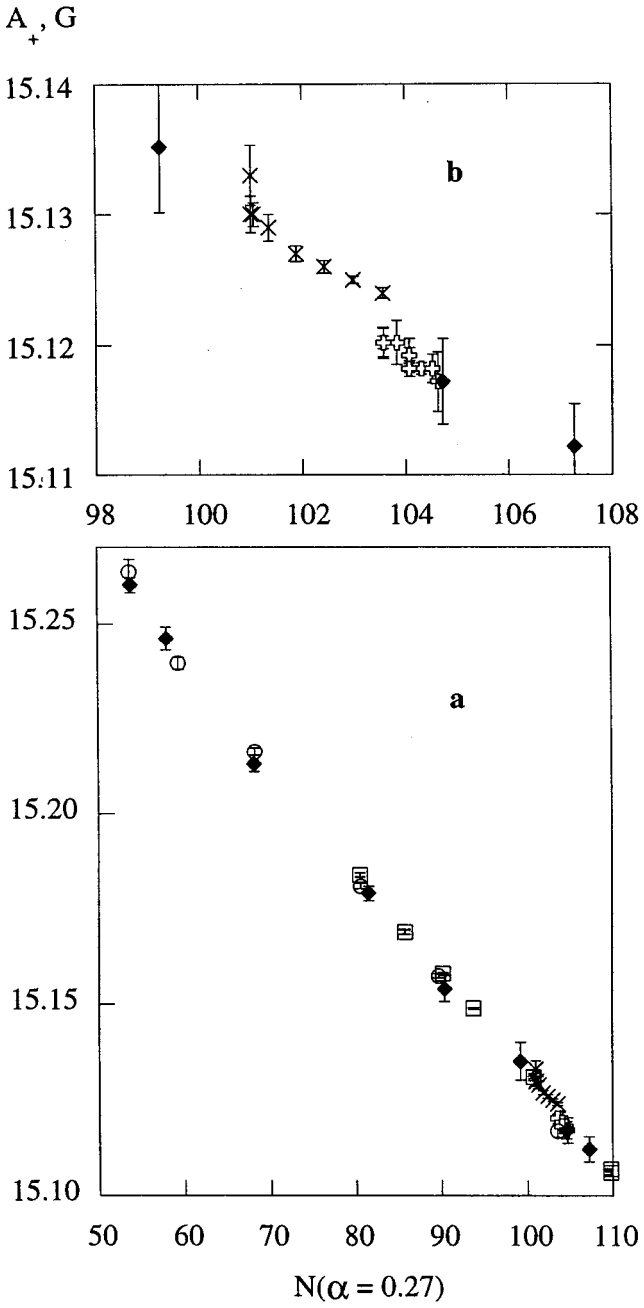

Figure 5. Hyperfine spacing A_+ vs the aggregation number computed from eqs 1, 2, and 8, holding α constant at 0.27, denoted by $N(\alpha = 0.27)$. (a). Two "zero salt" series (○ and □), a "reference" series (◆), and the two "constant C_{aq}" series using the same symbols as those in Figure 2. (b). Expanded scale near $N = 103$. Sample preparation errors would place error bars (not shown) of approximately ±0.7 molecules along the abscissa. A universal curve is indicative of a constant value of α.

becomes remarkable. Thus, in Table 1, we see reproducibilities ranging from about 2 mG to 0.2 mG. This latter figure is less than the uncertainty from the sweep width; thus this value, which is the standard deviation in 10 measurements, cannot be the accuracy of these measurements. The accuracy is limited by the accuracy of the NMR gaussmeter quoted by the manufacturer to be ±1 mG. In the final analysis, the absolute accuracy of the values of A_+ is probably limited by the small correction due to double spin probe occupancy as discussed in the appendix of ref 15. Fortunately, this systematic error, which would amount to about 4 mG, is unimportant in the method of eq 6 provided the samples are prepared with care to have the same surfactant: probe ratios. It would not be wise to prepare sample pairs using different sources of spin probe, for example.

Critique of Equation 3. The fact that ionic micelles grow with salt is a generally accepted fact. In fact, already in the 1950s, empirical equations of the same form as eq 8 were proposed where cmc + C_{ad} was the independent variable rather than C_{aq}, as is presently formulated. For work near the cmc, there is no difference in these two variables. See, for example, refs 27 and 28. Equation 3 makes the additional assertion that there is no difference in the growth induced by added counterions in the form of salt and those supplied by the surfactant. The detailed prediction of eq 3 has been tested in the literature for only 8 surfactants as follows: the sodium alkyl sulfates with chain lengths 8−14,[29,30] lithium dodecyl sulfate,[17] and cetyltrimethylammonium chloride and acetate.[31] In addition, preliminary work shows that eq 3 will likely hold for several other surfactants as well.

The implication of eq 3 being true is that the aggregation number of a micelle is independent of the concentration of micelles; i.e., only C_{aq} is important. This, in turn, implies that interactions between micelles are unimportant in determining their aggregation number. Figure 3 strongly suggests that eq 3 holds to high precision because values of α that are derived directly from values of A_+ are constant over a very wide range of micelle concentrations as long as the aggregation number is constant.

It is reasonable to assume that the size dispersion of the micelles is dependent only on N. Thus, when matching values of N in order to apply eq 6, one will also match the dispersions, which allows the method to be applied to either a number- or weight-averaged aggregation number. Therefore, any technique that consistently detects the same statistically weighted average aggregation number could be utilized.

We have restricted our measurements to values of N below 130, at which point the sphere−rod transition occurs.[15] If eq 3 holds up under further investigation for values of N below the sphere−rod transition, it will be an interesting question whether it continues to be valid above this point. Some other technique would be required to pursue this point.[15]

Critique of Equation 6. The strength of the definition eq 6 is that any experimental technique may be used that is capable of determining whether two values of N are equal. Since the aggregation number is not needed, precision in relative values is the important requisite. A further strength of eq 6 is that systematic errors tend to cancel because only differences in values of N are important. There can be little doubt that eq 6 can be applied to a wide variety of experimental techniques and to a wide variety of micelles. The requirements are two: the micelles grow with increasing C_{aq}, and the technique can distinguish two values of N. It remains to be seen if a particular technique can be applied with sufficient relative precision to yield useful values of α.

A weakness in eq 6 is that it is not useful at low values of S_t approaching the cmc_0 where S_t' would also be low and therefore near S_t. The precision of eq 6 declines as S_t approaches S_t'.

Applying the Spin Probe Technique to Other Investigations. The measurements in this study were extensive because we were interested in the question of the constancy of α to rather high values of surfactant concentration. We foresee that the general utility of the spin probe method will be in experiments that are more typical; i.e., those that extend to more modest values of S_t, say 100−200 mM, where an a priori assumption of a constant value of α is reasonable. In these types of studies, we envision preparing 8−10 samples, not the 82 samples

prepared for this study. If the variation of N with C_{aq} is known, then one could quickly determine a value of α that minimizes the difference in A_+ for various series of samples versus N, i.e., by finding a value of α that yields a common curve in Figure 5. Alternatively, if values of N are not known, one would search for a common curve for A_+ versus C_{aq}. Running the spectra, reducing the data, and preparing a figure such as Figure 5 requires about 2 days work.

Because of the simplicity of the method, it becomes feasible to investigate large numbers of systems. In addition to studying other surfactants, investigation of the variation of α with a number of experimental parameters such as temperature, chain length, counterion, and added nonelectrolytes becomes attractive.

The EPR method should be applicable to any micelle that fulfills the general criterion of growing with increasing C_{aq} and that possesses water in its polar shell which is expelled as the micelle grows. We believe this to include most micelles in the slow growth region where they are approximately spherical, i.e., below the sphere−rod transition.

We have employed 5DSE in this study but have previously found[16] that 16DSE, where the doxyl group is attached at carbon 16, gives the same results. We have given arguments that the doxylstearic acid esters labeled at any position should all give similar results,[15,16] and in unpublished work,[32] we have found this to be true. In general, we expect any spin probe to work, provided it is sufficiently hydrophobic to avoid appreciable partitioning into the aqueous phase and provided it possesses sufficient intramolecular flexibility to yield narrow line widths. However, we council avoiding 5-doxylstearic acid which is sensitive to changes in the pH.[33]

Conclusions

An unambiguous definition of α results from the hypotheses that the aggregation number and α depend only on C_{aq}. In effect, the aggregation number becomes an internal measure of the value of C_{aq}. When applied to SDS using a spin probe technique, the method yields a constant value of $\alpha = 0.272 \pm 0.017$ for aggregation numbers less than $N \approx 110$, which is in excellent agreement with literature values based on activity measurements,[13] micelle mobility measurements,[34] and radio isotope mobility measurements of the Na^+ ion.[23] The constancy of α is in accord with theoretical arguments based on the Poisson-Boltamann equation.[5]

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