

Aggregation Number-Based Degrees of Counterion Dissociation in Sodium *n*-Alkyl Sulfate Micelles

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Values of the degree of counterion dissociation, α , for sodium *n*-alkyl sulfate micelles, denoted by SN_cS , where N_c is the number of carbon atoms in the alkyl chain, are defined by asserting that the aggregation number, N , is dependent only on the concentration, C_{aq} , of counterions in the aqueous pseudophase. By using different combinations of surfactant and added salt concentrations to yield the same value of N , α can be determined, independent of the experimental method. Electron paramagnetic resonance measurements of the hyperfine spacings of two nitroxide spin probes, 16- and 5-doxylstearic acid methyl ester (16DSE and 5DSE, respectively), are employed to determine whether micelles from two samples have the same value of N to high precision. The EPR spectra are different for the two spin probes, but the values of α are the same, within experimental error, as they must be. In agreement with recent work on S12S and with prevailing thought in the literature, values of α are constant as a function of N . This implies that the value of α is constant whether the surfactant or added electrolyte concentrations are varied. Interestingly, α varies with chain length as follows: $N_c = 8$, $\alpha = 0.42 \pm 0.03$; $N_c = 9$, $\alpha = 0.41 \pm 0.03$; $N_c = 10$, $\alpha = 0.35 \pm 0.02$; $N_c = 11$, $\alpha = 0.30 \pm 0.02$ at 25 °C and $N_c = 13$, $\alpha = 0.22 \pm 0.02$; and $N_c = 14$, $\alpha = 0.19 \pm 0.01$ at 40 °C. A simple electrostatic theoretical description, based on the nonlinear Poisson–Boltzmann equation for the ion distribution around a charged sphere, was compared with the experimental results. The theory predicts values of α that are in reasonable agreement with experiment, nicely predicting the decrease of α as N_c increases. However, the theory also predicts that, for a given value of N_c , α decreases as N increases. Moreover, this decrease is predicted to be different if N is increased by adding salt or by increasing the surfactant concentration. A modification to the theory in which dissociated counterions contribute to the ionic strength while added co-ions (Cl^-) do not, brings theory and experiment into closer accord. Assuming α to be constant versus N permits a direct application of the aggregation number-based definition of α using time-resolved fluorescence quenching to measure values of N as well as other experimental parameters that vary monotonically with N , such as the microviscosity measured with spin probes and the quenching rate constant. For S13S micelles at 40 °C, $\alpha = 0.20 \pm 0.02$ is derived from N ; $\alpha = 0.21 \pm 0.02$ from the microviscosity, and $\alpha = 0.21 \pm 0.02$ from the quenching rate constants, in agreement with the hyperfine spacing results. The aggregation numbers for S13S are well described by the power law $N = N^\circ(C_{\text{aq}}/\text{cmc}_0)^\gamma$, where cmc_0 is the critical micelle concentration in the absence of added salt, $N^\circ = 67$, and $\gamma = 0.26$.

Introduction

The apparent degree of counterion dissociation, α , also called the degree of micelle ionization, is an important parameter in the physical description of aqueous surfactant solutions.^{1,2} Although ionic surfactants are strong electrolytes below the critical micelle concentration (cmc), that is, fully ionized, the charge density on the micellar surface is so high that a fraction, $1 - \alpha$, of the counterions condense onto the surface and reduce the net charge, so that α is often only 0.2–0.5.¹ This parameter significantly influences the surface properties of surfactants, such as the cmc, micellar size, reduction of interfacial (or surface) tension, etc.² Colloidal properties such as substrate binding efficiencies, transport properties, and phase transitions (e.g., from

spheres to rodlike structures) can also show significant dependencies on α .³

Many theoretical discussions regarding the formation of ionic micelles are based on a consideration of the electrostatic energy and the evaluation of this energy in connection with counterion binding.⁴ A particularly simple and elegant approach was developed by Evans, Mitchell, and Ninham (EMN),⁵ who analyzed in detail the “dressed micelle model”. Using their description for ion binding in micelles, α was calculated by solving the nonlinear Poisson–Boltzmann (P–B) equation for the ion distribution around a charged spherical structure. The EMN work⁵ showed, without resorting to Stern layers, how a counterion binding picture emerges. The model takes into account both the opposing interfacial forces at the micelle–water interface and the free energy change upon transfer of the hydrocarbon tails from water to an interior region that is nonpolar. Hayter,⁶ in a beautifully written paper, summarized

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TABLE 1: Parameters for the Aggregation Numbers of SN_cS , Eq 9, and the Spherical Limit (25 °C)

	cmc ₀	N^o	γ	$V, L mol^{-1} h$	$V_{tail}, \text{\AA}^3 i$	$N_{spherical\ limit}^j$
S8S ^e	0.134 ^a	38 ^d	0.25 ± 0.01 ^d	0.232	242.6	40
S9S ^e	0.0646 ^a	35 ^d	0.25 ± 0.01 ^d	0.246	269.5	44
S10S ^e	0.030 ^a	45 ^d	0.20 ± 0.01 ^d	0.260	296.4	52
S11S ^e	0.0141 ^a	52 ^d	0.18 ± 0.01 ^d	0.274	323.3	60
S12S ^e	0.0081 ^a	52 ^g	0.25 ± 0.01 ^g	0.288	350.2	69
S13S ^f	0.004 ^b	67	0.26 ± 0.02	0.302	377.1	79
S14S ^f	0.002 ^c	72 ^d	0.20 ± 0.01 ^d	0.316	404	89

^a Data taken from ref 18. ^b Data taken from ref 53. ^c Data taken from ref 36. ^d Data taken from ref 19 and recalculated using α from this work. ^e $T = 25$ °C. ^f $T = 40$ °C. ^g Data taken from ref 27. ^h The molar volumes of surfactant were calculated as $V = M/1000$, where M is the molecular weight of surfactant. ⁱ The volume (\AA^3) occupied by the saturated hydrocarbon chain calculated according to Tanford (p 52 of ref 54) as $V_{tail} = 27.4 + 26.9N_c$, assuming that the entire hydrocarbon chain is embedded in the core. ^j Values of the limiting aggregation numbers for spherical micelles calculated by eqs 11 and 13.

the work until 1992 and recast the solution of the P–B equation for the dressed micelle model self-consistently and solved for α analytically. A remarkably simple expression for α emerged, which we term EMNH theory.⁶

The degree of counterion dissociation has been measured experimentally by different techniques, including ultrafiltration,⁷ potentiometry,⁸ conductometry,^{9,10} and NMR spectroscopy.¹¹ But even for well-studied micellar solutions such as sodium dodecyl sulfate in water (with or without added salt) reported measurements of α vary over a very wide range, and there is strong evidence in the literature that many of the reported values of α are dependent on the methodology used for its measurement.¹²

In this work, we study a series of sodium *n*-alkyl sulfate micelles which we denote by SN_cS , where N_c is the number of carbon atoms in the alkyl chain. This series offers the possibility to change the size of the micelles in independent ways by changing N or N_c .

Recently, one of us proposed a definition of α which, with a relatively simple physical model and a few reasonable assumptions, allowed consistent values to be established that were independent of the experimental method used.¹³ The method is based on the hypothesis that the aggregation number, N , at a given temperature, is dependent only on the concentration, C_{aq} , of counterions in the aqueous pseudophase:

$$N = N(C_{aq}) \quad (1)$$

where C_{aq} may be found from the conventional pseudophase ion exchange mass balance relationship:¹⁴

$$C_{aq} = (\alpha C + (1 - \alpha)C_{free} + C_{ad})/(1 - VC) \quad (2)$$

where C , C_{free} , and C_{ad} are the molar concentrations of total surfactant, surfactant in free monomer form, and added counterion in the form of salt, respectively. The factor $1/(1 - VC) \equiv F(C)$, where V is the molar volume of the surfactant, takes into account the excluded volume of the micelles as previously discussed.¹³ The molar volumes are listed in Table 1.

The method relies on precise measurements of any physical quantity that varies monotonically as a function of N . Using electron paramagnetic resonance spectroscopy (EPR) of nitroxide free radical spin probes, a constant value for $\alpha = 0.272 \pm 0.017$ was reported¹³ for concentrations of S12S from 25 to 600 mM and added NaCl concentrations from 0 to 155 mM. The values of N varied from 54 to 110; thus, a constant value of α implies that it does not vary significantly with the micelle size. While the EMNH theory, as originally written, predicts somewhat constant values of α over this range of values of N , there is nevertheless some variation. Moreover, the value of α depends

on whether the size of the micelle is increased by increasing the surfactant concentration or by adding salt.

Some members of the SN_cS series have been investigated by NMR spectroscopy.¹⁵ From measurements of the chemical shifts of Na^+ as a function of surfactant concentration, those authors suggested¹⁵ that α was constant as a function of N_c . If this were to be so, then α would be a constant as a function of micelle size, whether N changes for a given value of N_c or the chain length varies.

In this paper we report an extension of the S12S study^{13,16} to the homologous series SN_cS , in each case varying N by changing both the surfactant and salt concentrations. We compare our results with the EMNH theory as originally proposed by Hayter⁶ and under other plausible assumptions. The purpose of the work is to (1) further test the hypothesis that α may be obtained using the assumption eq 1, (2) to test the EMNH theory as either N or N_c is varied, and (3) to test the hypothesis¹⁵ that α is constant as a function of N_c .

Experimental Section

Materials. SN_cS (Lancaster Synthesis, Inc., $N_c = 8-11, 13$, and 14, 99%) were used as received. Surface tension measurements were not carried out; however, freshly prepared samples were used for each experiment, most of which were completed within 2–3 days, minimizing the risk of hydrolysis. Distilled water was purchased from Arrowhead. Sodium chloride (Aldrich) was used as received. Stock solutions of the spin probes 16- and 5-doxylstearic acid methyl ester (16DSE and 5DSE, respectively) (Aldrich, used as received) in methanol were distributed to vials by weight, dried with a stream of nitrogen gas, and stored in the freezer until needed. A stock micelle solution was prepared in the following way: the vial was warmed to the room temperature and then SN_cS and water were added until the concentration of SN_cS was equal to 500 mM, and the spin probe concentration (16DSE or 5DSE) was equal to 1 mM. The solution was stirred for about 20 h before preparing samples with an appropriate concentration of surfactant and/or salt by adding distilled water and/or NaCl to the stock solution. This method of sample preparation guaranteed a constant spin-label: SN_cS molar ratio of 1:500.¹⁷

Two types of series of the samples were prepared which we term “zero salt” and “add salt”, respectively, the first with various concentrations of the detergent molecule in the absence of salt, prepared by diluting the stock solution with distilled water. The second was prepared with different NaCl concentrations while holding the concentration of SN_cS surfactants at a low, constant value, generated by mixing two solutions: one at the maximum desired salt concentration and one without any salt. An effort was made to produce “conjugate pairs” in the two series; i.e., the concentrations of the surfactant and salt were

chosen so that C_{aq} , eq 2, was the same for two samples. In planning the preparation of all samples, trial values of α must be assumed. The final results do not depend on this preliminary value as was discussed previously;¹³ however, the proximity of the values of C_{aq} in the conjugate pairs does depend on the value.

Aggregation numbers for all SN_cS are available in the literature,^{18–20} except for S13S. Thus, time-resolved fluorescence quenching experiments (TRFQ) were performed on this surfactant. Pyrene was used as the fluorescence probe and dimethylbenzophenone (DMBP) as the quencher, both obtained from Aldrich and used as received. A 20-mM stock solution of pyrene in ethanol was prepared. An aliquot of this stock solution was added to a vial and the solvent evaporated under a slow flow of N_2 gas. The pyrene concentration in the samples prepared for TRFQ experiments was kept at about 1/100 times the concentration of micelles, ensuring that the fraction of micelles with two or more pyrene molecules was negligible. The required amounts of S13S and 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 one quencher per micelle, which was then stirred gently for 12 h. An add-salt series with constant $[S13S] = 0.01$ M was prepared by mixing solutions of $[S13S] = 0.01$ M and 0.13 M NaCl with $[S13S] = 0.01$ M without added salt.

Methods. EPR. EPR experiments were performed using a Bruker 300ESP spectrometer operating at X-band. Instrumental conditions were the same as recently reported.²¹ Reported parameters derived from the spectra are the mean values of five measurements. Computer fits of the EPR spectra yielded line positions and line heights to high precision as discussed in detail previously.²²

The spin-probes 16DSE and 5DSE are very sparingly soluble in water; thus, the signal arising from probes partitioned into the aqueous phase is negligible. The measurements were carried out for all surfactants at 25 °C, except S13S and S14S. The Krafft points of S13S and S14S are higher than this temperature; therefore, their EPR spectra were recorded at 40 °C.

TRFQ. The fluorescence decay curves of pyrene in the presence and absence of DMBP were obtained using an FL900 lifetime measurement spectrometer of Edinburgh Analytical Instruments. Instrumental conditions were the same as reported in ref 20. The time-dependent fluorescence decay curves were fitted to the Infelta–Tachiya equation.^{23–25} These fits yielded negligible exit rate constants of the quencher; thus, the decay curves take the form

$$F(t) = F(0)\{-k_0t + \langle N_q \rangle [\exp(-k_q t) - 1]\} \quad (3)$$

where $F(0)$ denotes the initial fluorescence intensity, k_0 is the decay rate of excited pyrene in a micelle without quenchers, k_q is the rate constant for quenching of pyrene fluorescence by a single quencher, and $\langle N_q \rangle$ is the average number of quenchers per micelle. The derivation of eq 3 assumes that the micelles are monodisperse, and the probes and quenchers are distributed according to Poisson statistics.^{23,24,26} From values of $\langle N_q \rangle$, the micelle aggregation numbers are computed from

$$N = \langle N_q \rangle (C - C_{free})/[Q] \quad (4)$$

where $[Q]$ is the quencher concentration in mol L^{-1} .

Theory. Aggregation Number-Based Degree of Counterion Dissociation. In principle,¹³ a value of α is measured by preparing two samples yielding the same value of N , but with

different values of C and C_{ad} . For these two samples, the hypothesis, eq 1, states that the value of C_{aq} is the same for these two samples. This allows us to write the following:

$$F(C)\{\alpha C + (1 - \alpha)C_{free} + C_{ad}\} = F(C')\{\alpha C' + (1 - \alpha)C'_{free} + C'_{ad}\} \quad (5)$$

The free monomer concentration may be obtained using eq 5 of Quina et al.:²⁷

$$\log(C_{free}) = (2 - \alpha) \log(\text{cmc}_0) - (1 - \alpha) \log(C_{aq}) \quad (6)$$

where cmc_0 is the critical micelle concentration at $C_{ad} = 0$. Equation 6 shows that, for equal values of C_{aq} , $C_{free} = C'_{free}$. Now, $F(C) \approx F(C')$ for values of $C, C' \leq 100$ – 200 mM, and above these concentrations C_{free} is small compared with C . Thus, for equal values of N we have

$$F(C)\{\alpha C + C_{ad}\} = F(C')\{\alpha C' + C'_{ad}\} \quad (7)$$

And, solving eq 7 for α , for a given value of C_{aq} , we obtain

$$\alpha = \frac{F(C)C_{ad} - F(C')C'_{ad}}{F(C')C' - F(C)C} \quad (8)$$

By varying the combinations of C and C_{ad} , α becomes available as a function of C_{aq} . Note that knowledge of the values of N is not required to employ eq 8. Because any physical quantity that varies monotonically with N may be used to find conjugate pairs, eq 8 yields values of α that are independent of the experimental technique.

An alternative method to find values of α , assuming it to be constant, is to plot any physical quantity that varies monotonically with N , as a function of C_{aq} , adjusting α to find the best common curve as suggested by eq 5.

To simplify the language in this paper, we refer the computation of α using eq 8 or using eq 5 as follows: using eq 8 means a pairwise application to an approximately conjugate pair, making no assumption whether α is constant. Using eq 5 means that we search for a common curve with the implicit assumption that α is constant.

Variation of N with C_{aq} . In 1995 it was determined²⁷ that, for S12S micelles, the aggregation number shows a power law:

$$N = N^\circ (C_{aq}/\text{cmc}_0)^\gamma \quad (9)$$

where N° is the value of N at the cmc_0 and the exponent γ is an empirically determined constant. Further, eq 9 has been found to be valid for the sodium alkyl sulfates with chain lengths 8–12 and 14.^{19,20} The empirical parameters N° and γ obtained in ref 20 are presented in Table 1.

EMNH Theory. The EMNH theory⁶ treats micelles as highly charged spheres in an electrolyte bath. The nonlinear P–B equation which describes the ionic distribution about the micelle is solved from which the degree condensation of counterions onto the charged surface gives a natural estimate of the value of α . The original EMN treatment⁵ solved the P–B equation with approximate planar boundary conditions, leading to an inconsistency pointed out and solved by Hayter.⁶ Values of $\beta = 1 - \alpha$ are computed from eq 15 of Hayter⁶ from values of N , the radius of the charged sphere, R , and the ionic strength of the supporting electrolyte. Hayter computed⁶ this latter quantity assuming the electrolyte to be composed of the surfactant monomers and their counterions together with any added salt (both the ion common to the counterion and its co-ion). The counterions dissociated from the micelle were excluded from

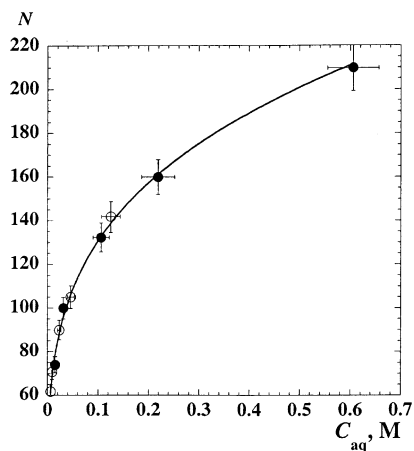


Figure 1. Aggregation number, N , vs the concentration of sodium ions in the aqueous phase, C_{aq} , for S13S micelles, $T = 40$ °C: (●) add NaCl; (○) zero NaCl. The abscissa was calculated from eq 2, varying α in search of the best common curve; in this case $\alpha = 0.20$. The solid line is eq 9; the values of N° and γ obtained are presented in Table 1. The horizontal error bars delimit $\alpha = 0.20 \pm 0.02$.

the electrolyte concentration. The dielectric constant of the supporting electrolyte enters the theory, which Hayter took to be that of pure water.⁶

Results

TRFQ Measurements: Aggregation Number and α for S13S Micelles. TRFQ experiments in S13S using pyrene and DMBP produced decay curves (not shown) similar to those in recent papers.²⁰ Fitting these curves to eq 3 yielded values of $\langle N_{\text{q}} \rangle$ and k_{q} .^{23,24,28} Aggregation numbers were computed from eq 4 setting $[Q] = [\text{DMBP}]$ because solubility measurements show that 99.6% of DMBP is dissolved in micelles.²⁹ Previous results using S12S by several investigators^{19,20} show that variations from sample to sample are about $\pm 5\%$ in N , which we adopt as the estimated relative error.

The resulting values of N are presented as a function of C_{aq} in Figure 1 for a zero-salt (open circles) and an add-salt (closed circles) series. Figure 1 is the result of the application of eq 5 to find the best value of $\alpha = 0.20$ found by minimizing the least-squares difference in the experimental results and eq 9. The solid curve is the least-squares fit to eq 9, yielding the values of $N^\circ = 67$ and $\gamma = 0.26$ which are reported in Table 1. The horizontal error bars in Figure 1 show the uncertainty in the value of C_{aq} due to a ± 0.02 uncertainty in the value of α . The vertical error bars indicate the relative error of aggregation number measurements, $\pm 5\%$.

Values of α from EPR. Three line-motional-narrowed EPR spectra of 16DSE or 5DSE, typical of nitroxide free radicals, were observed for all samples.³⁰ See, for example, Figure 1 of ref 29. The difference in resonance fields between center- and low-field lines, A_+ , is a sensitive measure of the relative value of N .^{13,17} for values of N below the sphere-rod transition. Above this transition, EPR is ineffective because A_+ no longer varies¹⁷ with C_{aq} ; thus, we confined the present study to those values of C_{aq} which resulted in monotonic variations of A_+ .

First, values of α were determined using eq 8, which makes no assumption about the constancy of α . For a nearly conjugate pair, equal values of N are indicated by equal values of A_+ in which case eq 8 gives the value of α immediately. If these values are slightly different, an interpolated value of NaCl concentration for the added-salt series is found before applying eq 8, as discussed in detail recently.¹³ For each conjugate pair, five EPR spectra were measured of each sample; pairing these yielded

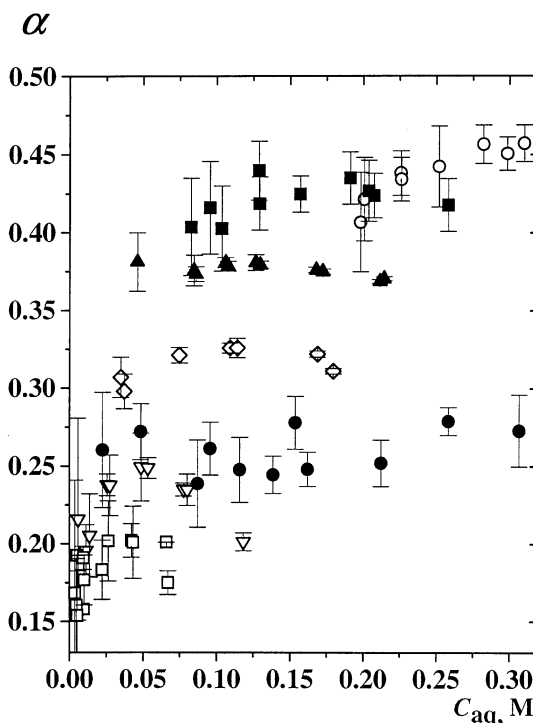


Figure 2. Degree of ionization, α , vs C_{aq} , for SN_cS micelles. Spin probe 16DSE. S8S (○), S9S (■), S10S (▲), S11S (◇), S12S (●) at 25 °C and S13S (▽), S14S (□) at 40 °C. The data for S12S are taken from ref 13.

five values of α from which mean values and standard deviations were calculated. This procedure was performed for every SN_cS surfactant using both 5DSE and 16DSE spin probes. The results using 16DSE are plotted vs C_{aq} in Figure 2; the error bars are the standard deviations. Figure 2 shows that α is constant vs C_{aq} , within experimental error for every surfactant as was the case with S12S employing 5DSE.¹³ Note that values of α may be reached without any knowledge of the values of N for these surfactants; no reference to N is needed to prepare Figure 2. Values of α averaged over all values of C_{aq} are presented in Table 2; the uncertainties are the standard deviations.

To compare experimental values of α with theory, they are needed as functions of N . To obtain α as a function of N , we employ eq 9, using the values of cmc_0 , N° , and γ presented in Table 1. These data are plotted in Figure 3a and can be compared with theoretical results in Figure 3b to be discussed below. For clarity, calculated values are shown here for only two of the surfactants. Data for S12S are taken from the literature.¹³

Employing the spin probe 5DSE, the observed data are similar to those in Figure 2, and the values of α obtained for every detergent are also constant within experimental error. The average values and standard deviations of α are presented in Table 2. Column 3 shows results obtained using the 5DSE spin probe and column 2 those obtained using the 16DSE probe. It is interesting to note that in contrast with earlier suggestions¹⁵ the value of α significantly decreases with increasing length of the surfactant carbon chain. We note that in many older determinations of α , including those of ref 15, it was implicitly assumed that α was constant vs C_{aq} . This is because the values of the various physical quantities were plotted vs C or C_{ad} , assuming a single value of α .

The dependence of the experimental values of α on N_c is shown in Figure 4 with open squares which are mean values

TABLE 2: Values of α Deduced from EPR Implementation of the Aggregation Number-Based Definition, Eq 1, and the Variation of the cmc_0 with Added Salt, Eq 10

	$\alpha_{16\text{DSE}}^c$	$\alpha_{5\text{DSE}}^c$	$\alpha_{16\text{DSE}}^d$	$\alpha_{5\text{DSE}}^d$	$\alpha_{16\text{DSE}}^e$	$\alpha_{5\text{DSE}}^e$	α^f	α^i
S8S ^a	0.432 ± 0.013	0.411 ± 0.042	0.419 ± 0.011	0.41 ± 0.04	0.411 ± 0.017	0.421 ± 0.017	0.345	0.42 ± 0.03
S9S ^a	0.418 ± 0.016	0.406 ± 0.011	0.411 ± 0.013	0.403 ± 0.008	0.404 ± 0.016	0.412 ± 0.017	0.426	0.41 ± 0.03
S10S ^a	0.375 ± 0.004	0.334 ± 0.019	0.371 ± 0.009	0.342 ± 0.023	0.340 ± 0.014	0.330 ± 0.013	0.362	0.35 ± 0.02
S11S ^a	0.316 ± 0.011	0.292 ± 0.012	0.315 ± 0.014	0.302 ± 0.019	0.291 ± 0.012	0.285 ± 0.012	0.433	0.30 ± 0.02
S12S ^a		0.277 ± 0.013 ^g	0.290 ± 0.020 ^h	0.272 ± 0.017 ^g			0.322	
S13S ^b	0.226 ± 0.020		0.221 ± 0.010		0.212 ± 0.011			0.22 ± 0.02
S14S ^b	0.182 ± 0.018		0.187 ± 0.009		0.195 ± 0.009			0.19 ± 0.01

^a $T = 25$ °C. ^b $T = 40$ °C. ^c The values of α were calculated according to eq 8 from the dependences of A_+ on C_{aq} . ^d The values of α were calculated according to eq 7 from the dependences of A_+ on C_{aq} . ^e The values of α were calculated according to eq 7 from the dependences of microviscosity, η , on C_{aq} . ^f The data taken from ref 18. ^g From ref 13. ^h From ref 16. ⁱ Unweighted average. Uncertainty is the sum of the random errors in one series of samples, the presumed 5% uncertainty from different series, and an estimated 2% systematic error due to the uncertainty in the value of V in eq 2, all added in quadrature.

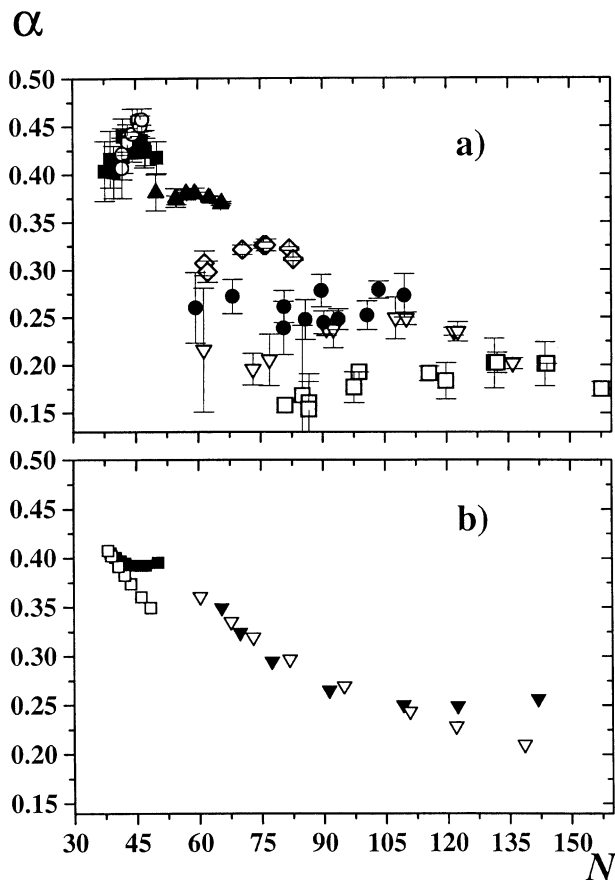


Figure 3. Degree of ionization, α , vs the aggregation number, N , of S_N,S micelles: (a) experimental values for S8S (○), S9S (■), S10S (▲), S11S (◇), S12S (●), S13S (▽), S14S (□); (b) calculated values for S9S, zero-salt (□) and add-salt (■); S13S, zero-salt (▽) and add-salt (▼), using the EMNH theory with the original assumptions. The abscissa was computed using eq 9 with the parameters in Table 1.

averaged over all values of N . The error bars are the standard deviations. The solid symbols represent theoretical calculations discussed below.

On the basis of the above results, we make the reasonable assumption that α is constant for a given surfactant and employ the other approach to find α based on eq 5, searching for the best common curve of A_+ as a function of C_{aq} . Representative results from this approach are presented in Figure 5 for $N_c = 8-11$, using the 16DSE spin probe. Open symbols represent experiments with zero-salt samples, and closed symbols represent those with add-salt. In Figure 5a, the abscissa assumes $\alpha = 1$, i.e., is equal to the total counterion concentration. The

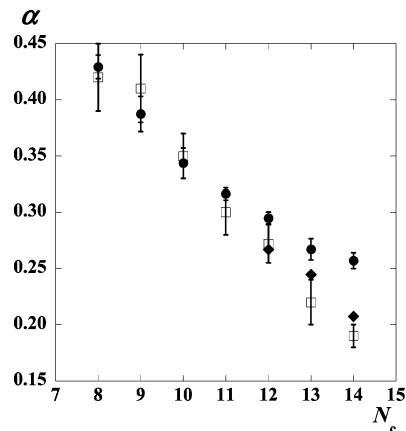


Figure 4. Ionization degree, α , vs the carbon chain length, N_c . The experimental values averaged over all N and all methods (□), the calculated values by EMNH theory in the spherical limit (●). The error bars on the experimental data are propagated random and systematic errors. See text. The error bars on the calculated data delimit the double-valued results for zero-salt vs add-salt. The symbols (◆) represent the calculated data, reducing the dielectric constant water to 70.6 for S12S at 25 °C; 66.7 for S13S and 63.6 for S14S at 40 °C.

value of α was varied by trial and error until a common curve was reached for each surfactant. The best common curves were estimated by plotting the mean-squared deviation of the data for S8S, S9S, S10S, and S11S from quadratic functions and for S13 and S14S from power trial functions. Figure 5b shows the common curves with the best values of α for each surfactant. In finding α by direct application of eq 8, it is desirable to prepare closely matched conjugate pairs to avoid large extrapolations of the values of NaCl concentration. In Figure 5b, our success in preparing conjugate pairs, i.e., in choosing the correct trial values of α , may be judged by the coincidence of the open and closed points. A few points are coincident and do not show in Figure 5b. The advantage of the method of eq 5 is that the precision in finding the best value of α does not depend on the values of α assumed to prepare the samples since there is no need for coincident points. If an incorrect value of α is assumed to prepare the samples, the correct value emerges anyway; only the positions of points in plots such as Figure 5b are displaced.

Plots similar to those in Figure 5 resulted from EPR measurements using the 5DSE spin probe. The values determined for α based on eq 5 with 16DSE and 5DSE are listed in columns 4 and 5 of Table 2, respectively. Except for S10S, values of α obtained with both spin probes are within the random experimental errors in the application of eqs 5 or 8 and thus they are not dependent on the spin probe. The same conclusion resulted from the use of 16DSE¹⁶ and 5DSE¹³ in

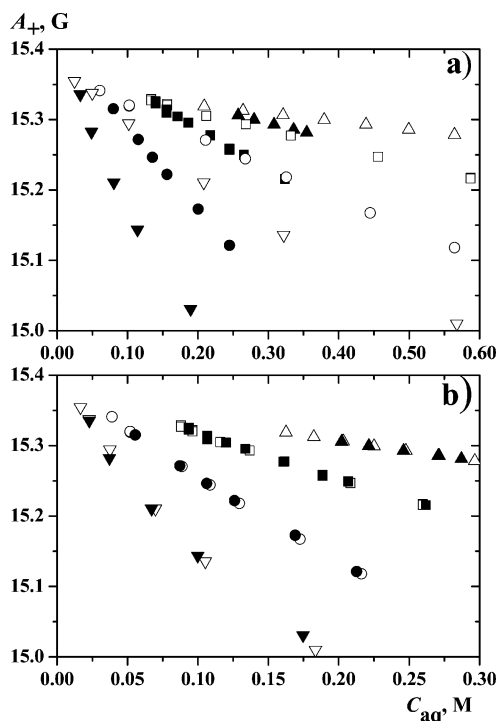


Figure 5. Hyperfine spacing A_+ vs C_{aq} for 16DSE at 25 °C: (a) abscissa computed from eq 2 with $\alpha = 1$ for all detergents and from (b) best fit values of $\alpha = 0.419$ for S8S (Δ , \blacktriangle), $\alpha = 0.411$ for S9S (\square , \blacksquare), $\alpha = 0.371$ for S10S (\circ , \bullet), $\alpha = 0.315$ for S11S (∇ , \blacktriangledown). Open and filled symbols represent zero-salt and add-salt, respectively. The concentrations of SN_cS surfactants are varied from cmc_0 to 500 mM; the concentration of NaCl is varied from 0 to 180 mM.

S12S. When other sources of error are considered (see below), the same conclusion may be reached for S10S.

We now turn to an application of eq 5 to another micellar property, the microviscosity, η , deduced from the rotational correlation times of the nitroxide moiety of either 5DSE or 16DSE. These measurements and calculations proceeded exactly as has been detailed in recent papers^{31,32} and are not described. The microviscosity depends on the environment of the spin probe and also is a monotonic function of N for SN_cS . Figure 6a,b presents the mean values of microviscosity, η , obtained from five spectra with 16DSE as spin probe: (a) for S8S, S9S, S10S, and S11S at $T = 25$ °C and (b) for S13S and S14S at $T = 40$ °C. Open symbols represent experiments with zero-salt samples, and closed symbols represent those with add-salt. We again employed eq 5 to estimate α . The value of α was varied by trial and error until a common curve was reached for each surfactant using quadratic trial functions for S8S–S11S and power functions for S13S and S14S. Solid lines show the common curves with the best values of α for each surfactant. Plots similar to those in Figure 6 resulted from EPR measurements using the 5DSE spin probe. The values determined for α based on eq 5 with 16DSE and 5DSE are listed in columns 6 and 7 of Table 2, respectively. As in the case of A_+ , comparison of columns 6 and 7 shows that the values of α obtained with both spin probes are within experimental error, and thus they are not dependent on the spin probe.

The final column of Table 2 reports the unweighted average values of α derived from EPR measurements of both A_+ and η . The uncertainties reported in columns 1–6 are random errors arising from measurements on one series of samples. We have no data to assess the errors involved in repeating presumably identical series in the present surfactants; however, a recent extensive data set in which four such series of aqueous solutions

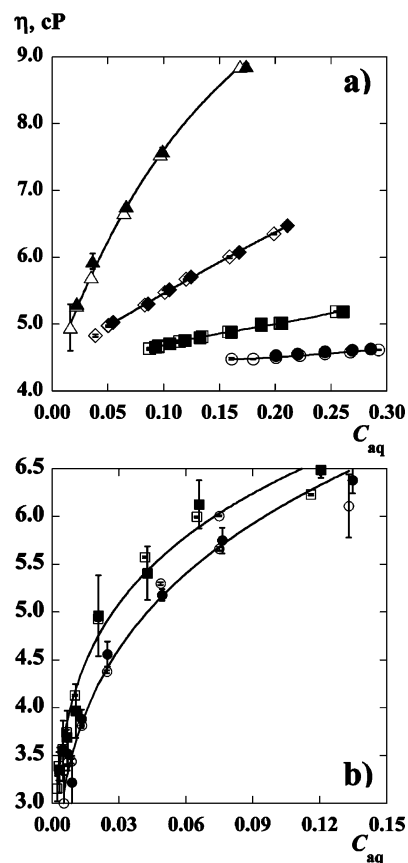


Figure 6. Microviscosity, η , vs C_{aq} , 16DSE. (a) S8S (\circ , \bullet), S9S (\square , \blacksquare), S10S (\diamond , \blacklozenge), S11S (Δ , \blacktriangle) at 25 °C; (b) S13S (\circ , \bullet), S14S (\square , \blacksquare) at 40 °C. Open and solid symbols are zero-salt and add-salt, respectively. The error bars are the standard deviations in five measurements. The solid lines are (a) quadratic trial and (b) power trial functions. The abscissa was computed from eq 2 varying α in search of the best fit. The best values of α are presented in column 6 of Table 2. Similar curves are obtained from 5DSE; the best values are given in column 7 of Table 2.

of tetramethylammonium dodecyl sulfate were prepared showed that this source of error is approximately $\pm 5\%$.³¹ In addition to the random errors, there is a systematic error due to the uncertainty in the value of V in eq 2. The excluded-volume effect reaches 14–19% in these experiments at high values of C . Ignoring this effect completely results in an increase in the value of α by approximately 10%; thus, an uncertainty in V of 20% leads to an uncertainty of $\pm 2\%$ in the values of α . The estimated uncertainties in the final column of Table 2 are the sums of the random errors in the present measurements, plus 5% presumed random error in multiple series, plus 2% systematic error. The uncertainties are presumed to be independent; thus, they are added in quadrature.

Values of α from the Quenching Rate Constant. The values of the quenching rate constants, k_q , vary monotonically with N . Therefore, we can use the dependence k_q vs C_{aq} to determine values of α , employing eq 5. Figure 7 presents the variation of k_q measured for S13S at 40 °C as a function of C_{aq} . Open and solid circles correspond to zero-salt and add-salt samples, respectively. The best common curve is obtained with $\alpha = 0.20 \pm 0.02$, using eq 5 under the assumption that α is constant for all N . The error bars are $\pm 5\%$.

Discussion

α Is Constant vs N . The present results together with those for S12S^{13,16} show that α remains constant, within experimental

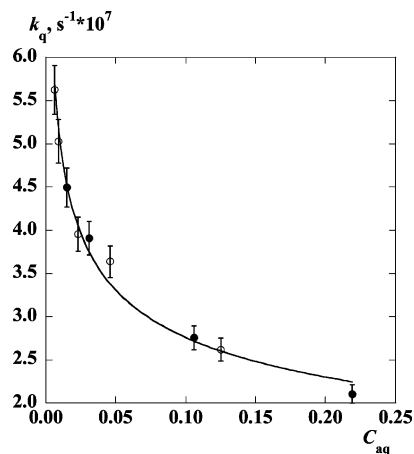


Figure 7. Quenching rate constant of pyrene by DMBP, k_q , vs C_{aq} for S13S micelles at 40 °C. Open and solid circles represent zero-salt and add-salt, respectively. The error bars are estimated from the nonlinear least-squares fit of the fluorescence decay curves to eq 3. The abscissa was computed from eq 2 varying α in search of the best common curve, a power function. The best power function calculated with the best value of $\alpha = 0.21$ is shown as the solid line.

error, as a function of N . Other experimental evidence that α is generally constant as a function of surfactant and salt concentrations in a wide variety of micelles has been summarized recently in ref 13. The phenomenon is often termed counterion condensation, and textbook discussions are available (e.g., ref 1), applicable to many systems exhibiting high charge densities, including micelles. Nevertheless, the error bars in Figure 2 of the present work and in Figure 3 of ref 13 are not sufficiently small to conclude that α is strictly constant so care is required. It would be interesting to apply the principle of eq 8 to other experimental quantities in the interest of improving the precision; however, the values of A_+ are already of high precision, so smaller error bars may be difficult to obtain. If one reaches the conclusion that α is indeed constant, then the strategy of searching for common curves such as those in Figure 5 becomes available, increasing the statistics because multiple samples are involved instead of just two. For further discussion of this point, see refs 16 and 30. We note that there are cases³⁰ in which excellent common curves are obtained whether α is assumed to be constant or slowly varying. For this reason one cannot take a common curve to mean that α is strictly constant. Care should be exercised in drawing theoretical conclusions from assuming that α is strictly constant. For example, Hall³³ has shown that a small variation in α with N , hard to detect experimentally, can account for the fact that S12S micelles grow with C according to eq 9 while also maintaining a small dispersion in N . With a strictly constant value of α , thermodynamics predicts a larger polydispersity than is observed experimentally.³³

α Decreases with Increasing N_c . As shown in Figure 4, our values of α decrease with increasing alkyl chain length, from 0.42 for S8S to 0.19 for S14S which represents a change in α by more than a factor of 2. It should be kept in mind that the results for S13S and S14S are at 40 °C while the rest are at 25 °C; therefore, variations of α with temperature could influence the plots in Figure 4 somewhat. These variations have been studied for S12S by Shanks and Franses³⁴ using conductivity methods. The values of α depend somewhat on the model used to interpret the data. Averaging over three salt concentrations and over three models yielded a negligible temperature variation of $\partial\alpha/\partial T = -0.0009 \pm 0.0007$ °C⁻¹ over the range $T = 25$ –60 °C. Data are not available for S13S or S14S; however, the

results in S12S suggest that the variation is quite small. In the theoretical calculations, the experimental temperature is used.

Numerous values of α are available in the literature with which to compare for S12S. See ref 13 for a survey. Much less data are available for the other SN_cS .

Evans³⁵ has reported values of the degree of the ionization for the S8S, S12S, and S14S surfactants, obtained using the conductivity technique at 40 °C. These data show the same trend for a change in α with chain length as those obtained in our present work. Despite the 15 °C temperature difference, Evans' absolute values for S8S ($\alpha = 0.415$) and S12S ($\alpha = 0.256$) are very close to our results (0.42 for S8S and 0.27 for S12S). For S14S, the Evans' reported value of $\alpha = 0.234$ ³⁵ differs significantly from our value: $\alpha = 0.19$. Part of this discrepancy may be the small value of the average aggregation number ($N = 55$) used for the calculations of α in ref 35. Recalculating α using $N^\circ = 72$ (Table 1) using Evans' method yields a value of 0.216, in better agreement with the aggregation number-based result.

The value of α determined here for S14S is equal to that obtained from activity and surface tension measurements, $\alpha = 0.19$, by Sasaki et al.³⁶

For S8S, α was reported to be 0.6 by Lindstrom et al., measured by the conductivity technique.³⁷ This is significantly larger than our value for S8S of 0.42. However, in that previous report³⁷ the authors employed a simplified method to estimate $\alpha = S_2/S_1$, where S_1 and S_2 are the slopes of the conductivity–concentration graph below and above the critical micelle concentration. We have recalculated α using their data³⁷ and Evans' approach³⁵ using the value of the equivalent conductivity of the Na^+ , $\Lambda_{Na} = 50.1$, $T = 25$ °C, $N = 38$. This gives $\alpha = 0.372$, much closer to our value.

A similar trend in the variation of α with surfactant chain length has been observed in studies of aqueous solutions of sodium alkanoates.³⁸ The values of α for these micelles changed from $\alpha = 0.35$ for $C_{10}H_{19}COONa$ to $\alpha = 0.12$ for $C_{15}H_{31}COONa$.

Huisman¹⁸ fit the values of the cmc_0 to its well-known³⁹ dependence on C_{ad} as follows:

$$\log(cmc_0) = -K_3 - K_4 \log(cmc_0 + C_{ad}) \quad (10)$$

where K_3 and K_4 are constants. An approximate value of α may be obtained from eq 10 because mass action theory predicts that $K_4 \approx 1 - \alpha$ in the limit of large aggregation numbers.^{40,41} This interpretation obviously requires an implicit assumption that α be constant. Column 8 of Table 2 gives these approximate values. The values of α estimated from eq 10 are similar to those based on eq 1; however, there are systematic differences. Gaillon and co-workers^{42,43} contend that, in some cases, eq 10 does and in other cases does not provide a reliable estimate of the value of α . This is a fact that needs to be kept in mind in comparing the values in Table 2.

Theoretical Estimates of the Values of α . We now turn to a comparison of the experimental results with theory. The beauty of the EMNH theory is its simplicity. Values of R , the surface density of charged headgroups and the dielectric constant, together with known values of C and C_{ad} lead to a unique value of α . The theory is applicable to spherical micelles; thus, the radius of the core, R_c , is fixed by values of N and the volume of the alkyl chain that is embedded in the core, V , as follows:

$$\frac{4}{3}\pi R_c^3 = NV_{\text{chain}} \quad (11)$$

There is some uncertainty concerning the number of alkyl hydrocarbons that ought to be embedded in the core; we simplify by assuming that all N_c carbons form the core. With this assumption, fixing N fixes R_c , leaving only the value of R and the dielectric constant as parameters that enter the theory. In computing the ionic strength, Hayter excluded the dissociated counterions and included the Cl^- co-ions.⁶ In addition, he assumed that the theory, strictly valid for spheres, is applicable to micelles over a wide range of values of N .

Hayter states⁶ that the theory is without adjustable parameters, and this is so if one accepts the implicit assumptions of the previous paragraph and two further assumptions. First, the value of R is assumed to be defined by the spherical surface that divides the polar shell into equal volumes, i.e.

$$R^3 = \frac{1}{2}(R_c^3 + R_m^3) \quad (12)$$

where R_m is the micelle radius, given by $R_m = R_c + t$, where t is the thickness of the polar shell. Second, the dielectric constant is assumed to be that of pure water.

Figure 3b shows representative theoretical values of α computed from EMNH⁶ for two of the surfactants, S9S and S13S, using the original assumptions of the theory. We follow Hayter's suggested solution of eq 15 in his paper⁶ to find values of α using a Newton's approximation, solving the equations in a spreadsheet. At low values of N , the theory is in rather good agreement with experiment for S9S while for S13S good agreement is only obtained at higher values of N . In both cases, at higher values of N there are two problems. First, the theoretical values decrease with increasing N while the experimental values do not, and second, different values of α are predicted for the same value of N if different values of C and C_{ad} are used. Thus, the theory predicts that α is a double-valued function of N . This disagrees with the assumption of eq 5 and disagrees with experiment. Indeed, not only does α seem to be the same for conjugate pairs at a given value of N , its also seems to be constant for all N .

In the EMNH theory,⁶ the double value of α for conjugate pairs arises from different values of the ionic strength due to the inclusion of the co-ion and the exclusion of the dissociated counterion in the calculation. Perhaps the co-ions ought to be excluded. At relatively low concentrations ($C_{\text{ad}} < 0.3$ M), the co-ions have a negligible effect on N , at least for inorganic ions.^{18,44} If the co-ions have no effect on N , why should they have an effect on α ? Figure 8 shows the computed values of α under various assumptions for the composition of the electrolyte bath for S10S. Using the original assumptions the open and closed squares result, illustrating the double-valued property. Excluding the co-ions gives the open and closed triangles, showing a decrease in the difference in the double values. The open squares are not affected by excluding the co-ions. Also displayed in Figure 8 is the effect of including the Na^+ counterions that are dissociated from the micelle as well as excluding the Cl^- co-ions. These are shown as open and closed circles, respectively. Including the dissociated counterions and excluding the co-ions removes the double-valued prediction of the EMNH; a single common curve results.

We now return to the theoretical values of α presented in Figure 4 as solid symbols. Because the theoretical results depend on N , these calculations were carried out at the values of N that correspond to the largest aggregation number consistent with a spherical shape, $N_{\text{spherical limit}}$. This avoids the question of whether the micelles are really spheres.⁴⁵ This limit is obtained when the length (\AA) of a fully extended chain, l_{N_c} , is equal to the

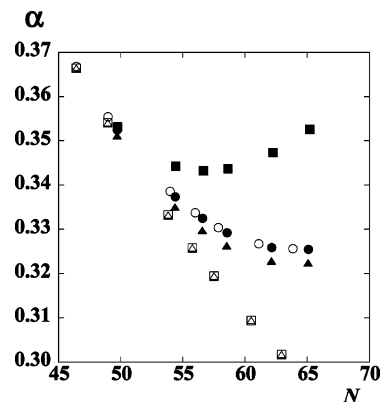


Figure 8. Calculated values of α vs N for S10S micelles. $T = 25$ °C. Solid and open symbols represent add-salt and zero-salt, respectively: original assumptions in the EMNH, \blacksquare and \square ; omitting the Cl^- co-ions from the computations, \blacktriangle and \triangle ; and, omitting the Cl^- co-ions and including the dissociated Na^+ counterions in the computations, \bullet and \circ . The double-valued nature of α is reduced by omitting the co-ions and is eliminated by also including the counterions. The concentrations of surfactant and salt used for the calculation of N were those of the experimental samples. The abscissa is eq 9 using the parameters of Table 1 and the theoretical values of α .

radius of the core of the micelle as follows:

$$R_c = l_{N_c} = 2.765 + 1.265N_c \quad (13)$$

where we have tacitly assumed that all N_c carbon atoms are embedded in the core. Table 1 gives the values of $N_{\text{spherical limit}}$.

In Figure 4, the solid circles are computed using the original assumptions in the EMNH theory. The upper and lower extent of each error bar indicate the extent of the double value of α from an add-salt or a zero-salt sample, respectively. One questionable assumption in the EMNH theory is the use of the dielectric constant of water to describe the vicinity of the charged sphere, if that sphere is supposed to reside within the polar shell as does eq 12. To explore briefly the effect of altering this assumption, the solid diamonds show the result of employing dielectric constants somewhat smaller than that of pure water as follows: 70.6 for S12S at 25 °C, 66.7 for S13S at 40 °C, and 63.6 for S14S at 40 °C.

The agreement between experiment and the EMNH in the spherical limit is already rather impressive, leaving the theory intact as written. The purpose of including the modification to lower dielectric constants is to demonstrate the magnitude and direction of this effect and to point out that rather small changes in the dielectric constant can significantly affect the theoretical values of α .

Comparison between Theory and Experimental Values of α Derived from Small-Angle Neutron Scattering (SANS).

Values of α may also be estimated from small-angle neutron scattering (SANS) experiments.⁴⁵ A comparison of the aggregation number based method and SANS is therefore worthy of discussion. The discrepancy between theory and the aggregation-number method prompted us to reexamine the remarkable agreement between the same theory and values of α derived from SANS for S12S. Hayter and Penfold⁴⁵ fit scattering profiles to a core-shell model, finding values of N and R_m from which the thickness, t , is evaluated, having fixed R_c from the model. Another fit parameter was the micelle charge, from which α may be computed. These parameters, together with known values of C and C_{ad} , are all that is required in the theory. The overall comparison between theory and SANS-based values of α , given in Table 2 of Hayter's paper,⁶ is impressive considering

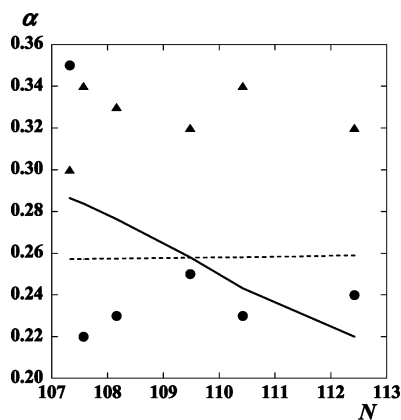


Figure 9. Degree of ionization, α , estimated from fitting SANS data⁴⁶ vs N , 25 °C. The solid circles correspond to using N as a fit parameter in the analysis of the SANS data and the solid triangles to fixing $N = 110$. The solid line is computed from the EMNH in its original form and the dashed line including the dissociated Na^+ and excluding Cl^- in the ionic strength. The abscissa is computed from eq 9 using the parameters in Table 1.

the simplicity of the model. In detail, however, there are discrepancies there similar to those in this paper, but of the opposite sense. Experimental SANS-based values of α decrease with increasing N faster than theory predicts by a factor of ~ 6 . Recently, SANS measurements of S12S with an approximately constant C_{aq} were published.⁴⁶ These values of α depended on whether the values of N were used as fit parameters or were constrained to the consensus values, i.e., eq 9. These α values are displayed in Figure 9; the solid circles correspond to using (variable) N as a fit parameter and the solid triangles to fixing $N = 110$. To display both on the same plot, the consensus value is used as the abscissa; a similar plot results from using the SANS-fit values. The solid line is computed from the EMNH in its original form and the dashed line including the dissociated counterions and excluding the co-ions from the computation of the ionic strength. In Figure 9, we see a similar discrepancy between experiment and theory using SANS as in Figure 3 using EPR; i.e., experiment yields constant values of α while the original theory predicts decreasing values as N increases. As Figure 9 makes clear, there is a coupling between the fit values of α and N , so the absolute magnitude depends on the fitting scheme; however, in the two cases depicted, the values of α are constant within experimental uncertainty.

To gain further insight into question of the appropriate ions to include in the computation of the ionic strength, we plot data taken from the literature for S12S in Figure 10. The symbols \times and $+$ are data from two add-salt series holding $[\text{S12S}]$ constant at 25 mM. The circles and squares are two approximately constant C_{aq} series. A plot of these data vs N is given in Figure 5 of ref 13. The abscissa in Figure 10a is computed from eq 2 employing $\alpha = 0.27$ (constant). In Figure 10b the abscissa is computed by using the value of α predicted by a the modified EMNH theory by including the dissociated Na^+ and excluding the Cl^- . Figure 10c is computed using the EMNH in its original form, excluding the dissociated Na^+ and including the Cl^- . While Figure 10a exhibits the best common curve as judged by the deviations from the power law trial function, Figure 10b is certainly satisfactory coming as it does from a simple theory. Figure 10c reiterates the discrepancy between the EMNH and the aggregation number-based definition of α .

Finally, we briefly explore the effect of altering the radius of the charged sphere as originally computed from eq 12. One

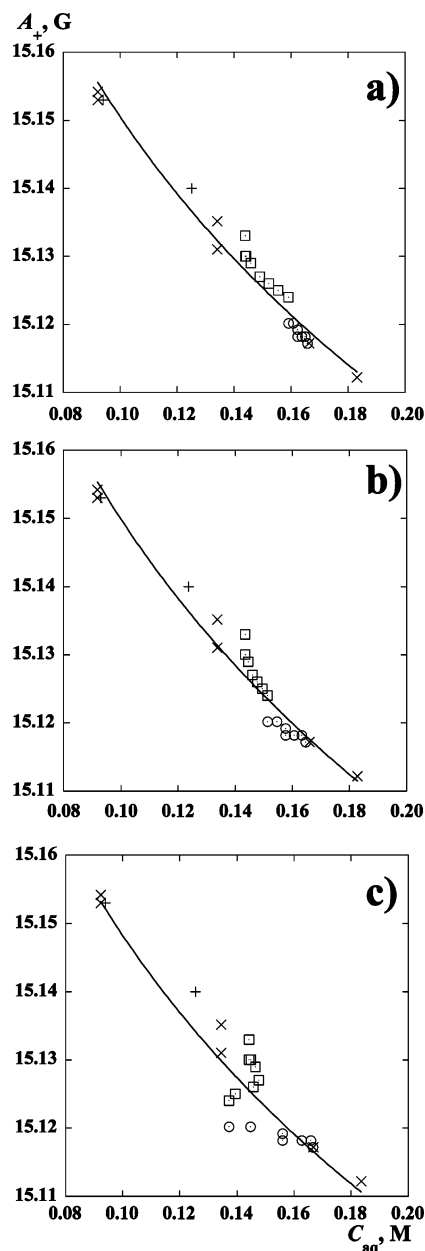


Figure 10. A_+ vs C_{aq} for S12S, 5DSE, 25 °C: C_{aq} was calculated from eq 2 using the following values of α : (a) a constant $\alpha = 0.27$; (b) the value of α calculated by EMNH including the dissociated Na^+ and excluding Cl^- from the computation of the ionic strength; and (c) calculated by EMNH in its original form. Data taken from ref 13.

might question that choice as follows: If we take the surface of the charged sphere to be within the polar shell, then some of the counterions that do not condense onto the surface still remain within the polar shell. One would expect that those counterions remaining within the polar shell would diffuse as a kinetic unit with the micelle and thereby not contribute to the values of α as determined by transport methods. Figure 11 shows the result of moving the surface of the sphere outward by 2 Å (40% of the shell thickness), circles, or inward by 0.5 Å, triangles, for two representative surfactants, S13S and S9S. Taken together, Figures 4 and 10 show that uncertainties in the dielectric constant, and the appropriate radius of the charged sphere can influence the results considerably.

In summary, the EMNH predicts reasonably the magnitude of α , in agreement with experiment, either SANS or the EPR implementation of the aggregation number-based definition. The

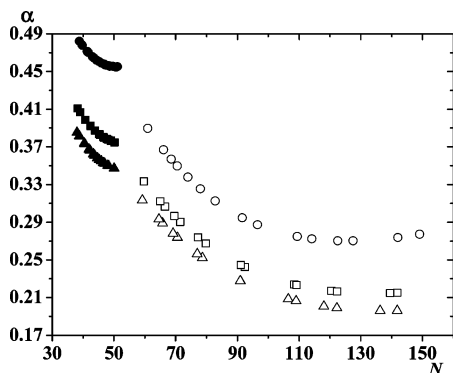


Figure 11. Theoretical values of α for S9S micelles, solid symbols, and S13S, open symbols, using EMNH theory including the Na^+ counterions that are dissociated from the micelle and excluding the co-ions, Cl^- . Placing the surface of the charged sphere in the P–B equation at R given by eq 12; i.e., the surface that divides the polar shell into equal volumes, as suggested by Hayter⁶ (\blacksquare , \square); placing it at $R + 2 \text{ \AA}$, (\bullet , \circ); and at $R - 0.5 \text{ \AA}$, (\blacktriangle , \triangle). The dielectric constants were those of pure water, 78.48 at 25 °C for S9S and 73.17 at 40 °C for S13S, and the thickness of the polar shell was taken to be 5 Å. The abscissa was computed from eq 9 using the theoretical values of α .

double-valued α can be eliminated by changing the composition of the electrolyte bath; however, we have not found a simple explanation for the variation with N . It is important to remember that the methods used to estimate values of α from the two techniques are entirely different. That is, SANS is *not* used to implement eq 8; values of α are derived by fitting scattering profiles.

Validity of N -Based α .³¹ There are several reasons why the aggregation number-based definition of α is of interest.³¹ First, the definition is independent of the experiment technique, not involving a decision on where and for how long the counterions reside. Second, as implemented by EPR, it is an extremely easy experiment. Because of the simplicity of the method, it becomes feasible to investigate large numbers of systems varying a number of experimental parameters such as the temperature, chain length, counterion, and added nonelectrolytes. The EPR technique can be performed using very small amounts of material. A typical sample in this work is of volume 50 μL because 50 μL disposable pipets are used to house the sample; however, this could be easily reduced to 20 μL using the same pipets. The use of flat cells would reduce the requirements further. Thus, for expensive or rare surfactants, quite small amounts of material could be used, the limiting factor being accurate determination of the concentrations. In the EPR approach, one works well above the cmc, so impurities are less of a problem than in techniques working near the cmc. The disadvantage of EPR or any other method employing eqs 5 or 8 is that one cannot evaluate α at surfactant concentrations near the cmc.³¹

The validity of the aggregation number-based definition of α , eqs 5 or 8, rests on two assumptions: (1) that N depends only on C_{aq} at a given temperature, eq 1, and (2) that α depends only on N . Assumption 2 seems to be borne out by the data. Not only is α the same for a given value of N , it appears to be approximately the same for all values of N below the sphere–rod transition. Values of α estimated from fitting SANS profiles are also dependent only on N as can be judged, for example, by a plot of α vs N for S12S taken from Table 2 of Hayter and Penfold⁴⁵ (not shown).

The validity of assumption 1 may be studied directly by methods that measure N or indirectly by those that measure quantities that vary monotonically with N . Thus far, direct

applications of the definition have been limited to TRFQ (this work and refs 16, 19) and SANS.⁴⁶ Although neither of these methods is sufficiently precise to explore whether α is constant or not or to define accurate values of α , they are important to ensure that the more precise, but indirect, methods are valid.

Figure 1 is an example of the direct application of eq 5 to TRFQ measurements of N for S13S. The data follow a satisfactory common curve when plotted vs C_{aq} computed using the average value $\alpha = 0.22$ taken from Table 2. Using eq 9 as the trial function, the minimum deviation of the data from a common curve occurs when $\alpha = 0.20$. Another example of a direct test of assumption 1 is given in Figure 5 of ref 46, showing a satisfactory common curve of N vs C_{aq} for S12S measured with SANS. For the other members of the SN_cS family, less extensive direct data are available in Table 2 of refs 16 and 19 where values of N for a conjugate pair for each surfactant are tabulated. The original pairs were prepared using values of α derived by Huisman from measurements of the cmc vs C_{ad} interpreted from eq 10. Recalculation of values of C_{aq} from the values of α given in Table 1 show only minor changes due to the relatively low surfactant concentrations used in ref 19. Therefore, the fact that the conjugate pairs yielded the same values of N support assumption 1, although again, the precision is not sufficient to provide accurate values of α .

Indirect applications of eq 8, making no assumption whether α is constant, have so far been limited to S12S¹³ and those in Figure 2, both using the property A_+ . Numerous other investigations have supported constant values of α ; thus, applications of eq 5 are likely to be reliable. In the past, these indirect applications have been derived from A_+ , the cloud temperature, and the Krafft temperature.^{47–49} Beyond the results shown in Figures 6 and 7, the quenching rate constants derived from TRFQ and microviscosity measurements measured by EPR have not been exploited to measure α . Unlike N and A_+ , these latter two properties are sensitive functions of temperature, so good temperature control is a requirement for successful implementation of the method.

The Power Law Eq 9 Describes All Members of the SN_cS Family. Micelles of S13S fit the growth law, eq 9, that has been found to describe micelle growth with increasing surfactant and/or salt concentrations in the slow-growth region for dodecyl sulfate micelles with counterions Na^+ ,²⁷ Li^+ ,⁵⁰ tetramethyl-, tetraethyl-, and tetrapropylammonium;³⁰ dodecyltrimethylammonium bromide and chloride;³¹ the sodium alkyl sulfates with chain lengths 8–12, 14,^{19,20} and cetyltrimethylammonium chloride and acetate.⁵¹ The only surfactant that we have studied that did not conform to eq 9 was tetrabutylammonium dodecyl sulfate, which is a very unusual surfactant indeed.⁵²

Conclusions

Application of the aggregation-number based definition of α to SN_cS shows that values of α are constant as a function of N and that they decrease as a function of N_c . Assuming α to be constant as a function of N , this definition was applied to S13S using four different experimental quantities: A_+ , N , the microviscosity, and the quenching rate constant of pyrene by DMBP. All yielded the same value of α within experimental uncertainty. The growth of micelles of S13S induced by increasing the surfactant concentration or by adding salt is described by the power law, eq 9, as are all other members of the SN_cS series, $N_c = 8–14$. The EMNH theory reasonably predicts the magnitude of experimental values of α , whether they are derived from the aggregation number-based definition or from fitting SANS profiles; however, two discrepancies in detail emerge.

The theory predicts (1) double values of α for the same value of N and (2) systematic decreases in α with N . Discrepancy 1 is eliminated by including counterions dissociated from the micelle and excluding co-ions in the computation of the ionic strength. The same expedient reduces discrepancy 2. Altering the position of the effective charged spherical surface and/or the dielectric constant can alter the results of the predictions significantly; however, no simple explanation to remove discrepancy 2 was found.

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