Effect of the Nature of the Counterion on the Properties of Anionic Surfactants. 2. Aggregation Number-Based Micelle Ionization Degrees for Micelles of Tetraalkylammonium Dodecylsulfates

Barney L. Bales,*,† Kaba Tiguida,# and Raoul Zana#

Department of Physics and Astronomy and the Center for Supramolecular Studies,
California State University at Northridge, Northridge, California 91330-8268, and Institut C. Sadron
(ICS–ULP), 6 rue Boussingault, 67000 Strasbourg, France

Tetramethyl-, tetraethyl-, tetrapropyl-, and tetrabutylammonium dodecylsulfate micelles in aqueous solution grow as either the surfactant or added electrolyte concentrations are increased. The variation in the aggregation number, N, of the first three surfactants is described as follows: $N = N^0(C_{aq}/cmc_0)^\gamma$ where N^0 is the aggregation number at the critical micelle concentration in the absence of added electrolyte, cmc_0, C_{aq} is the concentration of counterions in the aqueous phase, and γ is a constant. The values of N^0 are rather small, in the range 54 to 64 at 25°; 61 to 74 at 10°; and 51 to 56 at 40 °C. The values of γ are insensitive to temperature and are rather small; 0.05 to 0.1. In contrast, tetrabutylammonium dodecylsulfate grows nearly linearly with C_{aq}. The ionization degrees (α) of these micelles are studied by applying the hypothesis recently introduced (*J. Phys. Chem. B* **2001**, *105*, 6798) that the aggregation number at a given temperature is determined solely by C_{aq}, whether these counterions are supplied by the surfactant alone or by the surfactant plus added salt with a common counterion. In all cases, the values of α are larger than those obtained at the cmc_0 by conductivity. For comparison, cesium dodecylsulfate is also studied, where we find that α is equal to its value at the cmc_0.

Introduction

Ionic micelles in aqueous solution are known to be charged because a fraction, α, of their counterions dissociate into the aqueous pseudophase. The value of α for a given pure surfactant or a surfactant in the presence of additives[1] is important practically, because both the chemical[2,3] and physical[4,5] properties of the micelle viewed as a microreactor depend on its value. From a theoretical point of view, the value of α, and in particular whether it remains constant as diverse experimental parameters are varied, is particularly interesting.[2,6–10] Experimentally, it is often found[2,11–15] that α remains nearly constant as electrolyte or surfactant concentrations are varied. Theories based on a simple electrostatic view of the micelle surface as an example of a highly charged surface[6,8,9,16] have enjoyed some success because the constancy of α approximately emerges naturally,[6,8,9,16] although some variation in α is still predicted by theory (See the Electrostatic Theory section in the Discussion below). Nevertheless, there are a number of phenomena in micelles and other areas of colloid and interface science where the simple theories are not successful.[17] Even for micelles in which α is found to be constant for a given counterion, the change in the value of α upon substitution of another counterion, outside of indirect effects caused by a change in the aggregation number, cannot be predicted by theory.[17] In essence, the simple theories seem to work when short range, ion specific forces can be neglected. Recently, the inclusion of dispersion forces has been shown[17] to be a promising addition to the simple theories.

This work is part of a program to study the dodecylsulfate (DS⁻) micelle as the counterion is systematically made more bulky and hydrophobic. Part 1[18] of this series outlined the significance and the overall objectives of the work. Here we study tetramethyl-, tetraethyl-, tetrapropyl-, and tetrabutylammonium dodecylsulfate micelles (TMADS, TEADS, TPADS, and TBADS). We apply a new technique[14] to measure α under the assumption that α is constant as a function of the aggregation number. We find that the results are inconsistent with the condition that $\alpha = \alpha^0$, where α^0 is the value measured at the cmc by conductivity. For comparison with SDS and LiDS, we briefly study cesium dodecylsulfate (CsDS) where we do find that $\alpha = \alpha^0 = $ constant for this surfactant as has been found for all other cases studied to date.[13–15]

Materials and Methods

TAADS and CsDS were prepared from a sample of purified SDS by ion exchange as described in Part 1.[18] Salts were purchased in the highest purity available, in every case >98% as follows: CsCl and TMACl (Merck, Germany); TEABr (Aldrich); TEACl·H₂O, TBABr, TBACl, and TPACl (Fluka) and were dried overnight at 50 °C under vacuum before use. The spin probe 16-doxylstearic acid methyl ester (16DSE) was purchased from Adrich and used as received. The EPR sample preparation, data collection, and analysis procedures were identical to those recently detailed.[13]

Theory. *Micelle Ionization Degree.* Recently,[14] a definition of the micelle ionization degree based on the micelle aggregation number (N) was proposed. The fundamental hypothesis is that, at a given temperature, N is uniquely given by the concentration of counterions in the aqueous pseudophase, C_{aq}; that is, $N = N(C_{aq})$. C_{aq} is given by

$$C_{aq} = F(C)\{\alpha C + (1 - \alpha)C_f + C_{ad}\} \tag{1}$$

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* barney.bales@csun.edu.
† California State University at Northridge.
# Institut C. Sadron (ICS–ULP).

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where C, C_f, and C_{ad} are the molar concentrations of total surfactant, surfactant in free monomer form, and added common counterion in the form of salt, respectively. The quantity within the brackets would yield the counterion concentration if the counterions occupied the entire sample. The factor $F(C)$, which corrects this concentration for the volume excluded to the counterions by the micelles, is given by[3]

$$F(C) = \frac{1}{1 - VC} \qquad (2)$$

where V is the molar volume of the anhydrous surfactant in L mol^{-1}. This same factor is used to correct the uniform penetrating background[19] in the Hayter and Penfold approach to fitting small-angle neutron scattering data.[20] See Bales[14] for a detailed discussion of eq 1.

In principle, a value of α is measured by preparing two samples yielding the same value of the aggregation number, but with different values of C and C_{ad}. For these two samples, the hypothesis states that the value of C_{aq} is the same for these two samples. This allows us to write the following:

$$F(C)\{\alpha C + [1 - \alpha]C_f + C_{ad}\} = $$
$$F(C')\{\alpha C' + [1 - \alpha]C_{f'} + C'_{ad}\} \quad (3)$$

The free monomer concentration may be computed using eq 5 of Quina et al.[21] derived from the work of Sasaki et al.[12] and Hall,[22]

$$\log(C_f) = (2 - \alpha)\log(cmc_0) - (1 - \alpha)\log(C_{aq}) \quad (4)$$

where cmc_0 is the critical micelle concentration at $C_{ad} = 0$. Equation 4 shows that, for equal values of C_{aq}, $C_f = C_{f'}$. Now, $F(C) \approx F(C')$ for values of C, $C' < \approx 100-200$ mM, and above these concentrations C_f is small compared with C. In either case the terms involving C_f and $C_{f'}$ cancel in eq 3. Thus for equal values of N, we have

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

In practice, a measurement of α could proceed in various ways depending on whether the aggregation numbers are known and/ or whether the value of α is constant.

Values of N Unknown. Values of N are not needed to apply eq 5. In this case one can proceed directly by rearranging eq 5 to yield the value of α.

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

The experimental challenge in applying eq 6 is to find, by trial and error, pairs of samples that give the same value of N. Any property that varies monotonically with N could, in principle, be used to identify these pairs; however, the relative precision of the technique determines the accuracy of α. It is worth noting that the technique need not yield accurate results as long as it yields *reproducible* results so that different values of N may be distinguished. Supposing one has obtained such pairs, then α can be determined from eq 6. By varying the combinations of C and C_{ad}, α becomes available as a function of C_{aq}. This pairwise approach was carried out by Bales[14] by using an EPR technique that is indirect but shows excellent reproducibility. It was found[14] that α for SDS was constant with respect to C_{aq} over a large range of combinations of C and C_{ad} extending up to quite high surfactant concentrations.
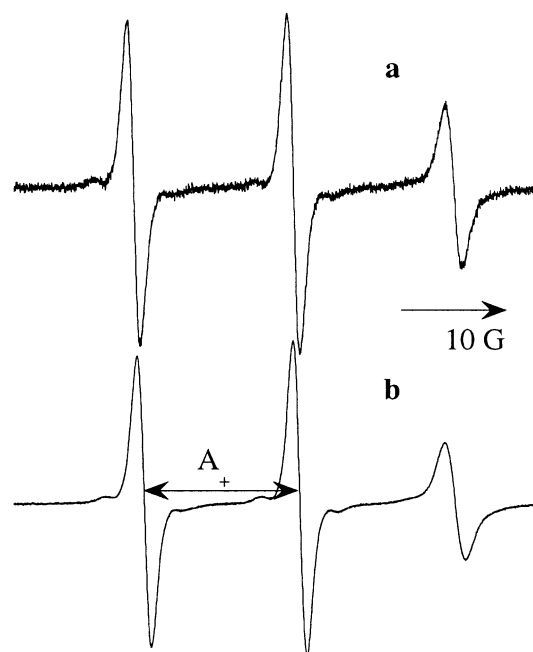

Figure 1. EPR spectra of 16DSE in (a) 25 mM TMADS and in (b) 400 mM TMADS. The receiver gain is a factor of 16 larger in (a) than in (b). The measurement of the hyperfine spacing A_+ is indicated.

EPR Technique to Measure α. A spin probe, sparingly soluble in water, is used in low concentration to report the polarity of its immediate surroundings in a micelle. The polarity is deduced from the experimental value of the nitrogen hyperfine spacing between the low- and center-field lines, A_+. See Figure 1. To apply eq 5 or 6, the only requirement is that the hyperfine spacing depends only on the aggregation number. This is tantamount to assuming that the spin probe reports the same average environment in two micelles if they have the same aggregation number. This has been amply demonstrated[13,14,23,24] and is expected a priori from what is known[25] about the mechanism of the effect of local electric fields on the hyperfine coupling. The only way we can imagine that the hyperfine coupling constant would be different in two micelles of the same size would be if the spin probe senses the nearest neighbor micelles or if the neighbors induced a change in the average location of the spin probe. Both of these possibilities appear to be unlikely in view of our present knowledge. Thus, EPR offers a precise experimental method to determine if two micelles have the same value of N, which permits the determination of values of α from eqs 5 or 6. Nevertheless, even with the excellent precision of the EPR technique, the results are subject to uncertainties due to the lack of statistics when only two samples are compared.

To improve the statistics, we make the reasonable assumption that α is constant. Under this assumption, rather than computing α for one pair of samples at a time using eq 6, a simpler approach that improves the statistics is suggested by eq 5. Equation 5 requires that all values of A_+ fall on a common curve when plotted versus the variable $F(C)\{\alpha C + C_{ad}\}$ constraining α to be constant. This approach has been demonstrated recently.[13]

Values of N Known. If values of N are known as a function of C_{aq}, it may be useful to plot values of A_+ versus N rather than $F(C)\{\alpha C + C_{ad}\}$ in a search for a common curve.

Variation of N with C_{aq}. In 1995 it was recognized[21] that, for SDS micelles, the aggregation number shows a power law dependence on C_{aq} as follows:

$$N = N^0(C_{aq}/cmc_0)^\gamma \qquad (7)$$

where N^0 is the value of N at the cmc_0 and the exponent γ is a constant. Equation 7 holds below values of N where a sphere-rod transition marks the beginning of much faster growth.[26,27] {In earlier papers,[15,21,23,28] eq 7 was written $N = \kappa_2 C_{aq}{}^\gamma$; eq 7 results by defining $N^0 = \kappa_2 (cmc_0)^\gamma$}. Since 1995, eq 7 has been found to be valid for nine other surfactants as follows: the sodium alkyl sulfates with chain lengths 8–14,[29,30] lithium dodecylsulfate,[24] cetyltrimethylammonium chloride and acetate,[31] dodecyltrimethylammonium bromide, and chloride (DTAB and DTAC).[13] We show in this work that TMADS, TEADS, and TPADS also conform to eq 7; interestingly, TBADS does not.

Results

Values of α from EPR Assuming a Constant Value of α. Figure 1 shows EPR spectra of 16DSE in (a) 25 mM and (b) 400 mM TMADS, respectively, in the absence of salt. The measurement of A_+ is indicated. The difference in the values of A_+ is barely perceptible on the scale of Figure 1. However, they are substantially different: $A_+ = 15.121 \pm 0.001$ G for 25 mM and $A_+ = 14.718 \pm 0.0003$ G for 400 mM. The uncertainties are the standard deviations in measurements of five spectra taken one after the other.

Figure 2a shows the variation of A_+ with $F(C)\{\alpha C + C_{ad}\}$ for CsDS at 30 °C where the abscissa is computed by fixing the value of α at $\alpha^0 = 0.18$ taken from Part 1[18] determined at the cmc_0 by the method of Evans.[32] We studied CsDS anticipating that this surfactant might show some interesting departures from the behavior for SDS and LiDS. In Figure 2a, for open symbols, C is varied in the absence of salt and for closed symbols, CsCl is added. For each sample, five points from five successive spectra are plotted, illustrating the reproducibility. The reproducibility of A_+ on a single sample is typically 1 mG while experience has shown[13–15] that discrepancies of about 3 mG can occur in samples presumably prepared identically. Figure 2a shows that, in the case of CsDS, the value of α determined at the cmc from conductivity measurements yields a satisfactory common curve for the EPR results holding $\alpha = \alpha^0$ (constant). If we search for the constant value of α that gives the best common curve, as determined by the minimum squared deviations from a quadratic trial function, we find that $\alpha = 0.20 \pm 0.01$. A value of $\alpha = 0.22 \pm 0.01$ is similarly found at 40°. Figure 2a shows that even with the cation Cs⁺, a constant value of α is obtained in dodecylsulfate micelles as was the case with SDS and LiDS. Figure 2a is the "normal" situation, having been found for several surfactants, using EPR,[13–15] time-resolved fluorescence quenching (TRFQ),[13,15] small-angle neutron scattering (SANS),[15,33] and Krafft temperature.[34] There is already abundant evidence that N depends only on C_{aq} and, in all the cases investigated so far, that α is constant.

However, contrast Figure 2a with Figure 2b representing EPR data on TMADS taken at 25 °C. Here, the value of α was fixed at the conductivity value $\alpha^0 = 0.20$ (value at the cmc) taken from Part 1.[18] Clearly a constant value of $\alpha = \alpha^0$ is unable to reconcile the results in Figure 2b.

Values of N^0 and γ from TRFQ Assuming a Constant Value of $\alpha = \alpha^0$. Figure 3a shows a plot of the aggregation numbers for TMADS taken from Part 1[18] versus C_{aq}/cmc_0 where C_{aq} is computed assuming a constant value[18] of $\alpha = \alpha^0 = 0.20$ The solid line is a least-squares fit of the data to eq 7 yielding $N^0 = 64.7 \pm 1.5$ and $\gamma = 0.111 \pm 0.011$.
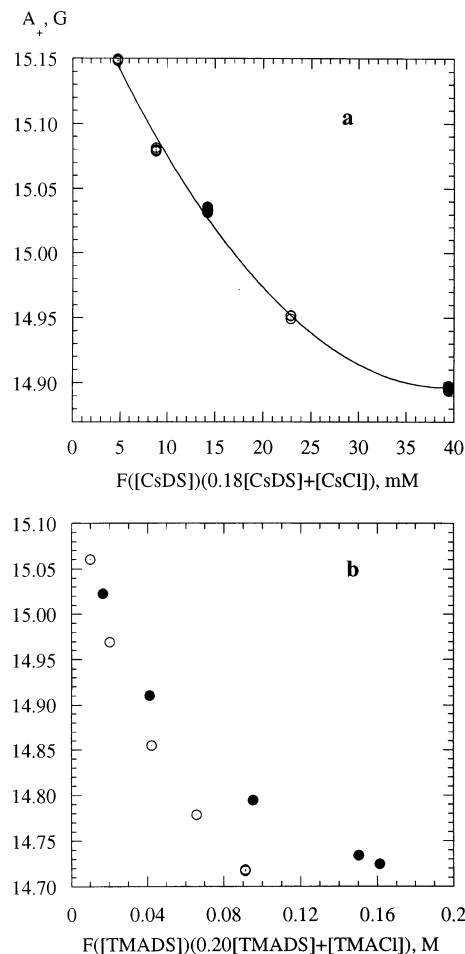

Figure 2. (a) A_+ versus $F(C)(0.18[CsDS] + [CsCl])$ at 30 °C; ○ zero salt; ● CsCl added. The data form a satisfactory common curve holding the value of α fixed at $\alpha^0 = 0.18$ found at the cmc_0 using the method of Evans.[32] (b) A_+ versus $F(C)(0.20[TMADS] + [TMACl])$ at 25 °C; ○ zero salt; ● TMACl added. The data do not form a satisfactory common curve holding the value of α fixed at $\alpha^0 = 0.20$ found at the cmc_0 using the method of Evans.[32]

Values of α from EPR Assuming a Constant Value of $\alpha \neq \alpha^0$. Since the aggregation numbers for TMADS may be described adequately by eq 7, it is convenient to plot the EPR data versus N rather than the variable $F(C)\{\alpha C + C_{ad}\}$ employed in Figure 2. A typical plot is shown in Figure 4a assuming $\alpha = \alpha^0 = 0.20$ (constant) and in Figure 4b after having successfully found a value of α consistent with both the EPR and TRFQ data. A trial value of α is used in eq 1 to compute C_{aq}; N follows from eq 7. One reason to use N as the abscissa in Figure 4 is that the trial function may be taken to be linear. A new assumed value of α is adopted and the whole procedure is repeated until a minimum value of the mean square deviations is found as described in detail in recent publications.[13,15] Since this best value of α is determined using values of N^0 and γ found from TRFQ under a hypothesis of $\alpha = \alpha^0$, the TRFQ data must now be re analyzed using the new value, after which the EPR analysis is repeated. After two iterations, the TRFQ data are shown in Figure 3b; the solid line corresponds to the best fit parameters $\alpha = 0.34$, $N^0 = 61.2 \pm 2.0$, and $\gamma = 0.119 \pm 0.013$. These values in eq 7 change only slightly from the values $N^0 = 64.7 \pm 1.5$ and $\gamma = 0.111 \pm 0.011$ found above using a value of α^0. For TMADS, we cannot distinguish between fits of TRFQ data to eq 7 using α or α^0; however, the EPR values are profoundly affected. The experiment depicted in Figure 4 was repeated two more times at 25 °C starting with

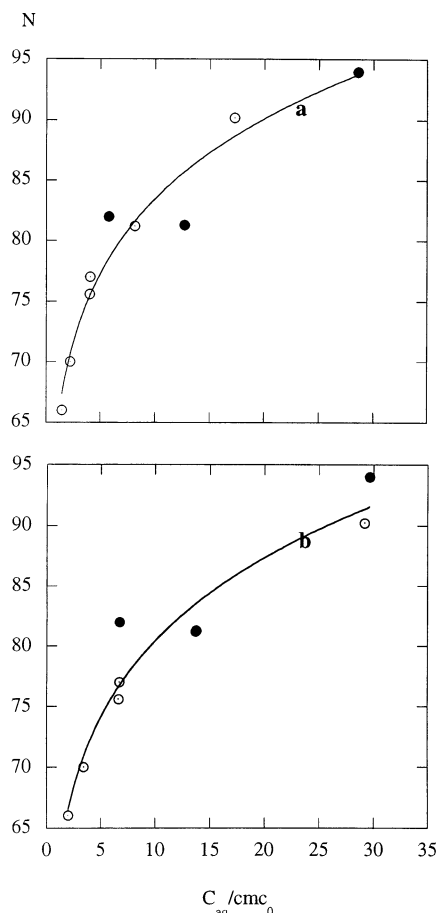Effect of the Nature of the Counterion

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Figure 3. (a) Aggregation numbers of TMADS from TRFQ versus C_{aq}/cmc_0 where C_{aq} is computed from eq 1 using a constant value of $\alpha^0 = 0.20$. (b) Using $\alpha = 0.34$. ○ zero salt; ● TMACl added. Note that the points with and without salt near $N = 82$ are coincident in 3b.
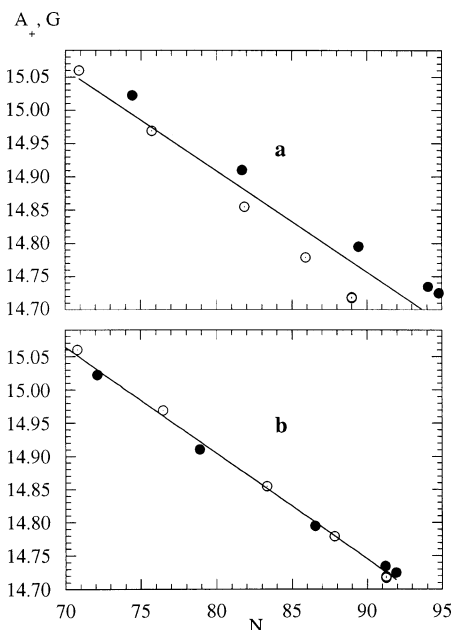

Figure 4. A_+ versus the aggregation number for TMADS computed from eq 7 using (a) constant $\alpha^0 = 0.20$, (b) constant $\alpha = 0.34$. ○ zero salt; ● TMACl added.

fresh samples and different combinations of salt and surfactant concentrations. The results are reported in Tables 1 and 2. The fourth column of Table 2 gives the root-mean-squared deviation of the results from the trial function, $\delta A_{+\text{RMS},}$ which we define

TABLE 1: Critical Micelle Concentrations in the Absence of Salt[a], Degree of Micelle Ionization from Conductivity,[a] and Fit of Aggregation Numbers[a] to Eq 7

	T, °C	cmc_0, mM	α^0	N^0	γ
TMADS	10	5.4	0.20	73.9 ± 1.6^b	0.100 ± 0.009^b
TMADS	25	5.4	0.20	61.2 ± 2.0^b	0.118 ± 0.012^b
TMADS	40	5.7	0.22	55.9 ± 2.7^b	0.101 ± 0.019^b
TEADS	10	3.8	0.20	69 ± 2^b	0.043 ± 0.01^b
TEADS	25	3.7	0.21	62 ± 2^b	0.049 ± 0.01^b
TEADS	40	3.8	0.23	53 ± 3^b	0.08 ± 0.02^b
TPADS	10	2.3	0.19	61 ± 2^b	0.05 ± 0.01^b
TPADS	25	2.2	0.20	54 ± 2^b	0.06 ± 0.01^b
TPADS	40	2.2	0.19	51 ± 3^b	0.05 ± 0.02^b
TBADS	10	1.3	0.19	NA^c	NA^c
TBADS	25	1.15	0.17	NA^c	NA^c

[a] Benrraou et al.[18] [b] Errors are derived in the standard way from the least-squares fits.[43] [c] Not applicable because the aggregation numbers for TBADS do not fit eq 7.

TABLE 2: Values of α Resulting from Fits to EPR an TRFQ

	T, °C	α, EPR	$\delta A_{+\text{RMS}}$, mG	α, TRFQ
TMADS	10	0.32 ± 0.02	4.9	
TMADS	25	0.34 ± 0.01	2.1	
TMADS	25	0.34 ± 0.01	2.9	
TMADS	25	0.31 ± 0.01	2.2	
TMADS	40	0.37 ± 0.02	2.0	
TEADS	10	0.37 ± 0.01	3.0	
TEADS	25	0.44 ± 0.02^a	3.5	
TEADS	25	0.40 ± 0.02^b	2.9	
TEADS	40	0.42 ± 0.02	2.8	
TPADS	25	0.45 ± 0.02	3.4	
TBADS	10	0.30 ± 0.01^c	0.8	0.35 ± 0.05^c
TBADS	25	0.28 ± 0.01^c	0.6	0.27 ± 0.02^c
TBADS	30	0.29 ± 0.01^c	0.6	
TBADS	25	0.33 ± 0.01^d	1.0	

[a] Salt TEABr. [b] Salt TEACl·H_2O. [c] Salt TBACl. [d] Salt TBABr.

to be the square root of $\sum (A_+(j) - A_+)^2$ divided by the number of points, where $A_+(j)$ are the experimental points and A_+ is the corresponding value from the trial function. The resulting values of $\delta A_{+\text{RMS}}$ are near the estimated reproducibility of 3 mG.

One experiment each was carried out with TMADS at 10 °C and 40 °C. Tables 1 and 2 summarize the results. Interestingly, the values of γ do not vary significantly with temperature for TMADS; within experimental uncertainty, all are equal to $\gamma = 0.11 \pm 0.01$. The values of N^0 decrease with increasing temperature as is usual with ionic micelles.[13,35,36]

Results from TEADS and TPADS are very similar to those shown in Figure 4. Self-consistent fits of the aggregation numbers to eq 7 and the EPR results are summarized in Table 2. For TEADS, both TEABr and TEACl·H_2O were used as added salts and yielded similar results (Table 2).

The behavior of TBADS is very different, as may be seen in Figure 5a which shows values of N for TBADS as a function of C_{aq} at 25 °C. In Figure 5a, C_{aq} is computed using $\alpha = \alpha^0 = 0.17$ from conductivity measurements;[18] open and filled symbols are derived from samples without and with added TBACl, respectively. Clearly, a common curve is not achieved holding the value of α constant at its value at the cmc_0. Employing trial constant values of α, a satisfactory common curve is achieved in Figure 5b with $\alpha = 0.27 \pm 0.02$. This best value was determined by finding the minimum least-squares difference of the data with a linear trial function over the range encompassing the salt-added data; that is, $C_{aq}/\text{cmc}_0 = 10$ to 57. We see that for TBADS, unlike TMADS in Figure 3, TRFQ yields definitive values of α from eq 5. Therefore, as with the other members of
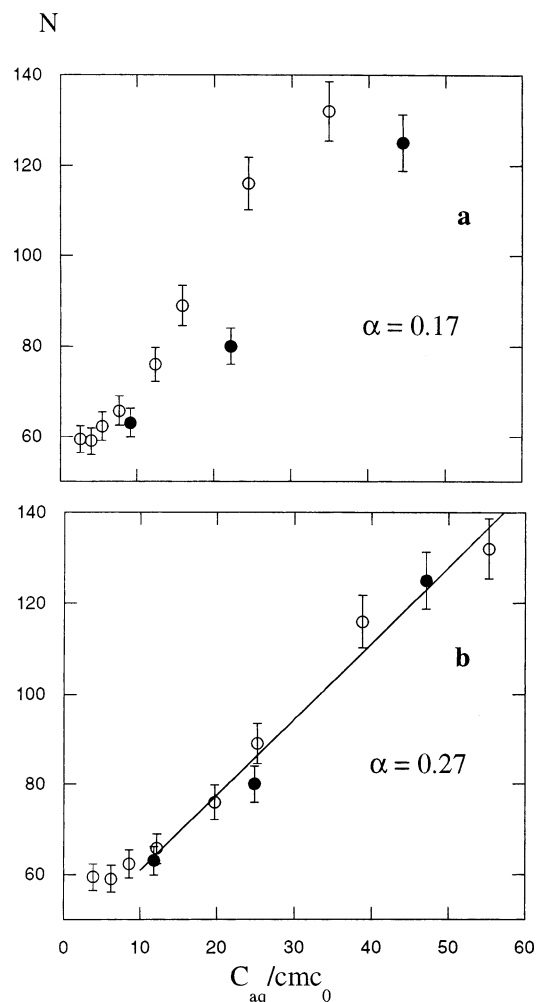
Figure 5. (a) Aggregation numbers of TBADS from TRFQ versus C_{aq}/cmc_0 where C_{aq} is computed from eq 1 using a constant value of $\alpha^0 = 0.17$. (b) Using a constant value of $\alpha = 0.27$. ○ zero salt; ● TBACl added. The error bars indicate a 5% uncertainty.
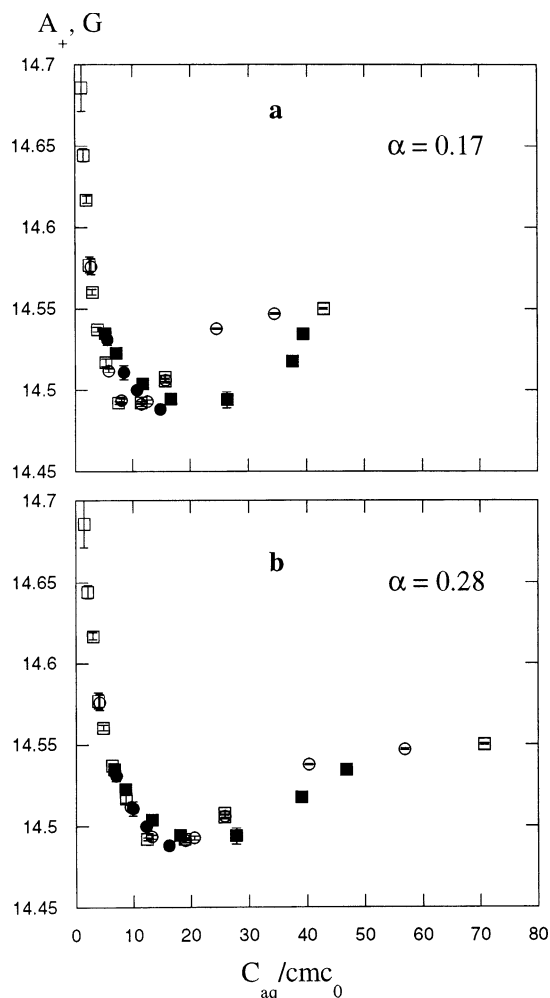

Figure 6. A_+ versus C_{aq}/cmc_0 computed using a constant value of $\alpha^0 = 0.17$ and (b) a constant value of $\alpha = 0.28$. ○ no TBACl; ● TBACl added; □ no TBABr; ■ TBABr added. The error bars are the standard deviations in five spectra. The reproducibility of the results from different sample preparations may be judged by the coincidence of the salt-free data in the two experiments.

the TAADS family, TRFQ shows that holding $\alpha = \alpha^0$ cannot describe the data. The systematics of growth are clearly different. Above values of $C_{aq}/cmc_0 \approx 7 (C_{aq} \approx 0.008$ M) the growth is linear, within experimental error.

Figure 6a shows values of A_+ in TBADS at 25 °C as a function of C_{aq} computed using $\alpha = \alpha^0 = 0.17$ and Figure 6b shows the same data using $\alpha = 0.28$, which was determined to be the best fit of the data for all values less than $C_{aq}/cmc_0 = 18$ for which the values of A_+ are monotonic functions of C_{aq}. The experiment was carried out twice, adding TBACl or TBABr, respectively. The reproducibility of the sample preparation may be judged by the coincidence of the salt-free results in the two experiments. The values of A_+ decrease to a minimum near values of C_{aq}/cmc_0 in the range 15−20 and then show an unprecedented increase. In every ionic surfactant studied to date,[13,23,24] plus TMADS, TEADS, and TPADS in the present work, A_+ has decreased monotonically to high surfactant concentrations. Therefore, EPR, on its own, could not be considered a reliable method to determine values of α because A_+ varies monotonically with C_{aq} over such a limited range. Nevertheless, since the same value of α is determined by EPR and TRFQ, confidence in the EPR method is increased. It is clear that a better common curve over the entire range of C_{aq} is found in Figure 6b than in Figure 6a, even though α was determined using only low values of C_{aq}. This supports the hypothesis that A_+ is the same if N is the same, even if A_+ is

not monotonic with N. Since TRFQ is a direct application of eq 5, the measured property being N itself, the fact that the TRFQ and EPR results are the same lends further support to the assumption that A_+ depends only on N. Applying eq 5 to EPR data at 10 and 30 °C yields the results in Table 2.

Discussion

TAADS Micelle Growth with C_{aq}. Equation 7 describes the aggregation numbers of TMADS micelles as determined by TRFQ with $\gamma = 0.11$ and $N^0 = 74$, 64, and 56 at $T = 10$, 25, and 40 °C respectively in the slow-growth regime, below any possible sphere-rod transition.[13] TMADS is the only surfactant in the TAADS family for which aggregation numbers have been studied in the literature using SANS[37]) at $T = 30$ °C. These are plotted in Figure 7 as a function of C_{aq}/cmc_0. The abscissa is computed from eqs 1 and 7 employing $\alpha = 0.34$. The solid line through the data is an unweighted least-squares fit of the SANS data[37] to eq 7 yielding $N^0 = 73.0 \pm 1.4$ and $\gamma = 0.077 \pm 0.008$ with a correlation coefficient of $r = 0.984$. Plotting the same data versus C_{aq}/cmc_0 assuming a constant value of $\alpha = \alpha^0 = 0.20$ gives a similar plot with $N^0 = 73$, $\gamma = 0.095$, and $r = 0.984$; that is, the plot gives an equally good fit. From these data, there is no means to investigate the value of α since only salt-free samples were studied by SANS.[37] The dashed line in

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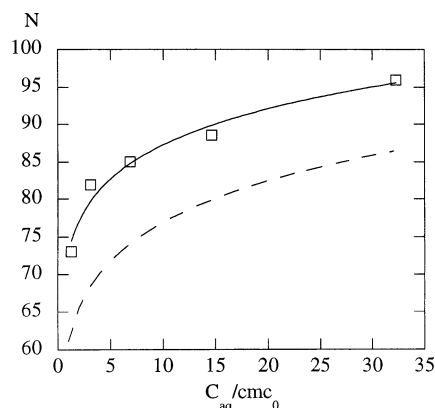*J. Phys. Chem. B, Vol. 108, No. 39, 2004* **14953**

Figure 7. Aggregation numbers[37] of TMADS in D_2O from SANS, 30 °C, □. Solid line is a fit to eq 7 yielding $N^0 = 73$ and $\gamma = 0.077$. Dashed line is the fit to eq 7 for the aggregation numbers in H_2O from TRFQ (this work). Abscissa computed using $\alpha = 0.34$.
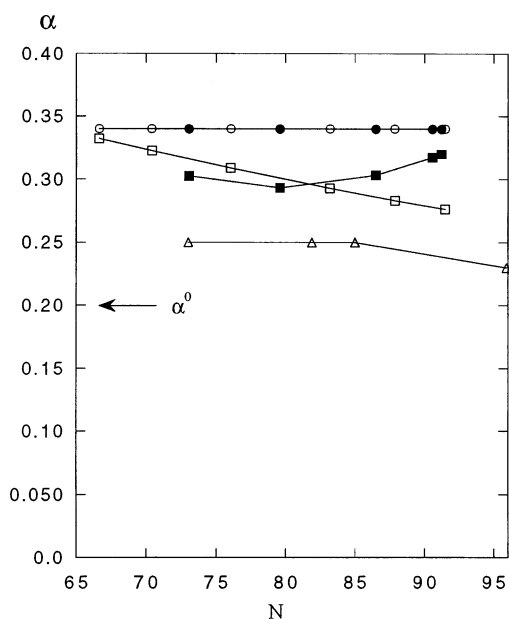

Figure 8. Experimental values of α versus N for TMADS from fits of EPR data assumed to be $\alpha = 0.34$, ○ no TMACl; ● TMACl. Theoretical predictions from electrostatic theory[9] for salt-free, □; and salt-added, ■ samples. The lines through these points are to guide the eye. Values obtained from SANS data,[37] △. These data correspond to the experiment yielding the data in Figure 4, similar plots result for all experiments.

Figure 7 is a plot of the best fit to the TRFQ data at 25°. The functional dependence of the aggregation numbers on C_{aq} using the two experimental methods is similar; however, as is often found to be the case,[13,21,37] the absolute values differ somewhat. We note that in the original publication[37] the SANS data in Figure 7 (see Figure 9 of Berr et al.[37]) were fit to the square root of the surfactant concentration, giving $N = 69 + 43[TMADS]^{1/2}$ with $r = 0.979$, but the same data are better described by eq 7. Experimental values of α may be estimated from SANS experiments;[37] these are plotted (triangles) in Figure 8.

TEADS and TPADS micelles also conform to eq 7. However, much less extensive aggregation number data are available[18] at present, so the parameters in Table 1 ought to be viewed with caution.

In eq 7, the meaning of N^0 is clear. There is a need for a better theoretical understanding of γ. MacKintosh et al.[38] have considered the effect of electrostatics on micelle growth using a sphero-cylindrical model. They properly predict that the micelles grow upon increasing either surfactant or electrolyte concentrations and find that there is a dilute region where the growth proceeds as a power law with an exponent less than 1/2. It is not obvious how γ ought to behave when the counterion is changed while maintaining the amphiphilic ion the same. Until we have a better understanding, we feel that it is important to avoid over interpreting γ. This is particularly so since accurate values of γ are not easy to obtain because they are very sensitive to the values of N at low values of C_{aq}; that is, they are very sensitive at low values of C in the absence of salt. With this caveat in mind, we note that the growth of dodecylsulfate micelles at 25 °C is described by values of γ as follows: 0.25 for SDS;[21] 0.18 for LiDS;[24] and now 0.11 for TMADS, 0.06 for TPADS, and 0.05 for TEADS, respectively.

Applying the Principle of Eq 3 to Obtain the Value of α. The results in Figure 4a for one experiment with TMADS and similar results in other TMADS experiments and in experiments with TEADS, TPADS, and TBADS at various temperatures show that α cannot be equal to α^0, if the fundamental hypothesis

$$N = N(C_{aq}) \text{ only} \tag{8}$$

is true. The hypothesis inherent in eq 8 has been tested with EPR,[13–15] TRFQ,[13,15] SANS,[15,33] and Krafft temperature[34] in a few surfactant systems with hydrophilic counterions. Therefore, the interpretation of the present results in terms of the behavior of α with N must be regarded with caution until eq 8 is more generally tested.

For dodecylsulfate micelles $\alpha = \alpha^0$, where α is defined by hypothesis by eq 8, whether either surfactant or salt concentration is varied with sodium,[14] lithium,[15] and cesium (Figure 2a) as counterions. In contrast with the inorganic counterions, dodecylsulfate micelles with any of the tetraalkylammonium counterions result in a value of α that is larger than α^0. A satisfactory account of the data can be achieved using a constant value of α. The interesting question of how a larger value of α as determined by eq 8 should converge to α^0 led to our investigating a model in which α is fixed to be equal to α^0 at the cmc$_0$ and allowed to vary linearly with N. This model fits the data very well; however, this variation yields an unprecedented *increasing* value of α with N. Thus, in the absence of any corroborating evidence, we do not yet present the results of the model. Should other methods point to such a model, it is important to keep in mind that the present work is also consistent with an increasing value of α.

We can only speculate on the reason that α is larger as determined by eq 8 above the cmc$_0$ than it is at the cmc$_0$ as determined from conductivity. The idea that a second, loosely attached layer of counterions could be responsible for the behavior of TAADS micelles (particularly TBADS) was introduced in Part 1. Such a layer is conceptualized in Figure 9 for the case of TMADS where two TMA$^+$ ions are shown associated with the micelle in a second layer. These would presumably be less mobile than their counterparts that reside in the aqueous phase. In carrying out the conductivity measurements, the ions in the second layer, Figure 9b, would contribute to the current less than those that are not associated with the micelle, Figure 9a. The slope of the conductivity versus surfactant concentration above the cmc$_0$ would be smaller in the scheme suggested in Figure 9 than it would be if all of the TMA$^+$ outside the Stern layer were free in the aqueous pseudophase. In applying Evan's method, the micelle would appear to be less charged (smaller value of α) than it would if only the counterions residing in the Stern layer were regarded
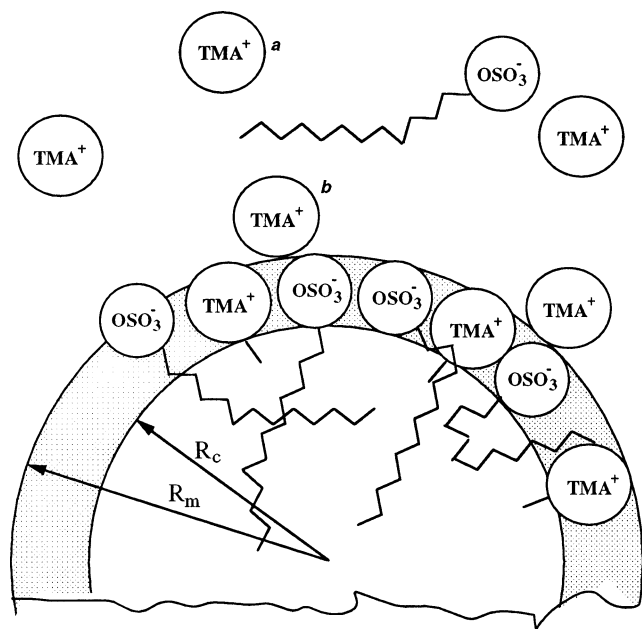
Figure 9. Schematic TMADS micelle drawn approximately to scale with a shell thickness of 0.5 nm. The model envisions possible alkyl chain intrusion into the polar shell due to the fact that the presence of hydrophobic TMA$^+$ counterion makes such intrusions more energetically favorable than in SDS. TMA$^+$ that conducts freely is depicted at (a) while a possible "second layer" of counterions with smaller mobility is suggested at (b).

as being condensed onto the micelle. A larger value of α arising from eq 8 would then be a consequence of including the counterions in the second layer in the accounting of C_{aq} but not in the conductivity. This view is plausible; however, it leads back to the problem that has plagued the determination of values of α over the years.[2] The value that emerges depends on the dividing line between "associated" and "disassociated" counterions.

Electrostatic Theory. To place the experimental results in context, we present the predictions of current electrostatic theory[9] for TMADS. Hayter[9] reported a self-consistent method of solving the Poisson–Boltzmann equation to derive values of α following the general outline of dressed micelles developed earlier by Evans et al.[6] The theory reproduced[9] experimental values of α derived from SANS for SDS quite well. In the calculations, the Debye length, which depends on the ionic strength, is calculated taking into account only C_{ad} and C_f; that is, the counterions dissociated from the micelle [in concentration $\alpha(C - C_f)$] do not enter into the calculations.

Figure 9 gives a schematic representation of the model. The thickness of the polar shell, $t = R_m - R_c$, where R_m is the radius of the micelle and R_c is the radius of the core, is taken to be $t = 0.5$ nm, the value that we have used in the past for SDS,[23] taken from high-resolution SANS.[39] Both the sulfate headgroup and the TMA$^+$ counterion are of similar size, fitting reasonably well within the 0.5 nm. Following Hayter,[9] we place the effective surface of the micelle at a position that divides the polar shell into equal volumes: $d = 0.28$ nm, where d is the distance to the surface from the micelle core. The results are plotted in Figure 8 as squares, filled for samples with added salt and open for salt-free samples. The lines through these points are to guide the eye. The calculations differ slightly from those in Hayter's paper[9] in that the electrolyte concentrations were corrected for the factor $F(C)$ in eq 1, as they should be, and C_f is used rather than cmc$_0$. The electrostatic theory does not account for the size or identity of the counterion directly;

these enter only indirectly through their influence on the values of N. An interesting facet of the theory is that different values of α are predicted for the same value of N if that value is produced with or without added salt. This difference in salt-added versus salt-free behavior is due to the fact that the co-ions (Cl$^-$ or Br$^-$) are included in the Debye screening length while the counterions that are dissociated from the micelle are not. As shown in Figure 8, the electrostatic theory predicts values of α that decrease monotonically with increasing N in the absence of salt while they go through a minimum and then increase with added salt. The experimental values of α derived from SANS are shown in Figure 8 as triangles. For SDS, dodecyltrimethylammonium chloride and bromide, and hexa-decyltrimethylammonium chloride, experimental values of α derived from fitting SANS data are in quite good agreement with the electrostatic predictions.[9] Figure 8 shows there is not as good agreement with theory in the present case; however, it should be noted that a value of α emerges from fitting of SANS data as an adjustable parameter that depends on the model used to separate the form and structure factors[40] and is not necessarily unique. Figure 8 shows that theory predicts values of α that are relatively constant in the case of TMADS; however, there is a definite trend to smaller values at larger values of N. Figure 8 supports the use of a constant value of α in the application of eqs 3 or 5, because both theory and SANS show rather constant values even though the absolute values are somewhat different. Further, the values of α from the present work as well as those from SANS are closer to the theoretical values than is the conductivity value of $\alpha^0 = 0.20$.

The fact that α cannot be equal to α^0 as TAADS micelles grow was deduced by applying the principle that N is uniquely given by C_{aq}. It is important to verify this fact by an independent method both to substantiate the result and to provide further support for the principle of eq 8. An indirect method to study α employing diffusion measurements by NMR as pioneered by Stilbs and Lindman[41] and applied to tetraalkyammonium dode-canoates[42] might be effective.

Search for a Sphere–Rod Transition in TMADS. One experiment was carried out to a high salt concentration, [TMACl] = 1.0 M, in the search for a possible sphere–rod transition in TMADS. The sphere–rod transition in SDS was manifested[23] by a leveling of the value of A_+ near [NaCl] = 0.4 M. The value of A_+ (not shown) decreased monotonically for TMADS over the entire concentration range, thus revealing no such transition. Aggregation numbers at high salt concentrations are not available. If we use the extrapolation of eq 7 to [TMACl] = 1.0 M as a rough guide, a value of $N \sim 110$ is predicted, well below the value of $N = 130$ for the sphere-rod transition in SDS.

Conclusions

Tetraakylammonium dodecylsulfate micelles grow as a power law of the concentration of counterions in the aqueous phase (eq 7) except for TBADS, which grows linearly above C_{aq}/cmc$_0$ ≈ 7. Combining TRFQ and EPR, we find that α measured using the principle that equal concentrations of counterions in the aqueous phase produce equal micelle aggregation numbers is larger than α^0 measured at the cmc using conductivity. The results are in surprisingly good agreement with simple electrostatic theory.

Effect of the Nature of the Counterion

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