Effect of the Nature of the Counterion on the Properties of Anionic Surfactants. 3. Self-Association Behavior of Tetrabutylammonium Dodecyl Sulfate and Tetradecyl Sulfate: Clouding and Micellar Growth

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The surfactants tetrabutylammonium dodecyl sulfate (TBADS) and tetradecyl sulfate (TBATS) have been synthesized by ion-exchange, and their self-association behavior has been investigated. The solutions of these surfactants show clouding and phase separation as the temperature is increased. The clouding temperature T_C of TBADS solutions has been found to be about 4−5 °C higher than for TBATS solutions in the whole range of composition up to a surfactant content of 64 wt %. The critical micellization concentration (cmc) of TBATS has been determined using the electrical conductivity method. The micelle aggregation numbers (N) have been determined using the time-resolved fluorescence quenching (TRFQ) method, with pyrene/dodecyl-pyridinium chloride as fluorescent probe/quencher pair. For the two surfactants, N increases with the surfactant concentration and above a threshold concentration with the temperature. This latter increase as well as the phase separation observed for TBADS and TBATS are very unusual features for ionic surfactants. At temperatures approaching T_C from below, the TRFQ data show evidence of quencher/probe migration between micelles. This process is shown to occur via collisions between micelles. Approximate calculations indicate that the maximum number of TBA$^+$ ions that can be packed at the TBADS micelle surface is smaller than the experimentally determined value of the number of bound TBA$^+$ ions. This result suggests that some bound TBA$^+$ ions must be located in an outer and probably incomplete second layer of bound TBA$^+$ ions. The origin of the attractive intermicellar interaction responsible for the observed phase separation is discussed on the basis of the existence of the second layer of bound TBA$^+$ ions and the capacity of TBA$^+$ ions to self-associate in water.

Introduction

This paper is part of a series that deals with the effect of the nature of the counterion of anionic surfactants on their self-association behavior and micellar properties of anionic micelles viewed as reaction medium. Part 1 in this series reported on the solution behavior and micellar properties of the surfactants SDS, CsDS, TMADS, TEADS, TPADS, and TBADS (sodium, cesium, tetramethyl, tetraethyl, tetrapropyl, and tetrabutylammonium dodecyl sulfates, respectively): critical micellization concentration (cmc), ionization degree (α), and micelle micropolarity, microviscosity, and aggregation number (N).[1] Micelle growth in solutions of tetraalkylammonium dodecyl sulfates (TAADS) upon increasing surfactant or added salt concentration was found to be rather limited despite the lower values of the cmc of TAADS with respect to SDS and CsDS.[1] A peculiar behavior was noted for TBADS, with values of N slightly increasing with, or independent of, temperature at a concentration of 35 mM. Higher concentrations were not investigated.[1]

In part 1, we also reported that TBADS solutions show clouding and phase separation as the temperature is increased.[1] The cloud temperature, T_C, was shown to be a function of the total concentration of TBA$^+$ ions in the aqueous phase, C_{aq},

irrespective of whether these ions originated from the ionization of micelles or from a TBA salt added to the TBADS solution.[2] The values of C_{aq} were calculated using a value of the micelle ionization degree that was quite close to that determined at the cmc, α°,[1] from the analysis of conductivity data using Evans method.[3] The tetrabutylammonium tetradecyl sulfate (TBATS) solutions also show clouding and phase separation upon heating.[4−6] Clouding and phase separation are usually observed with aqueous solutions of the *nonionic* poly(ethylene glycol) monoalkyl ether surfactants C$_m$EO$_n$ (m = alkyl chain carbon number; n = number of ethylene EO oxide units).[7] However, recently, clouding had been reported to occur with solutions of anionic surfactants in the presence of counterions that are large and of hydrophobic character as for instance tetrabutylammonium perfluoroalkanoates,[8,9] mixtures of sodium perfluorooctanoate and tetrapropylammonim bromide,[10] and mixtures of sodium alkyl sulfates (alkyl = octyl to octadecyl) and of tetrabutylammonium or tetrapentylammonium salts.[5,6,11−15] Clouding and phase separation have also been evidenced with solutions of the cationic surfactant erucyl-bis(hydroxyethyl)-methylammonium chloride in the presence of the hydrophobic counterions tosylate or salicylate[16] and with solutions of the cationic surfactants alkyltributylammonium bromides that have a large hydrophobic headgroup.[17−21] However, in contradistinction to these results, no clouding was observed with solutions of tetrabutylammonium dodecanoate[22] and of tetrabutylammo-

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nium tetradecanoate, octadecanoate, docosanoate, and tetracosanoate,[23] up to 98 °C.

Part 2 in this series reported on the growth and ionization of TAADS micelles.[24] The micelle aggregation number of CsDS and TAADS surfactants was found to increase with the counterion concentration in the aqueous phase, C_{aq}, whether the counterions are supplied by the surfactant alone or by the surfactant plus added salt, according to $N = N°(C_{aq}/cmc_0)^\gamma$, where γ is a constant and cmc_0 is the value of the cmc in the absence of added salt.[24] The micelle ionization degree α was determined using EPR probe measurements and a newly introduced hypothesis that the aggregation number is only determined by C_{aq}.[25] For CsDS, the value of α thus obtained agreed with that determined at the cmc from the analysis of conductivity data using Evans' method.[3] For all TAADS surfactants, the EPR method led to values of α larger than Evans' method. A possible reason for the observed difference is the crowding of the large TAA^+ ions at the surface of the dodecyl sulfate micelles.[1,24] The conductivity and EPR methods may also weigh the free and bound TBA^+ ions differently resulting in apparent differences in micelle ionization degree.[24]

Results reported for TBADS[1,24] and TBATS[4] show that the micelles of these two surfactants are still charged and of finite size up to a temperature only 0.5 °C below T_C. An attractive interaction between micelles that overcomes the electrostatic repulsion at high temperature must therefore exist for the phase separation to take place.

The peculiar behavior of TBADS noted in parts 1 and 2 led us to undertake a study of the effects of temperature on the self-association behavior and micellar properties of TBADS in aqueous solution in a large range of TBADS concentration. For the sake of comparison, measurements were also performed on the longer homologue TBATS. This surfactant has been shown to form elongated micelles at sufficiently high surfactant concentration and temperature.[5] The present study used essentially the time-resolved-fluorescence quenching (TRFQ) method for the determination of the values of the micelle aggregation number N. Our main purpose was to bring additional results characterizing the self-association behavior of TBADS and TBATS and to investigate further the still unclear origin of the attractive intermicellar interaction responsible for the phase separation.

At this stage, it is recalled that the TBA^+ ion is clearly hydrophobic. The literature reports evidence of TBA^+ self-association in aqueous solutions of TBA salts,[26-30] with an onset of association at around 0.8 M,[27] irrespective of the counterion (Cl$^-$ or Br$^-$). Besides, aqueous solutions of TBA salts have been reported to give rise to a microemulsion-like phase upon addition of benzene.[31]

Experimental Section

Materials. TBADS was synthesized by ion-exchange, starting from a solution of purified sodium dodecyl sulfate (SDS) as previously described.[1] At room-temperature TBADS is a colorless viscous liquid that does not crystallize even after over two years at 2 °C. TBATS was synthesized by neutralization of tetradecylsulfuric acid by tetrabutylammonium hydroxide (TBAOH, from Fluka, *purissimum* grade) under a nitrogen atmosphere. The tetradecylsulfuric acid was obtained by passage of a relatively dilute solution of sodium tetradecyl sulfate (from Fluka, purity > 98%) through a column filled with a strong cation-exchange resin (Merck, type I) in the protonated form. It was reacted with TBAOH as it came out of the ion-exchange column in order to avoid a possible acid hydrolysis. The

neutralization was monitored by measuring the pH. The resulting aqueous TBATS solution was freeze-dried, yielding a pale yellow viscous liquid at room temperature. It turned into a solid when maintained at 2 °C for about two weeks. Both TBADS and TBATS were stored in the dark at 2 °C in flasks protected from ambient moisture. TBADS was miscible in water up to the highest concentration tested in this work, about 64 wt %. The solubility of TBATS in water has been reported to be extremely high.[4] However, TBADS/water and TBATS/water mixtures showed clouding and phase separation upon heating (see below).[1,2,4]

The samples of pyrene and of dodecyl and tetradecyl pyridinium chloride (DPyCl and TPyCl, respectively) used in TRFQ studies were the same as in previous investigations.[32,33] Tetrabutylammonium chloride (TBACl, from Fluka) was dried before use at 40 °C, under vacuum and in the presence of phosphorus pentoxide.

The preparation of the solutions for TRFQ studies has been described.[1]

Methods. The cloud temperature, T_C, was obtained visually. The aqueous solutions of TBADS were contained in a small vial immersed in a temperature-controlled water bath. Clouding of solutions with TBADS content above 2 wt % was extremely sharp, occurring within 0.1 °C, and reproducible (indicating no significant evolution of the surfactant). The same value of T_C was measured upon increasing or lowering the temperature, provided that the temperature was varied slowly enough, indicating no hysteresis in the clouding phenomenon.

The micelle aggregation number (N) was determined using the TRFQ method[34-39] with pyrene as the fluorescent probe and DPyCl or TPyCl as quencher.[1,32,33] For solutions with concentrations up to 35 mM, the aggregation number was calculated using eq 4 in ref 1. For more concentrated solutions, the slope of the long time part of the fluorescence decay curve was found to be larger in the presence than in the absence of quencher, starting at a temperature that decreased upon increasing concentration. This behavior indicated the occurrence of a redistribution of the probe/quencher among micelles (migration) during the pyrene fluorescence lifetime.[34-39] The values of the aggregation number and of the pseudo first-order rate constants for intramicellar quenching, k_Q, and intermicellar migration, k_m, were obtained using the equations[37-39]

$$N = A_3\{(C - C_{free})/[Q]\}(1 + x)^2 \quad (1)$$

$$k_Q = A_4/(1 + x) \quad (2)$$

$$k_m = A_4 - k_Q \quad (3)$$

$$x = (A_2 - 1/\tau)/A_3 A_4 \quad (4)$$

In eqs 1–4, A_2, A_3, and A_4 are the parameters obtained from the fitting of the fluorescence decay eq 5 to the decay curve determined in the presence of quencher. C and $[Q]$ are the surfactant and quencher concentrations, respectively. The pyrene fluorescence lifetime in the micelles, τ, is determined from the fitting of eq 6 to the decay curve determined in the absence of quencher. Equations 1–4 were readily obtained from the reported expressions of A_2, A_3, and A_4.[34-39] In eq 1, C_{free} is the concentration of free surfactant. At each surfactant concentration, C_{free} is obtained by solving eq 7,[40,41] where C_{aq} is the total counterion concentration in the aqueous phase, given by eq 8. C_{ad} is the concentration of added common counterion and V is the molar volume of the anhydrous surfactant in L/mol. The density of the TBADS is taken equal to 1.0 g/mL. C_{free} is
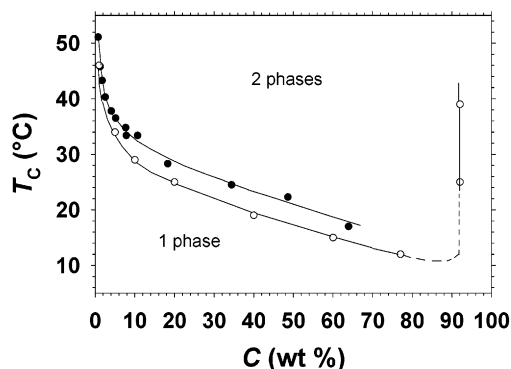
Figure 1. Variation of the cloud temperature T_C of TBADS (●) and TBATS (○) solutions with the surfactant concentration in wt %.

calculated after having determined the value of α but is not very sensitive to errors in this value. In eqs 5 and 6, I(t) and I(0) are the fluorescence intensities at time t and zero

$$I(t) = I(0) \exp\{-A_2 t - A_3[1 - \exp(-A_4 t)]\} \qquad (5)$$

$$I(t) = I(0) \exp(-t/\tau) \qquad (6)$$

$$\log C_{\text{free}} = (2 - \alpha) \log \text{cmc} - (1 - \alpha) \log C_{\text{aq}} \qquad (7)$$

$$C_{\text{aq}} = [\alpha C + (1 - \alpha)C_{\text{free}} + C_{\text{ad}}]/(1 - VC) \qquad (8)$$

The measurements of micelle aggregation number for TBADS were performed on solutions with concentration ranging between 15 and 210 mM, and in the temperature range from 10 to 40 °C for the solutions with cloud temperature $T_C > 40$ °C ($C \leq$ 50 mM) and between 10 °C and a temperature 0.5–1 °C below T_C for solutions with $T_C < 40$ °C ($C \geq 80$ mM). Some measurements were performed in the presence of added TBACl. For TBATS, the measurements were performed at only two concentrations up to a temperature 0.2 °C below T_C for the most concentrated solution.

Results

Clouding in TBADS Solutions. Figure 1 shows the variation of the cloud temperature (T_C) of TBADS solutions with the surfactant concentration expressed in weight percent (a concentration of 10 wt % corresponds to about 200 mM). For the sake of comparison, Figure 1 also shows the U-shaped cloud curve reported for TBATS.[4] The two curves run parallel, the curve for TBATS being shifted to lower temperatures by a constant 4–5 °C in the whole concentration range. The shape of these curves differ very much from those reported for the nonionic $C_m EO_n$ surfactants where a marked minimum occurs at a rather low surfactant concentration, usually below 5 wt % for a surfactant with a dodecyl chain.[7] This minimum defines the critical concentration and the critical temperature of the investigated $C_m EO_n$ surfactant.[7] The cloud curve for TBATS suggests that T_C is a minimum at about 80 wt %. Thus, the critical concentration in the TBATS/water mixture, if the minimum corresponds to a critical concentration, would be more than 1 order of magnitude larger than for $C_m EO_n$ surfactants. Above T_C, TBADS solutions separate into two liquid phases, a behavior similar to that reported for TBATS solutions.[4] For TBATS, Figure 1 shows that one liquid phase has a nearly constant composition, with about 92 wt % surfactant. The surfactant content of the second phase is fairly large. All of these results strongly differentiate clouding in TBA alkyl sulfate and in $C_m EO_n$ solutions. The cloud curves for TBADS and

TBATS resemble much those reported for the alkyltributylammonium bromide surfactants.[17–19,21] For both types of solutions, the cloud curve is U-shaped and presents a minimum at a fairly high surfactant concentration and T_C increases very rapidly at concentrations above this value. For instance, for the dodecyltributylammonium bromide surfactant, T_C is a minimum at about 63 wt % and increases very rapidly at concentrations above about 65 wt %.[17]

The cloud temperature of the TBADS solution decreases upon addition of TBACl.[2] This behavior indicates that the attractive intermicellar interaction responsible for the phase separation increases with the TBACl content. Recall that additions of salts to solutions of $C_m EO_n$ surfactants result in an increase or decrease of T_C depending on whether the added salt has a salting-in or salting-out effect on the surfactant.[42,43] We have shown elsewhere that the values of T_C for TBADS in the presence and absence of TBACl fall on a single curve when plotted as a function of the total counterion concentration in the aqueous phase, C_{aq}, given by eq 8.[2] This behavior is similar to the variations of the micelle aggregation number of various surfactants[44–47] and of the Krafft temperature of CsDS[48] in the absence and presence of added salt with the same counterion as the surfactant, when plotted against C_{aq}. The Krafft temperatures of sodium dodecyl sulfate and dodecyltrimethylammonium bromide also fit this scheme.[49]

cmc and Micelle Ionization Degree at the cmc. The values of the cmc of TBADS and of the micelle ionization degree at the cmc (α^0) have been reported in part 1.[1] The cmc value was found to be around 1 mM and varied little with the temperature T in the range 10–40 °C. The ionization degree at the cmc, as obtained from the analysis of the conductivity data on the basis of Evans' equation,[3] was around 0.18. It decreased very slightly upon increasing T, whereas it increased with T for all other ionic surfactants investigated, including the other TAADS surfactants.[1]

The cmc of TBATS measured by electrical conductivity was found to be 0.260 mM at 25 °C. This value compares well with the values 0.260 and 0.256 mM obtained at 20 and 40 °C from surface tension measurements.[4]

Micelle Polarity. The micelle polarity has been investigated by measuring the ratio I_1/I_3 of the intensities of the first and third vibronic peaks in the fluorescence emission spectra of pyrene. Recall that a larger value of this ratio reflects a larger polarity of the pyrene microenvironment.[36] The values of I_1/I_3 in TBADS and TBATS micelles at 25 °C are listed in Tables 1 and 2. The value of I_1/I_3 for TBADS is seen to be independent of both C and C_{ad} within the experimental error. The value of I_1/I_3 is lower in TBATS than in TBADS micelles. A similar decrease of I_1/I_3 upon increasing surfactant chain length has been noted for other surfactants series.[50] It probably reflects a lower polarity of the pyrene solubilization site (micelle palisade layer) resulting from the tighter packing of the surfactant with the longer alkyl chain.

For the sake of comparison, Table 3 lists the I_1/I_3 values for SDS, CsDS, and the four TAADS investigated to date. The values of I_1/I_3 are nearly the same for CsDS and SDS and clearly smaller than for the four TAADS surfactants. I_1/I_3 is a maximum for TEADS. Pyrene apparently senses a higher polarity in dodecyl sulfate micelles with *less* hydrophilic (TMA$^+$ and, even more so, TEA$^+$) or hydrophobic counterions (TPA$^+$ and TBA$^+$) than in dodecyl sulfate micelles with *strongly* hydrophilic counterions such as Na$^+$ or Cs$^+$. As discussed in part 1,[1] this result suggests that pyrene may be located closer to the surface of TAADS micelles than of SDS or CsDS micelles, owing to the attractive interaction known to occur between the π-electron

TABLE 1: TBADS: Values of I_1/I_3, Pyrene Lifetime in the Absence (τ) and Presence ($1/A_2$) of Quencher, Micelle Aggregation Number, and Intramicellar Quenching Rate Constant k_Q[a]

C (mM)	C_{ad} (M)	T (°C)	I_1/I_3	τ (ns)	$1/A_2$ (ns)	N	$10^{-7} \times k_Q$ (s^{-1})
14.9	0	10			386.4	61	0.76
C_{free} = 0.81 mM	0	25	1.37		367.4	58	1.41
	0	40			340.3	55	2.37
25.3	0	10			396.0	64	0.70
C_{free} = 0.58 mM	0	25	1.38		365.3	58	1.39
	0	40			342.1	58	2.25
35.0	0	10			388.2	64	0.73
C_{free} = 0.46 mM	0	25			364.4	62	1.36
	0	40			336.6	62	2.00
50.0	0	10		385	392.9	68	0.71
C_{free} = 0.35 mM	0	25	1.36	357.1	366.0	66	1.24
	0	40		345	326.7	75	1.51
80.1	0	10		379.6	386.9	68	0.71
C_{free} = 0.24 mM	0	25		357.1	350.0	76	0.98
	0	30		352	326.0	85	0.96
	0	35		348	303.4	95	0.92
	0	37		345	297.8	100	0.90
101.6	0	10		379.6	384.8	70	0.65
C_{free} = 0.20 mM	0	17		367	358.4	72	0.80
	0	25		357.1	317.9	89	0.80
	0	30		352	299.5	103	0.72
	0	35		348	279.0	117	0.69
152.4	0	10		387.0	376.2	75	0.59
C_{free} = 0.14 mM	0	17		378.1	343.4	92	0.54
	0	25	1.36	365.3	307.1	116	0.51
	0	30		359.0	284.7	132	0.49
	0	34		351.5	268.2	144	0.49
210	0	10		383.6	348.5	88	0.47
C_{free} = 0.11 mM	0	17		378.4	318.5	112	0.42
	0	25	1.38	361.4	276.8	133	0.43
	0	33		350.1	239.8	159	0.43
30.6	0.04504	10			374.7	78	0.66
C_{free} = 0.082 mM	0.04504	25	1.39		304.8	125	0.56
30.6	0.0200	10			389.7	69	0.64
C_{free} = 0.14 mM	0.0200	25	1.38		336.8	80	0.92
30.6	0.00497	10			394.6	65	0.67
C_{free} = 0.30 mM	0.00497	25	1.38		362.5	63	1.32
	0.00497	39			332.3	70	1.53

[a] Quencher: dodecylpyridinium chloride.

TABLE 2: TBATS: Values of the Pyrene Lifetime in the Absence (τ) and Presence ($1/A_2$) of Quencher, Micelle Aggregation Number, and Intramicellar Quenching Rate Constant k_Q

C (mM)	T (°C)	quencher	I_1/I_3	τ (ns)	$1/A_2$ (ns)	N	$10^{-7} \times k_Q$ (s^{-1})
37.07	9.9	DPyCl			390	82	0.44
37.07	25.2	DPyCl	1.32		369	89	0.77
37.07	41.2	DPyCl			325	119	0.96
37.07	43.6[a]	DPyCl			315	127	1.0
75.58	9.9	DPyCl		392	386	87	0.44
75.58	25.2	DPyCl	1.31	368	336	122	0.46
75.58	39.7[b]	DPyCl		345	285	180	0.43
78	25.2	TPyCl			338	127	0.43
78	39.5	TPyCl			286	188	0.38

[a] In the presence of quencher T_C = 43.8 °C. [b] In the presence of quencher T_C = 40.3 °C.

cloud surrounding pyrene and the positive charge of the quaternary ammonium ions.[51,52,53] Note that the I_1/I_3 values found for the micelles of the cationic tetradecyltrialkylammonium bromide surfactants are also quite high,[54] probably for the same reason. The lower I_1/I_3 values found for micelles with the more hydrophobic counterions TPA$^+$ and TBA$^+$ with respect to micelles with TEA$^+$ counterions may reflect a partial penetration of one or more of the alkyl chains of the TPA$^+$ and

TABLE 3: Values of I_1/I_3 for Dodecyl Sulfate Surfactants

surfactant	SDS	CsDS	TMADS	TEADS	TPADS	TBADS
I_1/I_3[a]	1.18	1.17	1.34	1.47	1.40	1.36

[a] Values at a concentration of 100 mM and 25 °C, except for CsDS at 30 °C.
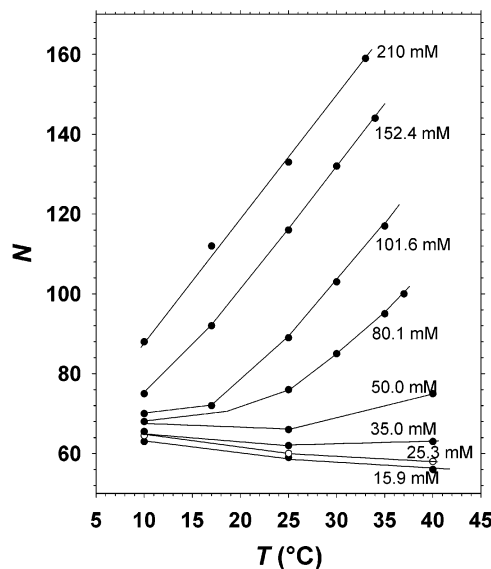
Figure 2. Temperature dependence of the aggregation number of TBADS micelles. The surfactant concentration is indicated on each plot. The solid lines are guides to the eye.

TBA$^+$ counterions into micelles, as discussed in part 1.[1] This effect would render the pyrene solubilization site less polar and may also move pyrene to a time-average site a bit deeper and thus less polar in the micelle. Also the pyrene/quaternary ammonium ion interaction may be weakened because the longer alkyl chains of the TPA$^+$ and TBA$^+$ ions prevent a close approach of the pyrene to the charged nitrogen atom.

Micelle Aggregation Number. The values of C_{free}, required for the calculation of the values of N on the basis of eq 1, were computed iteratively at 25 °C using eq 7.[1] They are given in Table 1 at each TBADS concentration investigated. The values of N listed in Table 1 all correspond to $C \gg C_{free}$, and errors in α and C_{free} had very little impact on these values. This permitted the use of the same values of C_{free} at all temperatures. For TBATS, the free surfactant concentration is even smaller than for TBADS and was neglected in calculating the N values listed in Table 2. The overall error on N, estimated to be about 5%, mostly arises from the fluorescence decay experiments and the data analysis.

Figure 2 shows the variation of N with T at different TBADS concentrations. The corresponding variations of the intramicellar quenching rate constant k_Q are represented in Figure 3. The plots in Figure 2 are seen to all extrapolate to the same value of about 65–70 at 5 °C. This value is only slightly larger than for the maximum spherical micelle formed by a surfactant with a dodecyl chain (about 60). The k_Q vs T plots also all extrapolate to the same value of about 6 × 10^6 s^{-1} at 5 °C.

Clear trends are seen in Figures 2 and 3 as T and C are increased. Thus, in the whole T-range, N increases with C. At low C, between 15 and 35 mM, N decreases and k_Q increases upon increasing T, a behavior similar to that reported for ionic surfactants.[55,56] At the intermediate concentrations 80.1 and 102 mM, N increases with T first slowly at low T then more rapidly and almost linearly at higher T. For these concentrations k_Q goes through a maximum, a behavior already noted for C_mEO_n

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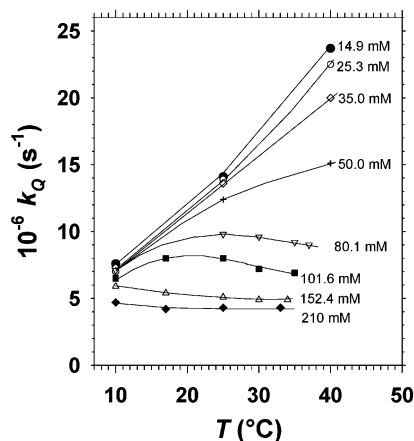*J. Phys. Chem. B, Vol. 108, No. 47, 2004* **18199**

Figure 3. Temperature dependence of the quenching rate constant of pyrene by dodecylpyridinium chloride in TBADS micelles. The surfactant concentration is indicated on each plot. The solid lines are guides to the eye.

surfactants when measurements are performed over a sufficiently large T range.[57,58,59,60] For C_mEO_n surfactants, the maximum in k_Q results from two opposite effects: the normal increase of k_Q with T and the increase of N with T that decreases k_Q.[57-60] The second effect becomes predominant at high T. For TBADS, at high C, in the range 150−210 mM, N increases almost linearly with T and the variation of k_Q with T is then dominated by this effect.

For the 101, 152, and 210 mM solutions, the highest temperature at which N was measured was only 0.5−1 °C below T_C. The plots in Figures 2 and 3 show no peculiar behavior of N and k_Q at the approach of the cloud temperature of the investigated solutions, indicating that there is no additional rapid growth associated with this approach. The micelles retain a finite size up to a temperature very close to T_C.

The values of N in the investigated T-range and at concentrations up to 80 mM are close to that for the maximum spherical micelle formed by a surfactant with a dodecyl chain, i.e., about 60. This remains true at higher C, up to 100 mM at relatively low temperature. At higher C and T, the values of N are well above 60 indicating that the micelles are probably no longer spherical.

The concentration-dependence of the product Nk_Q (not shown), which is inversely proportional to the micelle microviscosity,[61] supports this conclusion. At a given temperature, Nk_Q remains about constant as long as N has a value close to that for spherical micelles, then decreases; that is, the micelle microviscosity increases, at higher C, where the micelles are no longer spherical. The decrease of Nk_Q occurs at an increasingly lower T as C is increased. The increase of micelle microviscosity when one goes from spherical to elongated micelles is well documented.[62-64]

The effect of TBACl additions on the aggregation number of TBADS micelles at a surfactant concentration of 30.6 mM has been investigated. The results are summarized in the last three entries in Table 1. The aggregation number is increased by additions of TBACl. A similar behavior has been reported with other ionic surfactants.[55,65,66]

The behavior of TBATS micelles has been found to be qualitatively similar to that for TBADS, with larger values of N and lower values of k_Q for given values of C and T (see Table 2). Figure 4 shows that N increases with T, the more so the higher the surfactant concentration. As for TBADS, the two N vs T plots extrapolate at low temperature to the same value N = 85. This value is only slightly larger than for the maximum
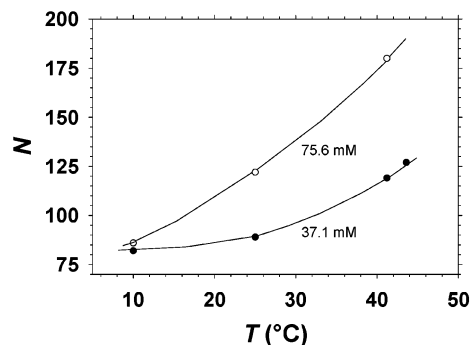

Figure 4. Temperature dependence of the aggregation number of TBATS micelles. The surfactant concentration is indicated on each plot. The solid lines are guides to the eye.
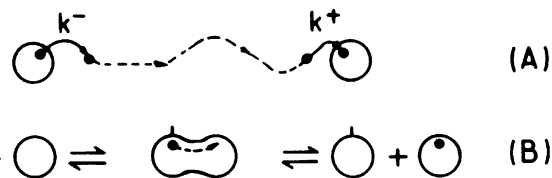

Figure 5. Possible mechanisms of probe/quencher migration between micelles.

spherical micelle formed by a surfactant with a tetradecyl chain, about 73. The TBATS micelles are thus expected to be spherical at low temperature and anisotropic at high temperature. Note that the fitting of eq 5 (valid for monodisperse micelles) to the fluorescence decay curves recorded for the determination of the values of N showed at 40 °C systematic deviations typical of polydisperse systems.[67]

Intermicellar Migration. At high concentration and sufficiently high temperature, the slope of the long time part of the decay curve in the absence of quencher yielded a value of the pyrene fluorescence lifetime, τ, that was larger than the apparent lifetime measured in the presence of quencher, $1/A_2$ (see Tables 1 and 2). This indicated that a redistribution of the probe and/or quencher occurred on the fluorescence time scale.[34-39] Fast probe/quencher redistribution can occur by two rather different mechanisms. In the first mechanism, the quencher present in a micelle exits from this micelle and associates to another micelle after diffusing in the intermicellar solution (see Figure 5, process A).[34-39] Pyrene redistribution is not considered in this mechanism because the pyrene residence time in micelles is much longer than the fluorescence lifetime.[68] The second mechanism involves collisions between micelles that set the micelle cores in contact or bring about a temporary merging of the collided micelles (referred to as *sticky* collisions below; see Figure 5 process B).[57-60,69,70] The pseudo first-order rate constant for migration, k_m, is given by eq 3.[34-39] These two mechanisms of intermicellar migration are characterized by very different variations of k_m on the micelle concentration [M] and the carbon number m of the alkylpyridinium quencher.[34-39] For the first mechanism, $k_m = k^-$, rate constant for the exit of the quencher from the micelle.[34-39] Thus, $A_4 - k_Q$ would be independent of [M] but would decrease rapidly upon increasing m. Indeed, the rate constant for the exit of a surfactant (including alkylpyridinium chlorides) from a micelle decreases exponentially upon increasing m.[71] For the second mechanism $k_m = k_c$ [M],[39] where k_c is the second-order rate constant for sticky collisions between micelles. $A_4 - k_Q$ would thus be independent of m and increase linearly with [M].[39,57]

In the present study, a choice between these two mechanisms was achieved by substituting the DPyCl quencher used in most

TABLE 4: Values of the Second Order Rate Constant for Sticky Micellar Collisions and of the Parameters Used in the Calculations

T (°C)	C (mM)	N	[M] (mM)	x	$10^{-6} \times A_4$ (s^{-1})	$10^{-8} \times k_c$ ($M^{-1}s^{-1}$)
30	101.6	103	0.982	0.055	7.55	4.0
30	152.4	132	1.15	0.125	5.46	5.3
30^a	210	149	1.41	0.21	5.22	6.4
33	210	158	1.32	0.238	5.30	7.7
34	152.4	144	1.06	0.141	5.59	6.5
35	101.6	117	0.87	0.072	7.44	5.7

^{a} Interpolated values.

of the reported experiments by the TPyCl quencher in experiments with TBATS, using nearly the same surfactant, pyrene, and quencher concentrations. The value of k^- for TPyCl is expected to be about 10 times lower than for DPyCl,[71] and should the second migration mechanism prevail, this would result in a significant difference in the values of A_2 and A_4 measured with the two quenchers. The values of A_2 remained nearly the same with the two quenchers (see Table 2). The value of A_4 was slightly smaller with TPyCl because quenching is somewhat slower than with the shorter chain DPyCl. Thus, probe/quencher intermicellar migration essentially occurs through collisions between micelles. The occurrence of such collisions suggests that the interaction between micelles must be attractive. This conclusion should not come as a surprise because the phase separation occurring at high temperature in TBADS and TBATS solutions would not take place in the absence of attractive intermicellar interactions since the micelles remain of finite size and electrically charged even at temperatures very close to T_C.[1,4] Recall that sticky intermicellar collisions have been reported to occur in micellar solutions of C_mEO_n surfactants when the temperature is in the range $T_C - 30 < T < T_C$.[57-60] Probe/quencher redistribution has been also reported to occur between water droplets in water-in-oil microemulsion systems.[69,70] With both systems, the interaction between micelles or between microemulsion droplets was attractive.

The values of the second-order rate constant for sticky collisions, k_c, have been calculated for several values of C and T. These values are listed in Table 4, together with the values of A_4, x, and N required for the calculations. The values of k_c are all in the 10^8 $M^{-1}s^{-1}$ range. At a temperature only 0.2−1 °C below T_C (last three entries in Table 4), the k_c values are still about 1 order of magnitude lower than for a diffusion controlled process. Table 4 shows that at a given temperature k_c increases with C and that at a given C it increases with T. Although the increase with T is the behavior always observed for a rate constant, the increase with C is more unusual. It arises because the micelle size increases with C, resulting in increasing intermicellar interactions that favor sticky collisions between micelles.

Discussion

Similarities and Differences in Behavior between TBA Alkyl Sulfates and C_mEO_n Surfactants. The results presented above revealed many similarities and also some differences in the behavior of the TBA alkyl sulfates and the nonionic C_m-EO_n surfactants in solution. Both systems show phase separation, and the phase separation temperature T_C decreases when the surfactant alkyl chain carbon number m is increased. However, the decrease of T_C upon increasing m is about two times smaller for TBA alkyl sulfates than for C_mEO_n.[7] Both types of surfactants are characterized by values of N that increase with T.[4] However growth and intermicellar migration of probe/

quencher via sticky collisions are less extensive for the TBA alkyl sulfate surfactants. Thus, the value of N for these surfactants can still be determined at temperatures 0.2−0.5 °C below T_C (see above). On the contrary, the determination of N is not feasible with the C_mEO_n surfactants already at temperatures several degrees below T_C because the value of N becomes too large and the intermicellar migration via sticky collisions too extensive.[57-60]

Crowding of TBA$^+$ Ions at the Surface of TBA Alkyl Sulfate Micelles. The experimental values of N and of α permit the calculation of the number of TBA$^+$ ions bound to TBA alkyl sulfate micelles from

$$n_{bound,exp} = N(1 - \alpha) \qquad (9)$$

This number can be compared to the number of TBA$^+$ ions that can be packed at the surface of the micelle core, taking into account the surface area covered by the sulfate headgroups and the void surface in packing TBA$^+$ ions and headgroups.

The calculations below refer to TBADS solutions at low concentration, close to the cmc, and 25 °C where the micelles can be considered as spherical. All of the dodecyl chains are assumed to reside in the core, approximated to be a sphere of radius R_{core} and of volume V_{core} given by

$$V_{core} = 4\pi R_{core}^3/3 = NV_{tail} \qquad (10)$$

In eq 10, $V_{tail} = 0.350$ nm^3 is the volume of a dodecyl tail.[72] This equation permits the calculation of R_{core} for any value of N. The bound TBA$^+$ ions are assumed to penetrate into the micelle core[1] over a distance d that can be estimated as follows. The much lower cmc value found for TBADS (about 1 mM)[1] with respect to SDS (8 mM) corresponds to a free energy of micellization, ΔG_M, about 2 kT more negative for TBADS than for SDS. This difference indicates that the maximum value of d is about 0.20 nm, on the basis of the free energy of micellization increment of −1.1 kT per additional CH$_2$ in the surfactant alkyl chain.[73] The surface area of the sphere that passes through the centers of such micelle-bound TBA$^+$ ions is given by

$$a = 4\pi(R_{core} + R_{TBA} - d)^2 \qquad (11)$$

In eq 11, R_{TBA} is the radius of the TBA$^+$ ion. Part of the surface area a is covered by the sulfate headgroups and is therefore not accessible to TBA$^+$ ions. Besides, some surface area is lost in packing sulfate headgroups and bound TBA$^+$ ions. The surface area available to TBA$^+$ ions becomes

$$S_A = 0.82a - Na_{sulfate} \qquad (12)$$

In eq 12, the factor 0.82 accounts for the void surface area in packing headgroups and bound counterions. The value 0.82 is equal to $0.746^{2/3}$, the constant 0.746 being the fraction of filled volume in a compact hexagonal packing of spheres, and the exponent 2/3 accounts for the fact that packing involves a surface (dimension 2) and not a volume (dimension 3). Note that the surface areas covered by one sulfate headgroup and by a TBA$^+$ ion are not equal. This introduces an error in the value of the factor 0.82, but this error should be acceptable at the level of approximation of the present calculations. Also, the packing factor 0.746 used above represents the maximum possible value. A more correct value would be that for the random close packing of spheres, 0.64.[74] In eq 12, $a_{sulfate} = 0.39$ nm^2 is the surface area occupied by a sulfate headgroup.[4]

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TABLE 5: Calculated Values of the Maximum Number of TBA Ions Bound to the TBADS Micelles[a]

R_{TBA} (nm)	d (nm)	$n_{bound,max}$
0.494	0	31
	0.1	26
	0.2	20
0.400	0	39
	0.1	31
	0.2	24

[a] Experimental value of the number of micelle-bound TBA ions at the cmc and 25 °C: 47 (see text).

The maximum number of TBA$^+$ ions, $n_{bound,max}$, that can be packed in contact with the core surface is thus

$$n_{bound,max} = S_A / \pi R_{TBA}^2 \qquad (13)$$

The values of $n_{bound,max}$ have been calculated using the two limiting values: R_{TBA} = 0.494 nm that comes from molecular models[75] and 0.400 nm that comes from partial molal volumes.[76] Table 5 lists the values of $n_{bound,max}$ calculated for different values of the penetration depth d. The experimental value of the number of bound TBA$^+$ ions calculated from eq 9 is 47, based on the reported values of N = 57 and α = 0.17.[1] This value is larger than all calculated values of $n_{C,max}$ listed in Table 5, even for the smaller value of R_{TBA} and when the TBA$^+$ ion is assumed to not penetrate the micelle, a rather unlikely situation. The simplest interpretation of these results is that the bound TBA$^+$ ions in excess of $n_{bound,max}$, that is $\Delta n = n_{bound,exp} - n_{bound,max}$, bind to the micelles on top of the first layer of bound TBA$^+$ ions, forming a second outer layer. This layer is incomplete as $\Delta n < n_{bound,exp}/2$. The possibility of TBA$^+$–TBA$^+$ contacts in the close vicinity of the micelle surface is supported by the tendency of TBA$^+$ to self-associate in water into ill-defined aggregates with multiple charge.[26–30] An ultrasonic absorption study[27] indicated an onset of aggregation of about 0.8 M for TBABr and TBACl. The concentration of bound TBA$^+$ ions in the spherical shell of thickness 1 nm (approximate diameter of the TBA$^+$ ion) surrounding the micelle surface is 1.25 M, on the basis of the values of N and α. Thus, the TBA$^+$ ions bound to the micelle surface may be associated with one another.

The above discussion referred to systems at the cmc and at 25 °C where the micelles are spherical. The aggregation number increases with C and T. If the ionization degree remains unchanged, as this has been evidenced for several surfactants,[25,40,77–79] crowding of TBA$^+$ ions at the micelle surface becomes more acute. Indeed the surface area per headgroup decreases as the aggregation number increases and a larger fraction of counterions may be located in the outer second layer of bound counterions. Crowding may then even occur for smaller tetraalkylammonium ions, such as TPA$^+$ ions.

Similar calculations were performed for TBATS micelles. They led to the same conclusion, namely the micelle surface does not offer enough surface area for binding the number of ions that can be calculated from the value of α (taken equal to that for TBADS micelles) and the experimental value of N. Thus, here again some bound TBA$^+$ ions must be located in an outer second layer, farther away from the micelle surface.

Attractive Interaction Responsible for Phase Separation in Micellar Solutions of TBA Alkyl Sulfates. It is now accepted that the attractive intermicellar interaction responsible for the phase separation occurring in C$_m$EO$_n$ solutions is due to the decreasing polar character of the poly(ethylene glycol) headgroup upon increasing temperature and the associated

removal of hydration water from the micelle palisade layer.[80] The origin of the attractive interaction between TBA alkyl sulfate micelles that gives rise to sticky intermicellar collisions and to phase separation is less well established. Three different explanations have been proposed. Kumar et al.[13] attribute the attractive interaction to changes of hydration of the micelle surface associated with the crowding of TBA ions at this surface. This explanation is somewhat similar to that proposed for the phase separation of solutions of C$_m$EO$_n$ surfactants[80] and of the cationic alkyltributylammonium bromide surfactants.[17–21] Raghavan et al.[16] suggest that the presence of hydrophobic counterions in an ionic surfactant solution may render the micelles pseudo-nonionic. However, this explanation probably does not apply because the TBA alkyl sulfate micelles have been shown to be substantially charged.[1,4] Last, Yu et al.[4–6] propose that the attractive intermicellar interaction originates from the bridging of micelles by TBA$^+$ ions which would have their butyl chains partially incorporated in two different micelles.

A previous study[2] of the cloud temperature in solutions of TBADS in the absence and presence of TBACl led us to propose a model similar to that postulated by Yu et al.[4–6] with the important difference that several TBA$^+$ ions may be involved in connecting two micelles. The approximate calculations detailed above indeed suggest the existence of a second outer layer of bound TBA$^+$ ions around TBA alkyl sulfate micelles. The intermicellar interaction may therefore be mediated by TBA$^+$ ions located in this second layer and/or by TBA$^+$ ions bound to this layer and thus still farther out in the solution. As the temperature or the concentration is increased, the micelle aggregation number increases and the micelles become elongated. More micelle-bound TBA$^+$ ions are then located in the second outer layer farther away from the micelle surface (see above) and participate in micelle bridging. Multiple bridging will increase until the occurrence of phase separation. In such a model, bridging involves three or more TBA$^+$ ions. Figure 6 schematically represents two dodecyl sulfate micelles bridged by four TBA$^+$ ions. Note that the observed decrease of T_C upon addition of a TBA salt to TBA alkyl sulfate solutions supports the postulated model. Indeed such additions increase the number of TBA$^+$ ions that can bind to the outer TBA layer and the probability of bridging between micelles, thus resulting in phase separation at a lower temperature.

Insight into the Behavior of TBADS Micelles from EPR. Figure 2 shows that the behavior of TBADS micelles with temperature is "normal" up to a threshold concentration of approximately 50 mM in the sense that the aggregation numbers decrease with increasing T. To gain insight into the behavior of TBADS micelles as a function of concentration, EPR measurements taken from ref 24 are given in Figure 7a which shows the hyperfine coupling spacing, A_+, as a function of the concentration at 25 °C. A_+ yields an estimate of the water volume fraction in the Stern layer.[81] At low concentrations, up to approximately 50 mM at 25° and 75 mM at 10°, the values of A_+ decrease with increasing concentration, a "normal" behavior that has been observed[78,81–83] in all ionic micelles studied to date. This decrease in A_+ has been interpreted[78,81–83] as follows: increasing surfactant concentration causes the micelles to grow. Provided that the micelles remain nearly spherical (globular) the headgroups and counterions occupy an increasing fraction of the volume in the Stern layer leaving less volume available to house water. In all of the previous cases,[24,78,81–83] the micelles are known to grow with surfactant concentration, while remaining nearly spherical or globular in shape.
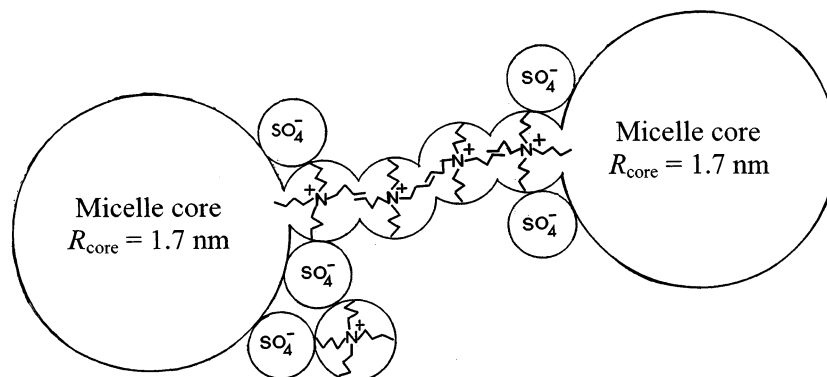
Figure 6. Schematic representation of the bridging between dodecyl sulfate micelles by TBA$^+$ ions, via hydrophobic interactions between butyl chains of the ions. The relative dimensions of the micelle, TBA$^+$ ions and sulfate headgroups are respected. For the sake of simplicity the micelle cores are represented with a spherical shape while they are more likely to be elongated at high T and C.
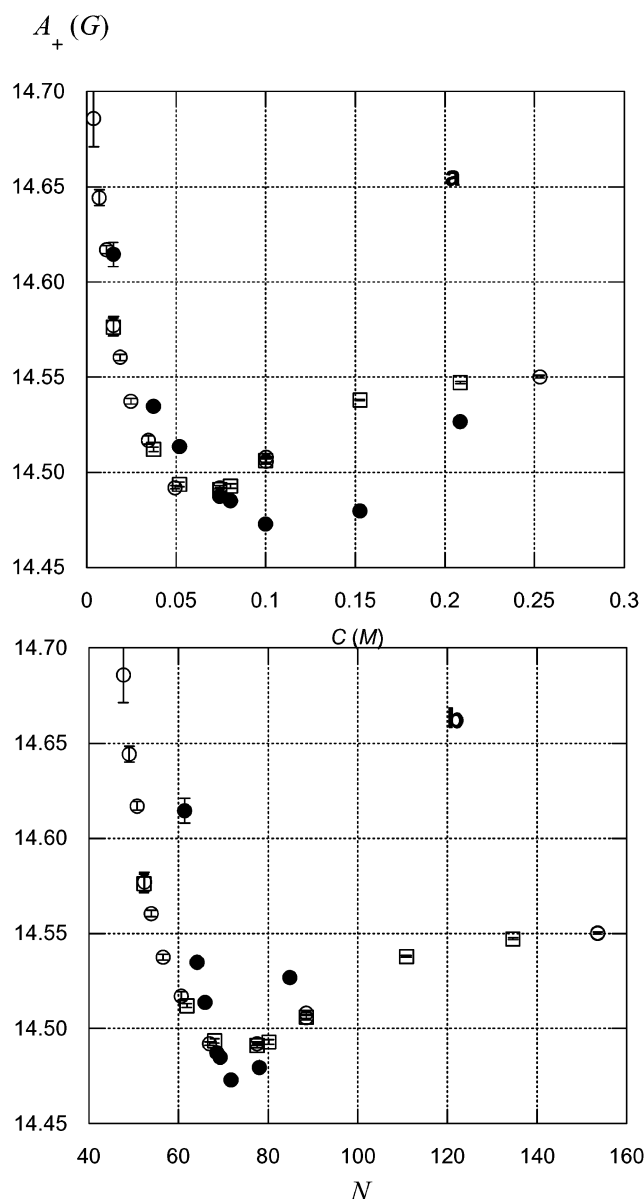

Figure 7. (a) Variation of the hyperfine spacing A_+ with the surfactant concentration at 25 °C (□, ○) and at 10° (●). The two symbols □ and ○ correspond to two different experiments using freshly prepared samples. (b) The same data plotted against the aggregation number.

The situation changes if a dramatic change in shape occurs. For example, by adding NaCl to SDS solutions, the so-called

sphere-rod transition may be induced. Above this transition, it was found[81] that values of A_+ no longer decreased, a fact that is understood to be due to the fact that growth along the long axis of a cylinder no longer reduces the water concentration in the Stern layer. Nevertheless, the results in Figure 7a probably are not due to a change in shape, because such an explanation would require that the largest globular micelle be dryer than the cylindrical micelles. This is unlikely because any reasonable transition from a globular to cylindrical shape would not involve an increase in curvature that is associated with higher water content.

A more likely explanation of the unusual results in Figure 7a showing that minima are attained near 60 mM and 100 mM for $T = 25$ and 10 °C, respectively, above which A_+ shows an unprecedented increase with C, is that they could signal a change in the time-averaged location of the probe. Such a behavior could be rationalized as follows: above a threshold concentration that depends on temperature, bridging of the type shown in Figure 6 could occur. The hydrophobic bridges could easily induce a slight change in the average position of the spin probe toward the bridge where a higher concentration of water could be encountered.

Figure 7b presents the same data as Figure 7a plotted against the aggregation number. The aggregation numbers in Figure 2 vary linearly with C as follows: $N = 46 + 425C$, $r = 0.995$, at 25° and $N = 60 + 120C$, $r = 0.969$, at 10°. Values of the abscissa of Figure 7b were computed from these linear relationships. The precision and ease of the EPR measurements allow precise data to be obtained at low values of C. N was computed from the same linear relationships for these values; however, below $N = 58$, the linearity of N with C has not been proved. Thus, the abscissa of Figure 7b is approximate below this value. From Figure 7b, we may conclude that the minima occur at the same value of N and at nearly the same water concentration. Thus, in these limited data, there appears to be a threshold value of N above which interesting behavior is manifest.

Regardless of the detailed explanation of the EPR results, it is clear that "normal" behavior gives way to "abnormal" behavior at about the same concentration as the threshold dividing normal and abnormal behavior in the aggregation numbers (see Figure 2).

Summary and Conclusions

The self-association of TBADS and TBATS in water has been investigated by means of TRFQ and cryo-TEM. The two surfactants show clouding and phase separation as the temperature is increased. They give rise to micelles that have an

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aggregation number that increases with temperature. The micelles are spherical at low T and C but grow at high C and/or T, probably becoming elongated. Nevertheless, they retain a finite size up to a temperature only 0.2−0.5 °C below T_C. Approximate calculations show that the micelle surface area is not sufficient for accommodating all micelle-bound TBA$^+$ ions and that some of these ions must be located in a second layer farther away from the micelle surface. The fraction of such ions increases with the micelle aggregation number, that is, with temperature and surfactant concentration. These ions and some other TBA$^+$ ions bound to them still farther away from micelle surface may form bridges between micelles. Increasing micelle bridging may be responsible for the phase separation observed in solutions of TBA alkyl sulfate micelles upon increasing temperature.

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