

Tetrabutylammonium Alkyl Carboxylate Surfactants in Aqueous Solution: Self-Association Behavior, Solution Nanostructure, and Comparison with Tetrabutylammonium Alkyl Sulfate Surfactants

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Received June 21, 2005. In Final Form: September 18, 2005

A series of long and ultralong chain tetrabutylammonium alkyl carboxylate (TBAC_m, TBA = tetrabutylammonium ion; C_m = carboxylate ion C_{m-1}H_{2m-1}CO₂⁻ of total carbon number *m*) surfactants have been obtained by direct neutralization of the fatty acids with *m* = 12, 14, 18, 22, and 24 by tetrabutylammonium hydroxide. Time-resolved fluorescence quenching has been used to determine the micelle aggregation number (*N*) of the surfactants with *m* = 12, 14, and 18 in the temperature range 10–50 °C and of the surfactants with *m* = 22 and 24 in the temperature range 25–60 °C. In all instances the values of *N* were well below those that can be calculated for the maximum spherical micelle formed by surfactants with the same alkyl chain as the investigated surfactants on the basis of the oil drop model for the micelle core. The microstructure of selected solutions of TBAC22 was examined using transmission electron microscopy at cryogenic temperature and compared to the microstructure of solutions of TBA dodecyl and tetradecyl sulfates. These observations generally confirmed the findings of TRFQ. The self-association behavior of these anionic surfactants with TBA counterions is explained on the basis of the large size and the hydrophobicity of the tetrabutylammonium ions. The important differences in behavior that have been evidenced between tetrabutylammonium alkyl carboxylates and alkyl sulfates are discussed in terms of differences in distribution of the surfactant electrical charge on the headgroup and alkyl chain predicted by quantum chemical calculations (*Langmuir* **1999**, *15*, 7546).

Introduction

The surfactants TAADS (TAA = tetraalkylammonium ion; DS = dodecyl sulfate ion) have been recently much investigated.^{1–4} The main purpose of these investigations was to bring new information on anionic surfactants with large TAA counterions whose self-association and phase behavior have recently attracted much interest.^{5–8} These studies also aimed at elucidating the clouding and phase separation occurring in TBADS and TBATS (TBA = tetrabutylammonium ion; TS = tetradecyl sulfate ion) upon heating.^{1–7} Clouding and phase separation upon increasing temperature are known to occur for solutions of the nonionic poly(ethylene oxide) monoalkyl ether surfactants (C_mEO_n; *m* = alkyl chain carbon number; *n* = number of ethylene oxide EO units).⁹ However, recently, several anionic surfactants with a large hydrophobic counterion have been reported to show clouding and phase

separation upon heating as, for instance, tetrabutylammonium perfluoroalkanoates,^{10,11} mixtures of sodium perfluorooctanoate and tetrapropylammonium bromide,¹² and mixtures of sodium alkyl sulfates (alkane = octane to octadecane) and tetrabutylammonium or tetrapentylammonium salts.^{5,7,8,13–16} Clouding and phase separation have also been observed with solutions of the cationic surfactant erucyl-bis(hydroxyethyl)methylammonium chloride in the presence of the hydrophobic counterions tosylate or salicylate,¹⁷ and with solutions of the cationic surfactants alkyltributylammonium bromides that have a large hydrophobic headgroup.^{18–22}

The studies of TBADS and TBATS showed that the large size of the TAA counterion can limit the size of anionic micelles and also restrict growth upon increasing surfactant concentration,^{1,4} in the same manner as the size

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of the headgroup of cationic surfactants.²³ At sufficiently high concentration the aggregation number of TBADS and TBATS micelles was found to increase with temperature,^{1,4} a behavior in line with the phase separation displayed by these surfactants and similar to that reported for C_mEO_n surfactants.^{24–27} The phase separation appears to be due to the crowding of the large TBA ions around the micelles that results in the location of some bound ions in an outer second layer of bound counterions⁴ and also to be due to the capacity of the TBA ions to self-associate in water into ill-defined charged aggregates.^{28–32} These two effects favor bridging between micelles by a short chain of TBA ions interacting with one another via hydrophobic interactions between butyl chains.

Following the above investigation of TBADS and TBATS the question arose as to why tetrabutylammonium salts of fatty acids do not show a behavior similar to TBA alkyl sulfates. Indeed, Jansson et al.³³ observed no clouding or Krafft phenomenon between 0 and 100 °C for aqueous solutions of TBA dodecanoate (TBAC12) and reported a near complete absence of mesophases in the phase diagram of the TBAC12/water system. A more recent study concerned TBA salts of long and ultralong fatty acids (up to the octacosanoic acid, $C_{27}H_{55}CO_2H$).³⁴ The TBA tetradecanoate and octadecanoate (TBAC14 and TBAC18, respectively) showed a behavior similar to TBAC12 with no clouding or Krafft phenomenon in the range between 2 and 98 °C, even for relatively concentrated solutions. No clouding was observed up to a temperature of 98 °C with the TBA salts of ultralong fatty acids: TBA docosanoate (TBAC22), TBA tetracosanoate (TBAC24), and TBA octacosanoate (TBAC28). However a gel phase and a two-phase range were observed with the surfactants TBAC22, TBAC24 and TBAC28 in the low temperature (T) range.³⁴ The partial phase behavior of these surfactants and a preliminary account of their self-aggregation behavior in water were reported.³⁴

The main purpose of this paper is to give more complete results on the self-association behavior of the TBAC m surfactants with $m = 12, 14, 18, 22,$ and 24 . Results on the microstructure of selected solutions of the TBAC22, TBADS, and TBATS surfactants will be also presented. Some complementary information on the long-term phase behavior of the ultralong chain alkyl carboxylates TBAC22 and TBAC24 is also given in this paper. An explanation of the difference of behavior between TBA alkyl sulfates and alkyl carboxylates is proposed.

Materials and Methods

Materials. The dodecanoic, tetradecanoic, octadecanoic, docosanoic, and tetracosanoic acids were of the best available grade (Fluka, *purissimum* grade in most instances), used as received. The tetrabutylammonium hydroxide (TBAOH, Fluka, *purissimum*) was received under the form of a 1.0 M aqueous solution. The molality of this solution was determined to within

0.1% by neutralization with a normalized HCl solution (Titrisol 0.100 M). Its density was also determined to within 0.1 mg/mL using a calibrated 10 mL pipet.

The TBA salts of the fatty acids were directly obtained as aqueous solutions of known concentration as follows. A known mass of fatty acid was mixed in a glass flask with a known mass of water and the stoichiometric equivalent weight of TBAOH solution. This ensured a stoichiometric neutralization of the fatty acid to within 0.1%, and the knowledge of the concentration in weight percent of the TBAC m solutions thus generated to within 0.1%. The flask was tightly sealed, the mixture stirred overnight, and heated when needed (in the case of the TBAC24 and TBAC28 surfactants). The resulting solutions were clear and transparent except that of TBAC28 which was weakly turbid. The concentrations of the TBAC m solutions so prepared ranged between 8 and 20 wt %. The density of these solutions was determined by weighing a known volume of solution using a calibrated pipet. The value of the density permitted the calculation of the molar concentration of the solution. The cmc values of TBAC12 and TBAC14 were measured using the electrical conductivity method, and found to be 7.4 ± 1 mM and 1.7 ± 0.03 mM, respectively, at 25 °C. The value for TBAC12 is only in fair agreement with that reported by Jonsson et al.³³ (5 ± 1 mM, from density measurements). The surfactants TBA dodecyl sulfate (TBADS) and tetradecyl sulfate (TBATS) came from the same batch as a in previous investigation.⁴

Methods. The aggregation number of the TBA surfactant micelles were determined using the time-resolved fluorescence quenching (TRFQ) method,^{35–39} with pyrene as the fluorescent probe and dodecyl, tetradecyl, or hexadecylpyridinium chloride as quenchers of the pyrene fluorescence (the longer the surfactant alkyl chain the longer the alkyl chain of the quencher used in the measurements).^{1,40,41} The fluorescence decay curves were recorded at 381 nm using an excitation wavelength of 335 nm by means of the single photon apparatus used in previous studies.^{1,40,41} The decay curves were determined in the absence and in the presence of quencher. Details on the analysis of the decay curves can be found in ref 4.

The nanostructures of selected solutions of TBAC22, TBADS, and TBATS were examined by cryogenic-temperature transmission electron microscopy (cryo-TEM). Details concerning such experiments (apparatus and specimen preparation) have been previously reported.^{42,43}

Results

Complementary Results on the Partial Phase Behavior of TBAC22 and TBAC24. We previously reported that the solutions of these two surfactants give rise to a gel phase when maintained at 2–3 °C for, e.g., a few hours.³⁴ Upon heating, the gel phase was found to separate into two phases, a lower phase that is a micellar solution of the surfactant and an upper phase that is the remaining part of the gel phase. The extent of the upper phase decreased as T was increased, until its complete disappearance.³⁴ Since that preliminary report, we observed that maintaining the gelled system at 2–3 °C for *several months* resulted in the appearance at the upper part of the system of a white phase whose extent first increased with time, and then apparently stabilized after 3–4 months. For the TBAC24 the viscosity of the lower phase was low (a magnetic stirrer would rotate in this

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phase at the temperature of 2–3 °C at which the system was obtained). However, in the TBAC22 system the lower phase was still very viscous (a magnetic stirrer did not rotate at the temperature of 2–3 °C). These results indicate that the gel phase that forms relatively rapidly when cooling the solutions of TBAC22 and TBAC24 is metastable. Thus, it is tempting to assume that the two-phase system that forms after several months is closer to, or represents, the true equilibrium state of the system. Similar to what was reported for the TBAC28 surfactant,³⁴ the upper white phase probably is a hydrated surfactant phase. Its formation means that TBAC22 and TBAC24 surfactants show the usual Krafft phenomenon that was not observed in the shorter time scale experiments previously reported³⁴ where only a gel phase was observed.

The effect of heating on the phase behavior of an 18.9 wt % TBAC24/water system, that had been obtained in the two-phase state after several months at 2–3 °C, was investigated. The slow heating first resulted in an increase of the viscosity of the lower phase, with the magnetic stirrer rotation becoming progressively more difficult and then blocked at around 15 °C. At 20 °C, the extent of the white upper phase was clearly decreased. At 25 °C, the white phase nearly completely disappeared, resulting in a system of relatively low viscosity. Note that the viscosity of the lower phase progressively decreased as the temperature was increased from 20 to 25 °C. In the reported short time scale experiments we observed that the gel phase formed by the TBAC24/water mixture turned into a two-phase system in the range 24.3–25.8 °C.³⁴ It thus appears that the upper “turbid phase” observed in the short time scale experiments turns into the solid white phase observed in the long time scale experiments reported above. Overall, the results suggest that the system requires an extremely long time to completely phase-separate into a dilute low viscosity surfactant solution and a hydrated surfactant phase, and also for the surfactant in the upper phase to turn into a solid or something close to that.

The effect of heating was examined for a 5 wt % TBAC22/water mixture in a less systematic way. The viscosity of the lower phase was observed to strongly decrease at above 14 °C, a temperature close to that where the gel phase formed by this system melted in the previously reported short time scale experiments.³⁴ The upper white phase did not completely disappear, probably because we were constrained to perform the experiments in a tube of relatively small diameter that did not permit efficient stirring of the system.

Fluorescence Decay. In the absence of quencher the pyrene fluorescence decay curves $\log I_F$ vs t (I_F = fluorescence intensity; t = time after excitation) of pyrene solubilized in TBAC m micelles were found to be linear. These plots yielded the pyrene fluorescence lifetime, τ , in its micellar environment. The values of τ were independent of the surfactant concentration, but they increased with m as previously pointed out,³⁴ indicating that the micelles of the longer surfactants provide a less polar environment to pyrene. Figure 1 shows that the variations of $\ln \tau$ with $1/T$ (T = absolute temperature in K) are linear and that the plots run nearly parallel for the various surfactants. The plots yield an activation energy of about 3 kJ/mol, irrespective of the surfactant chain length. This value is slightly smaller than those reported for ionic and nonionic surfactants.⁴⁴

The decay curves in the presence of a sufficient concentration of quencher were biphasic. The fitting of

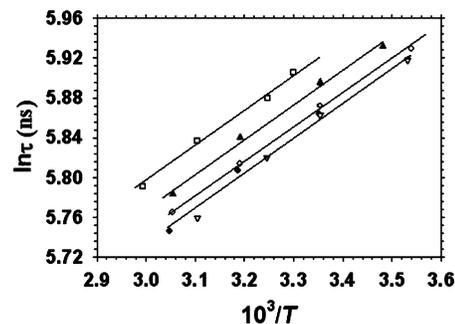


Figure 1. Semilogarithmic representation of the variation of the pyrene fluorescence lifetime with temperature in micelles of TBAC m surfactants: (∇) $m = 12$, $C = 198$ mM; (\bullet) $m = 14$, $C = 287$ mM; (\circ) $m = 18$, $C = 216$ mM; (\blacktriangle) $m = 22$, $C = 84.6$ mM; (\square) $m = 24$, $C = 49.6$ mM.

the appropriate decay equation (see eq 5 in ref 4) yielded the apparent pyrene fluorescence lifetime, $1/A_2$, the apparent intramicellar quenching rate constant, A_4 , and the apparent [quencher]/[micelle] molar concentration ratio, A_3 (the notations A_2 , A_3 , and A_4 are those used in most papers dealing with the TRFQ method applied to micellar systems).^{35–41} The expressions of A_2 , A_3 , and A_4 in situations where the quencher is *immobile* (no quencher migration from micelle to micelle in a time scale long with respect to the pyrene fluorescence lifetime) and where the quencher and/or probe are *mobile* (migration occurring in a time scale shorter than or comparable to τ) are given in refs 35–41. Experimentally, the *immobile* situation is characterized by $\tau = 1/A_2$ while the *mobile* situation corresponds $\tau > 1/A_2$. From the values of A_2 , A_3 , and A_4 one can calculate the values of the aggregation number, N , and of the pseudo first-order rate constants for intramicellar quenching, k_Q , and for intermicellar migration, k_m , using the following equations⁴

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

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

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

$$x = (A_2 - 1/\tau)/A_3A_4 \quad (4)$$

The immobile situation corresponds to $A_2 = 1/\tau$, i.e., $x = 0$. The expressions of N and k_Q then take their usual form.

At low values of C and T for all surfactants and at all values of C and T for TBAC22 and TBAC24 the fitting of the decay curves generally yielded $\tau = 1/A_2$, indicating an immobile situation (see Table 1). For lower values of m , higher C and/or T the mobile situation prevailed. The mechanism of quencher/probe redistribution is discussed below. The values of the aggregation number were obtained using eq 1.⁴

Micelle Aggregation Number. Figures 2–4 show the variations of the micelle aggregation number N with T for TBAC m solutions. The ultralong chain surfactants, TBAC22 and TBAC24 could not be investigated at low temperature because of the occurrence of the gel phase and/or the two phase range.³⁴

A first remark concerning the results in Figures 2–4 is that, at all values of m , C , and T , the values of N are small, well below those that can be calculated on the basis of the oil drop model for the micelle core for surfactants with an alkyl chain carbon number $m - 1$. This behavior was noted in ref 34 for N values at 25 °C and at one concentration. The results in Figures 2–4 extend this observation to higher C and also over a large T range.

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Table 1. Values of τ , $1/A_2$, N , k_Q , and k_c for the Investigated Surfactant Solutions

surfactant	T (°C)	τ (ns)	$1/A_2$ (ns)	N	$10^{-6}k_Q$ (s ⁻¹)	$10^{-7}k_c$ (M ⁻¹ s ⁻¹)
TBAC12 $C = 102.4$ mM	10		377	40.5	16	
	25		352	36	28	
	35		333	33	35	
	49		299	29	48	8.5
TBAC12 $C = 194.1$ mM	10	372				
	25	352				
	35	337				
	49	317				
TBAC12 $C = 286$ mM	10		370	38	15	
	25		335	35	28	
	35		291	34	38	7
	49		189	31.5	49	33
TBAC12 $C = 378$ mM	10		364	38	14	
	25		316	36	27	3.7
	35		251	36	36	12
	49		142	39	45	65
TBAC14 $C = 168.6$ mM	9.9 ^a	375	54	8.9		
	25.2	354	52	17		
	40.6	327	48	28		
	55.0	283	44	43		12
TBAC14 $C = 287$ mM	9.9 ^a	372				
	25.2	352				
	40.6	332				
	55.0	313				
TBAC14 ^a $C = 276.5$ mM	9.9		372	55	8.8	
	25.2		348	53.5	17	
	40.6		308	50	27	5
	55.0		225	45	37	27
TBAC18 $C = 216$ mM	10.0	375	375	82	4.8	
	25.1	355	361	87	7.3	
	40.5	335	327	85	12	
	54.0	319	304	80	17	6
TBAC22 $C = 84.6$ mM	9.3	382 ^a				
	25.1	364	357	104	3.8	
	40.4	344	339	106	6.7	
	54.0	325	327	102	9.8	
TBAC22 $C = 168.1$ mM	25.1		362	106	3.8	
	44.1		345	112	6.7	
	53.8		321	119	9.7	
			367	101	4.0	
TBA24 $C = 49.6$ mM	34.9	353	358	113	4.5	
	49.0	343	343	120	6.8	
	60.6	328	327	117	9.8	

^a The measurements at 9.9 °C were performed rapidly after reaching the equilibrium temperature. We checked that at the end of the experiment the system was still completely fluid (supercooled state) even though the temperature at which the experiment was performed was below the gelling temperature (about 13 °C). The lifetime measurement was also performed on the gelled system at 8.2 °C. The lifetime was measured to be 372.4 ns, a value lower than that for the liquid system.

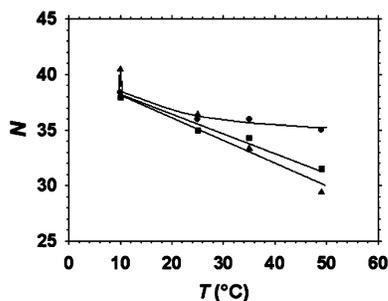


Figure 2. Temperature dependence of the aggregation number of TBAC12 micelles at surfactant concentration 102.4 (▲), 286 (■), and 378 mM (●).

Such low values of N indicate that the micelles are probably close to being spherical and of rather low polydispersity in aggregation number. The TRFQ results confirm the last conclusion as the fits of the decay equation to the

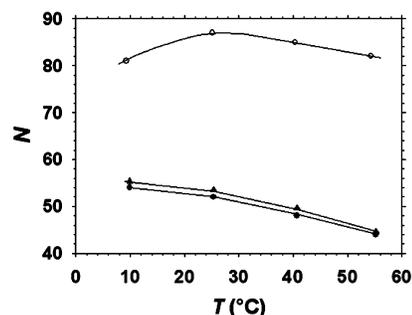


Figure 3. Temperature dependence of the aggregation number of TBAC14 micelles at surfactant concentration 278 (▲) and 168.6 mM (●) and of TBAC18 micelles at surfactant concentration 216 mM (○).

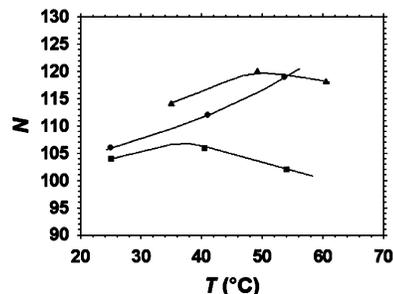


Figure 4. Temperature dependence of the aggregation number of TBAC22 micelles at surfactant concentration 84 (■) and 168.1 mM (●) and of TBAC24 micelles at surfactant concentration 49.6 mM (▲).

decay curves did not show the systematic deviations that usually reveal micelle polydispersity.^{4,38,45}

The results in Figures 2–4 show that the way N varies with T , up to temperatures of 50–60 °C, depend on both m and C . There is a gradual change from a decrease of N upon increasing T (for TBAC12 up to at least 378 mM and TBAC14 up to at least 278 mM; see Figures 2 and 3) to an increase of N with T (for TBAC22 at $C = 168$ mM; see Figure 4). This change involves two intermediate types of variation of N with T :

(i) At low values of m and high C , N first decreases and then tends to level off (see TBAC12 at $C = 378$ mM in Figure 2). N might have gone through a minimum at higher temperature, but the experiments were not possible because of the extensive quencher migration taking place with this system at high temperature.

(ii) At high value of m but relatively low C , N first increases with T , goes through a maximum, and then decreases (see TBAC18 at $C = 216$ mM, in Figure 3; see TBAC22 at $C = 84$ mM and TBAC24 at $C = 49.5$ mM, in Figure 4).

Briefly it can be said that the variation of N with T for micelles of TBAC m surfactants with low value of m is qualitatively similar to that of micelles of common ionic surfactants.^{44,46,47} For TBAC m surfactants with high values of m and at relatively high concentration the variation of N with T becomes similar to that of micelles of the nonionic ethoxylated surfactants C_mEO_n .^{24–27}

These results show similarities and differences with respect to those for TBADS and TBADS. Thus, similarly to TBADS at low C , N decreases upon increasing T for TBAC12 and TBAC14. TBAC22 shows an increase of N

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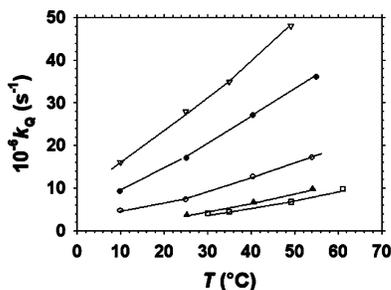


Figure 5. Temperature dependence of the intramicellar quenching rate constant for TBAC m micelles: (∇) $m = 12$, $C = 198$ mM; (\bullet) $m = 14$, $C = 287$ mM; (\circ) $m = 18$, $C = 216$ mM; (\blacktriangle) $m = 22$, $C = 84.6$ mM; (\square) $m = 24$, $C = 49.6$ mM.

with T at the fairly high concentration $C = 168$ mM, similarly to TBADS at the lower concentration $C \approx 80$ mM and TBATS at the still lower concentration of 37 mM. However, the main difference between TBA alkyl carboxylates and alkyl sulfates is that the increase of N with T is always relatively small for the former. In fact in some cases N starts decreasing after having increased a little (see Figures 3 and 4). All these results suggest that the effect responsible for the temperature-induced growth of TBA alkyl sulfate micelles is also present in TBAC m solutions but at a much lower level and it requires much larger values of C and/or m to become significant (compare results for TBAC12 and TBADS or TBAC22 and TBATS).

The results in Figures 2–4 suggest that for a hypothetical TBAC m surfactant the full N vs T plot would first show a decrease of N and a minimum, a maximum, and finally a decrease of N as T is increased. For a real TBAC m surfactant, only one part or the other of this full variation is observed, and this part depends on the values of m and C and of the covered T range. The decreases at low and high T probably correspond to the usual effect of T on the aggregation number of ionic micelles.^{44,46,47} The unusual behavior seen at intermediate temperatures has probably in part the same origin as discussed for the TBADS and TBATS. We reserve the discussion of these results for the Discussion.

Intermicellar Migration. As for TBADS and TBATS, at high C and sufficiently high T , 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 Table 1). This indicated that a redistribution of the probe and/or quencher occurred in the fluorescence time scale.^{34–39} Fast probe/quencher redistribution can occur by two rather different mechanisms. In the first mechanism (process A), the quencher present in a micelle exits from this micelle and associates to another micelle after diffusing in the intermicellar solution (see Figure 5 in ref 34). Pyrene redistribution is not considered in this mechanism because the pyrene residence time in micelles is much longer than the fluorescence lifetime.⁴⁸ The second mechanism (process B) involves collisions between micelles that set the micelle cores in contact or bring about their temporary merging (referred to as *sticky* collisions below; see Figure 5 in ref 34).^{24–27,49,50}

As in our previous study of the intermicellar migration in solutions of TBADS and TBATS⁴ an attempt was made to find out which of the processes A and B is operative in

TBAC m solutions. For this purpose TRFQ measurements were performed on the same surfactant solution using two alkylpyridinium quenchers of different alkyl chain lengths. The 283 mM TBAC14 solution that had been investigated using the quencher dodecylpyridinium chloride (DPyCl; see results in Table 1) was also investigated using tetradecylpyridinium chloride (TPyCl) at the same concentration as DPyCl, and 55 °C. At such a high temperature the difference between the values of τ (312 ns) and of $1/A_2$ in the presence of DPyCl (228 ns) is quite large. The fitting of the decay curve in the presence of TPyCl yielded the same value of $1/A_2$ as in the presence of DPyCl and a value of A_4 that was only a few percent smaller. These two results suggest that the intermicellar migration takes place through process B, i.e., via sticky collisions between micelles, as for TBADS and TBATS solutions. The bimolecular rate constant k_c for sticky collisions was calculated using eq 5 where $[M]$ is the molar micelle concentration.⁴

$$k_c = (A_4 - 1/\tau)/[M] \quad (5)$$

The values of k_c are listed in Table 1. They all range between $3.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $6.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, depending on m , T , and C . The largest value, obtained at 49 °C, is about 1 order of magnitude smaller than for a diffusion-controlled process. The value of k_c is seen to increase rapidly as the temperature or surfactant concentration are increased, and as the surfactant alkyl chain length is decreased (see Table 1). Indeed, as noted above significant migration is observed only for TBAC12 and TBAC14. For TBAC18 the difference between τ and $1/A_2$ is small even at 54 °C, indicating a rather weak intermicellar migration. As for the TBAC22 and TBAC24 the fittings yielded $\tau = 1/A_2$ at all values of T and C .

The very rapid variations of this rate with C and T (see Table 1) suggest that the intermicellar migration may involve several (more than two) species. If such is the case the bimolecular rate constant would be only an apparent rate constant that would depend on the surfactant concentration to some power. We cannot present at this stage a precise explanation for these observations.

Quenching Rate Constants. The values of the intramicellar quenching rate constant, k_Q , listed in Table 1, are represented as a function of temperature for the different surfactants in Figure 5. It is seen that at a given temperature the values of k_Q decrease by almost one order of magnitude in going from TBAC12 to TBAC24. Part of the decrease is due to the corresponding increase of aggregation number with the surfactant alkyl chain length. Nevertheless the values of Nk_Q (that is, corrected for the variation of N) still decrease upon increasing m , indicating that the micelle microviscosity increases with m , as was pointed out in our preliminary report.³⁴ This behavior is similar to that reported for other surfactant series,⁵¹ but the reported data did not extend to such long alkyl chains.

None of the systems investigated shows a variation of k_Q with T going through a maximum, a behavior observed in the nonionic C_mEO_n surfactants^{25–27} and also in TBADS.⁴ For those solutions, the micelle aggregation number increases rapidly with T at above a certain temperature. The maximum in k_Q occurs when the increase of k_Q with T is overcompensated by the decrease of k_Q upon increasing N . With TBA alkyl carboxylates the increase of N with T observed for some of the investigated

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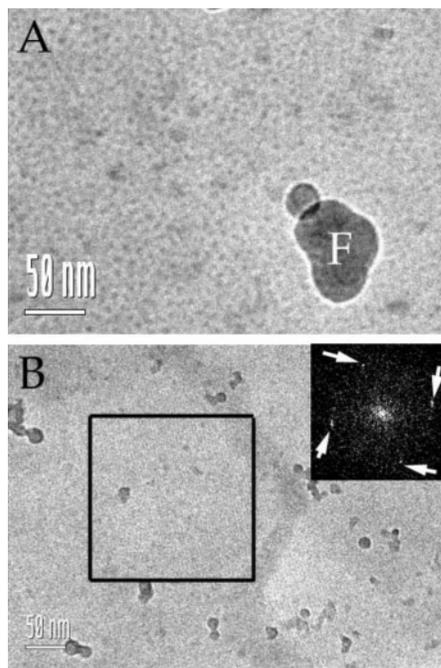


Figure 6. Cryo-TEM images of 5 wt % TBAC22 (≈ 86 mM) solutions: (A) at 25 °C, note spherical micelles, and “F” denotes a frost particle; (B) at 15 °C, an area of two sets of crossed parallel lines is marked by a black frame, where the fast Fourier transform (FFT) of the boxed area shows two sets of spots, suggesting two superposed lamellar liquid crystals of interlamellar spacing of approximately 5 nm.

solutions (see Figure 3) is never large enough for the associated decrease of k_Q to dominate the increase of k_Q with T .

Nanostructure in TBAC22, TBADS, and TBATS Solutions. Figure 6 shows representative micrographs for a 5 wt % TBAC22 (≈ 86 mM) solution at 25 and 15 °C. Spherical micelles are seen at 25 °C (Figure 6A), in agreement with the TRFQ results. The micrograph at 15 °C (Figure 6B), a temperature slightly above the temperature of 12 °C, above which the translucent gel formed by this surfactant turns into a micellar solution,³⁴ shows areas of parallel lines. Such an area of two sets of crossed parallel lines is marked by a black frame. Because of the low contrast it is difficult to see clearly those lines. However, their presence is clearly shown by the fast Fourier transform (FFT) of the boxed area in the form of two sets of stronger spots, located at the same distance from the center of the transform (arrows in the inset of Figure 6B). The speckle in the FFT is the result of the noise in the image. This result suggests two superposed lamellar liquid crystals of interlamellar spacing of approximately 5 nm (this value closely corresponds to the length of the surfactant alkyl chain, about 3 nm, increased by twice the diameter of the TBA ion, about 1 nm, suggesting that the lamellar structure is interdigitated). These lamellar domains are probably precursors of the structure taken by the surfactant at low temperature, when it forms the metastable gel phase. This “precursor phase” may occur at 15 °C in cryo-TEM while it has been observed to melt above about 13 °C in bulk phase because cryo-TEM observations are performed on vitrified liquid layers, 100–300 nm thick.^{42,43} It has been shown that when the investigated solution is close to a phase transition, its confinement as a thin layer or the flow during the preparation of cryo-TEM specimens may bring about this

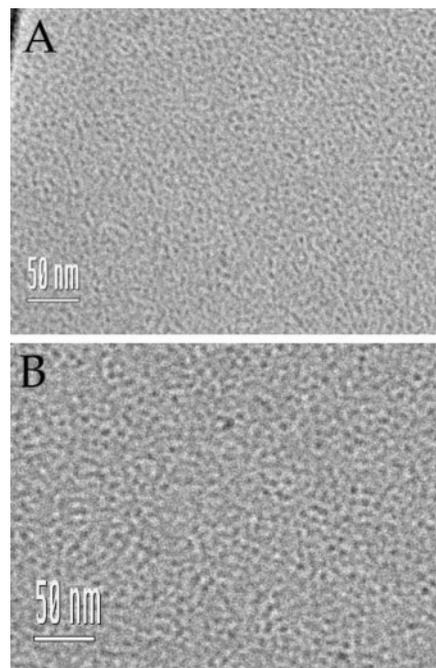


Figure 7. Vitrified 98 mM solution of TBADS at 20 (A) and 34 °C (B). Spherical or spheroidal micelles are seen at both temperatures.

phase transition.^{52,53} Also the difference may stem from some inaccuracies in determination of the phase-transition temperature and some precooling of the specimen as it approaches the cryogen, prior to vitrification.

Figure 7 shows representative electron micrographs for a 98 mM solution of TBADS at 20 and 34 °C. Spherical or spheroidal micelles are seen throughout the micrographs at both temperatures. Recall that the aggregation numbers measured by TRFQ at such values of the concentration and temperature are below 120. Thus, the micelles would have an aspect ratio of about 2 at most. Close inspection of the micrographs does suggest somewhat elongated spheroidal micelles. However, due to the overlap of several layers of micelles, because of the large depth field of the TEM, it is difficult to distinguish between spherical micelles and spheroidal micelles of axial ratio 2.

Figure 8 shows representative micrographs for a 65 mM TBATS solution at 25 and 40 °C. Spherical micelles are observed at 25 °C (Figure 8A), in agreement with the value of the micelle aggregation number $N = 110$, interpolated from the TRFQ results for this surfactant.⁴ The micrographs at 40 °C (Figure 8B) shows a mixture of spheroidal and relatively short threadlike micelles. At this temperature the value of N interpolated from the TRFQ data is of about 170.⁴ This value suggests that the average micelle should be slightly elongated, in agreement with the cryo-TEM observation. Thus, it can be now concluded with certainty that the TBATS micelles grow modestly with temperature, contrary to the conclusion reached in the light scattering studies of Yu et al.^{5,6} Recall that, as noted by those authors, the effect of intermicellar interactions which is responsible for the phase separation observed in TBADS and TBATS solutions at high T gives rise to a large contribution to the scattered intensity that predominates over the scattering arising from the particle

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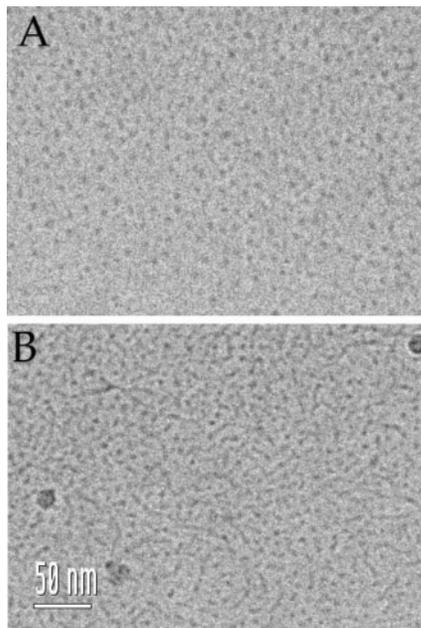


Figure 8. Cryo-TEM micrographs of a 65 mM TBATS solution: (A) spheroidal micelles observed at 25 °C; (B) at 40 °C a mixture of spheroidal and relatively short threadlike micelles.

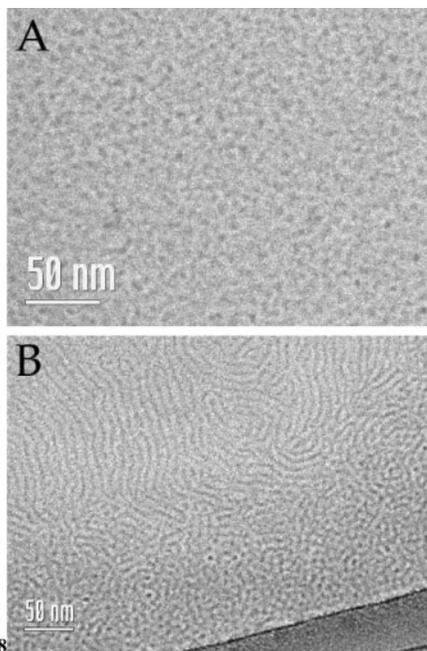


Figure 9. Cryo-TEM micrographs of TBATS solutions at 10 °C: (A) spherical or spheroidal micelles are seen in the 37 mM solution; (B) in a 65 mM solution, we observe short threadlike micelles (upper part of field of view) coexisting with spheroidal micelles in the lower part, where several overlapping layers of micelles are seen.

size. Information on the particle size then becomes difficult to obtain by light scattering. Cryo-TEM and TRFQ are not affected by these interactions.

Figure 9 shows representative micrographs of 37 and 65 mM TBATS solutions at 10 °C. Spherical or spheroidal micelles are seen for the 37 mM solution (Figure 9A) whereas the 65 mM solution (Figure 9B) shows short threadlike micelles coexisting with spheroidal ones. The value of the micelle aggregation number measured by TRFQ is consistent with spherical micelles for the 37 mM TBATS solution at 10 °C, in agreement with the cryo-

TEM imaging. However the two techniques apparently disagree on the micelle shape for the more concentrated solution, with the TRFQ still suggesting spheroidal micelles while the cryo-TEM shows short elongated micelles. The reason for this disagreement is probably a result of the high shear rate experienced by the specimen during preparation. The shear rates are higher in thinner areas of the specimen, away from the support film.^{53,54} Locally the concentration may increase, and our previous results indeed show that the aggregation number of TBADS micelles can grow rapidly with concentration.⁴ This is actually confirmed by the cryo-TEM micrographs in Figure 9.

Discussion

The results that are reported above can be briefly summarized in order to emphasize the main points to be discussed in this section.

(i) Aqueous solutions of TBAC m show no clouding and phase separation at high temperature, contrary to TBADS and TBATS solutions.

(ii) The TBAC m micelles have aggregation numbers that are significantly smaller than those for the maximum spherical micelles that surfactants with the same alkyl chain length usually form, at all investigated temperatures and concentrations. Also, they are smaller than those found for TBA alkyl sulfate micelles, at a given chain length.

(iii) The variation of N with T for TBAC m surfactants is rather complex as it depends on the values of m , C and the temperature range in which this variation is considered. Unusual variations of N with T have been observed with N going through a maximum or a leveling off upon increasing T (see Figures 2–4). In contrast for TBADS and TBATS N decreases upon increasing T at low C but increases with T at high C .

The above listed points are discussed below successively.

Comparison of the Phase Behavior of TBA Alkyl Sulfates and Alkanecarboxylates. The clouding and phase separation taking place in TBADS and TBATS solutions upon heating have been attributed to the formation of bridges between micelles.⁴ These bridges are made of micelle-bound TBA ions belonging to different micelles and interacting via hydrophobic interactions between butyl chains of TBA ions. Such bridge formation is favored by the well-known tendency of TBA ions to self-associate in aqueous solution at concentrations above, e.g., 0.8–0.9 M.^{28–32} Simple calculations based on the values of micelle aggregation number and ionization degree, that assume micelle-bound TBA ions located in a shell 1 nm thick around the micelle, yield values of the local TBA ion concentration even larger than 0.8–0.9 M. A second effect that favors micelle bridging is the fact that the number of bound TBA ions per micelle is such that the micelle surface does not offer enough surface area to accommodate all of these ions. Some of them form a second incomplete layer of bound ions farther away from the micelle surface.⁴ Both effects are taking place because TBA alkyl sulfate micelles are characterized by a relatively low degree of ionization, $\alpha < 0.2$ for TBADS.¹

The degree of ionization of TBAC m micelles is not known except that for TBAC12 with a reported value $\alpha = 0.26$ that has been determined using self-diffusion NMR.³³ As the aggregation number of TBAC12 micelles is 36 (see Table 1) the “experimental” value of the number of bound TBA ions per micelle is $n_{\text{bound,exp}} = (1 - 0.26) \times 36 = 27$.

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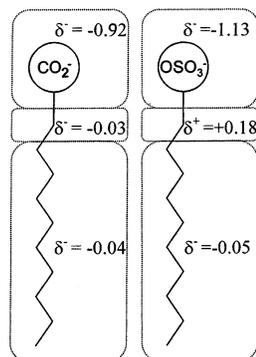


Figure 10. Distribution of the electrical charge on the dodecyl sulfate and dodecanoate ions according to the quantum chemical calculations of Huibers.⁵⁵

This number is well below the value calculated for the maximum number of TBA ions that can be packed at the surface of TBAC12 micelles, $n_{\text{bound, max}} = 52$ (the method of calculation is detailed in ref 4). In view of the low values found for the aggregation number of all TBAC m micelles, it is likely that $n_{\text{bound, exp}}$ is well below $n_{\text{bound, max}}$ for all TBAC m surfactants, contrary to the situation that prevails in TBADS or TBATS solutions. For the latter it is the crowding of bound TBA ions at the micelle surface that results in the formation of a second incomplete layer of bound TBA ions farther away from the micelle surface, and also in the high concentration of TBA ions in the close proximity of the micelles. These two effects favor micelle bridging by short chains of TBA ions and phase separation upon increasing temperature observed with these solutions. On the basis of our calculations such effects will be absent in TBAC m micellar solutions, thus the absence of phase separation.

One may then wonder why the ionization degree of TBA alkyl sulfate micelles is lower than that of TBAC m micelles. The answer probably lies in the quantum-chemical calculations of the electrical charge distribution in ionic surfactants reported by Huibers.⁵⁵ In classical models the charge of a surfactant ion is supposed to be localized on the headgroup. However, quantum-chemical calculations show that this charge is distributed on the headgroup and also on the alkyl chain.⁵⁵ Figure 10, based on the results of Huibers,⁵⁵ shows the charge distribution on a dodecyl sulfate ion and on a dodecanoate ion. The charge on the sulfate headgroup (-1.13) is larger than that on the carboxylate headgroup (-0.92). The extrapolation of these results to micelles of the two surfactants suggests that the alkyl sulfates micelles bind more TBA (and other ions) than alkyl carboxylate micelles because of the higher charge per headgroup, and thus have a lower degree of ionization.

Aggregation Number of TBAC m Micelles. The low values of the aggregation number of TBAC m micelles are probably also the result of the relatively low charge of the carboxylate headgroup. The main effect of this lower charge is that it results in more ionized micelles. For two surfactants having the same alkyl chain but differently charged headgroups, the lower the headgroup charge, the more ionized the micelles, the higher the cmc, and the smaller the micelles. Some support for this reasoning can be found by comparing the cmc values of alkyl carboxylates and alkyl sulfates. The cmc values of sodium undecyl sulfate and dodecanoate are 16 and 26 mM,⁵⁶ respectively. The difference between the cmc values of TBA undecyl sulfate and dodecanoate is even larger, with values of 2

(extrapolated value) and 7.4 mM (this work), respectively. This larger difference points out to the possible existence of a second effect of the larger ionization of alkyl carboxylate with respect to alkyl sulfate micelles. In our previous studies, we suggested that one or more butyl chains of the bound TBA ions may penetrate more or less into the core of dodecyl sulfate micelles, to explain the large decrease of cmc (by a factor 8) in going from SDS to TBADS.¹ The smaller decrease of cmc in going from sodium to TBA dodecanoate suggests that the penetration depth of TBA ions in dodecanoate micelles is less important than for dodecyl sulfate. This effect may also result in smaller micelles. NMR studies may provide more support to the points discussed above.

Effect of Temperature on the Aggregation Number of TBAC m Micelles. For ionic surfactants other than those with TBA counterions, it has been consistently observed that N decreases upon increasing T (behavior referred to as *normal* below). However, for TBAC m surfactants N decreases upon increasing T only at high or low temperatures. The decrease occurs at increasingly lower and higher T as m is increased and in some instances the decrease is not observed because of the restricted investigated T range (see the plot for TBAC22 at $C = 168.1$ mM in Figure 4). A small increase of N with T is observed in the intermediate T range (see Figures 3 and 4). The increase of N with T is much more important for TBADS and TBATS, particularly at relatively high concentrations, that are nevertheless well below those required for TBAC m surfactants. Apart from surfactants with TBA counterions, an increase of N with T has been observed in the case of C_mEO_n surfactants.^{24,27} The explanation for this increase lies in the change of the conformation of the poly(ethylene oxide) headgroup from a polar hydrophilic conformation to a less polar conformation as T is increased. This explanation is supported by theoretical calculations⁵⁷ and by measurements that show a decrease of the average hydration number of the ethylene oxide unit upon increasing T .^{58–60} Similarly, a conformation change that involves the TBA counterion may be responsible for the increase of the aggregation number noted for TBA alkyl sulfate and TBAC m micelles at sufficiently large values of m and C . Indeed, Chachaty et al.⁶¹ have shown by ¹³C relaxation rate measurements that the tributylammonium headgroups of alkytributylammonium bromide surfactants adopt a more compact conformation, with less extended butyl chains, as T is increased. The TBA ions at the micelle surface of the investigated anionic surfactants investigated here are expected to adopt a similarly more compact conformation as the temperature is increased. In this more compact conformation more TBA ions can be packed at the micelle surface. For TBADS and TBATS this possibility is crucial, because, as previously shown, there is not enough free surface area at the micelle surface for packing all bound TBA ions, and some bound ions are located on a second outer layer.⁴ A reduction of the TBA ion size upon increasing T would permit more ions to pack in the first layer of bound ions. This would result in a better

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neutralization of the micelle charge and in an increase of micelle size. Such an effect is expected to increase with the alkyl chain length (m) of the surfactant, because the micelle size increases, and the crowding of bound counterions at the micelle surface becomes more acute as m increases. This effect together with the *normal* behavior (decrease of N upon increasing T) can result in N vs T plots that show a monotonic decrease, a leveling off followed by an increase, or simply a monotonic increase in the limited range of temperature investigated (10–40 °C). The results for TBADS and TBATS confirm these expectations, with these varied behaviors effectively observed as T , m , and C are increased. In contrast, there is no crowding of TBA ions at the surface of TBAC m micelles (see above). Nevertheless, a more compact conformation of TBA ions would result in a tighter binding of TBA ions to alkyl carboxylate micelles. This effect by itself is sufficient to bring about an increase of N with T , although much smaller than for alkyl sulfates. In this case the normal behavior would dominate the variation of N with T except for very large values of m and at relatively high C , again as experimentally observed.

It is therefore suggested that the combination of the normal decrease of ionic micelle aggregation number upon

increasing T , together with the stronger binding of TBA counterions arising from their more compact conformation at higher temperature are responsible for the unusual changes of N with T observed for the TBA alkyl sulfate and alkyl carboxylate surfactants.

Conclusions

The alkyl sulfate and alkyl carboxylate surfactants with TBA counterions show important differences in phase behavior, self-association in water and microstructure in solution (micelle shape). To a large extent these differences can be explained on the basis of the relatively large difference in micelle ionization degree of these two types of surfactants. On the basis of the results of the quantum chemical calculations of Huibers,⁵⁵ it appears that the differences in micelle ionization degree reflect the fact that the distribution of the electrical charge over the sulfate and carboxylate headgroups are rather different, with the charge of the sulfate headgroup being larger than that of the carboxylate headgroup.

LA051665N