Effect of the Nature of the Counterion on the Properties of Anionic Surfactants. 1. Cmc, Ionization Degree at the Cmc and Aggregation Number of Micelles of Sodium, Cesium, Tetramethylammonium, Tetraethylammonium, Tetrapropylammonium, and Tetrabutylammonium Dodecyl Sulfates

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The surfactants cesium, tetramethylammonium, tetraethylammonium, tetrapropylammonium and tetrabutylammonium dodecyl sulfates (CsDS, TMADS, TEADS, TPADS, and TBADS) have been synthesized by ion-exchange. The critical micellization concentration in the absence of added salt (cmc) has been determined at 10, 25, and 40 °C using the electrical conductivity method. The cmc was found to decrease in the sequence CsDS > TMADS > TEADS > TPADS > TBADS. The value of the cmc depends very little on temperature, going through a shallow minimum around 25 °C for most surfactants investigated. The micelle aggregation numbers have been determined using the time-resolved fluorescence quenching method, with the pyrene/dodecylpyridinium chloride as fluorescent probe/quencher pair, at various surfactant concentrations and, in the case of TMADS, in the presence of tetramethylammonium chloride. The micelle ionization degree α_0 at the cmc has been determined from the electrical conductivity data and the values of the aggregation number extrapolated to the cmc. The micelle ionization degree was the largest for SDS (sodium dodecyl sulfate) and the smallest for TBADS. The micelle micropolarity, as determined by the pyrene polarity ratio I_1/I_3, was a maximum for TEADS. The micelle microviscosity, investigated using the fluorescent probe 1,3-dipyrenylpropane, increased in the sequence CsDS < SDS < TMADS < TEADS ≈ TBADS ≈ TPADS. At 10 °C, the micelle aggregation number decreases as the counterion radius increases, contrary to what was expected on the basis of the cmc values. At 40 °C, the sequence of the aggregation numbers is almost that expected from the cmc values. An intermediate result was obtained at 25 °C. The micelle aggregation number increased little with the surfactant concentration. The results are explained on the basis of the fact that the teraalkylammonium ions are so large that steric hindrance may impede their binding to the micelles, thereby restricting micelle size and limiting micelle growth.

Introduction

A survey of the literature shows that studies of the effect of the nature of the counterion on the self-assembly of cationic surfactants in aqueous solution vastly outnumber similar studies of anionic surfactants. Indeed cationic surfactants display dramatic effects associated with the nature of the counterion, such as micelle growth, viscoelasticity, shear-thickening, etc.[1,2] For instance, the cetyltrimethylammonium chloride micelles remain nearly spherical over a large range of concentration, even in the presence of NaCl.[3] On the contrary, the cetyltrimethylammonium bromide micelles grow with the surfactant concentration to become rodlike and the solution then displays high viscosity.[4] Micelle growth is even more pronounced in the presence of lyotropic counterions such as salicylate, chlorate and nitrate.[5−7] These differences in behavior reflect differences in the extent of counterion binding to micelles. Thus, the degree of counterion binding to cationic micelles increases in the order Cl⁻ < Br⁻ < nitrate⁻ < salicylate⁻.[7−9] This sequence of anions is a small part of the so-called Hoffmeister series, observed in many phenomena.[10,11] Specific interactions are involved in the

binding of anions to cationic micelles. These interactions are presently under intense investigation and their origin is not straightforward.[10,11]

The effect of the nature of the counterions in the case of anionic surfactants is much less dramatic. Thus, the critical micellization concentration (cmc) varies only little in going from lithium to cesium dodecyl sulfate.[12] The variations are not dramatic even when replacing the monovalent alkali metal ions by divalent cations such as Mg^{2+}, Co^{2+}, and Cd^{2+}. For instance in the case of the dodecyl sulfate surfactants, this substitution results in a decrease of the cmc (expressed in mole of surfactant ion per liter) by a factor of 2 and an increase of the micelle aggregation number from about 65 to 90.[13,14]

The cmc of the tetramethylammonium, tetraethylammonium and tetrapropylammonium dodecyl sulfates (TMADS, TEADS, and TPADS, respectively) have been reported.[12] The cmc decreases significantly in going from TMADS to TEADS and TPADS, as compared to the decrease noted in going from sodium dodecyl sulfate (SDS) to cesium dodecyl sulfate (CsDS). Recall that the TMA^+ ion is still relatively hydrophilic while the TEA^+, TPA^+, and TBA^+ (tetrabutylammonium) ions are increasingly hydrophobic. In fact the literature reports evidence of cation self-association in solutions of TPA^+ and TBA^+ salts.[15−19] Note that the ionization degree at the cmc and

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aggregation number of TEADS and TPADS micelle have not been reported. Some data exist for TMADS.[20,21] To the best of our knowledge, there are no reports on the micellization of tetrabutylammonium dodecyl sulfate (TBADS), but the micellization and micellar properties of tetrabutylammonium tetradecyl sulfate have been investigated.[22−24] Of particular interest are recent reports[25−27] that mixtures of SDS and tetrabutylammonium bromide show clouding, a phenomenon that is usually observed with nonionic surfactants of the poly(ethylene glycol) monododecyl ether type. Clouding was also reported to occur for tetrabutylammonium tetradecyl sulfate.[22−24]

The lack of information on the micelles of tetraalkylammonium dodecyl sulfates (TAADS) and the interesting clouding effects just mentioned led us to perform an extensive investigation of these surfactants. Our first aim was to fully characterize the micellar properties of these surfactants by determining the values of the cmc, the micelle micropolarity, the micelle ionization degree at the cmc, and the micelle aggregation number over wide ranges of concentration and temperature. Another aim of our work was to assess the properties of the micelles as reaction medium, i.e., by studying their hydration and microviscosity and the rate of bimolecular collisions in these micelles, as in previous studies.[28−31] For the sake of comparison we have also synthesized and investigated CsDS. Indeed the ionization degree at the cmc and the aggregation number of CsDS micelles have not been reported. In this first paper we report on the properties of micelles of CsDS, TMADS, TEADS, TPADS and TBADS: cmc, micelle ionization degree at the cmc, micelle micropolarity, and micelle aggregation number. Some information has also been obtained on the micelle microviscosity. The main conclusion inferred from the results is that the large size of the tetraalkylammonium ions probably limits the value of the aggregation number of TAADS micelles and restricts their growth upon increasing surfactant concentration.

Experimental Section

Materials. The surfactants were all prepared from a sample of purified SDS (Touzart-Matignon, France, crystallized twice from ethanol) by ion exchange, using a strong cation-exchange resin (Merck type I). A solution of SDS at a concentration of about 5 wt % was passed through a column of resin that had been treated as follows. The resin was first washed with a solution of SDS in order to eliminate impurities soluble in the surfactant solution. The failure to do so often results in solutions that are brownish after the first passage over the resin, even if the resin had been repeatedly washed with water. The resin was put in the acid form by using a large excess of a 7% aqueous hydrochloric acid solution and rinsed until complete elimination of the excess acid. It was neutralized by CsOH or tetraalkylammonium hydroxides (Fluka, purum or purissimum grade) and rinsed with deionized water until complete removal of any remaining excess base. The capacity of the resin was at least double the amount of sodium ion (from SDS) to be exchanged. The solid surfactants were obtained by freeze-drying of the ion-exchanged solutions. All surfactants were obtained as white powders, except TBADS, which is a colorless and viscous liquid at room temperature. The TAADS surfactants did not produce ashes when calcined at high temperature, contrary to SDS or CsDS (that yield sodium or cesium oxide) indicating that the exchange was quantitative (99% or so given the sensitivity of the scale used to weigh the amount of TAADS to be calcined and the eventually produced ashes).

The surfactants were stored in flasks protected from ambient moisture. CsDS was soluble in water above 28 °C and was therefore investigated at and above 30 °C. Results on the Krafft temperature of CsDS solutions in water and water + CsCl are reported and discussed elsewhere.[32] The other surfactants were readily soluble in water, forming transparent solutions at all temperatures, except TBADS. The solutions of this surfactant showed clouding above a temperature that decreased upon increasing surfactant concentration. The behavior of TBADS will be discussed in detail in part 5 in this series.[33]

The samples of pyrene, dipyrenylpropane and dodecylpyridinium chloride (DPC) were the same as in previous investigations.[34,35]

The solutions for TRFQ measurements were prepared by introducing a calculated amount of a stock solution of pyrene in ethanol in a volumetric flask, evaporating the ethanol, adding the proper amount of solid surfactant, some water and stirring for one night to achieve the solubilization of pyrene. The proper amount of an aqueous DPC stock solution was then added to the mixture. Water was finally added to the desired volume of solution, usually 5 or 10 mL. The pyrene concentration was around 2−4 μM in all solutions investigated, ensuring that the molar concentration ratio [pyrene]/[micelle] was below 0.02. The DPC concentration was adjusted to have a molar concentration ratio [DPC]/[micelle] close to 1. All solutions for fluorescence studies were deaerated by three successive freeze−pump−thaw cycles in order to remove the oxygen present in the solutions. The fluorescence cells were then filled with oxygen-free nitrogen at 1 atm in order to avoid a boiling of the solutions when performing experiments at 25 and 40 °C.

Methods. The cmc was obtained as the break in the plot of the electrical conductivity $K = B\kappa$ against the surfactant concentration C or in the plot of the equivalent conductivity $\Lambda = B(\kappa − \kappa_0)/C$ against $C^{1/2}$. The conductances κ of the surfactant solution and κ_0 of water were measured using an automatic precision bridge Wayne-Kerr type B 905 operating at 1 kHz. The cell constant B (cm^{-1}) was determined using a potassium chloride solution of known conductivity.[36a] The conductivity cell (Tacussel, France, type XE100) was made of two square platinum electrodes embedded in glass. This cell was immersed in the surfactant solution that was contained in a double-walled temperature-controlled glass container. The concentration of the surfactant was progressively increased by successive additions of aliquots of a stock surfactant solution of concentration about 10 times larger than the cmc. The constancy of the temperature during a conductivity run was better than 0.1 °C. The cmc values were determined to within ±3%.

The plots of K against C were also used to determine the value of the micelle ionization degree at the cmc, α^0, using eq 1, which is a modified form of the equation originally derived by Evans[37]

$$10^3\left(\frac{\mathrm{d}K}{\mathrm{d}C}\right)_{C>\mathrm{cmc}} = N^{0^{2/3}}\alpha^{0^2}\left[10^3\left(\frac{\mathrm{d}K}{\mathrm{d}C}\right)_{C<\mathrm{cmc}} - \lambda^0(X)\right] + \alpha^0\lambda^0(X) \tag{1}$$

In eq 1, $(\mathrm{d}K/\mathrm{d}C)_{C<\mathrm{cmc}}$ and $(\mathrm{d}K/\mathrm{d}C)_{C>\mathrm{cmc}}$ are the slopes of the conductivity plots below and above the cmc. $\lambda^0(X)$ is the limiting equivalent conductivity of the surfactant counterion. The values of $\lambda^0(X)$ used in the calculation have been obtained by interpolation or extrapolation from the tabulated values of $\lambda^0(X)$.[36b] N^0 is the aggregation number at the cmc. This number is obtained from the extrapolation of the N vs C plots to the cmc. The value of α^0, obtained from eq 1, is not very sensitive to the value of N^0 that is used in the calculation. The error on the value of α^0 was estimated to be of about ±5%.

The micelle aggregation numbers (N) were determined using the time-resolved fluorescence quenching method[38–42] with pyrene as fluorescent probe and DPC as quencher. The fluorescence decay curves (fluorescence intensity vs time) were recorded using the same single photon counting apparatus as in previous studies.[34,43,44] For each surfactant, a decay curve was determined for one solution containing pyrene and no quencher. This experiment yielded the pyrene lifetime τ in the micellar environment. The decay eq 2, where A_2, A_3, and A_4 are adjustable parameters, was fitted to the decay curve recorded for the solution containing pyrene and quencher.[38–42]

$$I(t) = I(0) \exp\{-A_2 t - A_3[1 - \exp(-A_4/t)]\} \quad (2)$$

In most instances A_2 was found to be very close to $1/\tau$, indicating the absence of significant redistribution of the quencher during the pyrene fluorescence lifetime. In such a situation $A_3 = $ [DPC]/[micelle], and $A_4 = k_Q$, the pseudo-first-order rate constant for the intramicellar quenching of pyrene by the dodecylpyridinium ion.[38–42] The micelle aggregation number N was obtained from

$$N = A_3(C - C_{\text{free}})/[\text{DPC}] \quad (3)$$

In eq 3, C_{free} is the concentration of free surfactant. For the 35 mM TBADS solution at 40 °C, A_2 was found to be slightly larger than $1/\tau$. A slight correction was therefore brought to the aggregation number calculated using eq 3 to account for this small quencher redistribution among micelles.[40–42]

At each surfactant concentration, C_{free} was obtained by solving the equation[45,46]

$$\log C_{\text{free}} = (2 - \alpha)\log \text{cmc} - (1 - \alpha)\log C_{\text{aq}} \quad (4)$$

where C_{aq} is the molar concentration of counterion in the aqueous phase, given by

$$C_{\text{aq}} = [\alpha C + (1 - \alpha)C_{\text{free}} + C_{\text{ad}}]/(1 - VC) \quad (5)$$

In eq 5, 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 surfactant is taken equal to 1.0 g/mM.[28–31] C_{free} is calculated after having determined the value of α but is not very sensitive to errors in this value. The overall error on the values of N is estimated to be about 5% and mostly arises from the fluorescence decay experiments and the analysis of the decay curves.

For each surfactant, except CsDS (see above), the measurements of aggregation number were performed at 10, 25, and 40 °C, over a concentration range from 25 mM to at least 100 mM for all surfactants. For TMADS the measurements extended up to 400 mM. Also some N values were determined in the presence of TMACl in order to check a law of variation of N with the counterion concentration in the aqueous phase.[28–31] For TBADS, only results at up to a concentration of 35 mM are presented in this paper. Results at higher concentration and/or in the presence of TBACl show a peculiar behavior that will be discussed in another part in this series, together with the clouding phenomenon observed for TBADS solutions.[33]

The pyrene-containing surfactant solutions for TRFQ measurements were also used to measure the ratio I_1/I_3 of the intensities of the first and third vibronic peaks in the fluorescence emission spectrum of micelle-solubilized pyrene. The value of this ratio provides qualitative information on the polarity sensed by pyrene at its micellar solubilization site.[40,47] Since all surfactants investigated are composed of the dodecyl sulfate ion,
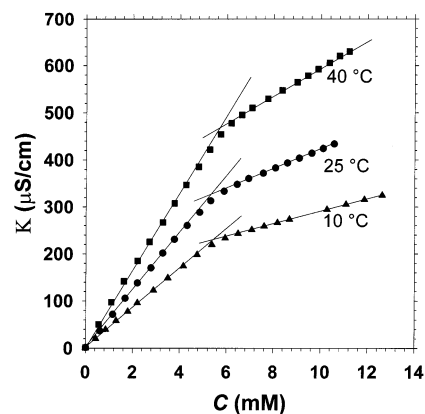

Figure 1. TMADS: Variation of the conductivity K with the surfactant concentration C.

TABLE 1: Values of the Cmc, of the Slopes of the Conductivity Plots below and above the Cmc, of the Aggregation Number at the Cmc, and of the Micelle Ionization Degree at the Cmc, α^0

surfactant	T (°C)	cmc[a] (mM)[a]	$(dK/dC)_{C<\text{cmc}}$ (S·cm²/equiv)	$(dK/dC)_{C>\text{cmc}}$ (S·cm²/equiv)	N^0	α^0
SDS	10	8.5	44.72	14.85	74	0.21
	25	8.0 [8.3]	65.8	23.97	62	0.23
	40	8.5	89.5	35.8	54	0.24
CsDS	30	6.2 [6.1]	102.8	28.2	85	0.18
	40	6.4	122.0	31.0	72	0.18
TMADS	10	5.4	41.9	13.0	76	0.20
	25	5.4 [5.52]	61.7	20.3	64	0.20
	40	5.7	82.2	29.0	57	0.22
TEADS	10	3.8	32.85	11.61	70	0.20
	25	3.7 [3.85]	48.14	17.78	63	0.21
	40	3.8	66.20	28.08	55	0.23
TPADS	10	2.30	29.15	10.38	62	0.19
	25	2.20 [2.24]	42.51	15.56	57	0.20
	40	2.20	60.71	21.09	53	0.19
TBADS	10	1.3	25.94	9.48	61	0.19
	25	1.15	40.58	19.40	57	0.17
	40	1.1	55.50	16.72	54	0.17

[a] Values from the K vs C plots. In brackets, cmc values from ref 12.

the comparison between the measured values of ratio I_1/I_3 measured for the different surfactants is much more meaningful than a comparison of I_1/I_3 values for two different surfactants. The fluorescence intensities were measured using a spectrofluorometer Hitachi F-4010, operated at an excitation wavelength of 335 nm.

The micelle microviscosity was investigated using the well-known viscosity-sensitive fluorescent probe 1,3-dipyrenylpropane (DPyP).[35] The quantity Q that is equal to the product of the ratio of the fluorescence emission intensities I_M (DPyP monomer emission near 378 nm) and I_E (DPyP excimer emission near 450 nm) by the excimer fluorescence lifetime τ_E was used to characterize the microviscosity. Indeed Q is proportional to the microviscosity.[35] The fluorescence intensities and lifetime were measured using the same spectrofluorometer and single photon counting apparatus as for the measurements described just above.

Results

Critical Micellization Concentration. Figure 1 illustrates the type of plots obtained for the variations of K with C. Table 1 lists the cmc values of the investigated surfactants at 10, 25,

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TABLE 2: Values of the I_1/I_3 Ratio at 25 °C, of the Micelle Aggregation Number, and of the Intramicellar Quenching Rate Constant for the Investigated Surfactants

surfactant	C (mM)	I_1/I_3	$C_{free}{}^a$ (mM)	10 °C		25 °C		40 °C	
				N	$10^{-7}k_Q$ (s^{-1})	N	$10^{-7}k_Q$ (s^{-1})	N	$10^{-7}k_Q$ (s^{-1})
SDS	50.1	1.20	4.9	81	1.86	65	3.44	56	6.04
	100.7	1.18	3.3	89	1.71	73	3.17	62	5.25
CsDS	25.3	1.22^b	4.8			91^b	3.1^b	75	4.6
	50.0	1.19^b	3.6			87^b	3.2^b	75	4.8
	99.9	1.17^b	2.4			99^b	2.9^b	83	4.3
TMADS	25.0	1.36	3.8	77	1.49	65	2.68	57	4.63
	49.2	1.35	2.7	80	1.34	70	2.58	62	4.52
	100.0	1.34	1.7	85	1.27	77	2.44	62	3.82
	200.9	1.31	1.0	94	1.19	81	2.16	73	3.81
	399.7		0.6	102	1.09	90	2.06	75	3.23
TEADS	25.3	1.47	2.4	71	1.18	64	2.17	57	3.65
	51.1	1.46	1.4	72	1.10	65	2.06	57	3.47
	99.8	1.47	0.9	76	1.08	69	1.92	64	3.14
TPADS	25.5	1.41	1.0	63	0.90	58	1.72	54	2.92
	50.0	1.40	0.6	65	0.88	60	1.60	55	2.63
	99.4	1.40	0.4	68	0.84	64	1.53	57	2.56
TBADS	14.9	1.37	0.8	61	0.76	58	1.41	55	2.37
	25.3	1.38	0.6	64	0.70	58	1.39	58	2.25
	35.0	1.36	0.5	64	0.73	62	1.24	62	2.00

^{a} Values computed at 25 °C (30 °C for CsDS) using eq 4 and values of α^0 from Table 1. ^{b} Values at 30 °C.

and 40 °C as obtained from the K vs C plots. The Λ vs $C^{1/2}$ plots (not shown) yielded slightly lower values of cmc, by about 3%. The cmc values at 25 °C obtained in this work are in good agreement with the values reported for some surfactants.[12] At 25 °C, the value of Λ extrapolated to zero concentration is 66.5 ± 1 S·cm²/equiv. This value is in good agreement with that calculated from the values of λ^0(dodecyl sulfate ion) = 21.6 S·cm²/equiv[48] and λ^0(TMA$^+$) = 44.9 S·cm²/equiv.[36b]

Table 1 shows that in all instances, the change of cmc with temperature is small. A rather flat minimum appears to occur at around 25 °C, on the basis of these limited data, for most of the investigated surfactants. Such a minimum has been reported to occur for SDS in a more detailed study.[49] At each temperature, the cmc decreases in the order SDS > CsDS > TMADS > TEADS > TPADS > TBADS, in agreement with previously reported results, for the first five surfactants.[12]

Micelle Polarity. The values of the pyrene polarity ratio I_1/I_3 at 25 °C are listed in Table 2. The value of this ratio decreases a little upon increasing surfactant concentration, as if the micelle palisade layer became less polar upon micelle growth associated with increasing concentration (see below). The values for CsDS and SDS are nearly equal and clearly smaller than the values for the four TAADS surfactants. This result indicates that pyrene senses a higher polarity in dodecyl sulfate micelles with *less* hydrophilic (TMADS and, to a lesser extent, TEADS) and hydrophobic counterions (TPADS and TBADS) than in SDS or CsDS micelles.

Micelle Aggregation Numbers. The values of N were calculated from eq 3 as follows. For each surfactant, values of C_{free} were computed by iteration starting from eq 4 and using the values of α_0 listed in Table 1. The values of C_{free} at 25 °C are given in Table 2. Note that the values of N all correspond to concentrations $C \gg C_{free}$. Thus, errors in α and C_{free} had very little impact on the computed values of N in Table 2. This permitted us to use the same values of C_{free} at all temperatures. The errors on the N values for CsDS are probably somewhat larger than for the other surfactants. Indeed, owing to a heavy atom effect,[50,51] pyrene is strongly quenched by the Cs$^+$ ion,
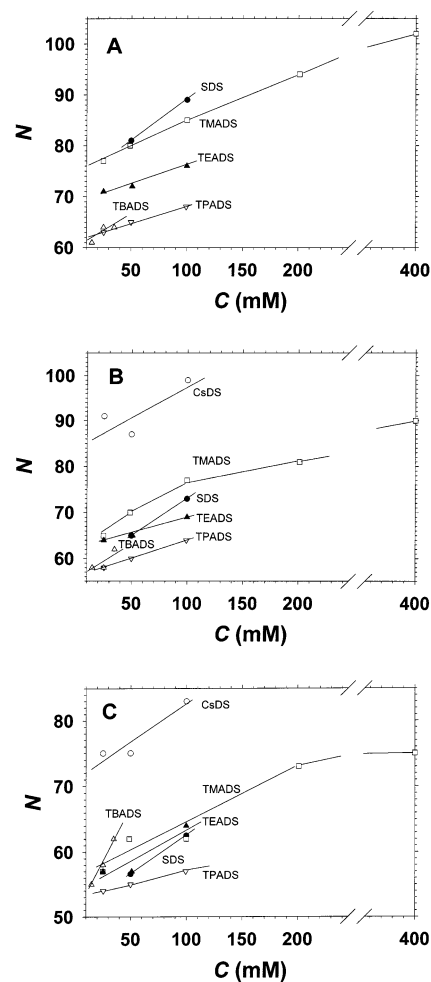

Figure 2. Variation of the micelle aggregation number with the surfactant concentration for SDS (●), CsDS (○), TMADS (□), TEADS (▲), TPADS (▽), and TBADS (△) at 10 °C (A), 25 °C (B; the results for CsDS are at 30 °C), and 40 °C (C).

just as it is quenched by the Tl$^+$ ion. Thus, in deoxygenated micellar solutions of CsDS, the pyrene lifetime was found to be $\tau = 55$ ns, while values of τ ranging between 350 and 370 ns were measured in solutions of all other surfactants investigated, at 25 °C. Such low values of τ resulted in larger errors in the values of N.

The results show the following trends.

1. For all surfactants, at a given temperature N increases with the surfactant concentration (see Figure 2), a behavior usual for ionic surfactants.[3,21,28,31,43]

2. For all surfactants, at a given concentration N decreases as the temperature is increased, a behavior also noted for ionic surfactants.[43] However the rate of variation of N with T becomes smaller in the sequence SDS > TMADS > TEADS > TPADS > TBADS.

3. At a given concentration and temperature N is larger for CsDS than for all other surfactants.

4. At 10 °C (Figure 2A) the aggregation number of SDS is close to, but larger than, that of TMADS and larger than that of all other TAADS. The micelle aggregation number decreases following the sequence: SDS ≈ TMADS > TEADS > TPADS ≈ TBADS. This is an unexpected behavior because in general, the value of the micelle aggregation number increases as the cmc value decreases.[52,53] Obviously such is not the case for the dodecyl sulfate surfactants investigated. Figure 2B and 2C show

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TABLE 3: Effect of Additions of TMACl on the Micelle Aggregation Number and Intramicellar Quenching Rate Constant in a 40 mM TMADS Solution

[TMACl] (mM)	I_1/I_3	C_{free} (mM)	10 °C		25 °C		40 °C	
			N	$10^{-7}k_Q$ (s^{-1})	N	$10^{-7}k_Q$ (s^{-1})	N	$10^{-7}k_Q$ (s^{-1})
21.4		1.6	92	1.25	82	2.40	72	3.93
59.0	1.36	1.0	94	1.16	81	2.23	70	3.69
143.9		0.7	106	1.03	94	1.96	84	3.40

that as the temperature is increased the sequence of micelle aggregation numbers becomes

CsDS > TMADS > SDS > TEADS ≈ TBADS >

TPADS at 25 °C

and

CsDS > TBADS > TMADS > TEADS > SDS >

TPADS at 40°C
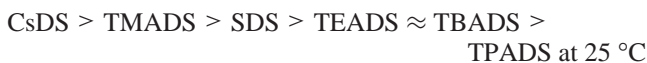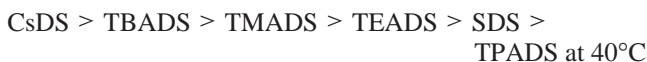
Thus, it appears that the sequence of the micelle aggregation number tends to become that expected on the basis of the cmc values as the temperature is increased, that is as the aggregation number decreases.

5. The values of N extrapolated to the cmc are all close to 60, except perhaps for CsDS. This value closely corresponds to that of the maximum spherical micelle that a surfactant with a dodecyl chain can form.[54,55] Up to the highest concentration investigated, the values of N remain consistent with micelles that are spherical or spheroidal as they do not differ very much from the value at the cmc. For instance for the 400 mM TMADS solution the value of N is only 1.4 times larger than at the cmc (92 vs 64). Thus, the micelle growth is relatively small for any of the TAADS surfactants, except TBADS where it is a bit more important,[33] under the experimental conditions of the present study.

6. The effect of additions of tetramethylammonium chloride (TMACl) on the aggregation number of TMADS micelles at a surfactant concentration of 40 mM has been investigated. The results are summarized in Table 3. It is seen that the aggregation number is increased in the presence of salt, as is always observed with ionic surfactants.[28,31]

Micelle Ionization Degree. The values of the micelle ionization degree at the cmc, α^0 for the investigated surfactants were calculated from eq 1 using the values of the slopes of the electrical conductivity vs C plots above and below cmc and of the aggregation number at the cmc, N^0, listed in Table 1. The results show that one goes from an increase of α^0 with T for SDS, TMADS, and TEADS, to a near constancy of α_0 for TPADS and CsDS, and to a decrease of α^0 when T increases for TBADS. Nevertheless, the overall variation of α^0 with T is small for all surfactants. The ionization degree is the largest for SDS and the smallest for TBADS. The differences are rather small at 10 °C but increase with temperature and become significant at 40 °C.

Intramicellar Quenching Rate Constant. The values of the intramicellar quenching rate constant k_Q are listed in Tables 2 and 3. As was found with other surfactants, k_Q increases much with temperature and decreases as N increases.[3]

For a given surfactant at a given temperature N increases and k_Q decreases with increasing concentration, while the value of the product Nk_Q varies very little if at all. The constancy of Nk_Q is consistent with the conclusion inferred from the values of N, namely, that the micelles are spherical or spheroidal up to the highest concentration investigated (see above). Indeed it
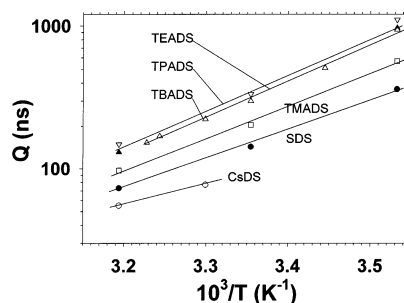
Figure 3. Variation of the microviscosity Q with $1/T$.

has been shown theoretically that for spherical micelles k_Q is nearly inversely proportional to N.[56]

Micelle Microviscosity. Figure 3 shows the variations of the quantity Q that is proportional to the microviscosity, with $1/T$, reciprocal of the absolute temperature. In the whole range of temperature the micelle microviscosity increases in the following sequence: CsDS < SDS < TMADS < TEADS ≈ TBADS ≈ TPADS. Thus, if we except CsDS where the strong quenching of the cesium ion may affect the results, the microviscosity appears to increase with the counterion radius. Besides, the plots are linear in the investigated range of temperature, in the semilog representation used. The slope of the plots has been used to determine the value of the activation energy $E_{DPyP}*$ of the micelle microviscosity, as sensed by the probe DPyP.[35] The values of $E_{DPyP}*$ listed in Table 4 increase in the same sequence as the microviscosity Q.

Information about the micelle microviscosity can also be obtained form the values of the product Nk_Q. Recall that the value of Nk_Q is inversely proportional to the microviscosity of the micelle.[57] Figure 4 shows the variations of Nk_Q with $1/T$ are linear in a semilog representation used. The results indicate that in the investigated range of temperature the microviscosity increases in the following sequence: CsDS ≈ SDS < TMADS < TEADS < TPADS < TBADS, that is with the radius of the counterion, as also found with DPyP. The values of $E_{TRFQ}*$ determined from the plots in Figure 4 are listed in Table 4. They increase in the sequence SDS ≈ CsDS < TMADS < TEADS < TPADS < TBADS, nearly as obtained with DPyP. However the values $E_{TRFQ}*$ are well below those of $E_{DPyP}*$.

Discussion

Cmc and Free Energy of Micellization. Using the values of the cmc and of α^0 in Table 1 we have calculated the value of the free energy of micellization $\Delta G°_M$ of the investigated surfactants from the equation[12]

$$\Delta G°_M = RT(2 - \alpha^0)\ln \text{cmc} \qquad (6)$$

In eq 6, the cmc is expressed in mole fraction. The values of $\Delta G°_M$ are listed in Table 4. The free energy of micellization is seen to become increasingly negative with increasing size of the counterion, indicating that micellization is favored by the increased hydrophobicity of the TAA$^+$ ion.

Two limiting models are used to discuss the values of $\Delta G°_M$. A first model assumes a simple binding of the TAA$^+$ ions to the micelle surface (adsorption model). The TAA$^+$ ion is modeled as a tetrahedron with the charged nitrogen atom at its center and the four terminal methyl groups of the alkyl chains at its four apexes. In this model the centers of any three terminal methyl groups define an equilateral triangle that is one of the four faces of the tetrahedron. The contact between a TAA$^+$ ion and the micelle is assumed to involve one face of the TAA$^+$

TABLE 4: Energy of Activation of the Microviscosity E^* and Free Energy of Micellization $\Delta G°_M$ at 25 °C

surfactant	SDS	CsDS[a]	TMADS	TEADS	TPADS	TBADS
E_{DPyP}^* (kJ/mol)	38.8 (36.4)[b]	27.3	43.5	47.8	47.8	47.8
E_{TRFQ}^* (kJ/mol)	19.6	19.6	20.4	21.5	23.9	24.4
$\Delta G°_M$ (kJ/mol)	−38.8	−41.1	−41.2	−42.6	−45.2	−48.9

a Value at 30 °C. *b* Value reported in ref 35.
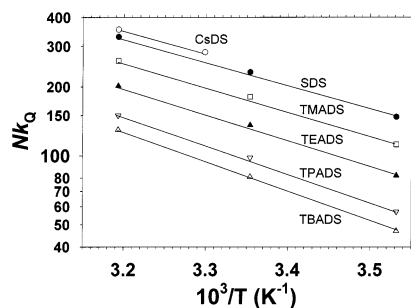
Figure 4. Variation of Nk_Q with $1/T$.

tetrahedron and to occur at one of the fatty patches present at the micelle surface. In this model the interaction involves three of the four alkyl chains of a bound TAA^+ counterion. The values of $\Delta G°_M$ in Table 4 yield increments in free energy per methylene group of − 0.47, −0.87, and −1.2 kJ/mol, in going from TMADS to TEADS to TPADS and to TBADS. In view of the assumptions underlying this model it is obvious that these increments represent lower bound values. Nevertheless, these values are much smaller than the free energy of micellization of −3.3 kJ/mol of CH_2 found for surfactants when the methylene group belongs to the surfactant alkyl chain.[12]

The other limiting model assumes that the TAA^+/micelle interaction involves the penetration of a single alkyl chain of the TAA^+ ion into the dodecyl sulfate micelle. This is equivalent to assuming a mixed micellization between TAA^+ and dodecyl sulfate ions. In this model the change of $\Delta G°_M$ in going from TPADS to TBADS, i.e., −3.7 kJ/mol, would be associated with the additional methylene group of the alkyl chain that is penetrating the micelle. This value is close to that for the micellization of one methylene group of the main surfactant alkyl chain. The agreement may be fortuitous. However, some results below (see below, section on intramicellar quenching rate constant) lend support to this model of the TAA^+/micelle interaction. Also, a study of the behavior of TMADS at the air−solution interface concluded to a penetration of part of the TMA^+ ions in the dodecyl sulfate layer.[58]

Micelle Polarity. As pointed out above pyrene senses a higher polarity in TAADS micelles than in SDS or CsDS micelles that have more hydrophilic counterions. A possible explanation for this counterintuitive result is that pyrene is located closer to the surface of the micelle of these surfactants than in SDS or CsDS micelles. Recall that an attractive interaction between pyrene and quaternary ammonium headgroups has been evidenced.[59−61] This interaction occurs between the π-electron cloud surrounding pyrene and the positive charge of the quaternary ammonium headgroup. A similar attractive interaction between pyrene and micelle-bound TAA^+ counterions may draw pyrene closer to the micelle surface. Such an interaction would be modulated by the size of the TAA^+ counterion. This may explain why I_1/I_3 is a maximum for TEADS. A full explanation of these results must wait for other data on the location of pyrene in, and the hydration of, the micelle palisade layer of the TAADS surfactants.

Variation of the Micelle Aggregation Number with the Counterion Size. For homologous series of surfactants in the

absence of additive, it is usually observed that the aggregation number N increases as the cmc decreases, in agreement with the prediction of theoretical treatments of the micellization.[52,53] However, the results in Figures 2A-C show a more complex behavior, particularly at 10 °C, where the sequence of micelle aggregation is opposite to that expected on the basis of the cmc values. It is only at 40 °C that the sequence of aggregation number starts showing some of the trends expected on the basis of the cmc values.

The literature reports one notable exception to the rule of a correlated decrease of cmc and increase of N. It concerns the effect of the headgroup size in the case of the tetradecyltrialkyl-ammonium bromide surfactants, $C_{14}H_{29}N^+(C_nH_{2n+1})_3,Br^-$. For these surfactants the values of both the cmc and N decrease as the size of the trialkylammonium headgroup increases.[62,63] This effect was explained in terms of a geometric steric hindrance (overlap) between the large trialkylammonium headgroups at the micelle surface. Rough calculations based on the values of bond angles and bond lengths showed that, as the size of the trialkylammonium headgroup increased, the geometric surface area covered by the headgroup became larger than the surface area available per surfactant at the micelle surface.[62,63] This hindrance constrains the micelles to take up a lower aggregation number. Indeed, for a given surfactant chain length, the surface area per headgroup at the micelle surface increases as the aggregation number decreases.[55,64] An overlap of the headgroups can be thus avoided by a reduction of the value of N.

A similar explanation may hold for the TAADS surfactants. The TAA^+ ions (radii increasing from 0.347 nm for TMA^+ to 0.494 nm for TBA^+)[36c] may be so large that the micelle surface does not offer sufficient surface area to accommodate all TAA^+ counterions that must bind to the micelles to ensure their stability. Therefore, the micelles take up lower values of N that correspond to larger surface area per headgroup in order to pack the counterions at the micelle surface.

A model very similar to that in ref 62 has been used to check this possibility. The surface area S_M of a dodecyl sulfate micelle of aggregation number N, the surface area S_{HG} covered by the N sulfate headgroups, and the surface area S_C occupied by the $(1 − \alpha^0)N^0$ bound TAA^+ ions, have been calculated. The results showed that $S_C > S_M − S_{HG}$, for TPA^+ and TBA^+. This result holds even if the TAA^+ ions are assumed to penetrate in the micelle core by 0.1 nm. S_C is still larger than $S_M − S_{HG}$ for TEA^+ but the difference is relatively small. For TMA^+, S_C is close to $S_M − S_{HG}$ at the cmc but would become smaller for the larger N values measured at higher concentration. The calculations are not reported in view of their very approximate character. In particular the water hydrating headgroups and counterions has not been taken into account. However it is noteworthy that from a qualitative viewpoint the inclusion of hydration water would further reduce the space available to counterions. It remains that the model used supports the explanation given above concerning our observations regarding the measured values of N for the TAADS micelles in terms of steric hindrance arising from the large size of the bound TAA^+ ions. This steric hindrance is also going to restrict the growth of the micelles upon increasing surfactant concentration.

If one accepts that for TPA^+ and TBA^+ $S_C > S_M - S_{HG}$, such a result means that the number of bound counterions is larger than the number of counterions that can be packed at the micelle surface. A tentative explanation of this unusual result is that most bound TAA^+ ions form a rather compact layer around the dodecyl sulfate micelle surface and that a few TAA^+ ions bind to this layer, forming a largely incomplete second layer. The existence of TAA^+-TAA^+ contacts in the micelle vicinity is supported by the tendency of TPA^+ and TBA^+ to self-associate in water into ill-defined aggregates with multiple charge.[15-19]An ultrasonic absorption study[19] indicated an onset of aggregation of about 1.5 and 0.8 M for TPA^+ and TBA^+, respectively. The concentration of bound TBA^+ ions in the spherical shell of thickness 1 nm (diameter of the TBA^+ ion) surrounding the micelle surface is 1.25 M, on the basis of the values of N^0 and α^0. The corresponding concentration is 1.4 M for TPADS. Thus, a few TAA^+ ions may be associated with TAA^+ ions bound to the micelle surface via hydrophobic interactions rather than being directly bound to the micelle surface, in the case of TPADS and particularly TBADS micelles. The existence of some TAA^+ ions bound to the micelles in this manner solves the problem of packing a number of counterions larger than the maximum number that can be packed at the micelle surface. The existence of such ions may also provide an explanation for the clouding of TBADS solutions upon increasing temperature. This will be discussed more at length elsewhere.[33]

The above discussion referred to the situation of the systems at the cmc, at 25 °C. As the surfactant concentration is increased the aggregation number increases. If the ionization degree remains unchanged, as this has been evidenced for a number of surfactants,[27] crowding of the TAA^+ ions at the micelle surface becomes more acute. Crowding may even occur for TMA^+ ions. More counterions may bind on top of the first layer of bound counterions, as discussed above. Another possibility is that the micelle ionization degree increases. Such an effect would result in a restricted micelle growth, as is experimentally observed (see N values for TMADS. In view of the lower cmc of TMADS with respect to SDS or CsDS one would have expected TMADS micelles to grow more rapidly with concentration than SDS or CsDS micelles). This intriguing possibility is presently being tested.

Effect of Temperature on the Micelle Aggregation Number. The N values represented in Figure 2A–C show that at 10 °C N(SDS) is larger than N(TAADS) in the investigated concentration range. At 25 °C, however, N(TMADS) becomes larger than N(SDS), and at 40 °C only N(TPADS) is still smaller than N(SDS). Thus, as the temperature increases the sequence of aggregation number tends to become normal, that is the surfactant with the lowest cmc tends to form the largest micelles. This effect of temperature can be explained with the model of micelle size controlled by the counterion size discussed in the preceding paragraph. Indeed, as the temperature increases, the micelle size decreases and the ionization increases, except for TBADS, which is not considered here. Estimates similar to the ones described above show that the problem of counterion overlap then becomes less acute. Indeed, there is more surface area available per headgroup at the surface of the micelle core and there are fewer counterions to pack on this surface. The result is that the micelles can then form with an aggregation number closer to that expected in the absence of counterion overlap. Then the change of N with counterion size tends to be the expected one.

Microviscosity. The concept of micelle microviscosity has been discussed.[35] In the present study, all the investigated surfactants share the same surfactant ion. Therefore, comparisons of values of microviscosity when changing only the surfactant counterion are meaningful, contrary to studies which compare values of the microviscosity of micelles with different surfactant ions. The microviscosity reported by DPyP as well as by the pair pyrene/dodecylpyridinium$^+$ is that at their preferential site of solubilization, that is in the micelle palisade layer. Indeed DPyP, pyrene and the pyridinium$^+$ group are aromatic and thus located in the micelle palisade layer.[40,65,66]

Our measurements do not yield absolute values of the microviscosity and the data obtained with DPyP and the pair pyrene/dodecylpyridinium$^+$ cannot be directly compared. Nevertheless both types of measurements indicate an increase of microviscosity with the counterion radius. The micelles of SDS and CsDS show a relatively large difference of aggregation number but a relatively small difference of microviscosity. On the other hand the micelles of SDS and TMADS are characterized by rather close values of the aggregation number but by differing values of the microviscosity. In view of these results we tentatively attribute the increased microviscosity of TAADS micelles with increasing TAA^+ radius to the progressive penetration of the alkyl chains of bound TAA^+ ions into the dodecyl sulfate micelle core discussed above. This would slow the diffusive motion of the probe and quencher that would then report a higher microviscosity.

The values of the activation energy of the microviscosity (Table 4) obtained with DPyP are much larger than with the pyrene/dodecylpyridinium$^+$. This result appears to be of general character. Indeed it also holds for the cationic surfactant dodecyltrimethylammonium bromide (DTAB). The reported values of N and k_Q for this surfactant[31] yielded $E_{TRFQ}* = 20.8$ kJ/mol, as compared to $E_{DPyP}* = 50.3$ kJ/mol. The microviscosity of DTAB micelles has also been investigated using the spin probe 5-doxylmethylstearate (5-DSE).[31] The results yielded an activation energy $E_{5-DSE}* = 29.3$ kJ/mol. This value is also lower than that from DPyP measurements but higher than when using the pair pyrene/dodecylpyridinium$^+$. The differences between the values of $E_{TRFQ}*$, $E_{DPyP}*$, and $E_{5-DSE}*$ probably reflect the different types of motion involved with these different probes. Indeed, TRFQ involves the translational motions pyrene and of the dodecylpyridinium ion. The DPyP probe undergoes a butterfly-like motion of the pyrenyl moieties. Last, the spin probe undergoes a rotational motion. The applicability of the Stokes–Einstein–Smolukhovsky equation using the values of the microviscosity found for TMADS micelles with the spin probe 5-DES will be addressed in a future paper.

Analogies between the Effect of the Nature of the Counterion and of the Surfactant Ion on the Self-Association Properties of Ionic Surfactants. The analogy in behavior between the TAADS surfactants and the tetradecyltrialkylammonium bromide (TTrAAB) surfactants concerning the effect of the size of the headgroup on the micelle aggregation number has been pointed out above. In both instances, the micelle aggregation number decreases upon increasing size of the counterion with TAADS surfactants and of the headgroup with TTrAAB surfactants. Also, in both series, the micelle microviscosity increases with the size of the counterion or of the headgroup whereas the micelle polarity (measured by the value of the pyrene intensity ratio I_1/I_3) increases mainly in going from the methyl to ethyl homologue.[63]

There are other instances where an effect observed by changing the nature or structure of the counterion is also

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observed when performing a similar modification of the surfactant ion. Take for instance the gemini surfactants $C_{12}H_{25}(CH_3)_2N^+(CH_2)_s{}^+N(CH_3)_2C_{12}H_{25}\cdot 2Br^-$.[68] The plot of the micelle aggregation number, at low to moderate surfactant concentration, as a function of the carbon number s of the polymethylene spacer $(CH_2)_s$ shows a minimum at around $s = 8-10$.[68] For the anionic surfactants $Pyr^+(CH_2)_sPyr^+\cdot 2C_{12}H_{25}SO_3^-$, with bispyridinium bolaform counterions (Pyr^+ stands for pyridinium), the micelle molecular weight at the cmc was found to be a minimum at $s = 10$.[69] In both series of surfactants, the observed minimum was explained in terms of a penetration of the polymethylene group of the spacer or of the counterion into the micelle core, when it became long enough.[68,69]

Another example concerns the organized phases produced by surfactants containing chiral atoms. The gemini surfactant $C_{16}H_{33}(CH_3)_2N^+(CH_2)_2{}^+N(CH_3)_2C_{16}H_{33}\cdot tartrate^{2-}$, where the $tartrate^{2-}$ counterion contain chiral carbons, gives rise to twisted ribbons (helical structures)[70] whereas the surfactant $C_{16}H_{33}$-$(CH_3)_2N^+(CH_2)_2{}^+N(CH_3)_2C_{16}H_{33}\cdot 2Br^-$ does not show such structures. The gemini surfactant $[Na_2O_3POCH_2CHOC(O)$-$C_{17}H_{35}]_2(CH_2CH_2)$, where the chiral carbon atoms are located in the surfactant ion, also gives rise to helical fibrillar structures.[71]

The number of examples in which the character of an aggregate of ionic surfactant can be modified through manipulation of the amphiphilic ion or the counterion is expected to continue to grow, as more systems are investigated.

Summary and Conclusions

The surfactants CsDS, TMADS, TEADS, TPADS, and TBADS have been characterized by the value of the cmc and micelle ionization degree at the cmc, the micelle polarity and viscosity, and the micelle aggregation number. Both the cmc and the micelle aggregation number N have been found to decrease as the radius of the counterion increases, whereas it is usually observed that N decreases as the cmc increases. Two effects appear to be responsible for this unusual behavior: first, the large size of TAA^+ ions and, second, their hydrophobic character that is well demonstrated for TEA^+, TPA^+, and TBA^+ by their self-association in water. We proposed on the basis of a simple model that the TAA^+ ions are so large that steric hindrance impedes their binding to the micelles and thus limits the value of the aggregation number and the growth of the micelles. This situation led us to tentatively conclude that a few bound TAA^+ ions may not in contact with the micelle surface but are associated with TAA^+ ions directly bound to this surface, via hydrophobic interactions. This is particularly true for TPA^+ and TBA^+. This aspect of TAADS micellar solutions and the possibility that one of the alkyl chains of the largest TAA^+ ions (TPA^+ and TBA^+) may penetrate into the micelles deserve further investigation. Small-angle neutron-scattering experiments with variable contrast using selectively labeled surfactants (on the chain and on the counterion) coupled with time-resolved fluorescence quenching determination of micelle aggregation numbers of the labeled surfactants may help understanding the behavior of these surfactants.

References and Notes

(1) Rehage, H.; Hoffmann, H. *Mol. Phys.* **1991**, *74*, 933.

(2) Hoffmann, S.; Rauscher, A.; Hoffmann, H. *Ber. Bunsen-Ges. Phys. Chem.* **1991**, *95*, 153.

(3) Malliaris, A.; Lang, J.; Zana, R. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 109.

(4) Candau, S. J.; Hirsch, E.; Zana, R. *J. Phys. (Paris)* **1984**, *45*, 1263.

(5) Shikata, T.; Imai, S.-I.; Morishima, Y. *Langmuir* **1997**, *13*, 5229.

(6) Appell, J.; Porte, G.; Khatory, A.; Kern, F.; Candau, S. J. *J. Phys. II (Fr.)* **1992**, *2*, 1045.

(7) Gamboa, C.; Sepulveda, L. *J. Colloid Interface Sci.* **1986**, *113*, 566.

(8) Sepulveda, L.; Cortes, J. *J. Phys. Chem.* **1985**, *89*, 5322.

(9) Gaillon, L.; Lelievre, J.; Gaboriaud, R. *J. Colloid Interface Sci.* **1999**, *213*, 287.

(10) Ninham, B. W. *Adv. Colloid Interface Sci.* **1999**, *83*, 1.

(11) Alfridsson, M.; Ninham, B. W.; Wall, S. *Langmuir* **2000**, *16*, 10087 and references therein.

(12) Mukerjee, P. *Adv. Colloid Interface Sci.* **1967**, *1*, 241.

(13) Baumuller, W.; Hoffmann, H.; Ulbricht, W.; Tondre, C.; Zana, R. *J. Colloid Interface Sci.* **1978**, *64*, 418.

(14) Satake, I.; Iwamatsu, I.; Hosokawa, S.; Matuura, R. *Bull. Chem. Soc. Jpn.* **1963**, *36*, 204.

(15) Tamaki, K. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2764.

(16) Wen, W.-Y.; Saito, S. *J. Phys. Chem.* **1964**,*68*, 2639.

(17) Wirth, H. E.; LoSurdo, A. *J. Phys. Chem.* **1968**, *72*, 751.

(18) Wirth, H. E.; LoSurdo, A. *J. Phys. Chem.* **1972**, *76*, 130.

(19) Blandamer, M. J.; Foster, M. J.; Hidden, N. J.; Symons, M. C. R. *Trans. Faraday Soc.* **1968**, *64*, 3247.

(20) Szajdzinska-Pietek, E.; Maldonado, R.; Kevan, L.; Berr, S. S.; Jones, R. R. *J. Phys. Chem.* **1985**, *89*, 1547.

(21) Berr, S. S.; Coleman, M. J.; Jones, R. R.; Johnson, Jr., J. S. *J. Phys. Chem.* **1986**, *90*, 6492.

(22) Z.-J. Yu; G. Xu *J. Phys. Chem.* **1989**, *93*, 7441.

(23) Z.-J. Yu; Z. Zhou; G. Xu *J. Phys. Chem.* **1989**, *93*, 7446.

(24) Z.-J. Yu; Zhang, X.; Z. Zhou; G. Xu *J. Phys. Chem.* **1990**, *94*, 3675.

(25) Kumar, S.; Sharma, D.; Kabir-U-Din *Langmuir* **2000**, *16*, 6821.

(26) Kumar, S.; Aswal, V. K.; Naqvi, A. Z.; Goyal, P. S.; Kabir-U-Din *Langmuir* **2001**, *17*, 2549.

(27) Kumar, S.; Sharma, D.; Khan, Z. A.; Kabir-U-Din *Langmuir* **2001**, *17*, 5813.

(28) Bales, B. L.; Shahin, A.; Lindblad. C.; Almgren, M. *J. Phys. Chem. B* **2000**, *104*, 256 and references therein.

(29) Ranganathan, R.; Peric, M.; Medina, R.; Garcia, U.; Bales, B. L. *Langmuir* **2001**, *17*, 6765.

(30) Bales, B. L. *J. Phys. Chem. B* **2001**, *105*, 6798.

(31) Bales, B. L.; Zana, R. *J. Phys. Chem.* B **2002**, *106*, 1926.

(32) Bales, B. L.; Benrraou, M.; Zana, R. *J. Phys. Chem.* B **2002**, *106*, 9033.

(33) Bales, B.; Benrraou, M.; Zana, R. Manuscript in preparation.

(34) Petit-Agnely, F.; Iliopoulos, I.; Zana, R. *Langmuir* **2000**, *16*, 9921.

(35) Zana, R. *J. Phys. Chem.* **1999**, *103*, 9117 and references therein.

(36) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed. (revised); Butterworths: London, 1959: (a) p 462; (b) p 465; (c) p 124.

(37) Evans, H. C. *J. Chem. Soc.* **1956**, 579.

(38) Tachiya, M. *Chem. Phys. Lett.* **1975**, *33*, 289.

(39) Infelta, P. P. *Chem. Phys. Lett.* **1979**, *61*, 88.

(40) Zana, R. In *Surfactant Solutions. New Methods of Investigation*; Zana, R., Ed.; Marcel Dekker Inc.: New York, 1987; p 241.

(41) Almgren, M. *Adv. Colloid Interface Sci.* **1992**, *41*, 9.

(42) Gehlen, M. H.; De Schryver, F. C. *Chem. Rev.* **1993**, *93*, 199.

(43) Malliaris, A.; Le Moigne, J.; Sturm, J.; Zana, R. *J. Phys. Chem.* **1985**, *89*, 2709.

(44) Alargova, R. G.; Kochijashky, I. I.; Sierra, M. L.; Zana, R. *Langmuir* **1998**, *14*, 6599.

(45) Sasaki, T.; Hattori, M.; Sasaki, J.; Nukina, K. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1397.

(46) Hall, D. G. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 1121.

(47) Kalyanasundaram, K.; Thomas, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 2039.

(48) Mukerjee, P.; Mysels, K. J.; Dulin, C. I. *J. Phys. Chem.* **1958**, *62*, 1390.

(49) Flockhart, B D. *J. Colloid Interface Sci.* **1961**, *16*, 484.

(50) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: London, 1970; p 209.

(51) Kalyanasundaram, K. In *Photochemistry in Microheterogeneous Systems*; Academic Press: Orlando, FL, 1987; p 93.

(52) Israelachvili, J. N.; Mitchell, D. J.; Ninham, B. W. *J. Chem. Soc., Faraday Trans.* **1976**, *72*, 1525.

(53) Nagarajan, R.; Ruckenstein, E. *J. Colloid Interface Sci.* **1979**, *71*, 580.

(54) The aggregation number of the maximum spherical micelle formed by a surfactant with an alkyl chain containing m carbon atoms is calculated using the expressions given by Tanford[55] for the length and volume of the alkyl chain.

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(55) Tanford, C. *J. Phys. Chem.* **1972**, *76*, 3020.

(56) Van Der Auweraer, M.; De Schryver, F. C. *Chem. Phys.* **1987**, *111*, 105.

(57) Lianos, P.; Lang, J.; Strazielle, C.; Zana, R. *J. Phys. Chem.* **1982**, *86*, 1019.

(58) Su, T. J.; Lu, J. R.; Thomas, R. K.; Penfold, J. *J. Phys. Chem. B* **1997**, *101*, 937.

(59) Lianos, P.; Zana, R.; Viriot, M. *J. Phys. Chem.* **1984**, *88*, 1098 and references therein.

(60) Bacaloglu, R.; Bunton, C.; Ortega, F. *J. Phys. Chem.* **1989**, *93*, 1497.

(61) Sabaté, R.; Gallardo, M.; Esterlich, J. *J. Colloid Interface Sci.* **2001**, *233*, 205 and references therein.

(62) Zana, R. *J. Colloid Interface Sci.* **1980**, *78*, 330.

(63) Lianos, P.; Zana, R. *J. Colloid Interface Sci.* **1982**, *88*, 594.

(64) Tanford, C. *J. Phys. Chem.* **1974**, *78*, 2469.

(65) Handa, T.; Matsuzaki, K.; Nakagaki, M. *J. Colloid Interface Sci.* **1987**, *116*, 50.

(66) Macanita, A.; Costa, F.; Costa, S.; Melo, E.; Santos, H. *J. Phys. Chem.* **1989**, *93*, 336.

(67) Bales, B.; Tiguida, K.; Benrraou, M.; Zana, R. Manuscript in preparation.

(68) Danino, D.; Talmon, Y.; Zana, R. *Langmuir* **1995**, *11*, 1448.

(69) Moroi, Y.; Matuura, R.; Tanaka, M.; Murata, Y.; Aikawa, Y.; Furutani, E.; Kuwamura, T.; Takahashi, H.; Inokuma, S. *J. Phys. Chem.* **1990**, *94*, 840.

(70) Oda, R.; Huc, Y.; Candau, S. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 2689.

(71) Sommerdijk, N. A. M.; Lambermon, M. H. L.; Feiters, M. C.; Nolte, R. J. M.; Zwanenburg, B. *Chem. Commun.* **1997**, 1423.