Physicochemical Properties of α,ω-Type Surfactant in Aqueous Solution. Bis(triethylammonium) 1,20-Eicosanediyl Disulfate

Kenji IKEDA,* Motoharu ISHIKAWA, Masaaki YASUDA, Kunio ESUMI, Kenjiro MEGURO,
William BINANA-LIMBELE,† and Raoul ZANA†
Department of Applied Chemistry, Institute of Colloid and Interface Science, Science
University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162
†CNRS, Institut C. Sadron (C.R.M.-E.A.H.P.), 6 rue Boussingault, 67083 Strasboug-Cedex, France

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The physicochemical properties of the α,ω-type (bolaform) surfactant, bis(triethylammonium) 1,20-eicosanediyl disulfate (α,ω $C_{20}N_2Et_6$), in aqueous solution have been investigated by means of surface tension, electrical conductivity, dye solubilization and time-resolved fluorescence quenching. The critical micelle concentration of α,ω $C_{20}N_2Et_6$ was 1—1.3×10^{-3} mol dm^{-3}. The micelle ionization degree of the surfactant was larger than a conventional surfactant having the same head group. From surface tension measurements, the molecular area of α,ω $C_{20}N_2Et_6$ at the air-water interface was found to be about twice as large as that of a normal type surfactant, such as sodium dodecyl sulfate (SDS). This reveals that α,ω $C_{20}N_2Et_6$ probably forms vertical looping ("wicket-like" conformation) at the air-water interface. By time-resolved fluorescence quenching measurements, the aggregation number of α,ω $C_{20}N_2Et_6$ micelle was found to be strongly dependent on the concentration, but only slightly dependent on the temperature. At low concentrations the aggregation number is close to half that corresponding to a normal type surfactant having a chain length that is that of the bolaform. The solubilizing power of a micellar solution of α,ω $C_{20}N_2Et_6$ toward Orange OT was 7.6×10^{-3} mol of dye per mol of surfactant, that is, a value smaller than that of SDS.

α,ω-Type (bolaform) surfactnts have hydrophilic head groups at both ends of the hydrophobic alkyl chain. Interest in bolaform surfactants has increased steadily in recent years from the stand points of both fundamental investigations and applications.[1—14)] The investigations of α,ω-type surfactants in aqueous solutions have shown the following. First, the propensity of micelle formation of the α,ω-type surfactants is generally lower, the size of their micelles is smaller,[8,9,11—13)] and their cmc is generally higher than that of single head surfactants of comparable chain length.[7—9)] Second, the α,ω-type surfactants have been shown to adopt a folded, wicket-like, conformation at the air-water interface.[6,8)] Third, it was suggested that these surfactants may exist in a predominantly folded conformation in micelles.[9c)] As regards to the last point, a study for providing direct evidence on the conformation of these surfactants in micellar solutions, performed by using ^{13}C and ^{14}N NMR relaxation techniques,[13)] suggested that bolaform surfactant chains adopt a predominantly stretched form in micelles. Recently, we have reported on the properties of α,ω-type cationic surfactant.[12,13)] However, there have been a few reports about other types α,ω surfactant, i.e. the anionic or nonionic type.

In this study, as one of the systematic investigations with α,ω-type surfactants, the physicochemical properties of the anionic surfactant bis(triethylammonium) 1,20-eicosanediyl disulfate in aqueous solution have been investigated by means of surface tension, electrical conductivity, dye solubilization and time-resolved fluorescence.

Experimental

Materials. Bis(triethyl ammonium) 1,20-eicosanediyl disulfate was synthesized by using eicosanedioic acid (Okamura Oil Mill Ltd.) as the starting material via 1,20-eicosanediol. Eicosanedioic acid was reduced to 1,20-eicosanediol by using borane-THF complex (Aldrich Chem. Co.). The diol was recrystallized twice from benzene and dried for 48 h under vacuum. Its purity was confirmed by IR spectroscopy. The diol was reacted with chlorosulfuric acid to give 1,20-eicosanedisulfonic acid which was neutralized with triethylamine. The bolaform was recrystallized three times from an acetone–ethanol mixture and three times from an ethyl acetate–ethanol mixture; it was then washed twice with diethyl ether and dried for more than 72 h under vacuum. The white crystalline product was found to be more than 99% pure by elemental analysis, isotachophoresis (IP-3A: Shimadzu Co., Ltd.), NMR, and surface tension. *N*-Phenylbenzoylacetamide (BZAA), ammonium 8-anilino-1-naphthalenesulfonate (ANS) (Wako Pure Chemical Industries. Ltd.) and benzoylacetone (BZA) (Tokyo Kasei Co.) were used without further purification. Yellow OB and Orange OT (Tokyo Kasei Co., recrystallized twice from ethanol) were used as dyes.

Measurements and Methods. The surface tensions of aqueous surfactant solutions were measured by a Wilhelmy-type surface tensiometer (Shimadzu ST-1) at 25 °C. The establishment of equilibrium was checked by repeated measurements in 5-minute intervals. The electrical conductivity of the solution was measured by means of a conductivity meter (Model CM-30ET Toa Denpa Co.) at 25±0.1 °C. The fluorescence and UV spectra of each sample were measured with a fluorescence spectrophotometer (Hitachi 650-10S) and a UV spectrophotometer (Hitachi 220A). The emission and excitation slits were set at 10 nm for ANS and at 1 nm for pyrene. Pyrene and ANS were excited at 335 and 365 nm, respectively. The concentrations of these probes were kept at 5.0×10^{-5} mol dm^{-3} for ANS and 1.6×10^{-6} mol dm^{-3} for pyrene. The emission intensity was measured from 350 to 600 nm.

The solubilization measurements of water-insouble dyes were carried out as follows. After an excess amount of water-insoluble dye was added to the surfactant solutions, the solutions were shaken for 48 h in order to reach a solubilization equilibrium. After centrifugation (5000 rpm, 30 min) of these suspensions, the supernatant solutions were taken, and diluted by ethanol. The optical density of the solution at each absorption maximum was measured with a UV spectrophotometer; the dye concentration was determined from calibration curves.

Prior to fluorescence measurements the solutions were bubbled with argon for about 20 min for deoxygenation. The fluorescence decay experiments were performed with the same photon-counting apparatus as in our previous studies,[15] modified by the use of an amplifier and single-channel analyzer (Ortec, type 590), which ensured rejection of multiphoton events and, thus, permitted a higher count rate. The measurements were performed at concentrations of 0.05, 0.1, 0.197, 0.296, 0.302 $\mathrm{mol\,dm^{-3}}$. The fluorescence decay curves were determined at low pyrene concentration (generally around 10^{-5} $\mathrm{mol\,dm^{-3}}$) in the absence and in the presence of the quencher *N*-dodecylpyridinium chloride (DPCl) at a concentration such that the [DPCl]/[micelle] molar concentration ratio, *R*, was around 1. The decay curves were computer-fitted to Eqs. 1 and 2 in both absence and presence of the DPCl:

$$I = I(0)\exp(-t/\tau_0) \qquad (1)$$

and

$$I = I(0)\exp[-A_2t - A_3(1-\exp(-A_4t))], \qquad (2)$$

respectively, after convolution with a lamp curve, using a nonlinear weighted least-squares procedure. The fitting yielded τ_0, fluorescence lifetime of micelle-solubilized pyrene in the absence of quencher and constants A_2, A_3, and A_4. In general, it was found that $\tau_0 > A_2^{-1}$. This result indicated that the quencher was not completely immobile on the fluorescence timescale. However, the use of the full expressions of A_2, A_3, and A_4 values in such a situation[16] yielded $A_3 = R$ because of the high concentration of quencher used in the experiments in view of the small aggregation number of the bolaform micelles. The aggregation number *N* was obtained from

$$N = R(C - \mathrm{cmc})/[\mathrm{DPCl}], \qquad (3)$$

where *C* is the concentration of the surfactant and cmc its critical micelle concentration

The aggregation number of α,ω $\mathrm{C_{20}N_2Et_6}$ micelles was also determined by the static fluorescence quenching method.[26] The quenching of the fluorescence emission (at 372 nm) of micelle-solubilized pyrene by *N*-hexadecylpyridinium chloride (CPCl) was measured at increasing contents of quencher and constant concentration of pyrene (1×10^{-5} $\mathrm{mol\,dm^{-3}}$) and surfactant. The slope of the line obtained by plotting $\ln I_0/I$ (where I and I_0 are the fluorescence intensities with and without a quencher) versus the quencher concentration yields the micelle aggregation number.

Results and Discussion

Surface Tension. Figure 1 shows a plot of the equilibrium surface tension, γ, versus the log of the concentration *C* (in molarity) of an α,ω $\mathrm{C_{20}N_2Et_6}$ aqueous solution. The γ_{cmc} value of α,ω $\mathrm{C_{20}N_2Et_6}$ was slightly higher than those for the corresponding normal-type surfactants, i.e., alkyl hydrogensulfate. Figure 1 shows that the break in the γ vs. $\log C$ curve at the cmc is nearly as sharp as for normal-type surfactants such as sodium dodecyl sulfate (SDS). However, there appears to be a small decrease of γ upon increasing *C* at above 3×10^{-3} $\mathrm{mol\,dm^{-3}}$. The critical micelle concentration of α,ω $\mathrm{C_{20}N_2Et_6}$ from the surface tension was 1.0×10^{-3} $\mathrm{mol\,dm^{-3}}$. Surface area calculations were based on the Gibbs adsorption equation,

$$\Gamma = -(1/nRT)(\partial\gamma/\partial \ln a), \qquad (4)$$

where γ, Γ, and a denote the surface tension in $\mathrm{mN\,m^{-1}}$, the surface excess in $\mathrm{mol\,cm^{-2}}$, and the activity of the surfactant, respectively. The factor $n=3$ in the denominator is applicable for a 2:1 electrolyte with no added salt; and for a dilute solution a is substituted for by the concentration, *C*. In Eq. 5, where N_A is Avogadro's number,

$$A = 10^{16}/\Gamma N_\mathrm{A} \qquad (5)$$

gives the surface area *A* in Å^2 per molecule. The surface area was calculated from γ vs. $\log C$ plots. α,ω $\mathrm{C_{20}N_2Et_6}$ had a surface area of 66.1 Å^2/molecule, which is very close to twice the value of 33.0 Å^2/molecule for SDS obtained by other workers.[17] Therefore, α,ω $\mathrm{C_{20}N_2Et_6}$ seems to form vertical looping, "wicket-like" conformation, at the air-water interface. This picture is consistent with that suggested by other reports.[2,6,8]

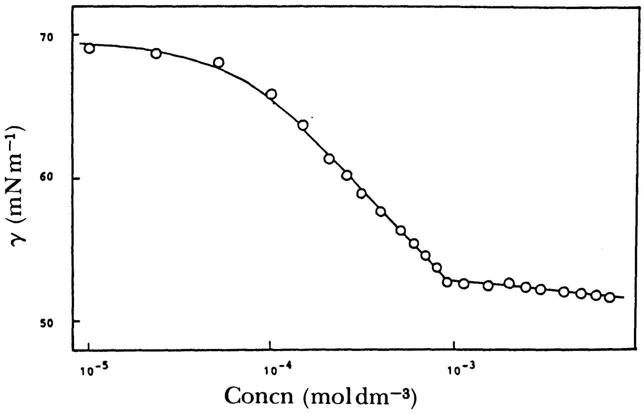

Fig. 1. Plot of surface tension, γ, against log concentration

Conductivity. The variations of the conductivity κ with concentration *C*, and of the equivalent conductivity Λ with the square root of the concentration expressed in equivalent per liter $(2C)^{1/2}$ are shown in Fig. 2. Each plot shows a sharp break at a concentration corresponding to the critical micelle concentration (cmc): 1.3×10^{-3} $\mathrm{mol\,dm^{-3}}$ from the κ-plot and 1.25×10^{-3} $\mathrm{mol\,dm^{-3}}$ from the Λ-plot. The slope of the Λ vs. $(2C)^{1/2}$ plot is close to the limiting slope expected for a 2:1 electrolyte in the range 3×10^{-4}—10^{-3} mol $\mathrm{dm^{-3}}$ (below 3×10^{-4} $\mathrm{mol\,dm^{-3}}$, the error on κ is too large for meaningful calculations of Λ-values.) The

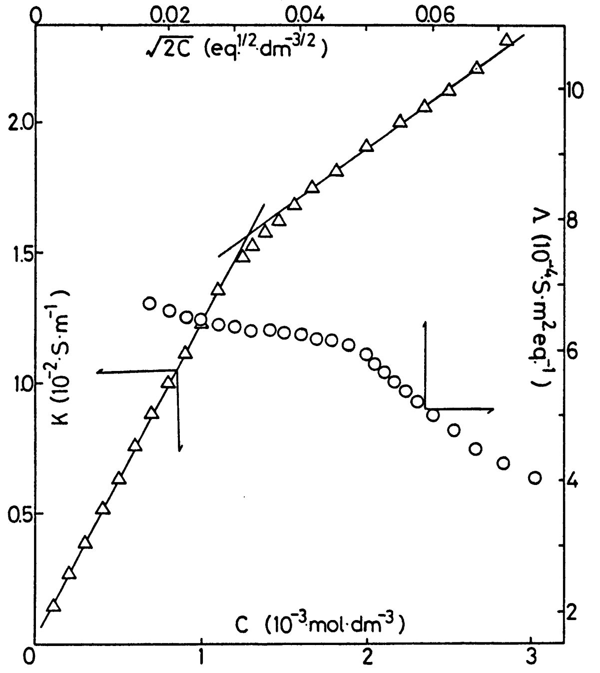

Fig. 2. Electrical conductivity–concentration of α,ω $C_{20}N_2Et_6$ (Δ) and equivalent conductivity–(concentration)$^{1/2}$ (O) curves.

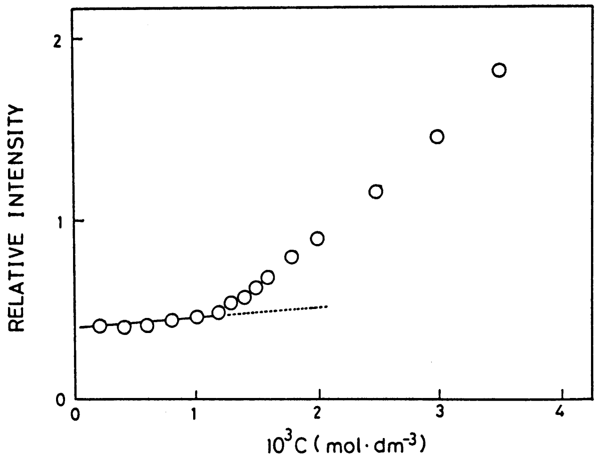

Fig. 3. Variation of the intensity of fluorescence of ANS as a function of α,ω $C_{20}N_2Et_6$ concentration.

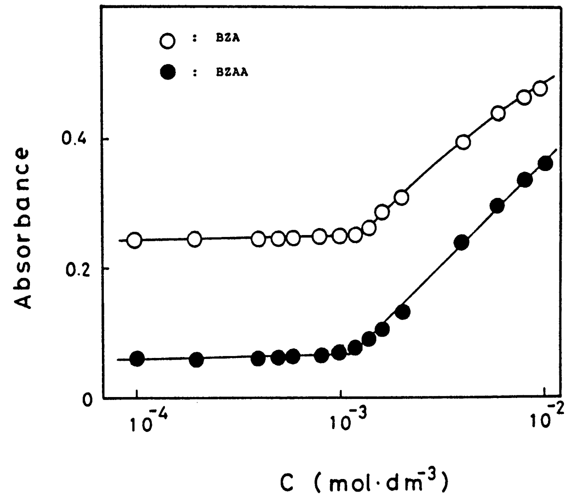

Fig. 4. UV absorbance of BZA and BZAA as a function of α,ω $C_{20}N_2Et_6$ concentration.

Table 1. cmc of α,ω $C_{20}N_2Et_6$ at 25 °C

Method	10^3cmc/mol dm^{-3}
Surface tension	1.0
Equivalent conductivity	1.3
Solubilization (ANS)	1.25
(BZA)	1.2
(BZAA)	1.2

micelle ionization degree, α=0.38, was obtained as the ratio of the slopes of the κ vs. C plots above and below cmc. This value is slightly larger than that of SDS micelles: 0.32, obtained as part of this work from the κ vs. C plot for this surfactant.

Solubilization of Dyes. The solubilization properties of aqueous solutions of α,ω $C_{20}N_2Et_6$ were studied by using ANS, BZA, BZAA, pyrene, Yellow OB, and Orange OT. The absorption and fluorescence spectra of organic compounds solubilized in micelles provide information about micellar properties. ANS is an indicator for the determination of the cmc of a surfactant because the quantum yield of this fluorescence probe is much higher in a nonpolar medium than in a polar solvent like water.[8,18,19] Figure 3 shows that the fluorescence intensity of ANS increased steadily at C above 1.25×10^{-3} mol dm^{-3}, which can be considered as the cmc of α,ω $C_{20}N_2Et_6$. This cmc value agrees with those obtained by electrical conductivity and surface tension.

The keto-enol tautomerisms of BZAA and BZA were also used to probe for micelle formation. The keto-form structure is predominant when the probe is in water. The change from a keto-form to an enol-form structure occurs when the polarity of the probe environment is decreased.[20] The cmc value (1.2×10^{-3} mol dm^{-3}) determined from the change of the probe absorbance, associated with this conformational transition (Fig. 4) agrees with those from other methods. All the cmc values obtained by several methods are listed in Table 1.

The fluorescence probe pyrene was used to investigate the polarity of α,ω $C_{20}N_2Et_6$ micelles. The ratio I_1/I_3 of the intensities of the first and third vibronic peaks of pyrene increases upon going from aliphatic to polar solvents and can be used as an indicator of the effective local polarity of the pyrene solubilization site in the micelles.[21] Figure 5 shows that I_1/I_3 decreases with an increasing α,ω $C_{20}N_2Et_6$ concentration from a value above 1.8 below cmc to a value of 1.42 at a concentration of 0.1 mol dm^{-3}, well above cmc. This last value is well above that found with normal-type surfactants, such as SDS, and indicates that pyrene senses

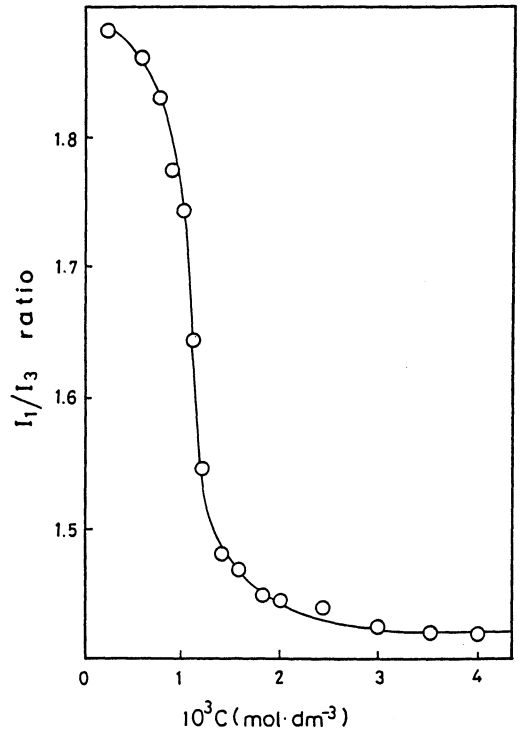

Fig. 5. Variation of the I_1/I_3 intensity ratio for pyrene in aqueous solutions of α,ω $C_{20}N_2Et_6$ as a function of the surfactant concentration.

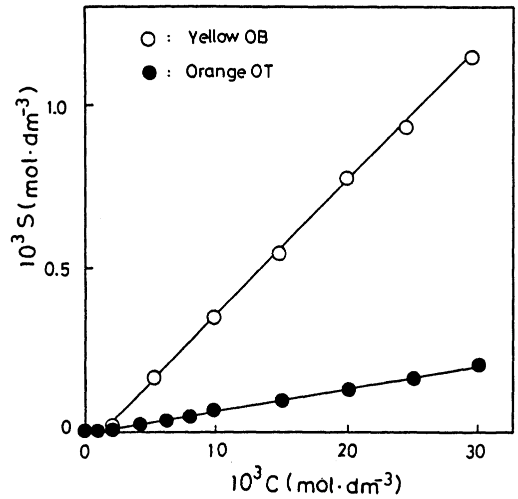

Fig. 6. Solubility of Yellow OB and Orange OT in α,ω $C_{20}N_2Et_6$ solutions as a function of concentration.

a fairly polar environment in α,ω $C_{20}N_2Et_6$ micelles. These micelles may not be as well organized as a normal-type surfactant micelle and allow somewhat more extensive pyrene-water contacts in the micelle palisade layer where pyrene preferentially resides.[21)]

Table 2. Aggregation Number of α, ω $C_{20}N_2Et_6$ Micelles as a Function of Temperature and Concentration

T	C/mol dm^{-3}				
°C	0.05	0.1	0.197	0.296	0.302
25	20±2	29±3	39	—	44
30	19	—	—	—	—
35	—	—	39	—	—
40	18.5	—	39	46	48
50	17±2	—	37	—	47

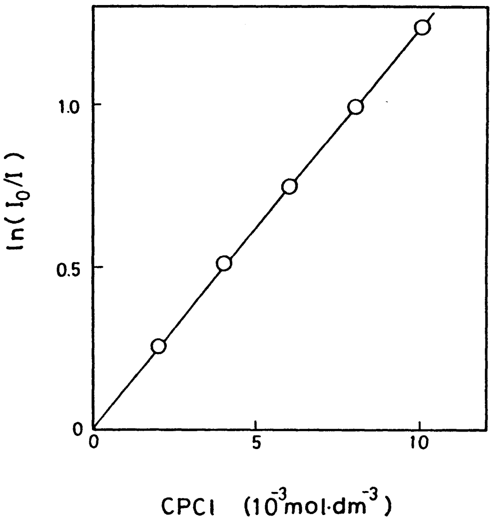

Fig. 7. Variation of $\ln I_0/I$ with the CPCl concentration in a 2×10^{-2} mol dm^{-3} solution of α,ω $C_{20}N_2Et_6$.

The molar concentrations of Yellow OB and Orange OT solubilized in α,ω $C_{20}N_2Et_6$ solutions are plotted against the surfactant concentration in Fig. 6. The solubilities of Yellow OB and Orange OT increased rapidly and linearly above the cmc. The slope of the line yields the number of moles of solubilized dye per mole of micellar surfactant, i.e., the solubilizing power. For α,ω $C_{20}N_2Et_6$ micelles, the solubilizing power was 4.49×10^{-2} and 7.64×10^{-3} mol of dye per mol of surfactant for Yellow OB and Orange OT, respectively. The value for Orange OT was smaller than that of the conventional surfactant micelles such as SDS: 9.90×10^{-3} for Orange OT. If the solubilizing power is expressed in moles of solubilized dye per mole of surfactant head groups, the value of α,ω $C_{20}N_2Et_6$ then appears to be much smaller than that of SDS. However, the solubilizing power of different surfactants should be compared at a constant solubilizing volume, which is proportional to the alkyl chain length, that is the number of carbon atoms, to the third power. The solubilizing power of α,ω $C_{20}N_2Et_6$ expressed in moles of dye per mole of surfactant head groups was thus found to be 6.6×10^3 when corrected by the factor $(12/10)^3$, that is a little smaller than for SDS.

Aggregation Number. Table 2 lists the values of the micelle aggregation number, N, at several temperatures and surfactant concentrations, obtained from time-resolved fluorescence quenching experiments. Static fluorescence quenching experiments using pyrene as probe and N-hexadecyl pyridinium chloride (CPCl) as quencher yielded a linear $\ln I_0/I$ vs. quencher concentration plot (see Fig. 7) from which the value N=15 was obtained by using Eq. 3 in Ref. 22, at $C=2\times10^{-2}$ mol dm^{-3} (25 °C), in good agreement with the results in Table 2. The aggregation number greatly increased with concentration. This increase is somewhat comparable to that found for SDS, where N increases from 65 to 110 when the concentration goes from 0.1 to 0.6 mol dm^{-3}.[23] Notice that a 0.3 mol dm^{-3} α,ω-type surfactant corresponds to 0.6 mol dm^{-3} of a classical surfactant with an alkyl chain equal to half that of the α,ω-type surfactant. Studies with another bolaform surfactant, 1,20-bis(triethylammonio)eicosane dibromide, referred to as $C_{20}Et_6$, have yielded an aggregation number which showed only little dependence on the concentration.[25] This difference with α,ω $C_{20}N_2Et_6$ may be due to the fact that the head-group size in $C_{20}Et_6$ is much larger than in α,ω $C_{20}N_2Et_6$. It will, thus, form small micelles and will have a lesser tendency to grow upon increasing concentration since its stacking parameter[24] (volume/surface area per head group × alkyl chain length) is smaller. On the other hand, it is noteworthy that $C_{20}Et_6$ and α,ω $C_{20}N_2Et_6$ have nearly the same aggregation numbers at low concentration: 17—20, and that these values are close to that calculated with the oil drop model for a classical surfactant with a 10 carbon atom alkyl chain. Finally, Table 2 shows that the aggregation number of α,ω $C_{20}N_2Et_6$ in an aqueous solution depends little on the temperature in comparison with normal type surfactants. Dodecyltrimethylammonium chloride (DTAC), dodecyltrimethylammonium bromide (DTAB), and SDS show a linear, or nearly linear, decrease of N upon increasing temperature.[26—28] For normal-type surfactants, the larger the value of N at low temperature, the steeper the decrease of N upon increasing the temperature.

One last point must be made. From the analysis of the pyrene fluorescence decay curve in presence of DPCl, we have been able to extract the rate constant k^- for the exit of the quencher dodecylpyridinium ion from α,ω $C_{20}N_2Et_6$ micelles. Although these values are fairly inaccurate, because of the small magnitude of k^- with respect to the quantity A_4, they all turned out to be in the range $1—2\times10^5$ s^{-1}. The residence time of the probe in the bolaform micelle is, thus, 5 to 10 μs. This value is comparable to that for other surfactants having the same chain length.[29]

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