Fluorescence Study of Premicellar Aggregation in Cationic Gemini Surfactants

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The aggregation behavior of four series of bis(quaternary ammonium halide) surfactants (gemini surfactants) having diethyl ether, dihydroxybutyl, monohydroxypropyl, and dimethylene phenylene spacer groups has been studied using steady-state and time-resolved fluorescence spectroscopy. Aggregation numbers were determined using the time-resolved single photon counting method with pyrene as the probe. At certain surfactant concentrations, aggregation numbers of 2, expressed as gemini molecules per micelle, were obtained in all four series when the number of carbon atoms in the alkyl chain length (*n*) increased beyond a maximum. These long-chain geminis also have a critical micelle concentration (cmc) greater than expected on the basis of plots of log cmc vs n for the shorter chain homologues. This deviation has been attributed to the formation of premicellar aggregates in the surfactant concentration region between the observed and the expected cmc values. The aggregation numbers obtained here indeed point to the existence of dimers in this region. Steady-state fluorescence measurements of I_1/I_3 values, which are indicative of the polarity of the probe environment, are followed as a function of surfactant concentration. These ratios are used to compare cmc values obtained by surface tension methods as well as to confirm the more hydrophilic nature of systems where dimers are thought to be present.

Introduction

Gemini surfactants (containing two hydrophobic and two hydrophilic groups in the molecule) continue to be of interest due to the enhanced surface properties that they exhibit¹⁻³ and the consequent implied applications. Traditional surfactant applications, such as detergent formulation, benefit from the existence of synergism between gemini and conventional surfactants.⁴⁻⁸ The wider range of structures for gemini aggregates vs conventional surfactant aggregates suggests novel applications. Thus, the presence of threadlike aggregates results in increased viscoelasticity,^{9,10} indicating a method of modifying the rheology of solutions. Use of conventional surfactants in the newest technologies, such as microelectronics, results in very thin, uniform surfactant layers that might function as resistors or chemical sensors.¹¹ Research involving substitution of gemini for conventional surfactants in this area is inevitable. Another area of interest is electrokinetic chromatography, where gemini surfactants give better

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separation than conventional surfactants.^{12,13} The patent literature currently includes mainly simple substitution of gemini for conventional surfactants without delving into the exceptional properties of the former.¹⁴ Regardless of the application, the need for fundamental research on the structure/performance relationships in gemini surfactants is clear.

In a recent paper,¹⁵ we reported on the physicochemical properties and aggregation behavior of bis(quaternary ammonium halide) gemini surfactants. Surface and interfacial tension measurements indicated aberrant behavior in those compounds having an alkyl chain length of 18 or greater in an aqueous solution and at 16 in 0.1 M NaCl. Steady-state fluorescence experiments, employing pyrene-3-carboxaldehyde as the probe, implied a different aggregation process for long-chain geminis as compared to that for short-chain geminis and conventional surfactants. A multistep aggregation process, as surfactant concentration is increased, is observed in the former case as compared to a simple two-step process in the latter case.

In this paper, we have determined aggregation numbers for four series of bis(quaternary ammonium halide) surfactants having diethyl ether $[(C_nN)_2O]$ (1), 2,3dihydroxybutyl $[(C_nN)_2(OH)_2]$ (2), 2-hydroxypropyl $[(C_nN)_2-$ OH] (3), and p-dimethylene phenylene $[(C_nN)_2Ar]$ (4) spacer groups. Aggregation numbers were determined by fluorescence spectroscopy using the time-resolved single

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$$\begin{array}{c} |_{\textcircled{\tiny \textcircled{\oplus}$}} \\ -N - CH_2 - CH - CH_2 - N - \\ R & OH & R \end{array} \qquad 2CI^-$$

$$-\overset{\text{l}}{\overset{\text{h}}{\underset{\text{R}}{\overset{\text{h}}{\underset{R}{\overset{\text{h}}{\underset{R}}{\overset{\text{h}}{\underset{R}}{\overset{\text{h}}{\underset{R}}{\overset{\text{h}}{\underset{R}}{\overset{\text{h}}{\underset{R}{\overset{h}}{\underset{R}}{\overset{h}}{\underset{R}}{\overset{h}}{\overset{h}}{\underset{R}}{\overset{h}}{\overset{h}}{\underset{R}}{\overset{h}}{\overset{h}}{\underset{R}}{\overset{h}}{\overset{h}}{\underset{R}}{\overset{h}}{\overset{h}}{\underset{R}}{\overset{h}}{\overset{h}}{\underset{R}}{\overset{h}}{\overset{h}}{\underset{R}}{\overset{h}}{\overset{h}}{\underset{R}}{\overset{h}}{\overset{h}}{\underset{R}}{\overset{h}}{\overset{h}}{\underset{R}}}{\overset{h}}{\overset{h}}{\underset{R}}{\overset{h}}{\overset{h}}{\underset{R}}}{\overset{h}}{\overset{h}}{\overset{h}}{\overset{h}}{\underset{R}}}{\overset{h}}{\overset{h}}{\overset{h}}{\underset{R}}}{\overset{h}}{\overset{h}}{\overset{h}}{\underset{R}}}}}}}}}}}}}}}}}}}$$

(3)

Figure 1. Molecular structures of bis(quaternary ammonium halide) surfactants. R is an alkyl chain where n = 10-20 carbon atoms.

photon counting method with pyrene as the probe.^{16–23} Following aggregation number as a function of surfactant concentration as well as comparison with I_1/I_3 ratios and surface tension values as a function of surfactant concentration provides a scenario of the aggregation behavior of aberrant (long chain) as well as nonaberrant (short chain) geminis.

Materials and Methods

Materials. The surfactants used in this study are shown in Figure 1. Their synthesis and purification followed procedures reported for previous investigations. $^{15,24,25}\,Pyrene$ (Aldrich, 99.9% pure) was used throughout as the fluorescent probe. All solvents were of spectral grade purity.

Steady-State Fluorescence Measurements. Fluorescence spectra were obtained on a Perkin-Elmer model LS-50B instrument. Emission spectra were taken at an excitation wavelength of 338 nm with a band-pass of 4 nm. Raman emission, expected at 382 nm, was insignificant under these conditions. I_1/I_3 values obtained from emission spectra were reproducible within ± 0.02 .

Dynamic Fluorescence Spectroscopy. Measurements. Time-resolved fluorescence measurements were carried out using a time-correlated single photon counting system constructed in the laboratory of Professor L. Davenport, Fluorescence Institute of Brooklyn Čollege, CUNY, following the procedures of Badea and Brand.²⁶ Samples were excited at 340 nm using a thyratrongated nanosecond flashlamp filled with nitrogen. Emission was monitored at 372 nm using a monochromator and detected with a photomultiplier tube. The timing system was set at 0.432 ns/ channel, appropriate for the lifetime of pyrene. A scatter solution of aqueous Ludox (colloidal silica, DuPont) was used to collect the lamp response function needed for recovery of the decay parameters. Additionally, a solution of anthracene in methanol was used as a standard to determine the color-shift parameter²⁷ (Q-shift) as well as to judge the success of the experiment based

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on the ability to recover a single exponential lifetime with a good statistical fit.

Analysis of the Decay Data. The aggregation number was estimated from the decay profile of pyrene fluorescence following the procedure of Atik et al.¹⁸ Studies using pyrene alone^{18-21,23} are based on the ability of the pyrene monomer to form an association complex or excimer. If the excimer is present, the fluorescence decay curve will show two components: a fast one associated with micelles having solubilized two or more pyrene molecules and a slow one corresponding to decay of the pyrene monomer.

Quenching is assumed to follow a first-order rate process,28 and the time dependence of fluorescence intensity is

$$I(t) = I(0) \exp[-k_1 t - n\{1 - \exp(-k_q t)\}]$$
(1)

where I(0) is the fluorescence intensity at zero time, k_1 is the first-order rate constant for unquenched fluorescence, *n* is the average number of quenchers per micelle, and k_q is the firstorder quenching rate constant. It should be noted that eq 1 is valid for the case of immobile reactants, i.e., when the residence time of the fluorescent molecule and the quencher inside the micelle is longer than the unquenched lifetime of the fluorescent probe. Equation 1 has been used extensively for micellar solutions in water, particularly with pyrene as the probe.^{17,29} Rewriting eq 1 in logarithmic form

$$\ln[I(t)/I(0)] = -k_1 t - n\{1 - \exp(-k_0 t)\}$$
(2)

For very long times, when all the excimer has decayed, eq 2 reduces to

$$\ln[I(t)/I(0)] = -k_1 t - n \tag{3}$$

The limiting slope of a plot of $\ln[I(t)/I(0)]$ vs *t* is $-k_1$. Extrapolation of the linear region to t = 0 is -n.

A series of curves with varying quencher (excimer) concentration produce parallel, linear tails in the logarithmic representation. This shows that no migration of the quencher has occurred, an assumption inherent in eq 1.

From the value of *n*, the surfactant aggregation number, *N*, is calculated

$$N = n[C_{\rm s} - \rm{cmc}]/C_{\rm py} \tag{4}$$

where $C_{\rm s}$ is the total surfactant concentration and $C_{\rm py}$ is the concentration of pyrene. An effective aggregation number can be determined as long as a well-developed tail, characterized by k_1 , can be identified.²² Decays were shifted to t = 0, assumed to be at the maximum of fluorescence intensity *I*(0). Linear regression analysis at long times provides the slope, $-k_1$, and the intercept, -n. The reciprocal of k_1 is equal to the monomer decay constant, τ_2 .

While we realize that use of a separate chemical species added to the system as a quencher is the preferred method for determination of aggregation numbers,²⁹ we were unable to apply this method due to experimental constraints. At the low surfactant concentrations used in this study, it was impossible to apply the accepted protocols for [probe]/[micelle] and [quencher]/ [micelle] ratios^{30,31} and still obtain a reasonable signal-to-noise ratio. Furthermore, the question of lamp instability during the long collection times needed for such experiments is another factor.

The reproducibility of our results was within 10%, and agreement with aggregation numbers for conventional surfactants was excellent. Only spectra that met the criterion of reaching the linear tail of the decay were considered.

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Table 1. cmc Determination of $(C_nN)_2O$ by Surface Tension and Fluorescence Methods in H_2O at 25 °C

compd	surface tension ^a (mol/L)	expected cmc ^b (mol/L)	<i>I</i> ₁ / <i>I</i> ₃ (mol/L)
$\begin{array}{c} (C_{12}N)_2O\\ (C_{14}N)_2O\\ (C_{16}N)_2O\\ (C_{18}N)_2O\\ (C_{20}N)_2O\end{array}$	$\begin{array}{c} 5.2\times10^{-4}\\ 5.8\times10^{-5}\\ 6.6\times10^{-6}\\ 1.4\times10^{-6}\\ 4.0\times10^{-6} \end{array}$	$\begin{array}{c} 5.2\times10^{-4}\\ 5.8\times10^{-5}\\ 6.6\times10^{-6}\\ 7.5\times10^{-7}\\ 8.0\times10^{-8} \end{array}$	$\begin{array}{c} 3.0 \times 10^{-4} \\ 2.5 \times 10^{-5} \\ 7.0 \times 10^{-6} \\ 2.9 \times 10^{-6} \\ 2.5 \times 10^{-6} \ (1 {\rm st \ cmc}) \\ 8.0 \times 10^{-6} \ (2 {\rm nd \ cmc}) \end{array}$

^a Reference. ^b Extrapolated from linear plots of log cmc vs n.

Results and Discussion

Determination of the critical micelle concentration (cmc) for the diethyl ether series $[(C_nN)_2O]$ in H_2O at 25 °C by steady-state fluorescence is shown in Figures 2–4. The commonly used method of following the ratio of intensity of the first and third peaks of the pyrene emission spectrum, I_1/I_3 , as an indication of the polarity of the probe environment is employed.^{32,33} The first drop in the value of I_1/I_3 , as a function of surfactant concentration, denotes a more hydrophobic probe environment and signals a nascent aggregation process. A gradual decline in the I_1/I_3 parameter after this initial drop is reached implies a concurrent gentle increase in aggregation number. Conversely, a sharp drop implies rapid conversion from a monomer to a micelle.

Values of the cmc determined by this method and previously reported values of the cmc determined by surface tension¹⁵ are listed in Table 1 for comparison. It is well-established that plots of log cmc vs number of carbon atoms in the alkyl chain (*n*) for conventional surfactants, from data obtained either by surface tension or by fluorescence, are linear.^{15,34} Table 1 lists expected cmc's for n = 18 and 20, which are obtained by extrapolation of these plots for n = 18 and 20. Positive deviation from linearity, reflecting abnormally high cmc's and indicative of premicellar aggregates, 15,24,25,35 occurs for the $(C_{18}N)_2O$ and $(C_{20}N)_2O$ compounds. Figures 2-4 also show the aggregation behavior for $(C_{12}N)_2O$, $(C_{18}N)_2O$, and $(C_{20}N)_2O$, respectively, as a function of surfactant concentration. In Figure 2, the cmc value for $(C_{12}N)_2O$ from fluorescence measurements, taken as the initial break in the I_1/I_3 vs $\log C_{\rm s}$ curve, is very near the cmc value from surface tension measurements. Within 1 order of magnitude greater than this surfactant concentration, the aggregation numbers are 35, reported as gemini molecules/micelle for consistency with previously published literature.9,36 Multiplication by a factor of 2 is required for comparison of these aggregation numbers with conventional surfactants having dodecyl chains, yielding N = 70 alkyl chains/micelle, a value typical of a spherical, monodisperse micelle near its cmc.^{37,38} Using this method of time-resolved fluorescence, a value of 70 ± 5 is obtained for dodecyltrimethylammonium bromide (DTAB) in H₂O at 25 °C, within experimental error of a published value of 65 in H₂O at

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Figure 2. I_1/I_3 and N vs log C_s for $(C_{12}N)_2O$ in aqueous solution using pyrene at 25 °C: \bullet , I_1/I_3 ; \triangle , N.



Figure 3. I_1/I_3 and Nvs log C_s for $(C_{18}N)_2O$ in aqueous solution using pyrene at 25 °C: \bullet , I_1/I_3 ; \triangle , N.

20 °C. 39 For tetradecyltrimethylammonium bromide (TTAB), our value of 80 \pm 10 is comparable to literature values of 97 39 and 70. 21

Deviation from expected cmc behavior, and its implied cause, i.e., premicellar aggregates, begins in this system when the alkyl chain reaches 18 carbons. Figure 3 and Table 1 show that cmc values from I_1/I_3 and surface tension data are in agreement for ($C_{18}N$)₂O, but now, in contrast to the situation with the lower homologues of the (C_nN)₂O series where the I_1/I_3 cmc values are slightly smaller than the surface tension cmc values, the former value is now slightly larger. At this surfactant concentration, the aggregation numbers begin to increase. Furthermore, in the concentration region between the observed and the expected cmc's (Table 1), the aggregation numbers are close to 2. This is additional evidence in support of the suggestion by us^{15,24,25} and others^{35,40–42} of the existence

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Figure 4. I_1/I_3 and Nvs log C_s for $(C_{20}N)_2O$ in aqueous solution using pyrene at 25 °C: \bullet , I_1/I_3 ; \triangle , N.

of premicellar aggregation in these compounds and permits us to postulate the existence of gemini dimers in this surfactant concentration region. Note that the aggregation numbers for $(C_{18}N)_2O$, determined up to over 1 order of magnitude above the cmc, are smaller than for the $(C_{12}N)_2O$ at surfactant concentrations in the same region relative to its cmc. This is reasonably a consequence of the heterogeneous distribution of micellar sizes, due to the presence of dimers or other submicellar units, in the aberrant $(C_{18}N)_2O$ system.

Figure 4 shows the data for $(C_{20}N)_2O$, whose cmc is more highly displaced than that of $(C_{18}N)_2O$. The I_1/I_3 data indicate two cmc's for the $(C_{20}N)_2O$, at 2.5×10^{-6} and 8×10^{-6} M, while the surface tension data indicate a single cmc at 4.0×10^{-6} M. It is likely that the fluorescence method is more sensitive than surface tension measurements in this case. The $\gamma_{\rm cmc}$ value for $(C_{20}N)_2O$ is 55 dyn/cm at equilibrium, ¹⁵ and instrumental limitations at high surface tension and low surfactant concentration make equilibrium surface tension values difficult to obtain. A plateau with $N=2.4\pm0.4$ between the expected and the second cmc indicates dimer formation. Aggregation numbers for the $(C_{20}N)_2O$ begin to increase gently at the second cmc, correlating with a gentle slope in the I_1/I_3 vs log $C_{\rm s}$ curve.

Figure 5 shows the aggregation numbers of the three members of the $(C_n N)_2 O$ series as a function of normalized surfactant concentration, C_s/cmc_{py} , where the cmc value is that observed using pyrene. A value of C_s /cmc below 1 indicates the region between the expected and the observed cmc's, i.e., the premicellar region. In the immediate vicinity of the cmc, $(C_{12}N)_2O$ has aggregation numbers within the literature range³⁹ for conventional surfactants with 12 carbon atoms. Both (C₁₈N)₂O and (C₂₀N)₂O exhibit dimers for C_s/cmc below 1 with an increase in aggregation number (N) at the observed cmc. Note that these aggregation numbers are smaller than expected for conventional surfactants with alkyl chain lengths of 18 and 20, respectively. Furthermore, the expected pattern of increase in *N* with alkyl chain length is reversed. Because these aggregation numbers are an average value, the inclusion of dimers will result in smaller aggregation numbers. $(C_{20}N)_2O$ dimers exist over a wider surfactant concentration range than $(C_{18}N)_2O$; hence, the aggregation numbers are smaller for the same value of C_{s} /cmc. The significantly greater population of dimers for $(C_{20}N)_2Ovs$ $(C_{18}N)_2O$ helps to explain the poor surface reduction, γ_{cmc} ,



Figure 5. Aggregation number (*N*) vs normalized surfactant concentration (C_s /cmc) for (C_nN)₂O surfactants in aqueous solution at 25 °C: \bullet , ($C_{12}N$)₂O; \Box , ($C_{18}N$)₂O; \triangle , ($C_{20}N$)₂O.



Figure 6. Aggregation number (*N*) vs normalized surfactant concentration (C_s /cmc) for (C_nN)₂(OH)₂ in H₂O at 25 °C: \blacktriangle , ($C_{16}N$)₂(OH)₂; \bigoplus , ($C_{12}N$)₂(OH)₂ and ($C_{14}N$)₂(OH)₂ (one point each, labeled as text).

for $(C_{20}N)_2O$ relative to $(C_{18}N)_2O$, ¹⁵ as the nonasymmetric dimers do not contribute to surface tension reduction.

For the $(C_n N)_2 O$ series, I_1/I_3 values along the plateau above the observed cmc are 1.31, 1.32, and 1.24 for the C12, C18, and C20 compounds, respectively (Figures 2-4). We expect a decrease in I_1/I_3 values as the alkyl chain increases, reflecting the less polar environment of the micelle-solubilized pyrene.^{32,38} On the basis of this, we might expect the values for the C18 and C20 compounds to be somewhat lower. Our numbers indicate a relatively higher polarity felt by the pyrene, possibly a more waterpermeated structure. For this surfactant concentration region, i.e., within 1 order of magnitude above the observed cmc, the presence of dimers in the heterogeneous aggregate mixture may contribute to the increased polarity detected by the fluorescence measurement. In turn, this helps explain the fact that smaller than expected aggregation numbers are observed for the geminis than for conventional surfactants with alkyl chain lengths of 18 and 20.

Aggregation numbers for the $(C_nN)_2(OH)_2$ series where n = 12, 14, and 16 in aqueous solution at 25 °C are shown in Figure 6. The $(C_{12}N)_2(OH)_2$ and the $(C_{14}N)_2(OH)_2$ aggregation numbers are 34 and 54 gemini molecules/



Figure 7. I_1/I_3 and N vs surfactant concentration (C_s) for $(C_{16}N)_2(OH)_2$ in H_2O at 25 °C: \bullet , I_1/I_3 ; \Box , N.

micelle, respectively, at surfactant concentrations just above their cmc values. Stated as alkyl chains/micelle, our aggregation numbers of 68 and 108 are close to the respective literature values of 65 and 97 for DTAB and TTAB.³⁹ The data therefore indicate that $(C_{12}N)_2(OH)_2$ and $(C_{14}N)_2(OH)_2$ have spherical, monodisperse micelles above their cmc's. Danino et al.⁹ have reported on C12 geminis with methylene spacers of various lengths and also report only spherical, monodisperse micelles at surfactant concentrations just above the cmc. For the corresponding spacer length, s=4, an aggregation number of 40 gemini molecules/micelle is reported at $C_s = 3$ mM.

 $(C_{16}N)_2(OH)_2$ shows a very small degree of aberration in water at 25 °C, with a narrow concentration range between the expected and the observed cmc values of 1.6 \times 10⁻⁵ and 2.4 \times 10⁻⁵ M, respectively. An aggregation number of 2, indicating dimers, was found in this region. Linear increase in *N* begins at the observed cmc, with a value of N = 70 gemini molecules/micelle (140 chains/ micelle) reached at C_s /cmc = 10 (Figure 6). An aggregation number of 108, determined by fluorescence quenching, is reported for hexadecyltrimethylammonium bromide (CTAB) at 25 °C and $C_s/cmc = 25.4^3$ An aggregation number of 160 for CTAB obtained by small-angle neutron scattering (SANS) studies⁴⁴ at $C_{\rm s}/\rm{cmc} = 100$ is comparable to that of the gemini surfactant on a per chain basis. Figure 7 clearly shows that the increase in aggregation number begins at the cmc of 1.8×10^{-5} M as determined by fluorescence measurement. The surface tension method cmc value was in good agreement (2.4×10^{-5} M).

Aggregation numbers for the $(C_nN)_2$ OH series, obtained in 0.1 M NaCl at 50 °C, are shown in Figure 8. For this system, interfacial properties at the air/liquid interface²⁴ and at the hydrocarbon/liquid interface¹⁵ begin to exhibit anomalous behavior beginning at n = 14. Figure 8 shows a linear increase in the aggregation number of $(C_{12}N)_2$ OH as the surfactant concentration increases above the cmc. Premicellar aggregates are indicated for the $(C_{14}N)_2$ OH and $(C_{16}N)_2$ OH compounds. As with the $(C_nN)_2$ O series, the expected pattern of increase in N with alkyl chain is reversed when aberrant behavior is encountered. $(C_{12}N)_2$ -OH has smaller N values than $(C_{14}N)_2$ OH, as expected,



Figure 8. Aggregation number (*N*) vs normalized surfactant concentration (C_s /cmc) for (C_n N)₂OH in 0.1 M NaCl at 50 °C: •, (C_{12} N)₂OH; \Box , (C_{14} N)₂OH; \triangle , (C_{16} N)₂OH.



Figure 9. Aggregation number (*N*) vs normalized surfactant concentration (C_s /cmc) for (C_n N)₂Ar in 0.1 M NaCl at 50 °C: •, (C_{12} N)₂Ar; \Box , (C_{14} N)₂Ar; Δ , (C_{16} N)₂Ar.

whereas $(C_{16}N)_2OH$ exhibits smaller aggregation numbers than $(C_{14}N)_2OH$ at the same normalized surfactant concentration.

Anomalous surface tension behavior has been reported for the $(C_nN)_2$ Ar series in 0.1 M NaCl at 50 °C beginning at $n = 14.^{24}$ Figure 9 shows aggregation numbers of 2.0 \pm 0.5 in the surfactant concentration range between the expected and the observed cmc for $(C_{14}N)_2Ar$ and $(C_{16}N)_2$ -Ar, specifically at $C_{\rm s}$ /cmc values of 0.76 and 0.60, respectively, increasing in the range above the observed cmc. Aggregation numbers for the (C₁₆N)₂Ar compound as a function of surfactant concentration are plotted in Figure 10 along with $(C_{16}N)_2$ OH for comparison. Both compounds were investigated under identical conditions of ionic strength and temperature; hence, the effect of the very different spacers on the aggregation number may be inferred. Aggregation numbers for (C16N)2Ar and (C16N)2-OH are roughly the same at the same surfactant concentrations (Figure 10) as well as at the same normalized surfactant concentrations (Figure 11). It appears that the difference between rigid hydrophobic and flexible hydroxylated spacers does not affect the aggregation behavior of gemini compounds of the same alkyl chain length.

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Figure 10. Aggregation number (*N*) vs log C_s in 0.1 M NaCl at 50 °C: \bullet , (C₁₆N)₂OH; \Box , (C₁₆N)₂Ar.



Figure 11. Aggregation number (*N*) vs normalized surfactant concentration ($C_{\rm s}$ /cmc) in 0.1 M NaCl at 50 °C: •, (C_{16} N)₂OH; \Box , (C_{16} N)₂Ar.

Menger et al.⁴⁵ have recently compared geminis with acetylenic spacers to those with flexible spacers and concluded that the chemical nature of the spacer is not the ultimate cause of nonlinear behavior. This validates the pattern we have seen, in that compounds with both flexible and rigid spacers show nonlinear surface tension patterns as well as the existence of dimers in the region between the expected and the observed cmc as the alkyl chain length increases beyond a limit dependent on system conditions.

When studied at 0.1 M NaCl and 50 °C, $(C_{18}N)_2Ar$ displays extremely unusual properties. It exhibits two cmc's in its surface tension curve: the first at 2.1×10^{-6} M and the second at 7.6×10^{-5} M.⁴⁶ The expected cmc for $(C_{18}N)_2Ar$ is 5.0×10^{-9} M.²⁴ Aggregation numbers for this compound are shown in Figure 12. Between the expected cmc and the first cmc, there are dimers that begin to grow rapidly, reaching an aggregation number of 61 at 9.0×10^{-6} M surfactant concentration. There is a precipitous drop in *N* to a value of 1.9 ± 0.5 (dimer) at $C_s = 1.0 \times 10^{-5}$ M. An I_1/I_3 ratio of 1.46 at $C_s = 1 \times 10^{-5}$ M confirms its



Figure 12. Aggregation number (*N*) vs log C_s in 0.1 M NaCl at 50 °C for $(C_{18}N)_2$ Ar.



Figure 13. Surface tension and aggregation number (*N*) vs log C_s in 0.1 M NaCl at 50 °C for $(C_{18}N)_2Ar: \bigcirc$, surface tension; \bullet , *N*.

hydrophilic environment.³² At $C_{\rm s} = 9.0 \times 10^{-6}$ M, I_1/I_3 is 1.13, indicating a hydrophobic (micellar) environment.³² The dimers begin to grow as surfactant concentration increases, and the second cmc is reached. A value of N= 63 is attained at $C_{\rm s} = 3.8 \times 10^{-4}$ M. Figure 13 is an overlay of aggregation numbers onto the surface tension plot. The symmetry between the two is evident.

The size of an aggregate is a thermodynamic balance between energy and entropy factors.⁴⁷ A shift in this balance, causing entropy to become the determining factor, might account for the sudden reformation of dimers between 9.0×10^{-6} and 1×10^{-5} M surfactant concentration. For amphiphilic structures, the repulsive energy between headgroups is at a minimum when the headgroup attains an optimal value (a_0).⁴⁷ Entropy factors dictate the smallest possible aggregates; yet, very small structures are energetically unfavorable as they force the surface area to increase above its optimal value to satisfy the packing constraints. The observation of dimers in a surfactant system would therefore indicate an overwhelm-

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 (46) Song, L. D. Ph.D. Thesis, City University of New York, 1997.

⁽⁴⁷⁾ Israelachvili, J. N. Physical Principles of Surfactant Self-Association Into Micelles, Vesicles and Microemulsion Droplets. In *Surfactants in Solution*; Mittall, K. L., Bothorel, Eds.; Plenum: New York, 1986; Vol. 4, p 3.

ing entropy consideration. Whether this marked change in aggregation number between the first and the second cmc is unique to this gemini system with a rigid hydrophobic spacer or is more common and to what it is due may be an interesting subject for further investigation.

To date, studies of aggregation behavior of gemini surfactants have focused mainly on the shorter chain compounds where aberrant behavior is not an issue and at concentrations well above the cmc. A recent small-angle neutron study on the ortho isomer of $(C_8N)_2Ar$ detected the presence of two cmc values.⁴² In the region between the first and the second cmc, investigators found aggregation numbers of 3–7, indicating the formation of premicelles and subsequent formation of normal micelles after the second cmc. In this case, aberrant behavior was due to conformation (ortho vs para) rather than alkyl chain length; however, the similarity between aggregation patterns of this compound and those of $(C_{18}N)_2Ar$ is striking.

Conclusion

We have continued our study of the structure/performance relationship of dimethyl alkylammonium bromide gemini surfactants begun in an earlier paper.¹⁵ It was shown that unusual interfacial properties occurred when the alkyl chain length reaches 16 carbons in a 0.1 M NaCl solution, regardless of the chemical nature of the spacer. Compounds with a rigid, hydrophobic spacer (4) have been added here. Aggregation behavior of these surfactants, investigated by fluorescence spectroscopy, also deviates from expected patterns at longer alkyl chain length for all spacer types.

In 0.1 M NaCl solution, surfactants with alkyl chains of 12 and 14 carbons and either diethyl ether (1) or 2,3-

dihydroxybutyl (2) spacers have aggregation numbers similar to DTAB and TTAB, respectively, on an alkyl chain per micelle basis. Beginning with 16 carbon atoms, aggregation numbers indicate the presence of dimers (2 gemini molecules per micelle) in the surfactant concentration region between the observed cmc and the expected cmc, as determined by plots of log cmc vs *n*. For 2-hydroxypropyl (3) and *p*-dimethylene phenylene (4) spacers, dimers are observed beginning with an alkyl chain length of 14 carbons.

Furthermore, as the surfactant concentration range between the observed and the expected cmc increases, we observe a reversal of the expected pattern of increase in N with alkyl chain length. A heterogeneous aggregate mixture, which includes dimers, would help to account for this. Steady-state fluorescence measurements of I_1/I_3 values, which are indicative of the polarity of the probe environment, confirm a more hydrophilic nature of systems where dimers are thought to be present.

Finally, the ($C_{18}N$)₂Ar compound, which shows two cmc values in its surface tension curve, also has two regions in which aggregation number measurements indicate the presence of dimers. In this respect, this gemini is similar to ($C_{20}N$)₂O, which shows two cmc values from its I_1/I_3 fluorescence data (Figure 4). There may be a similar pattern of aggregation numbers as in ($C_{18}N$)₂Ar; however, the small concentration range between the first and the second cmc makes measurement difficult. Further investigation of very long chain geminis, the existence of multiple cmc's, and the nature of the aggregates may prove interesting for future study.

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