Conformational Analysis of (Phenylenedimethylene)bis(*n*-octylammonium)dibromides in Aqueous Solution. Conformational Change upon Micellization

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Three gemini surfactants, in which two quaternary ammonium species ($CH_3(CH_2)_7N^+(CH_3)_2$) are linked at the polar headgroups by *o*-, *m*-, or *p*-phenylenedimethylene spacers, have been synthesized. The critical micelle concentration (cmc) of these surfactants in aqueous solutions was determined by electrical conductivity. Selective-decoupling ^{13}C NMR and ^1H NMR spectra were measured at various concentrations below and above the cmc. The selective-decoupling ^{13}C NMR results revealed that the specific rotational isomers about the CH_2-aromatic carbon single bonds for the gemini surfactant having a *m*-phenylenedimethylene spacer are preferentially stabilized upon micellization, while for the gemini surfactant having an *o*-phenylenedimethylene spacer, the presence of only the conformation in which the aromatic ring is sandwiched between two *n*-octyl chains was confirmed. Furthermore, it was found that variation in the stacking pattern of the aromatic rings after micellization of the surfactants is reflected in the ^1H spectral features of the aromatic protons. Comparison is made with the conformations of bis(quaternaryammonium) bromides with flexible spacer chains ($(CH_2)_s$) and of the corresponding *n*-alkylammonium bromide monomeric surfactants.

Introduction

The conformational change of molecules in a dissociation−association system has fundamental significance, since it serves as an important model for the relationship between the functional appearance and the conformational change of biological substances. In particular, conformational studies of surfactant molecules in an aggregated structure assist our understanding of the physicochemical properties of phospholipid bilayers with respect to their relationship to the structure of biomembranes.

We have already reported that one specific isomer, of the possible rotational isomers about the CH_2-CH_2 single bonds for the hydrocarbon moiety of simple surfactant molecules, is preferentially stabilized upon the formation of micelles.[1−6] It has been demonstrated for simple soap molecules (potassium *n*-pentenoate and potassium *n*-hexenoate), by measurement of the concentration dependence of the Raman scattering intensity of the accordion vibrational mode, that the population of the extended form (all-trans) of the hydrocarbon chain increases upon micellization.[1,5] For potassium *trans*-3-hexenoate,[2] potassium *trans*-4-pentenoate, and potassium *trans*-5-hexenoate,[6] micellization leads to a conformational change about the C−C single bond adjacent to the C═C double bond. These observations apply to surfactant molecules possessing longer hydrocarbon chains. A conformational change due to micellization has also been observed in the ^1H NMR[7−9] and Raman scattering[4,10−13] spectra of the polar parts of surfactant molecules.

The interaction between surfactant and proteins has been extensively studied, and the secondary structural change caused by surfactant binding of a protein has been observed. The α-helical content of bovine serum albumin decreases with an increase in the concentration of sodium dodecyl sulfate, and conformational changes about the C−S−S−C bonds of the protein molecule also occur.[14] The study of surfactant−protein interactions has important biological implications with respect to the lipid-membrane−protein interaction in biomembranes. The interaction between biological macromolecules could possibly result in a conformational change of the molecules. The interaction of DNA with histones brings about a conformational change in the DNA or the histones, and a conformational change due to a higher degree of association of the histone octamer has been observed.[15]

Such a conformational change should also affect the morphology of aggregates, including biomembranes and their model systems, since the type and structure of the self-assembly system depend on their geometrical packing parameters,[16] which are determined from the conformational structure.

Zana and Talmon[17] have used cryogenic transmission electron microscopy to investigate the microstructures of the aggregates of the dimeric surfactants, bis(quaternary ammonium bromides), in which two alkyldimethylammonium bromide chains are linked by a polymethylene chain. They found that the dimeric surfactants with a short spacer form long threadlike and entangled micelles, while those with a longer spacer form spherical micelles. These observations reveal that the length of a spacer affects the morphology of spontaneous curvature in molecular membranes. Thus, it is evident that the morphology of an aggregate strongly depends on the structure of a dimeric surfactant. In particular, variation in the length of a spacer chain changes the packing parameters. Moreover, conformational change of the dimeric surfactants probably occurs upon formation of the aggregates, leading to a further change of the packing parameters. Accordingly, this process affects the morphology of aggregates.

Diamant and Andelman[18] have presented a theoretical explanation for the experimental results obtained by Zana and Talmon[17] for dimeric surfactants. In this theory, it was suggested that the attractive and repulsive interactions of

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surfactant molecules and the conformational entropy of the spacer chain are dominant factors in elucidation of the shapes of aggregates formed in the aqueous solution. A conformational change of surfactant molecules upon micellization may vary the conformational entropy of the spacer chain.

To discuss quantitatively the relationship between the geometrical parameters and morphological characteristics, it is necessary to make a detailed investigation of the conformation of a surfactant molecule in an aggregate and the conformational change upon formation of its micelles in aqueous solution.

Stein and Gelman[19] synthesized amphiphiles with a unique headgroup topology, in which two carboxylates were rigidly held on a dibenzobarrelane skeleton. Nussler and Engberts[20] investigated the relationship between amphiphilic structure and aggregate morphology in 1,4-dialkylpyridinium salts, while Menger and Yamazaki[21] studied amphiphiles, in which the hydrophobic moiety was a polynuclear aromatic ring system or a hyperextended linear chain. In 1991, the name "gemini surfactants" was assigned by Menger and Littau[22] to a group of amphiphilic molecules having a long hydrocarbon chain, an ionic group, a rigid spacer, a second ionic group, and another hydrocarbon tail. Furthermore, Menger and Littau[23] reported a new class of self-assembling molecules for "gemini surfactants". They measured the surface tension and surface pressure for three series of gemini surfactants and discussed the molecular orientation at the air/water interface using the film-balance method. The remarkable properties of these "gemini surfactant" solutions were attributed to distortion of the water−structure by the two hydrophobic chains in the molecules.[24,25] It is evident from these observations that the molecular orientation at an interface is strongly related to the conformation of a molecule. Therefore it is highly desirable to make detailed studies of molecular conformations by use of spectroscopic methods in order to investigate the orientation of molecules at an interface.

In this present study, the so-called "gemini surfactants", in which two *n*-alkyldimethylammonium bromide moieties are connected by phenylenedimethylene spacer groups, have been synthesized, and the conformational change of these surfactants after micellization has been analyzed by use of the selective-decoupling ^{13}C NMR spectroscopic method.[26] The molecular conformations of bis(quaternaryammonium) bromides with flexible spacer chains ($(CH_2)_s$) and of the corresponding *n*-alkyltrimethylammonium bromide monomeric surfactants are discussed and compared with those for the geminis with rigid spacers.

Takeuchi et al.[26] used the selective decoupling ^{13}C NMR technique to analyze the structure of pentalenolactone and showed that this technique is very powerful for reliable structural elucidation of complex molecules. We briefly describe this technique for the further application to determination of the conformations of other gemini surfactants. In the completely proton-decoupled ^{13}C NMR spectrum, the resonance signals of all carbon-13 nuclei are observed as a singlet and do not involve any information on the coupling between the ^{13}C-nucleus and the proton. In contrast, in the nondecoupled spectrum, the resonance signal of each carbon-13 nucleus is observed as multiplet as a consequence of $^{13}C-^{1}H$ coupling (direct and long-range $^{13}C-^{1}H$ couplings), and, on the whole, the spectrum becomes very complex. However, when only the resonance signal of a specific proton interacting with a ^{13}C-nucleus is decoupled by using an appropriate weak power, one can eliminate selectively the effect of either a long-range or a direct $^{13}C-^{1}H$ coupling and extract the $^{13}C-^{1}H$ coupling through the three bonds, thereby providing direct information of the conformations about the CH_2-C (aromatic carbon) single bond.

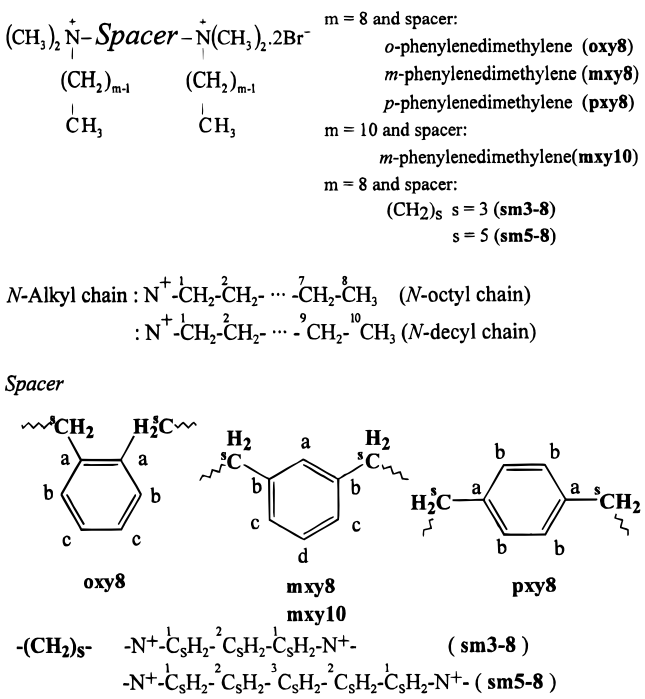


Figure 1. Numbering scheme of gemini surfactants.

TABLE 1: Elemental Analysis of oxy8, mxy8, pxy8, sm 3-8, sm 5-8 and sm 6-8

geminis		C %	H %	N %
oxy8	calcd	58.13	9.41	4.84
	found	58.24	9.71	4.53
mxy8	calcd	58.13	9.41	4.84
	found	57.95	9.63	4.39
pxy8	calcd	58.13	9.41	4.84
	found	57.80	9.78	4.45
sm 3-8	calcd[a]	49.99	10.22	5.07
	found	49.87	10.32	4.88
sm 5-8	calcd[b]	54.25	10.38	5.06
	found	54.04	10.53	4.59
sm 6-8	calcd	55.91	10.47	5.02
	found	55.53	10.72	4.68

[a] Calculated for dihydrated molecules. [b] Calculated for hemihydrated molecules.

Experimental Section

Materials. (Phenylenedimethylene)bis(*n*-alkylammonium) dibromide surfactants and bis(quaternaryammonium bromides) (Figure 1) were synthesized as follows.

For **oxy8**, **mxy8**, **pxy8**, and **mxy10**, reactions of *n*-octyldimethylamine and *n*-decyldimethylamine with the corresponding phenylenedimethylene dibromide[27,28] were performed in dried ethanol under reflux ($T = 353$ K) for 24 h so as to ensure as complete bisquarternization as possible. Bis(quaternaryammonium) bromides (**sm3-8** and **sm5-8**) were synthesized by reactions of *N,N′*-tetramethylpropane and -pentane with *n*-octylbromide in the same manner.

The two series of dimeric surfactants thus synthesized were recrystallized in various solvent mixtures (ethanol−ether or acetone−ether). Sample identification was confirmed by NMR and elemental analysis (Table 1). The reactants were purchased from Tokyo Kasei Co. and were purified before use. The isotopic purity of the D_2O (EURISO−TOP) used for NMR measurements was 99.8%. The samples of the monomeric

surfactants, *n*-octyltrimethylammonium bromide (OTAB, 98%) and *n*-cetyltrimethylammonium bromide (CTAB, 98%) were purchased from Tokyo Kasei Co. and were used without purification.

Conductivity Measurements and CMC Determinations. The electrical conductivity of the sample solutions was measured with a Conductivity Meter CM-11P (TOA−Electronics Ltd.) at 25.0 ± 0.1 °C. The critical micelle concentrations (cmc) were determined from plots of specific electrical conductivity against surfactant concentration.

^{13}C- and ^{1}H-NMR Measurements. ^{13}C NMR spectra were recorded on a Varian Unity-400 *plus* spectrometer operating at 100.58 MHz at 30 °C, using an acquisition time of 2.560 s under deuterium internal lock. Proton noise decoupling and selective decoupling carbon-13 chemical shifts (δ, ppm) were determined by use of 128 000 points in the time domain (sweep width 25 000 Hz). 3-(Trimethylsilyl)propanesulfonic acid sodium salt (DSS) was used as an external reference, and no susceptibility correction was made. All ^{13}C NMR measurements were made in 5 mm NMR sample tubes at 30 °C. The estimated accuracy of the observed ^{13}C NMR chemical shifts is ±0.004 ppm.

^{1}H NMR spectra were also recorded on a Varian Unity-400 *plus* spectrometer operating at 399.96 MHz at 30 °C, using an acquisition time of 10.924 s. Proton chemical shifts (^{1}H, δ, ppm), which are given relative to the signal of an external reference, were determined by use of 128 000 points in the time domain (sweep width: 5999.7 Hz). All ^{1}H NMR measurements were made in 5 mm NMR sample tubes at 30 °C, and the estimated accuracy of the observed ^{1}H NMR chemical shifts is ±0.0002 ppm.

Power Optimization for Selective Decoupling ^{13}C NMR Measurements. Decoupling was carried out only for the aromatic protons, and the pulse sequence is schematically shown in Figure 2A. The magnitude of decoupling power was optimized in order to obtain the true aromatic C-13 nucleus−$^{s}CH_2$-proton coupling constant. As is shown in Figure 2B, the ^{13}C NMR spectra of the 1,4-dioxane-benzene-d_6 solution (dioxane 40%) were measured for the various proton decoupling powers in the range of 25−45 dB. In this power range, only the protons of benzene-d_6 which remained undeuterized were completely decoupled. As a consequence, it was found that the decoupling power 25 dB does not bring about a decrease of the coupling constant in the dioxane-CH_2 spin system. Thus, it was concluded that a decoupling power of 25 dB is optimal for selective decoupling of only aromatic protons in the present gemini surfactant molecules.

In these experiments, therefore, aromatic protons were completely decoupled, while the spin-coupling between the $^{s}CH_2$ protons and aromatic carbon-13 nuclei remained constant, and no reduction of the ^{13}C−^{1}H coupling constant for the $^{s}CH_2$ groups was found.

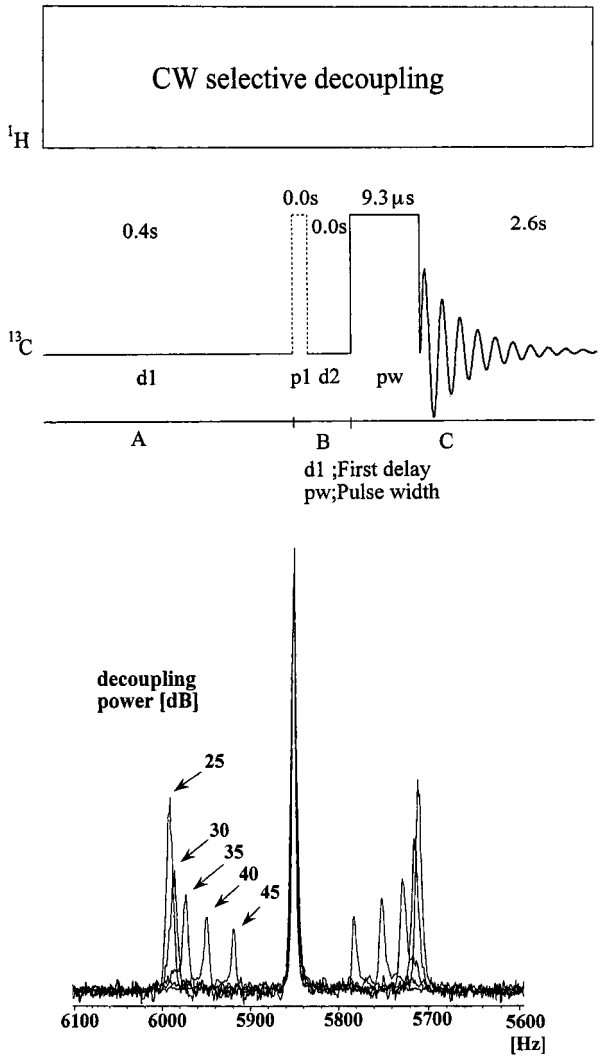


Figure 2. Pulse sequence ([A]) used for selective decoupling and ^{13}C NMR spectra ([B]) of the 1,4-dioxane-benzene-d_6 solution (dioxane 40 wt %) measured for various frequency settings of the proton-decoupler to optimize decoupling power.

TABLE 2: Critical Micelle Concentrations at 25 °C

Gemini surfactants	CMC [wt %]	CMC [mol l^{-1}]	α^a
oxy8	1.36	0.0235	0.616
mxy8	1.31	0.0226	0.618
pxy8	1.42	0.0245	0.538
sm3-8	0.71	0.0138	0.702
sm4-8	1.39	0.0262	0.674
sm5-8	1.43	0.0263	0.693
sm6-8	1.41	0.0252	0.672

[a] α: degree of ionization.

Results

This present study mainly concerned with the two series of gemini surfactants with rigid spacers and flexible spacers. The geminis with rigid spacers (*o*-, *m*-, and *p*-phenylenedimethylene) were synthesized in order to examine how the relative geometric disposition of the *n*-octyl chains affects the micellar behavior of the gemini molecules. The dimeric surfactants with flexible spacers (short polymethylene spacers ($(CH_2)_s$, s = 3, 4, 5, and 6)) were also synthesized to allow comparison with the micellar behavior of the geminis. In particular, the conformation about the CH_2−CH_2 single bond adjacent to the two nitrogen atoms, for the *n*-octyl and spacer chains, has been examined as a measure of the flexibility of the polymethylene chains.

The specific electrical conductivity for the two series of surfactants in aqueous solutions was measured at various concentrations. Plots of conductivity against concentration furnished two straight lines which intersected at the cmc. The cmc values thus obtained are listed in Table 2 together with the values (α) of degree of ionization obtained from the slopes of the straight lines.

The concentration dependence of the ^{1}H- and ^{13}C NMR spectra of these gemini surfactants in D_2O solutions has been investigated in detail. Figure 3 parts A and B shows the ^{1}H- and ^{13}C NMR spectra, respectively, of mxy8 (as a representative

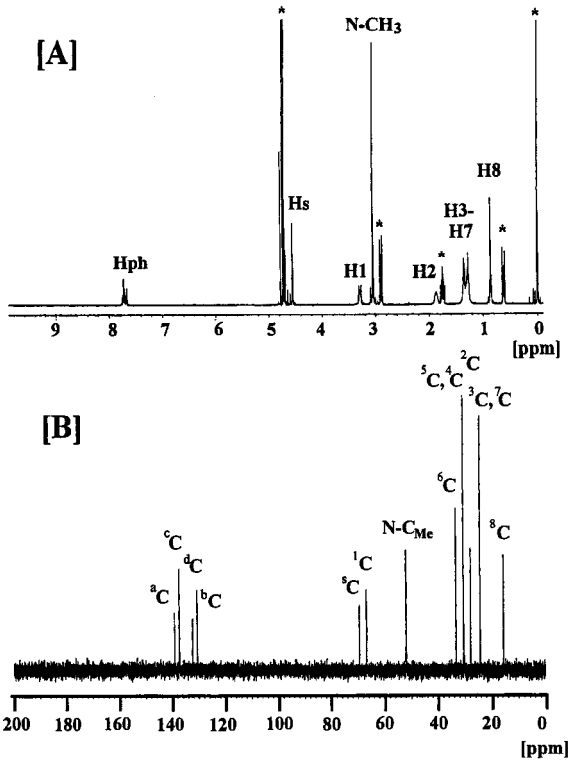


Figure 3. The ^{1}H NMR ([A]) and ^{13}C NMR ([B]) spectra of mxy8 (1.0 wt % in D_2O) as a representative of the gemini surfactants. Shift assignments (H_{ph}: aromatic protons, ^{s}H: $^sCH_2$ protons, H1, H2, H3−H7 and H8, corresponding to the $^1CH_2$, $^2CH_2$, $^3CH_2$-$^7CH_2$, and $^8CH_2$ protons, respectively) are shown. The ^{1}H signals marked with an asterisk show the resonance lines coming from the internal DSS reference. The ^{13}C chemical shifts (δ ppm) of each ^{13}C resonance signal for the 1.0 wt % mxy8 solution are 139.12 (^{a}C), 130.58 (^{b}C), 137.32 (^{c}C), 132.38 (^{d}C), 69.41 (^{s}C), 51.96 (N−CH_3), 66.74 (^{1}C), 27.79 (^{2}C), 24.23 (^{3}C), 30.41 (^{4}C, ^{5}C), 33.23 (^{6}C), 24.23 (^{7}C), and 15.65 ppm (^{8}C) relative to the DSS reference.

of the gemini surfactant series) together with assignment of their ^{1}H resonance peaks. The ^{13}C chemical shifts of mxy8 only are listed in the legend of Figure 3. The extents ($\Delta\delta = \delta$ (3 wt %)$-\delta$ (1 wt %), ppm) of the ^{13}C chemical shift change upon micelle formation are 0.32−0.34 ppm for oxy8, 0.36−0.45 for mxy8, and 0.33−0.40 ppm for pxy8, indicating that the $\Delta\delta$ value is almost independent of the relative geometric disposition of the *n*-octyl chains.

In this present study, detection of the conformational change of the phenylenedimethylene spacer portion, which is brought about by micellization, is focused mainly on the use of selective decoupling ^{13}C NMR and ^{1}H NMR spectra. Selective decoupling ^{13}C NMR spectra [26] of the sample solutions of the three gemini surfactants were therefore measured below and above the cmc. In these spectra, the splitting of the aromatic ^{13}C resonance signal which is due to spin-coupling with the aromatic protons disappears, and only splitting of the aromatic C-13 resonance line, which is caused by the interaction between the aromatic C-13 nucleus and the four protons of the two $^sCH_2$ groups, is observed.

pxy8. For the pxy8 ((*p*-phenylenedimethylene)bis(octylammonium) dibromide) sample solutions, a conformational change should not be reflected in the selective-decoupling ^{13}C NMR spectra, since the *ipso*-carbon (^{a}C) is not influenced by the conformation of the *n*-octyl chain and, moreover, the four ^{b}C carbons are equivalent. Indeed, although selective decoupling ^{13}C NMR spectra were measured at various concentrations under the standardized decoupling conditions, it was found that

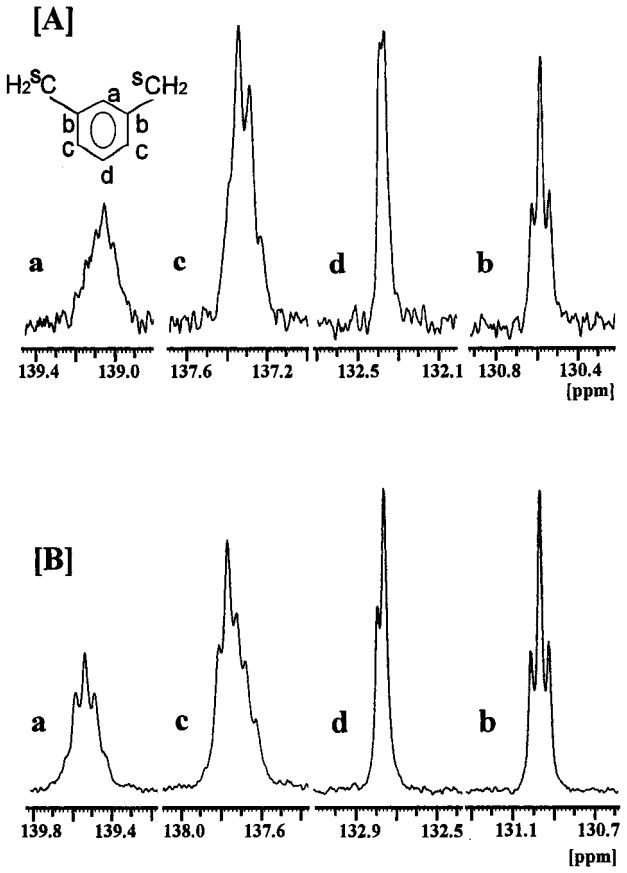


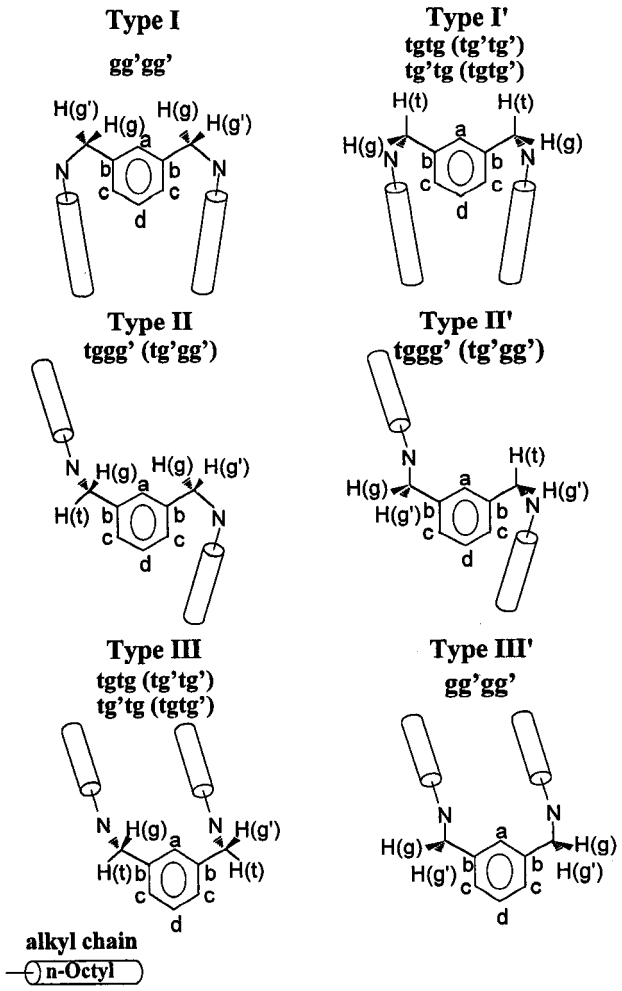
Figure 4. Selective decoupling ^{13}C NMR spectra of aromatic ^{13}C carbons (^{a}C(a), ^{b}C(b), ^{c}C(c), and ^{d}C(d)) for mxy8 in monomeric, 1.0 wt %, ([A]), and micellar, 3.0 wt %, ([B]) solutions.

the resonance spectral features of the ^{a}C and ^{b}C carbons were characteristic of a triplet signal, and this feature did not change above and below the cmc. The selective-decoupling ^{13}C NMR spectrum does not provide any information on the effect of micellization of pxy8, indicating either that the exchange among coexistent conformers occurs faster than the NMR time scale or that other magnetic nonequivalent conformers of pxy8 do not coexist.

Menger and Littau[23] studied the molecular orientation of (*p*-phenylenedimethylene) bis(stearylammonium) dibromide by the film-balance method and showed that the gemini surfactant molecules may take up an all-trans conformation at the air/water interface and that the water molecules remain incorporated into the hydrophilic portion of the monolayer, even in the condensed state. For the pxy8 molecules with short hydrophobic chains, we may assume that a conformation, similar to the all-trans conformation, exists in the micellar state together with other possible conformers.

mxy8 and mxy10. Figure 4 shows selective decoupling ^{13}C NMR spectra of the aromatic ^{13}C-carbons (^{a}C, ^{b}C, ^{c}C, and ^{d}C) coupled with the *m*-phenylenedimethylene CH_2 protons for the mxy8 gemini surfactant. It should be noted that for the resonance signals of the ^{a}C, ^{c}C, and ^{d}C carbon nuclei there exists a marked difference in the spectral features between monomeric and micellar solutions, although such a difference is not found for the ^{b}C resonance signal. This observation indicates that selective decoupling ^{13}C NMR spectra of aromatic carbon-13 nuclei reflects a conformational change about the two $^sCH_2$−^{b}C single bonds, due to the formation of micelles.

We may expect six skeletal structures for an mxy8 molecule in solution, as shown in Figure 5A, since three rotational isomers



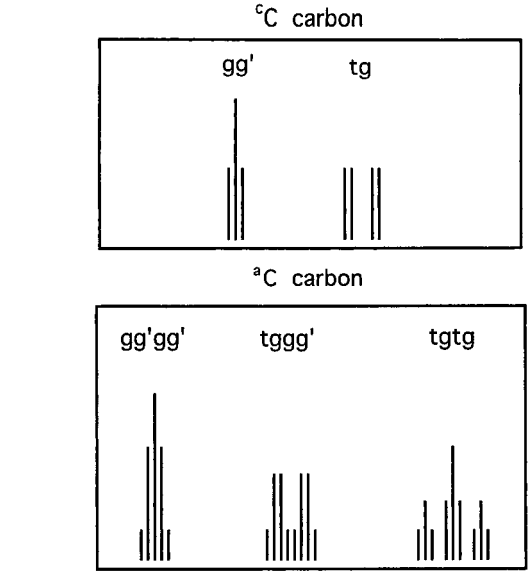


Figure 5. Possible skeletal structures ([A]) of an mxy8 molecule (the $^{b}C-^{a}C$ bond is a criterion for types I, II, and III and the $^{b}C-^{c}C$ bond is a criterion for types I′, II′, and III′) and possible splitting patterns [B] for the ^{13}C NMR signals of the ^{a}C and ^{c}C carbons.

(trans, gauche, and gauche′) about the $^{s}CH_2-^{b}C$ single bond are possible. For types I, II, and III, the $^{b}C-^{a}C$ bond is a criterion for the configurations of trans, gauche, and gauche′, while for type I′, II′, and III′, the $^{b}C-^{c}C$ bond is a criterion for the three conformers. In the type I structure, both of the $N^{s}C^{b}C$ planes are coplanar with the benzene plane, and in the Newman projection the two *n*-octyl-N segments are in the trans configuration with respect to the $^{a}C-^{b}C$ bond. For type I′, both of the $^{t}H^{s}C^{b}C$ planes are coplanar with the benzene plane and the two *n*-octyl-N segments extend in the direction of the gauche (or gauche′) configuration. In the type II (or type II′) structure, one of the two $N^{s}C^{b}C$ planes is coplanar with the benzene-ring plane, while the other plane is not. That is, one of the two *n*-octyl-N segments is in the trans configuration with respect to the $^{b}C-^{a}C$ (or $^{b}C-^{c}C$) bond, while the other *n*-octyl-N segment extends in the direction of the gauche (or gauche′) configuration. In type III, the two *n*-octyl-N segments both extend in the direction of the gauche (or gauche′) configuration. For type III′, both of the $N^{s}C^{b}C$ planes are coplanar with the benzene-ring plane, and the two *n*-octyl-N segments are in the trans configuration with respect to the $^{b}C-^{c}C$ bond.

The spectral feature of the ^{a}C carbon resonance depends strongly upon the mode of spin−spin coupling through the three bonds (vicinal coupling) between the ^{a}C nucleus and the four protons of the two $^{s}CH_2$ groups, which varies with the conformations (trans (t), gauche (g), and gauche′ (g′) with respect to the $^{b}C-^{a}C$ bond) about the $^{s}CH_2-^{b}C$ single bonds. We note the presence of the four protons of the two $^{s}CH_2$ groups and express the configurations of these protons by use of a combination of t, g, and g′, as seen in Figure 5. Thus, the quintet lines for type I, the double−quartet lines for type II and the triple−triplet lines for type III are all possible for the splitting features of the ^{a}C carbon resonance, due to coupling with the four protons (Figure 5B).

For the aromatic ^{b}C carbon, spin−spin coupling through the two bonds (geminal coupling) between the $^{s}CH_2$ protons and ^{b}C nucleus does not depend on the conformation about the $^{s}CH_2-^{b}C$ single bond. Therefore, the $^{2}J_{CH}$ value, which is obtained from the splitting feature of the ^{b}C carbon signal, does not provide any information for such a conformation.

The splitting pattern of the ^{c}C carbon resonance signal, unlike that of the ^{a}C nucleus, reflects only the conformation about the one $^{s}CH_2-^{b}C$ single bond. When the two protons of the $^{s}CH_2$ group take the tg form with respect to the $^{b}C-^{c}C$ bond (the two $^{s}CH_2$ groups of type I′ and one of the $^{s}CH_2$ groups of type II′), the ^{c}C carbon resonance provides the double−doublet signals (Figure 5B), while for the gg′ form of the two protons (one of the $^{s}CH_2$ groups of type II′ and both for type III′) the signal pattern of the ^{c}C carbon resonance becomes a triplet.

The ^{d}C nucleus is very weakly coupled with the protons of the two $^{s}CH_2$ groups through the four bonds, and the value of the coupling constant ($^{4}J_{CH}$) is very small. Therefore, the ^{d}C carbon resonance is observed as a singlet signal. When the exchange between all the conformers occurs within the NMR time scale or when an mxy8 molecule takes up only one conformation, the signal of the ^{d}C resonance should be observed as a singlet. Conversely, when many conformations coexist and the exchange between these conformations occurs more slowly than with the NMR time scale, the number of resonance lines should equal the number of all the conformations, and the ratio of intensities of the resonance lines should also be equal to the ratio of populations of these conformations.

We may therefore describe the conformational change of an mxy8 molecule upon micellization, based on the results of the selective decoupling ^{13}C NMR spectra. For the micellar solution of mxy8, the splitting pattern of the ^{a}C carbon resonance spectrum is obviously characteristic of quintet-lines (gg′gg′) (Figure 4B, indicating that the conformation of type I is preferentially stabilized upon micellization. Conversely, for the sample solution below the cmc, as shown in Figure 4A, a

spectral pattern of the ^{a}C carbon resonance is found in which the quartet lines (a part of tggg′) are superimposed upon the quintet lines (gg′gg′), implying that type I and type II conformations coexist below the cmc.

For the spectral feature of the ^{c}C-13 resonance, it is evident that the splitting pattern characteristic of the gg′ form becomes predominant upon micellization, although the two splitting patterns characteristic of the different species of two gg′ forms are superimposed upon each other. This observation indicates the absence of type I′ and II′ conformations and is consistent with the splitting pattern obtained from a ^{a}C carbon resonance.

The ^{d}C carbon resonance of the monomeric and micellar solutions of mxy8 consists of two resonance peaks. Below the cmc, the intensity of the resonance peak at low field is almost equal to that of the high field peak, while above the cmc the high field peak increases in intensity. Such a variation of the ^{d}C carbon resonance peaks also reflects a conformational change, which is expected from analysis of the splitting pattern of the ^{a}C carbon resonance. From consideration of the ^{a}C and ^{d}C carbon intensities, the peak of the high field ^{d}C resonance comes from a type I structure and that of the low field resonance comes from a type II. The difference in the ^{d}C carbon chemical shift between the two resonance peaks may be caused by the magnetic environmental difference of the ^{d}C carbon in solution, in addition to the difference in charge density of the ^{d}C carbon, due to the conformational change about the two $^{s}CH_2-^{b}$C single bonds mentioned above.

For mxy10 with *n*-decyl chains, selective decoupling ^{13}C NMR spectra of the aromatic ^{13}C-carbons coupled with the *m*-phenylenedimethylene CH_2 protons were also measured. The results showed that the spectral features both below and above cmc were very similar to those for mxy8 (spectra not shown), revealing that a conformational change, similar to that of mxy8, occurs for the mxy10 molecule upon micellization.

oxy8. For the oxy8 sample solutions, selective decoupling ^{13}C NMR spectra were also measured under the same selective decoupling conditions as were used for the pxy8 and mxy8 samples.

The dominant feature of the ^{a}C-13 resonance was a quintet, caused by spin−spin coupling through both two and three bonds between the ^{a}C-13 nuclei and *o*-phenylenedimethylene CH_2 protons. The quintet-splitting feature is characteristic of the gg′ form. The values of two coupling constants obtained from the observed spectra are $J_1 = 4.19$ Hz and $J_2 = 3.82$ Hz for the monomeric solution (1 wt %) and $J_1 = 3.82$ Hz and $J_2 = 3.81$ Hz for the micellar solution (3 wt %), indicating that there is no marked difference in the *J* values between the monomeric and micellar solutions. Since the observed *J* value is a weighted average of the *J* values in the monomer and micellar states, for the sample solutions of low micellar concentration the *J* value in the monomeric state will make a major contribution to the coupling constant and will dominate the observed value. Therefore, when the original gg′ form is stabilized in both the monomeric and micellar states, then a marked difference in the *J* values will not be observed. Consequently, micellization of the oxy8 surfactant does not result in a conformational change about the $^{s}CH_2-^{a}$C single bonds. The latter case implies that the protons of $^{s}CH_2$ do not take up the trans position with respect to the $^{a}C-^{b}$C bond and that the two *n*-octyl-N segments are in a trans configuration with respect to the $^{a}C-^{a}$C bond, as shown schematically in Figure 6. We suggest that the latter case may predominate in the oxy8 solution.

The spectral feature of the ^{b}C carbon resonance is characteristic of a triplet signal. However, micellization changes this feature to one in which the two triplet signals arising from two different conformers are superimposed. This observation indicates that these conformers are magnetically nonequivalent, due to the conformational change about the two $^{s}CH_2-^{a}$C single bonds. Moreover, exchange between these conformers occurs slowly compared with the NMR time scale. The observed difference in chemical shift may be caused by a stacking of the benzene planes due to micelle formation.

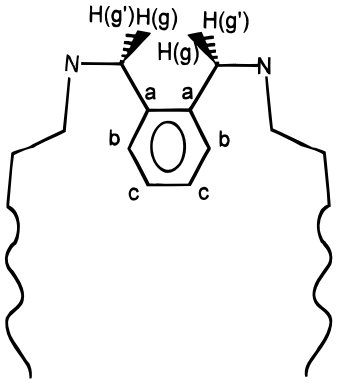


Figure 6. Configurations of the two *n*-octyl-N segments in an oxy8 molecule.

For the ^{c}C carbon nucleus, the spectral features of the selective decoupling ^{13}C resonance are found to be singlet for both the monomeric and micellar solutions, since the spin coupling through the four bonds between the $^{s}CH_2$ proton and ^{c}C carbon nuclei is very weak. At the ^{b}C carbon, two resonance peaks caused by the two conformers are observed. Conversely, the ^{c}C carbon of oxy8 provides only a singlet signal.

^{1}H NMR Spectral Variation of Aromatic Protons upon Micellization. Figure 7 shows the aromatic region of the ^{1}H NMR spectra of mxy8 and oxy8 in D_2O solution at different concentrations. The assignment of the ^{1}H signals, which were made from the splitting patterns, are also shown in the legends to this figure. For the mxy8-D_2O solutions (Figure 7A), the spectral feature of the aromatic protons depends strongly upon concentration. Below the cmc, this feature does not change, while above the cmc it varies rapidly with an increase in concentration. The ^{a}CH proton resonance is a singlet, and the downfield shift upon micellization is about 0.05 ppm. The ^{c}CH proton resonance is a doublet and micellization does not bring about any ^{1}H chemical shift change. The ^{d}CH proton resonance is a double−doublet, and a very small upfield shift is observed upon micellization. No change is observed in spin−spin coupling, despite the change in chemical shift upon micellization. Such a variation in the spectral feature reflects a change in the nature of stacking about the aromatic rings of the nearest neighboring molecules.

For the oxy8-D_2O solutions (Figure 7B), the spectral features of the aromatic protons also depend on concentration. Below the cmc, the spectral feature is a singlet, while above the cmc it changes rapidly to the AA′BB′ pattern with an increase in concentration. The difference in the chemical shifts between the ^{b}CH and ^{c}CH proton resonance peaks is ca. 0.07 ppm. In the oxy8 molecule, the stacking effect of this benzene ring may be larger than that for the mxy8 molecule.

Conformation of the *N*-Terminal CH_2-CH_2 Segment for the *n*-Octyl Chain. For the oxy8-, mxy8-, pxy8-, and mxy10-D_2O solutions, ^{1}H NMR spectra of the $^{1}CH_2$ protons for the *n*-octyl and *n*-decyl chains were used to investigate the conformation about the $^{1}CH_2-^{2}CH_2$ single bond. The ^{1}H resonance lines which are observed at 3.25−3.35 ppm are

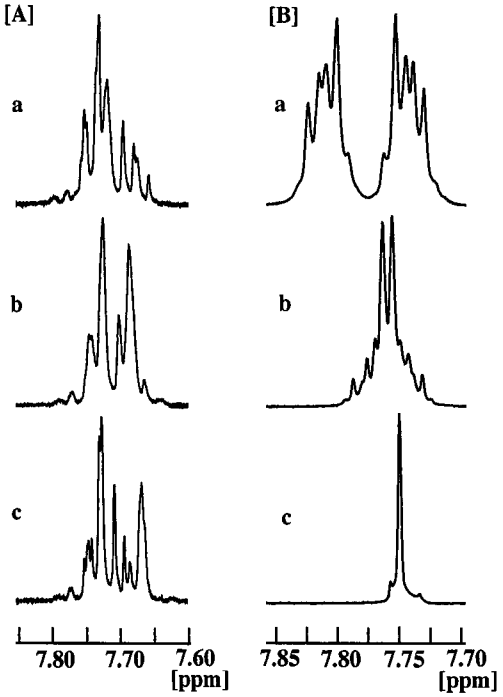


Figure 7. Concentration dependence of the ^{1}H NMR spectra of mxy8 ([A], a: 5.0, b: 3.0, and c: 1.0 wt %) and oxy8 ([B], a: 4.0, b: 3.0, and c: 1.0 wt %) in D_2O. For the spectrum (a) of mxy8 the resonance signals at 7.71, 7.74, and 7.67 ppm are assigned to the Ha, Hc, and Hd aromatic protons, respectively, and for the spectrum (a) of oxy8 the signals at 7.81 and 7.74 ppm are assigned to the Hb and Hc aromatic protons, respectively.

TABLE 3: ^{1}H NMR Vicinal Coupling Constants (Hz) and Estimated Populations (%) of Trans and Gauche Forms

Gemini surfactants[a]			J_{AX}	$J_{AX'}$	J_{AA}	$J_{XX'}$	P_g	P_t
oxy8	$^1C-^2C$	(1 wt %)$_{mon}$	12.2	4.7	−12.2	−12.4	11	89
		(3 wt %)$_{mic}$	12.2	4.8	−12.4	−12.6	11	89
mxy8	$^1C-^2C$	(1 wt %)$_{mon}$	12.2	4.9	−12.8	−13.0	11	89
		(3 wt %)$_{mic}$	12.4	4.6	−12.9	−12.7	9	91
mxy10	$^1C-^2C$	(0.4 wt %)$_{mon}$	12.4	4.7	−12.8	−12.5	9	91
		(2 wt %)$_{mic}$	12.5	4.6	−12.5	−11.0	8	92
pxy8	$^1C-^2C$	(1 wt %)$_{mon}$	12.3	4.7	−12.5	−12.5	10	90
		(3 wt %)$_{mic}$	12.4	4.7	−12.7	−12.9	9	91
sm 3-8	$^1C-^2C$	(2 wt %)$_{mic}$	12.4	4.5	−10.3	−10.2	9	91
	$^1C_S-^2C_S$	(2 wt %)$_{mic}$	11.8	4.9	−9.8	−9.8	16	84
sm 5-8	$^1C-^2C$	(3 wt %)$_{mic}$	12.2	4.6	−12.9	−12.7	11	89
	$^1C_S-^2C_S$	(3 wt %)$_{mic}$	11.8	5.1	−9.8	−9.8	16	84

[a] The symbols mon and mic show monomeric and micellar states, respectively.

assigned to the CH_2 protons adjacent to the nitrogen atom in the *n*-octyl chain. In the ^{1}H NMR spectrum the four protons of the $^1CH_2-^2CH_2$ segment provide a splitting pattern which is typical of an AA′XX′ system: the resonance signals of the two $^1CH_2$ protons correspond to the AA′ part. Thus the spectral feature reflects the conformations of the *N*-terminal CH_2-CH_2 segments. To examine the conformations about the CH_2-CH_2 single bonds, the LAOCOON III program[29] was used to calculate the ^{1}H NMR spectrum of the *N*-terminal CH_2-CH_2 protons. Vicinal coupling constants (J_{AX}, $J_{AX'}$, J_{AA}, and $J_{XX'}$), obtained by comparing the observed spectrum with the calculated best fit spectrum, are listed in Table 3.

The populations of the trans and gauche isomers are expressed[30−32] by eq 1

$$P_g = 1 - P_t = (J_t - J_{AX'})/(J_t - J_g) \quad (1)$$

where the J_g and J_t values $J_g = 4.14$ and $J_t = 13.22$ Hz[32] are a set of correct values for vicinal $^1H-{}^1H$ coupling constants for CH_2-CH_2 segments in the gauche and trans configurations. The calculated populations of the gauche and trans isomers for the three gemini surfactant solutions are also listed in Table 3. It is seen that there is no marked difference in population between the two solutions, indicating that the trans form is preferentially stabilized both below and above the cmc.

For the micellar solutions of the dimeric surfactants (sm3-8 and sm5-8), the conformations about the *n*-alkyl $^1CH_2-^2CH_2$ and about the spacer $^1CsH_2-^2CsH_2$ single bonds were investigated by using the ^{1}H NMR spectral analysis mentioned above. The P_t and P_g values thus calculated are also listed in Table 3. It is found that although the trans form is predominant for these conformations, there exists a difference in population between the $^1CH_2-^2CH_2$ and the $^1CsH_2-^2CsH_2$ segments. That is, for the *n*-octyl chain segment the P_t value tends to increase, compared with that for the spacer segment.

For the monomeric surfactants OTAB and CTAB, ^{1}H NMR spectral analyses for the conformation of the $^1CH_2-^2CH_2$ segment were made, leading to the conclusion of predominant stabilization of the trans form both below and above the cmc: ^{1}H NMR parameters for the OTAB micellar solution (8 wt %) were 12.4 Hz for J_{AX}, 4.7 Hz for $J_{AX'}$, −12.5 Hz for J_{AA}, and −12.3 Hz for $J_{XX'}$ and the estimated P_t value = 91%, while those for the OTAB micellar solution (0.3 wt %) were 12.4 Hz for J_{AX}, 4.7 Hz for $J_{AX'}$, −13.6 Hz for J_{AA}, and −12.5 Hz for $J_{XX'}$ and the P_t value = 91%. This result shows that the ^{a}-$CH_2-{}^bCH_2$ segment adjacent to the polar group is in an extremely restricted state because of its proximity to the bulky $(CH_3)_3N^+$ group.

Discussion

Menger et al.[23] used surface tension, film balance, and other methods to investigate the aggregation behavior of the geminis pxy8, pxy12, pxy16, and pxy18, (which correspond to compounds C-8, C-12, C-16, and C-18, respectively, in the abbreviations adopted by Menger et al.) and discussed possible orientations for these geminis at an air/water interface. They concluded that a conformational change of pxy18 (from the conformation lying flat on the water surface to that (the so-called "horseshoe" type structure) standing up vertically to the *p*-phenylenedimethylene plane) is made possible by compressing the monolayer.

One can estimate the cross section per molecule from the pressure−area isotherms. In particular, the value of the cross section, which is obtained as the process varies dynamically from the expanded state to the condensed state, provides significant information about the molecular orientation. It may also be expected that a conformational change should occur during the process of such a phase transition. Elucidation of such a conformational change on the water surface may lead to an understanding of the physicochemical property of the thin film.

The determination of a reliable molecular structure which is stabilized in the micellar state may be useful for estimating the molecular orientation of the geminis at the air/water interface and for determining any structural variation caused by this orientation. For example, when the gemini molecules oxy8 and pxy8 are adsorbed at the air−water interface, it may be estimated that the $N-{}^sC-{}^aC-{}^aC-{}^sC-N$ and $N-{}^sC-{}^aC-{}^bC-{}^aC-{}^sC-N$ skeletons containing the benzene ring are oriented vertically to the air/water interface, since these planes are rigid and planar, as discussed below.

Comparison of the hydrophobicity of the spacers suggests that the three spacers (*o*-, *m*-, and *p*-phenylenedimethylenes)

of the geminis should correspond to the polymethylene spacer $(CH_2)_8$. However, comparison of the distance between the two polar groups shows that the N···N distances for oxy8, mxy8, and pxy8 correspond approximately to those for sm3-8, sm4-8, and sm5-8, respectively, since geometrical calculation of the N···N distances for the extended polymethylene spacers of these compounds are 5.83 Å for oxy8, 7.25 Å for mxy8, 7.31 Å for pxy8, 4.96 Å for sm3−8, 6.26 Å for sm4−8, and 7.44 Å for sm5-8. Therefore, the series of these gemini molecules correspond to the dimeric surfactants with shorter polymethylene spacers ($(CH_2)_s$, $s = 2-6$).

In our previous small-angle neutron scattering study of the dimeric surfactant system[33] with $m = 10$ and shorter $(CH_2)_s$ spacers ($s = 2-6$), we showed that the aggregation number of a minimum micelle formed by the dimeric surfactants depends to only a small extent on the length of a spacer methylene chain, implying that the *n*-decyl group of the dimeric surfactants plays an important role in formation of a minimum micelle. Therefore, for oxy8, mxy8, pxy8, and mxy10, we may assume that two *n*-octyl chains strongly contribute to the micellar behavior.

We may use the P_t (or P_g) value as a measure of order in the *n*-octyl chain and in the polymethylene spacer. For oxy8, mxy8, and pxy8, it may be assumed that the $^1CH_2-^2CH_2$ segments of the *n*-octyl chains, on the whole, are in the highly ordered state both below and above the cmc. The reason is probably due to presence of the bulky polar groups, which hinder the free rotation about the CH_2-CH_2 single bond. For the dimeric surfactants (sm3-8 and sm5-8) with flexible spacers, it was found that the $^1CH_2-^2CH_2$ segments of two *n*-octyl chains are in an extremely restricted state, while the extent of ordering for the $^1C_sH_2-^2C_sH_2$ segment of the flexible spacer tends to decrease. This fact may indicate that it is the *n*-octyl chain rather than the spacer which plays an important role in determining the micellar behavior of these surfactants as well as that of the geminis.

Depending on the relative geometric disposition of the two $^sCH_2$ groups in the spacers, such a restricted state should not be neglected, even if it is small in extent, since the P_t values actually tend to increase in the order oxy8 < mxy8 < pxy8. This trend may be related to the stabilization of a specific isomer for the gemini molecules upon micellization.

For the conformation of an oxy8 molecule stabilized in the micellar state, it should be noted that the N−^{s}C−^{a}C−^{a}C−^{s}C−N skeleton of *o*-phenylenedimethylene is planar and the conformation about the rigid ^{a}C−^{s}C single bond is gauche. Moreover, as mentioned in the Results the two *n*-octyl-N segments are in a trans configuration with respect to the ^{a}C−^{a}C double bond. Accordingly, when two *n*-octyl-N segments take up a fully extended form, we may assume that the two *n*-octyl chains are not parallel to each other and fan out toward the methyl terminals of the *n*-octyl chains. Furthermore, in this molecular conformation, a phenylene ring of the spacer may be placed in the hydrophobic region rather than the hydrophilic region. Therefore, when the oxy8 molecules taking up such a conformation form micelles, the packing feature of *n*-octyl chains must become loose, since there exists a vacant space between the *n*-octyl chains and the *o*-phenylene ring, leading to the tendency for an increase in the gauche-population. That is, this loosely packed state may bring about a decrease in the P_t value.

For the mxy8 molecules in the micellar state, as mentioned above, the type I structure is predominantly stabilized, implying that the N−^{s}C−^{b}C−^{a}C−^{b}C−^{s}C−N skeleton takes up the all-trans form. Therefore, when the mxy8 molecules form micelles, the *n*-octyl chains within these micelles may be densely packed, compared with the case of oxy8. This dense packing may result in an increase in the trans population (P_t).

For the mxy10 micelles, it was also found that the P_t value for the $^1CH_2-^2CH_2$ segments of the main chain tends to increase. This tendency may indicate that the increased length of the main chain brings about a densely packed state of the *n*-decyl chains in the micelle due to an increase in aggregation number, a tendency which may promote a further restricted state for the $^1CH_2-^2CH_2$ segment.

In fact, it is evident that there exists a difference in the position of the phenylenedimethylene spacer between the type I structure and the stabilized oxy8 structure. This difference should change the balance of the hydrophobic and hydrophilic portions of the micelles and may affect the micellar structure. Thus, detailed studies of the micellar structures for these geminis are strongly desirable.

^{1}H NMR spectral variation of aromatic protons upon micellization (Figure 7) provides information on the environment of the benzene ring for mxy8 and oxy8. For mxy8, a singlet signal of the Ha proton tends to shift downfield (from 7.67 to 7.71 ppm) with an increase in concentration. The doublet signal of the Hc proton at 7.74 ppm is not dependent on concentration. The Hd signal, which is observed as a double−doublet, shifts upfield (from 7.69 to 7.67 ppm) as the concentration increases. The reason the ^{1}H chemical shift change of the Hc protons does not depend on concentration may be due to the reorientational effect of the benzene plane. The ^{1}H signals of the aromatic protons are sensitive to the variation in the environment. In fact, it has already been reported that they shift downfield in a hydrophilic environment but upfield in a hydrophobic environment.[34] Accordingly, we may use the direction of the change in the ^{1}H chemical shift upon micellization as a measure of the environment. Thus, it may be assumed that the Hd proton is placed on the side of the hydrophobic core, and the Hc protons may be close to the border region between the hydrophilic layer and the hydrophobic core. For the oxy8 molecules, the ^{1}H signals of the Hc aromatic protons do not change with increasing concentration, while the signals of the Hb protons shift downfield (from 7.75 to 7.81 ppm) upon micellization. This observation shows that the Hb protons at least of a benzene ring may be located in the aqueous region. Thus, we may estimate approximately the environment of a benzene moiety in the micellar state.

The molecular conformations of the oxy8 and mxy8 molecules which are stabilized upon micellization, which have been elucidated in this present study, can be used to calculate the packing parameters for these molecules in micelles.[16] For surfactant molecules of optimal area a_0, hydrocarbon volume v, and critical chain length l_c, the packing parameter is defined as v/a_0l_c. The relationship between the packing parameters of a surfactant and micellar shape has been shown by Israelachvili et al.[16] Accordingly, the packing parameters calculated for the oxy8 and mxy8 molecules in the micellar state are useful for estimation of micellar shape. For calculation of the packing parameter, the optimal area a_0 and critical chain length l_c can be determined from the molecular model. However, the hydrocarbon volume v depends on the extent of hydration of the hydrophobic portion.

The parameters were calculated for oxy8, mxy8, and pxy8, assuming that the two *n*-octyl chains and the benzene ring belong to the hydrophobic core and are unhydrated. The packing parameters, which were calculated for the stabilized conformation of an oxy8 molecule and for the type I structure of a mxy8 molecule, are 0.39−0.40 and 0.35, respectively. For

the molecular model of pxy8, in which two *n*-octyl segments are perpendicular to the *p*-phenylenedimethylene plane containing two nitrogen atoms, the calculated parameter is 0.33. On the basis of these parameters, we assume that the micellar shape for oxy8 may be cylindrical and that for mxy8 and pxy8 may be spherical.

If we assume that the aromatic carbons as well as some of the methylene groups of the *n*-octyl chain are also hydrated by their location in the water phase, the parameters (0.32−0.33) which are characteristic of a spherical shape are obtained. Thus, the position (environment) of a benzene ring in the micelle is important for estimation of the shape of the micelle.

Consideration of the results of the change in the ^{1}H NMR chemical shift suggests that the packing parameters of the mxy8 and oxy8 molecules may become smaller (ca. 0.33) and leads us to the assumption that both mxy8 and oxy8 adopt a spherical shape.

Conclusion

Three gemini surfactants (oxy8, mxy8, and pxy8) with *o*-, *m*-, and *p*-phenylenedimethylene spacers have been synthesized. The conformational changes caused by micellization of these surfactants, and their related compounds in D_2O were investigated by selective-decoupling ^{13}C NMR and ^{1}H NMR methods.

It was found that introduction of rigid spacers into the gemini surfactants promotes stabilization of the distance between the two hydrophilic groups, since the specific conformation of the spacer portion is preferentially stabilized upon micellization. For the two series with rigid and flexible spacers, the conformation of the two *n*-octyl chains tends to take up an all-trans conformation, implying that the two *n*-octyl chains play a significant role in micellar behavior. For the dimeric surfactants with flexible spacers, the population of the trans form of the $^1C_sH_2$-$^2C_sH_2$ segment of the spacer tends to decrease upon micellization, indicating that the steric compressive strain of the polymethylene spacer, caused by aggregation of the two *n*-octyl chains, may bring about an increase in the gauche-population. Conversely, for the dimeric surfactants with aromatic spacers, the population of the trans form of the $^1CH_2$-$^2CH_2$ segments of the two *n*-octyl chains tends to decrease upon micellization.

For the oxy8 molecules, the micelles are in a loosely packed state owing to the presence of gauche forms in the skeleton of the rigid spacer, because of preferential stabilization of a specific conformation upon micelle formation.

Since the difference in energy between the rotational isomers for the mxy8 molecules in D_2O may be small, we may speculate that the hydrophobic interaction between the two *n*-octyl chains and the aromatic ring plays a critical role in preferential stabilization of type I in the micellar state. We may therefore conclude that for oxy8 and mxy8 the benzene ring of the spacer is directed toward the hydrophobic core and that the plane containing the two nitrogen atoms and the two methylene-carbon atoms of the rigid spacer is coplanar with the plane of the benzene ring.

Preferential stabilization of a specific conformation probably occurs on the water surface when these molecules are adsorbed at the air/water interface.

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