Kinetics of the Self-Assembly of Gemini Surfactants

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ABSTRACT: A stopped-flow technique combined with pulsed-field-gradient spin-echo nuclear magnetic resonance (NMR) measurements was used to study the kinetics of exchange, size, and shapes in micellar systems of cationic surfactant dimers of the alkanediyl-α-ω-bis(dodecyldimethylammonium bromide) type, with alkanediyl being 1,2-ethylene, 1,3-propylene, and 1,4-butylene. By measuring the slow relaxation time for micelles, τ_2, the micelle lifetime as a function of spacer length was obtained and was further confirmed by micelle exchange measurements by NMR diffusometry. The micelle lifetimes for the gemini surfactants were found to be in orders of magnitude longer than for the corresponding conventional surfactants. All three cationic surfactant dimers showed an increase in micelle size in one direction, i.e., became prolates, as the concentration was increased. The growth of the micelles was most pronounced for the gemini surfactants with the shortest linker unit, i.e., ethylene.

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KEY WORDS: Dimeric, gemini surfactants, kinetics of micellization, lifetime of micelles, NMR, self-diffusion, slow relaxation time, stopped flow.

The association of many classes of surface-active molecules into micellar aggregates is a well-known phenomenon. Micelles are in dynamic equilibrium, constantly disintegrating and reforming. Two relaxation processes (1–25) are involved in micellar kinetics. The first one is a fast relaxation process referred to as τ_1 (generally on the order of microseconds), which is associated with the quick exchange of monomers between micelles and the surrounding bulk phase. This process can be considered a collision between surfactant monomers and micelles. The second relaxation time, τ_2 (on the order of milliseconds), is attributed to the micelle formation and dissolution process (i.e., the lifetime of the micelle). It has been shown that in certain surfactants, such as nonionic surfactants and mixed surfactant systems, τ_2 can be as long as minutes! For example, the τ_2 of a 0.80 mM solution of the nonionic surfactant Synperonic A7 (C_{13}–$C_{15}E_7$) is 150 s (2).

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Abbreviations: CMC, critical micelle concentration; DTAB, dodecyltrimethylammonium bromide; HDO, water with one proton replaced by deuterium; NMR, nuclear magnetic resonance; PFG-SE, pulsed-field-gradient spin-echo; SDC, self-diffusion coefficient.

Figure 1 shows the two characteristic relaxation times, τ_1 and τ_2, associated with micellar solutions. Micelle formation and disintegration are analogous to the equilibrium between water and water vapor at a given temperature and pressure. For a closed system containing water and water vapor in equilibrium, the number of water molecules per unit area per second evaporating from the surface is equal to the number of water molecules condensing at the surface. Thus, the total number of molecules in the vapor phase or in the liquid phase does not change with time, so the rate of condensation is equal to the rate of evaporation. The same principle holds for a micellar solution. Under equilibrium conditions, the rate of micelle formation is equal to the rate of disintegration into surfactant monomers.

The lifetime of micelles has been shown to significantly influence technological processes involving a rapid increase in interfacial area, such as foaming, wetting, emulsification, solubilization, and detergency (2,26–34). First, the available monomers adsorb onto the freshly created interface. Then additional monomers must be provided by the breakup of micelles. Especially when the free monomer concentration is low, the micellar breakup time is a rate-limiting step in the supply of monomers (26).

In recent years dimeric, or gemini, surfactants have attracted much attention, and several reviews on this new type of surfactant have been published (35–42), mainly involving the thermodynamic properties [e.g., critical micelle concentration (CMC), adsorption energy, area per molecule] of these systems (43–45). These gemini surfactants are made up of two surfactant monomers linked at the polar group of each monomer by a linker, or spacer, moiety. The length and type of this spacer moiety dictates the conformation of the
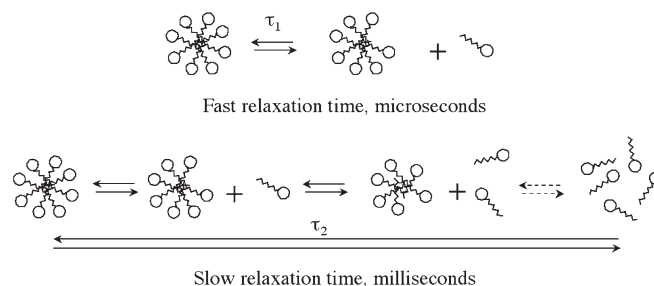

FIG. 1. Mechanisms for the two relaxation times, τ_1 and τ_2, for a surfactant solution above the critical micelle concentration (CMC).

dimeric molecule. The result is a small molecule with a high diffusion rate, high surface activity, and low CMC (36–50).

Recently, attention has turned to the kinetics of association and dissociation of gemini surfactant micelles (42,51,52). Ultrasonic absorption performed on short-chain gemini surfactants with eight-carbon tails and relatively short alkyl spacers (e.g., 8–3–8 and 8–6–8 geminis) have shown that the exit rate constant of a gemini molecule from a micelle is much smaller than that of an equivalent monomer (51). Other studies using the pressure-jump relaxation technique have shown that the fast and slow relaxation processes characterized by the relaxation times discussed above (τ_1 and τ_2) also exist for gemini surfactants, and that the residence time of a gemini molecule in a micelle is approximately 1,000 times longer than for the corresponding conventional surfactants (52), indicating that the lifetime of gemini surfactant micelles is very long.

In this work we have used the stopped-flow method with optical detection as well as self-diffusion nuclear magnetic resonance (NMR) to determine the effect of spacer group length on the relaxation kinetics and the size and shape of micelles of a series of gemini surfactants. Monolayer desorption experiments were used as a tool to study the alignment of the surfactants. To our knowledge, no previous study on gemini surfactants has combined the NMR self-diffusion technique with a stopped-flow method, and we believe this combination of techniques is a powerful one.

EXPERIMENTAL PROCEDURES

Materials. The high-purity-grade dyes Eosin Y ($C_{20}H_6Br_4Na_2O_5$, anionic) and Merocyanine 540 ($C_{26}H_{32}N_3NaO_6S_2$, anionic) were supplied by Acros Organics (Fair Lawn, NJ). Rhodamine B was from Sigma-Aldrich (St. Louis, MO). Alkanediyl-α,ω-bis(dodecyldimethylammonium bromide) (i.e., 12–n–12) gemini cationic surfactants with ethylene (12–2–12), propylene (12–3–12), and butylene (12–4–12) spacer groups were synthesized according to published procedures (53). Surfactant 12–2–12 was prepared by reacting 1-bromodecane with 1,2-ethylenediamine in a molar ratio of 2.1 to 1. Surfactants 12–3–12 and 12–4–12 were prepared by reacting 1-aminododecane with 1,3-dibromopropane and 1,4-dibromobutane, respectively, using a molar ratio of amine to bromo compound of 2.1 to 1. The surfactant Triton X-100 was from Union Carbide Corp. (New York, NY). All solutions for the stopped-flow method were prepared using water that was both deionized and distilled. All experiments were carried out at 23 ± 1°C unless otherwise stated.

For NMR measurements, D_2O from Dr. Glaser AG Basel (Basel, Switzerland) were used, and all measurements were carried out at 21°C. CMC of the gemini surfactants were determined using a Sigma 70 tensiometer from KSV (Helsinki, Finland).

Sample preparation. Samples for NMR measurements were prepared by mixing the surfactant and D_2O and allowing it to equilibrate overnight. Seven samples per surfactant were prepared with concentrations of 10, 15, 22, 32, 46, 68, and 100 × CMC.

Stopped-flow method. The stopped-flow method is generally used to measure the kinetics of micelle disintegration of nonionic surfactants. It is necessary to use a dye to obtain information about the micellar kinetics. A number of dyes or fluorescent compounds show an appreciable change in the extinction coefficient, depending on the medium in which the dye resides. Eosin, Merocyanine, and Rhodamine (Fig. 2) have different light absorbance characteristics, depending on whether they are present in an aqueous phase or in an oily phase. Because the interior of a micelle is oily in nature, these dyes absorb or emit differently inside and outside the micelles. This allows us to follow the relaxation kinetics upon a quick temperature, pressure, or (in this case) concentration jump by using spectrophotometric detection methods (54).

Eosin Y, for example, has a maximum light absorbance at 518 nm in water. This maximum shifts to 538 nm in the presence of micelles (55,56) as the dye partitions between the aqueous and micellar phases. As is shown in Figure 3, the maximum shift in absorbance occurs at 542 nm. The absorbance of 542 nm wavelength light increases with an increase in surfactant concentration (54). Therefore, if the 542-nm absorbance peak is monitored for different surfactant concentrations before and after quick dilution, the kinetics of micelle breakup over time can be followed (Fig. 4). A schematic of the technique is shown in Figure 5.

In all the experiments with dyes, the dye concentration was held constant at 0.019 mM. The gemini surfactant concentration ranged from 10 to 50 mM. Thus, the dye-to-surfactant molar ratio ranged from 0.0019:1 to 0.00038:1.

NMR diffusometry. Self-diffusion NMR experiments measure the echo-attenuation for a species moved by its Brownian motion labeled by pulsed magnetic-field gradients. The time duration between the gradient pulses is Δ. For a monodispersed sample, the echo-decay can be described by
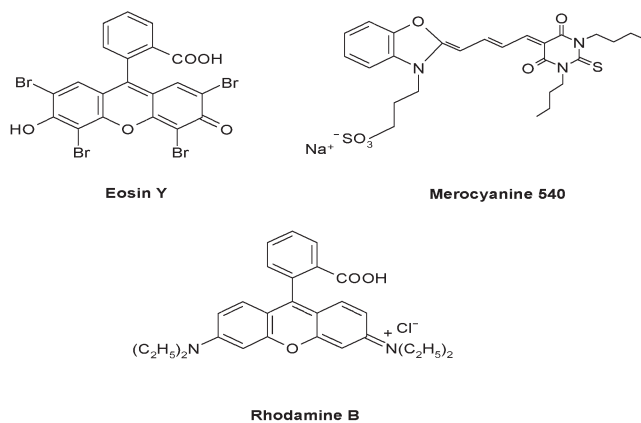
$$I/I_0 = e^{-bD} \qquad [1]$$

FIG. 2. Molecular structures of Eosin Y, Merocyanine 540, and Rhodamine B dyes (Acros Organics, Fair Lawn, NJ).
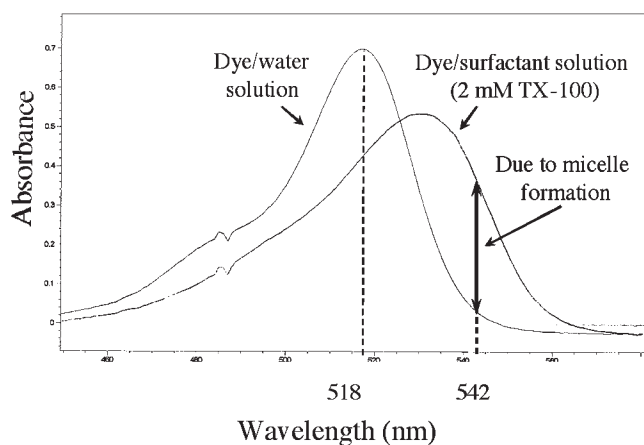
FIG. 3. Absorbance spectra of Eosin Y in water and 2 mM Triton X-100 (TX-100) solution (Eosin Y concentration: 0.019 mM; Acros Organics) (53).
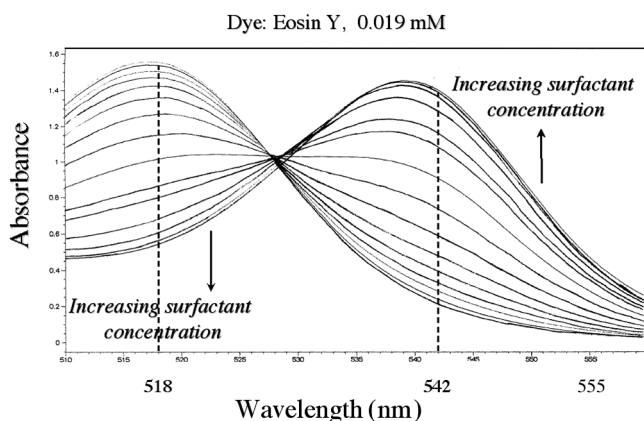

FIG. 4. Absorbance spectra of Eosin Y (Acros Organics) in water as a function of surfactant concentration (53).

where I is the intensity of the signal, I_0 the intensity at the gradient strength equal to zero, D the diffusion coefficient, and the constant b for a sinus-shaped gradient pulse:

$$b = \gamma^2 g^2 \delta^2 (4\Delta - \delta)/\pi^2 \qquad [2]$$

where δ is the duration of the gradient pulse and γ is the gyromagnetic ratio of ^{1}H. The diffusion coefficient is then evaluated by a single or biexponential least-squares fit.

Self-diffusion coefficients (SDC) were measured with the pulsed-field-gradient spin-echo (PFG-SE) NMR technique by using a stimulated echo with a time duration between the two first 90° pulses of 5 ms. All samples were measured with a sinus-shaped gradient with constant experimental times (Δ) and gradient durations (δ) of 100 and 4 ms, respectively. The gradient steps were varied in 20–32 steps, depending on the attenuation of the echo-decay.

Samples with a concentration $22 \times$ CMC were also used for exchange studies by varying the experimental time (Δ) from 50 to 800 ms. Here, the number of gradient steps was 25 for all Δ, but the increment was varied so that the interval of k was constant for all Δ.
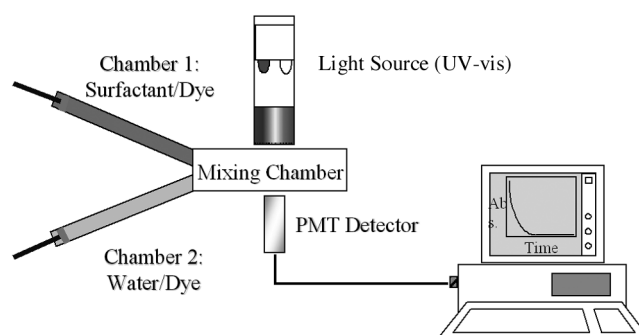

FIG. 5. Schematic diagram of a stopped-flow apparatus with optical detection. UV-vis, ultraviolet-visible; PMT, photomultiplier tube.

All experiments were carried out on a Varian 500-MHz spectrometer equipped with a diffusion probe (Doty Scientific, Inc., Columbia, SC).

RESULTS AND DISCUSSION

Stopped-flow experiments. In a recent publication Ulbricht and Zana (52) showed that gemini surfactants with short spacer groups do in fact show typical micelle formation and breakup kinetics. Using the pressure-jump technique with conductivity detection, they found that the same quaternary ammonium bromide-based gemini surfactants as were used in this study displayed fast (τ_1) and slow (τ_2) relaxation time constants. Interestingly, they found that the fast relaxation time constant, τ_1, is about 10^3 times larger than for similar conventional surfactants. This surprising observation implies that the residence time of a single gemini surfactant molecule within the micelle is very long. A possible explanation for this behavior is that surfactant dimers with a short spacer group experience increased energy due to steric hindrance between the two adjacent chains. This steric hindrance may force the dimer molecule to adopt a conformation where the two alkyl chains are in a *trans* position with respect to one another (52), causing the molecule to enter and exit the micelle in a stepwise process involving first one alkyl chain and then the other. This should be a much slower process than that by a conventional monomeric surfactant molecule. By this line of reasoning, the steric hindrance would decrease as the spacer group increased in length, allowing the gemini to enter and exit the micelle much more quickly.

Figure 6 shows the slow relaxation time (τ_2) of the 12–2–12, 12–3–12, and 12–4–12 gemini surfactants using the stopped-flow method with Merocyanine 540 dye. This figure clearly shows that the micelle lifetime for these geminis is quite long—on the order of tens of seconds. The figure also shows that the lifetime decreases with increasing spacer chain length, which seems to follow the above argument regarding steric hindrance of individual chains in the molecule. Another possible reason for a decrease in micelle lifetime with increased spacer chain length is the effect of molecular packing within the micelle.
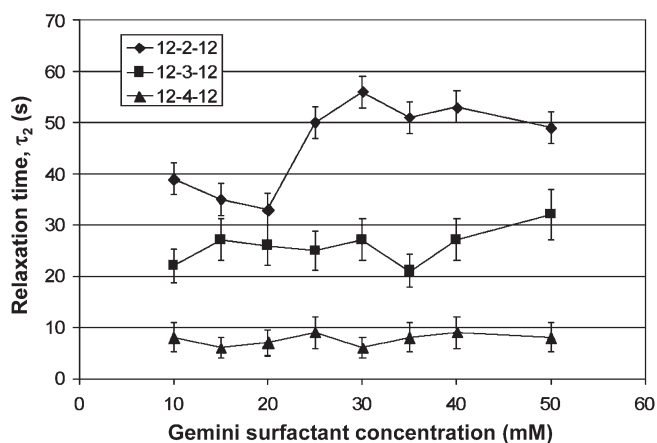
FIG. 6. Micelle stability of 12–2–12, 12–3–12, and 12–4–12 gemini surfactants at 25°C using the stopped-flow method.

The CMC values for the series of gemini surfactants, 12–2–12, 12–3–12, and 12–4–12, were determined from surface tension vs. log concentration plots to be $6.7 \cdot 10^{-4}$, $7.2 \cdot 10^{-4}$, and $8.6 \cdot 10^{-4}$, respectively. As Figure 7 illustrates, gemini surfactants with shorter spacer groups, such as the 12–2–12 gemini, seem to be able to pack more tightly in the micelle and in a monolayer than those with longer groups, such as the 12–4–12 gemini. Closer packing would increase the tail–tail hydrophobic interactions and increase the stability of the monomers within the micelle.

Furthermore, whereas the 12–3–12 and 12–4–12 geminis show a relatively flat τ_2 profile, the data suggest that some type of transition is encountered for 12–2–12 in the 20–25 mM concentration range. Zana and Talmon (49) showed, for the 12–2–12 gemini, a transition from short to long, wormlike micelles at approximately 25 mM. This transition is possibly seen here. Unfortunately, the stopped-flow instrument used was unable to determine the micelle stability
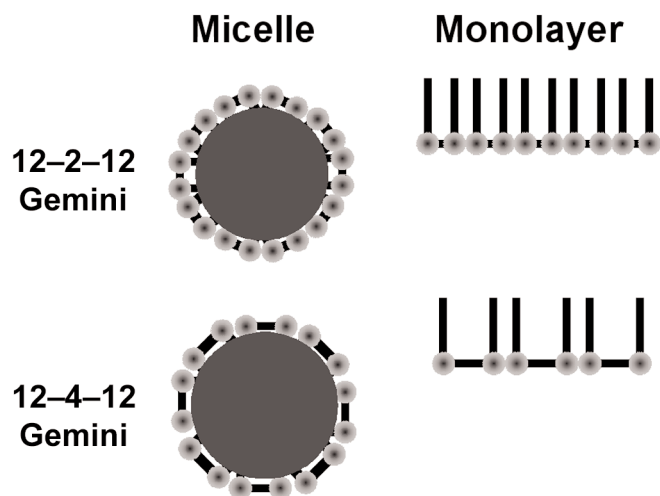
of these surfactants above approximately 50 mM. It was also unable to detect a transition from spherical to cylindrical micelles for the 12–3–12 and 12–4–12 gemini surfactants.

Monolayer experiments. The aspect of gemini surfactant micelles that allows them to have such a long lifetime compared with conventional surfactants appears to be the surfactant monomer's rate constant of exit from the micelle (51). Similarly, the desorption rate constant of this surfactant from an air/water interface is probably quite small (i.e., the molecule tends to remain adsorbed much longer at the interface). To study the desorption rate of the gemini surfactants from interfaces, a simple experiment was devised whereby small amounts of surfactant were spread onto a clean air/water interface, and the surface tension was monitored over time (Fig. 8) to determine the rate of desorption of the molecules from the surface.

The equilibration times for the geminis are much longer than that of dodecyltrimethylammonium bromide (DTAB), and the equilibration time increases with decreased spacer length of the geminis. These results are in agreement with the statement of Ulbricht and Zana (52) that gemini surfactants with longer spacer groups desorb more quickly than those with shorter spacer groups. The results are also in agreement with the surfactant micelle kinetics data (Fig. 6) showing the breakup time of 12–4–12 gemini micelles to be the shortest of the three gemini surfactants studied. The results shown in Figure 9 also make sense when one considers the probable molecular packing of the gemini surfactants at the air/water interface, as depicted in Figure 7. The 12–2–12 gemini surfactants most likely will pack much more tightly than the 12–3–12 and 12–4–12 gemini surfactants. The increased chain–chain interactions slow the desorption of molecules from the surface to the bulk solution. Also, because surface tension is ultimately a measurement of the crowding of molecules at the interface, it is not surprising that the 12–2–12 gemini surfactant solution yields the lowest equilibrium surface tension, whereas 12–4–12 yields the highest surface tension of the three gemini surfactants studied.
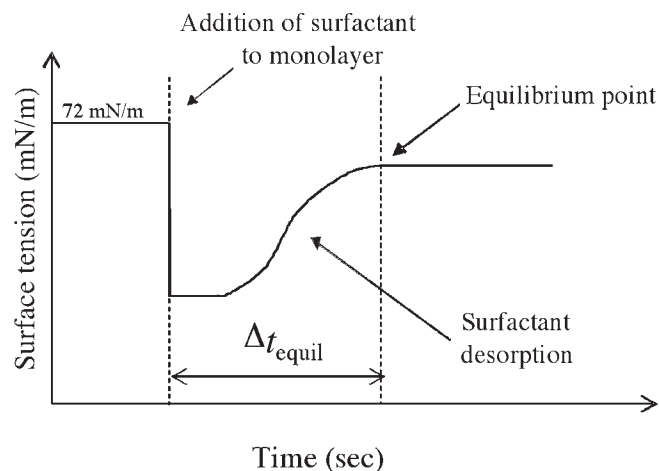

FIG. 7. Schematic illustration of the effect of the gemini spacer group on molecular packing within a micelle and a monolayer. 12–2–12 gemini surfactants are able to pack more closely than 12–4–12 gemini surfactants.

FIG. 8. Sample surface tension vs. time curve for surfactant desorption measurements. Δt_{equil}, time needed to reach equilibrium.
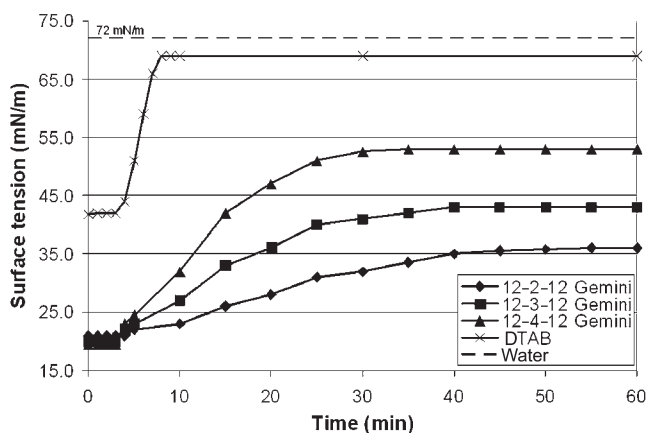
FIG. 9. Surface tension vs. time after spreading 100 µL of 1:1:3 methanol/chloroform/*n*-hexane + surfactant (1 mg/mL ratio) solution onto a clean surface of 0.05 M NaCl. The surface tension was measured by the Wilhelmy plate method using a 2.54 × 1 cm platinum plate. DTAB, dodecyltrimethylammonium bromide.

Self-diffusion NMR experiments. One of the most powerful ways to determine the size, size distribution, and shape of micelles is to measure the SDC of all the components in the solution. In favorable cases, the technique can also be used to determine the exchange dynamics in a micellar solution. When there is fast exchange between micelles and free surfactants (fast compared with the self-diffusion time, which may vary from *ca.* 10 ms up to 5 s) the obtained SDC is an average of all possible states of the surfactant, and the value can be used to calculate the micelle size from an averaged diffusion coefficient if the CMC is known. If the exchange dynamics are slow or in the intermediate time scale, the micelle size and/or size distribution is directly obtained from the measured diffusion constant through the Stokes–Einstein relation. The first test to determine the exchange rate is to vary the experimental diffusion time. This was done for all surfactants for a range of diffusion times (Δ), and the result is shown in Figure 10 for one concentration above the CMC.

The results presented in Figure 10 indicate that since the signal decay for the 12–2–12 surfactant expresses two distinctly different self-diffusion coefficients, the exchange dynamics are slow compared with all diffusion times used in the experiments (longest 800 ms). Both the 12–3–12 and the 12–4–12 surfactants experience fast exchange dynamics, as seen from their averaged signal decay, which shows an averaged SDC.

Once established, the exchange dynamics can be used to interpret the raw diffusion data, and the next step is to discuss the dependence on concentration. The obtained SDC is a direct measure of micelle size only in the region of unrestricted diffusion, i.e., in the very dilute region where intermicellar interaction can be neglected. By measuring the SDC in this region, one may assume a micelle shape and calculate the relevant size parameters. However, one test to discriminate between a spherical micelle and an oblate- or prolate-shaped micelle is to consider how the SDC depends on concentration. A spherical micelle will be much less hin-
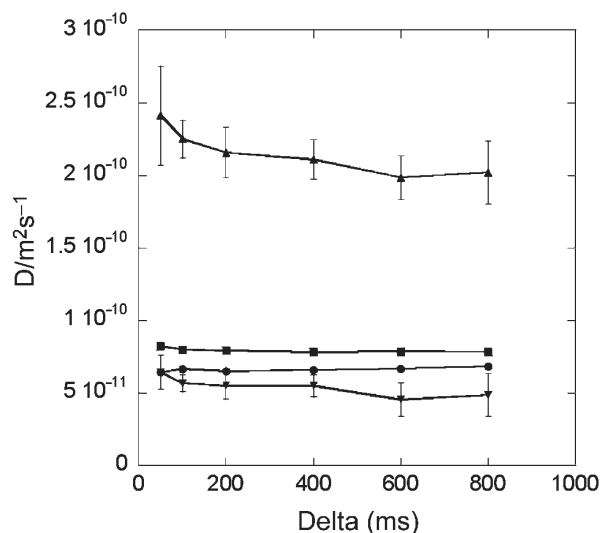

FIG. 10. The diffusion coefficient Δ as a function of the experimental time span (Δ). (▲) D1 12–2–12, (▼) D2 12–2–12, (●) 12–3–12, and (■) 12–4–12. Surfactant concentrations were two times the CMC. The propylene and butylene spacer showed a fast exchange, which averaged the diffusion coefficient for monomers and micelles. The ethylene spacer had two different diffusion coefficients, the slower originating from micelles and the faster from monomers.

dered in diffusion by the presence of other micelles than a prolate- or oblate-shaped micelle. Figure 11 shows results from the 12–3–12 and 12–4–12 gemini surfactants with DTAB used as a reference. (DTAB is known to form spherical micelles under these conditions.)
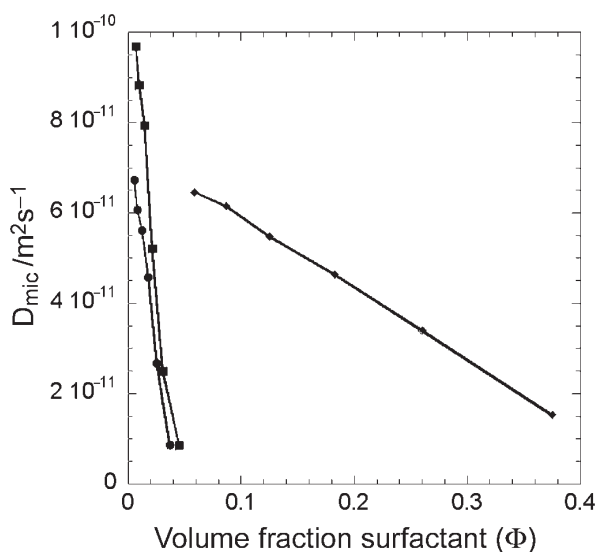

FIG. 11. Volume fraction of micelles as a function of the diffusion coefficient for the geminis with a propylene (●) and butylene spacer (■) and the corresponding conventional surfactant DTAB (◆). DTAB shows a decrease in diffusion coefficient characteristic of that of a spherical micelle, whereas the values for the other surfactants indicate larger aggregates. Data for the ethyl spacer are lacking due to phase separation of the samples at higher volume fractions. For abbreviation see Figure 9.

By using the experimentally determined CMC values, the SDC values of the micelles were calculated from the experimentally obtained SDC values. The first important feature in Figure 11 is the marked difference in slope between the two geminis on the one hand and DTAB on the other. For spherical micelles, the following expression was shown to describe the SDC data well (57,58):

$$D = D_0(1 - k\Phi) \qquad [3]$$

D_0 is the SDC at infinite dilution, k is a constant that for spherical micelles is around or slightly above 2, and Φ is the volume fraction of micelles. Equation 3 has been found to be valid for several cationic surfactants, giving k values of 2.2–2.3 (59). It should be noted here that the equation is only applicable to spherical micelles. If the data are not well described by Equation 3, as revealed either by differences in the functional form or by k being much larger than 2, it can be used only in the most qualitative way as an indication of the micelles not being spherical. The diffusion data for

DTAB, shown in Figure 11, fit Equation 3 perfectly with $k = 2$ and $D_0 = 7 \cdot 10^{-11}$ m^{2}s^{-1}. From the Stokes–Einstein relation, the hydrodynamic radius of a DTAB micelle can then be calculated to 2.8 nm, in good agreement with literature values. For the two gemini surfactants, however, a k value of 20 or more is obtained, indicating nonspherical micelles. Evidently, the micelle SDC values for the 12–3–12 and the 12–4–12 geminis decrease rapidly as a function of concentration due to large obstruction effects exerted by neighboring nonspherical micelles.

The next step in the procedure is to measure the SDC for the solvent. Similar to the situation for micelles, the obstruction of solvent molecules depends on the shape of the micelles present in solution. In such experiments it is difficult to separate spherical micelles from prolates since they give similar obstruction effects. Oblate-shaped micelles, however, are much more effective in obstructing the diffusion path for solvent molecules and give a much slower SDC. The SDC of HDO (a small amount of protons is always present in D$_2$O) is shown in Figure 12 (left *y* axis and filled
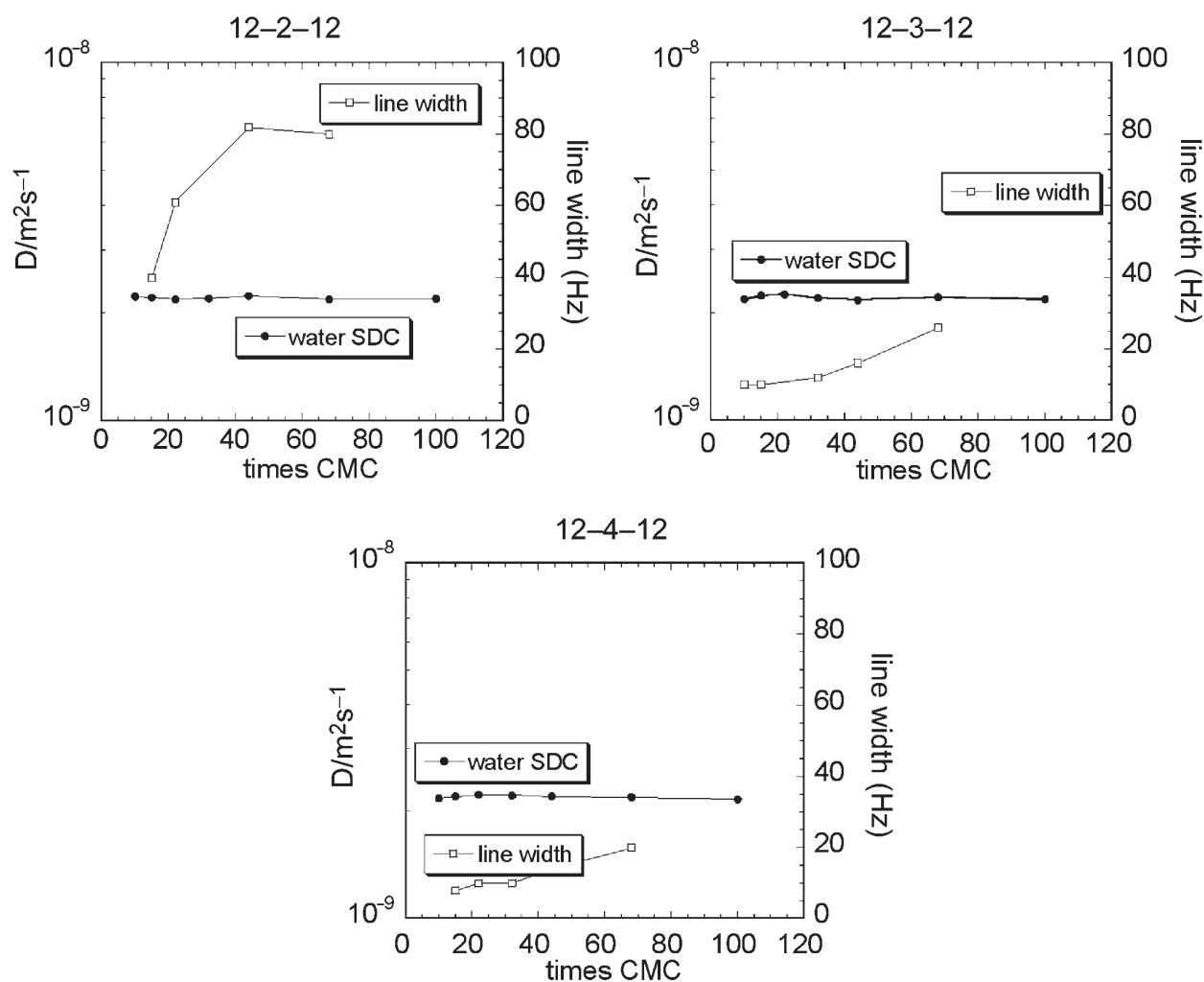

FIG. 12. Line widths of the signals from the protons of the N-methyl groups of the surfactant (right *y* axis and open squares) and the self-diffusion coefficient (SDC) for water (left *y* axis and filled squares). For other abbreviation see Figure 1.

circles). From the rather fast solvent diffusion, the fact that the solvent diffusion rate is relatively independent of the surfactant concentration, and the diffusion data of the surfactant, it can be concluded that the micelles are prolate shaped (60).

There is no dependence of the SDC of HDO on the concentration of micelles for any of the gemini surfactants. Together with the micelle SDC data, this indicates that the micelles are growing in one dimension as the concentration is increased above the CMC, i.e., into prolates. Also given in Figure 12 are the line widths of the signals from the protons of the N-methyl groups of the surfactant (right *y* axis and open squares). Small micelles are characterized by a short correlation time, which is due to micelle rotation and tumbling but also to the diffusion of surfactant molecules within the micelle. A short correlation time means a long NMR relaxation time and thus narrow lines in the NMR spectrum. Broad lines in the spectrum are normally indicative of large aggregates. One can clearly see that the proton line widths increase for all geminis above the CMC and that the increase is most pronounced for the 12–2–12 and least pronounced for the 12–4–12 surfactant. Thus, the results from the self-diffusion measurements on H_2O show that the growth of the micelle size with increasing surfactant concentration is more pronounced when the spacer length is short.

Taken together, the NMR self-diffusion experiments are consistent and show that all the gemini surfactants exhibit micelle growth in one dimension as the surfactant concentration increases. The growth is more pronounced the shorter the spacer unit, which is most likely due to increasing geometrical constraints in the formation of aggregates with decreasing length of the connecting unit. The NMR measurements also confirm the results from the stopped-flow experiments that the surfactant with an ethylene spacer has slower exchange dynamics of the micelles than the other two surfactants.

Gemini surfactants are attracting attention because of their unusual solution characteristics, which, in turn, are mainly related to the size and shape of the micelles, as well as to the micelle kinetics. The strong dependency of the viscosity on the surfactant concentration is a property of practical importance for solutions of certain gemini surfactants. For cationic geminis, this effect is known to be more pronounced for surfactants with very short spacer units. The work presented in this paper confirms that the length of the spacer unit is crucial for the solution behavior of such geminis. More specifically, the results indicate that to obtain the truly unique properties of C12 cationic gemini surfactants, an ethylene spacer should be used.

ACKNOWLEDGMENTS

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