Gemini surfactants, the effect of hydrophobic chain length and dissymmetry

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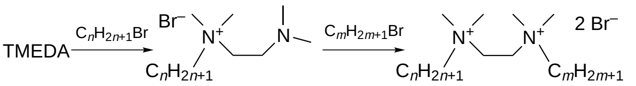
The synthesis of a new series of dimeric surfactants is reported; chain length and dissymmetry are shown to be critical factors for the richness of phases observed in water.

In recent years, bis(quaternary ammonium) gemini surfactants have received increasing attention. Dimeric compounds with the structure C_sH_{2s}-α,ω-($Me_2N^+C_mH_{2m+1}Br^-$)$_2$ which are referred to as *m-s-m*, show very low critical micellar concentrations (cmc) compared to the corresponding monomeric surfactants.[1] Some have been found to form giant worm-like micelles[2] at low concentration without any salt or hydrophobic counterions as was the case for the classically studied systems.[3,4] Zana and co-workers have reported detailed studies about the effect of the spacer chain length on the cmc of these surfactants as well as on the morphology of their aggregates.[5] Trimeric quaternary ammonium surfactants have also been prepared.[6] In this communication, we report on a new series of surfactants *n*-2-*m*, and on the effect of the dissymmetry of surfactant molecules on their self-assembled structures in aqueous solutions.

Their synthesis proceeds in two steps from *N,N,N′,N′*-tetramethylethylenediamine and two *n* and *m*-alkyl bromides. Thus, the diamine (0.1 mol) and the first alkyl bromide (0.8 equiv.) were heated in MeCN (250 ml) at 40 °C for 3 days. After evaporation and crystallisation from Et_2O, the corresponding pure alkyl dimethyl[1-(2-dimethylamino)ethyl] ammonium bromide was isolated in 70–80% yield. This compound (20 mmol) and the second alkyl bromide (4 equiv.) were refluxed in EtOAc (250 ml) for 2 days. After evaporation, the residue was recrystallised several times from $CHCl_3$–acetone yielding the *n*-2-*m* surfactant (50–60%).



When dissolved in water, the different surfactants assemble into various phases depending on their structure (Fig. 1). The symmetrical surfactants 14-2-14, 16-2-16, 18-2-18, as well as the almost-symmetrical surfactants 16-2-14 and 18-2-16 form turbid and rather viscous solutions which present a transition to isotropic and strongly viscoelastic phases upon heating. Rheometric studies (see below) allowed this latter phase to be characterised as entangled worm-like micelles. For the symmetrical surfactants, the solutions at room temperature are slightly birefringent. As shown in Fig. 2, DIC microscope observations reveal the presence of aggregated clusters of long and entangled tubule-like structures above 0.4, 0.2 and 0.1% for 14-2-14, 16-2-16 and 18-2-18 respectively. These tubules are quite stable and static, and their diameters do not exceed a micron. The phase observed with 16-2-14 at room temperature is somewhat different. It is also viscous, but shows much higher birefringence than those mentioned above. Microscopic observations show some indication of a lamellar phase. The phase observed with 18-2-16 also shows high birefringence, but the structure observed under the microscope was more reminiscent of a tubular phase. These structures as well as the nature of the transparent phase in-between are currently being investigated in detail by neutron scattering as well as with cryo-TEM.

The transition temperatures of these tubular/lamellar phases to worm-like micelles strongly depend on the overall length ($n + m$) as well as on the dissymmetry ($n - m$) of the surfactants (Fig. 1). The tubular/lamellar phases are more stable for longer chain lengths. In the symmetrical series, we observed a 15 °C drop in the transition temperature when both chains of a surfactant are shortened by two carbons, leading to transitions at 60, 45 and 30 °C for 18-2-18, 16-2-16 and 14-2-14 respectively.† Interestingly, the same 15 °C drop in transition temperature occurs when only one chain of a symmetrical surfactant is shortened by two carbons (*e.g.* from 18-2-18 to 18-2-16 or from 16-2-16 to 16-2-14). For example, 18-2-16 and 16-2-16, or 16-2-14 and 14-2-14 have almost identical transition temperatures. Thus, symmetry is a critical factor for the formation of the tubular/lamellar phases. In the range of *n* and *m* studied, these phases were never observed for $n - m > 2$ even for 18-2-14 which has the same overall chain length as 16-2-16.

Rheometric studies of the worm-like micellar phases obtained at high temperatures were performed, and we investigated the concentration dependence of the viscosity at low shear rate for various surfactants to determine the crossover concentration (overlap concentration) between dilute and semi-dilute regimes. Here, the crossover between these two regimes occurs when the micellar lengths become comparable to the screening length of electrostatic interactions. For salt-free worm-like micellar solutions, this happens approximately at the concentration at which the average distance between micelles equals the average length of micelles. As shown in Fig. 3, the overlap concentration of 16-2-16 is ten times lower than that of 14-2-14, which is itself ten times lower than that of 12-2-12. This can be

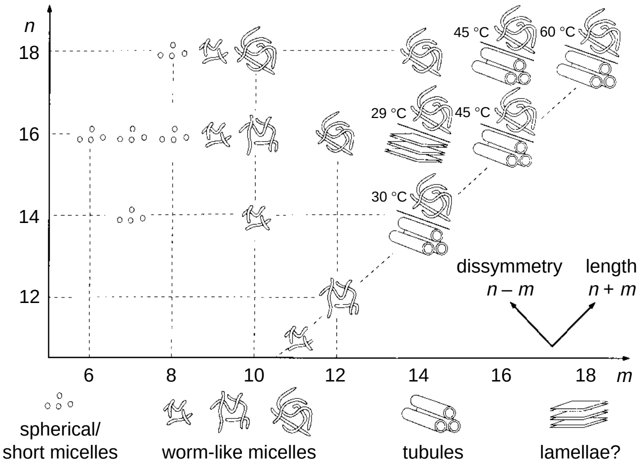


Fig. 1 Phases observed in aqueous solutions of *n*-2-*m* surfactants as a function of *n* and *m*. The investigated concentrations were between 0.1 and 10% w/w (*ca.* 1.6–160 mM). Transition temperatures are indicated whenever a phase transition was observed upon heating. The worm-like micelles are divided into three categories according to their overlap concentrations: (*i*) lower than 0.5% w/w for the longer micelles; (*ii*) between 0.5 and 2%; (*iii*) between 2 and 10%.

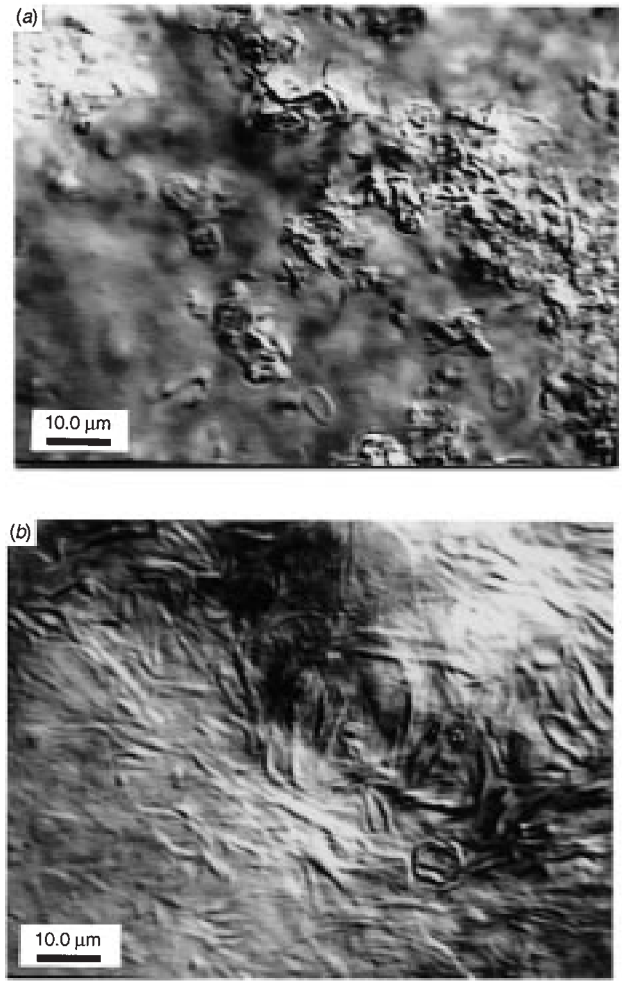


Fig. 2 Tubule-like structures at room temperature in 1% solutions of (*a*) 16-2-16 and (*b*) 18-2-18. Observations were made with a video-enhanced differential interference contrast (DIC) Zeiss Axiovert 135 Microscope using a 100× objective (numerical aperture 1.3). The images were processed using a Hamamatsu CCD camera (C2400-77) and an Argus20 real time image processor.

understood geometrically as an increase of the spontaneous curvature for shorter hydrophobic chains.[7] A higher curvature reduces the cap-energy and favours the formation of shorter micelles.[8] It is striking that a 0.1% solution of 16-2-16 (1.6 mM) shows a viscosity of 0.15 Pa s at temperatures as high as 45 °C! In order to study the effect of the dissymmetry, we compared surfactants with the same $n + m$, but with different $n - m$: 12-2-12 *vs*. 14-2-10, 14-2-14 *vs*. 16-2-12 and 16-2-16 *vs*. 18-2-14. In all these cases, the symmetric surfactants showed higher viscosity and lower overlap concentrations. Thus, the dissymmetry also causes an increase of the spontaneous curvature. This effect is particularly pronounced when one chain is less than half the length of the other. The solutions are then fluid at all temperatures and at concentratons as high as 20%, indicating the presence of spherical or short micelles only. Rather than being true geminis, these surfactants feature a single hydrophobic chain linked to a very voluminous and polar head, which leads to a large spontaneous curvature.

The cmcs of the surfactants were measured by conductimetry. They show a monotonous decrease as the overall hydrophobic chain length is increased. The smallest measured cmc was that of 16-2-18, at 17 µM. The cmc of 18-2-18 was too low to be evaluated accurately with this technique. Surfactants with equal $n + m$ such as 12-2-12, 10-2-14 and 8-2-16, or 14-2-18 and 16-2-16 have similar cmcs. Unlike the other properties of the surfactant aggregates presented above, the cmc does not depend on the symmetry but only on the overall hydrophobicity of the surfactant.

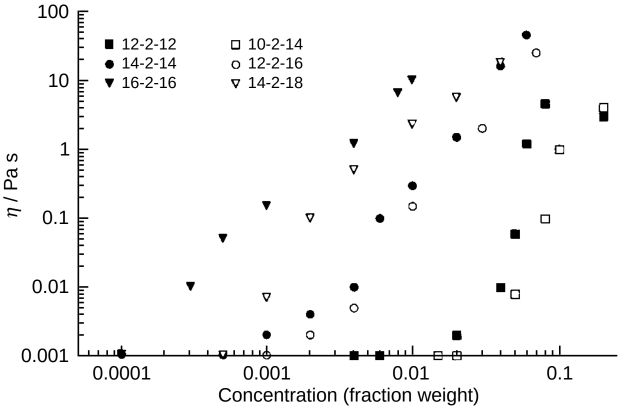


Fig. 3 The low-shear viscosity (η) of 12-2-12, 14-2-14, 16-2-16, 14-2-10, 16-2-12 and 18-2-14 as a function of concentration at 45 °C. Measurements were performed with a Rheometrics Fluid Spectrometer RFS II.

In conclusion, we have been able to correlate the morphology and the physical properties of the phases formed by new gemini surfactants with structural elements such as overall chain length and symmetry. Both decreasing the chain length and decreasing the symmetry result in larger spontaneous curvatures. This latter factor is particularly significant, allowing one to assess the arrangement of the surfactant hydrophobic chains in the various phases. Indeed, the increase in curvature for dissymmetric surfactants implies that in an aggregate, two diametrically opposed surfactant molecules cannot compensate their dissymmetry by overlapping their longer hydrophobic chains (see Graphical Abstract). The formation of pairs of surfactants spanning across a membrane in an arrangement comparable to that of bolamphiphiles is probably entropically disfavoured, and the thermal disorganisation of the hydrophobic chains proscribes such an overlap at the low concentrations studied. We are currently pursuing investigations to see whether interdigitation is possible in concentrated solutions of surfactants as was observed for hydrated dissymetrical phospholipids in the gel state.[9]

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Footnotes and References

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† These transition temperatures are those of 1% solutions, they increase slightly with concentration. Typically, we observed a variation of about 2 °C between 0.1 and 2% solutions.

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