T. Janicke, B. F. Chmelka, data not shown.
24. P. Laszlo, Ed., *NMR of Newly Accessible Nuclei* (Academic Press, New York, 1983), vol. 2.
25. V. K. Malinovsky and A. P. Sokolov, *Solid State Commun.* **57**, 757 (1986).
26. J. A. Tossell and P. Lazzeretti, *J. Non-Cryst. Solids* **99**, 267 (1988).
27. The authors thank D. Lewis (Chemagnetics) for technical assistance with the DOR probe. J.W.Z. thanks U. Werner-Zwanziger for several helpful discussions. Supported by NSF under grant nos. DMR-9115787 (J.W.Z.), DMR-9222527 (B.F.C.), and DMR-9257064 (B.F.C.).

6 March 1995; accepted 26 June 1995

Branched Threadlike Micelles in an Aqueous Solution of a Trimeric Surfactant

Dganit Danino, Yeshayahu Talmon,* Hélène Levy, Gerard Beinert, Raoul Zana

Very long threadlike micelles observed in aqueous solutions of some surfactants have attracted much attention because of the peculiar rheological properties of these systems. Molecular dynamics simulations have suggested that branched threadlike micelles should exist in concentrated solutions of dimeric surfactants. Here experimental evidence, obtained from transmission electron microscopy at cryogenic temperature, is presented of branched threadlike micelles in aqueous solutions of a triquaternary ammonium (trimeric) surfactant made up of three amphiphilic moieties connected at the level of the headgroups by two propanediyl spacers.

Surfactants and, more generally, amphiphiles self-associate in water and form micelles, vesicles, and lyotropic liquid crystalline phases. Theory (*1*, *2*) predicts many possible micelle shapes of which only three have been found experimentally: spherical or spheroidal micelles, disk-shaped micelles, and elongated micelles (*3*). Elongated micelles come in a wide variety of forms: from short rigid rods to flexible "giant" micellar threads that are micrometers in length (*3*). Threadlike micelles usually develop from spheroidal micelles when a relevant system parameter is altered (*4*–*6*). This change of shape is well understood within the framework of existing theories (*1*, *2*). Thus, micelle growth from spherical to threadlike micelles takes place if the difference between the standard chemical potentials of the surfactant in the cylindrical part (μ^0_c) of an elongated micelle and in a spherical micelle (μ^0_s), $\Delta\mu^0 = \mu^0_c - \mu^0_s$, is negative. Values of $\Delta\mu^0$ as low as -0.1 to $-0.2k_BT$ (where k_B is Boltzmann's constant and T is temperature) are sufficient to bring about an enormous micellar growth (*5*).

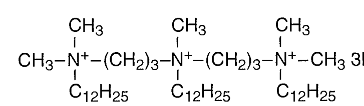
Transmission electron microscopy at cryogenic temperature has been extensively used to obtain direct visualization of threadlike micelles in aqueous solutions of pure conventional surfactants and of surfactant mixtures (*3*, *4*, *7*). Dimeric surfactants, made up of two identical amphiphilic moieties [$C_mH_{2m+1}(CH_3)_2N^+ Br^-$] connected at the level of the charged nitrogen atoms by a polymethylene spacer $(CH_2)_s$, have been found to form very long threadlike micelles at relatively low concentrations of 1% or less, provided the spacer is short enough (*8*).

Recently the possible existence of cross-links, connections, or seams between long and entangled threadlike micelles attracted much interest (*2*, *5*, *9*, *10*). Such cross-links would result in the formation of connected networks of elongated micelles, which are likely to have interesting rheological properties. Several experiments led to the postulation of the existence of such networks (*2*, *5*, *9*). Drye and Cates (*10*) investigated theoretically the formation of cross-links between threadlike micelles. They concluded that for conventional surfactants the free energy cost for forming a cross-link is much higher than for forming a hemispherical end-cap terminating a cylindrical micelle. This is because the surfactant layer at the seam between two branches is concave, whereas it is convex in the cylindrical part of the micelle, where the layer curvature is essentially equal to the spontaneous curvature. Therefore, a seam forms only when the system contains almost no end-caps, that is, when the micelles are extremely long (*10*). This is probably the case at the very high salt concentration at which some of the above-mentioned experiments were performed.

Molecular dynamics simulations of aqueous solutions of dimeric surfactants have accounted for the formation of elongated micelles. They also predicted that these elongated micelles should be branched or cross-linked (*11*). Furthermore, the simulations showed that the two alkyl chains of a given dimeric surfactant are radially oriented and roughly parallel in the cylindrical parts of the branched micelles; however, they are almost perpendicular when the surfactant molecule is located at a seam between two branches, with one chain oriented radially with respect to one branch and the other oriented radially with respect to the other branch (*12*). This very peculiar packing of the chains probably decreases the free energy cost associated with the formation of connections between threadlike micelles to a value that must be comparable to that of forming hemispherical end-caps which terminate elongated micelles. Thus, dimeric surfactants and their higher homologs trimeric surfactants potentially provide an easier way to obtain connected or branched threadlike micelles.

Here we present transmission electron micrographs taken at cryogenic temperatures showing branching in the threadlike micelles formed by a triquaternary ammonium tribromide (trimeric) surfactant that we synthesized and purified (*12*). Molecular dynamics simulations have not been performed yet for trimeric surfactants. It is likely, however, that the mechanism of reduction of the free energy cost for forming a seam holds and is even amplified with trimeric surfactants.

The trimeric surfactant we synthesized and purified (*12*), which is referred to as 12-3-12-3-12 following the terminology previously used (*8*, *12*, *13*), is shown in Scheme 1. This surfactant can be formally



Scheme 1.

considered as the trimer of the conventional surfactant dodecyltrimethylammonium bromide, which forms only spheroidal micelles even at fairly high concentration and ionic strength.

A 2% aqueous solution of the trimeric surfactant was studied by transmission electron microscopy at cryogenic temperatures (cryo-TEM). Thin vitreous samples were prepared under controlled temperature and 100% relative humidity as previously described (*8*). Some representative micrographs are shown in Fig. 1. A very long threadlike micelle is seen in the center of Fig. 1A. The featureless background is vitreous ice. In the central area of the field of view no overlap of micelles has occurred; thus, the branching of this long micelle (marked by arrow heads) can be easily seen. The clarity of the images of the meeting points of the three segments at each branching point strongly suggests that these are true branches. Furthermore, it is highly unlikely that the numerous branching points seen in

D. Danino and Y. Talmon, Department of Chemical Engineering, Technion-Israel Institute of Technology, Haifa 32000, Israel.
H. Levy, G. Beinert, R. Zana, Institut C. Sadron, 6 Rue Boussingault, 67000 Strasbourg, France.

*To whom correspondence should be addressed.

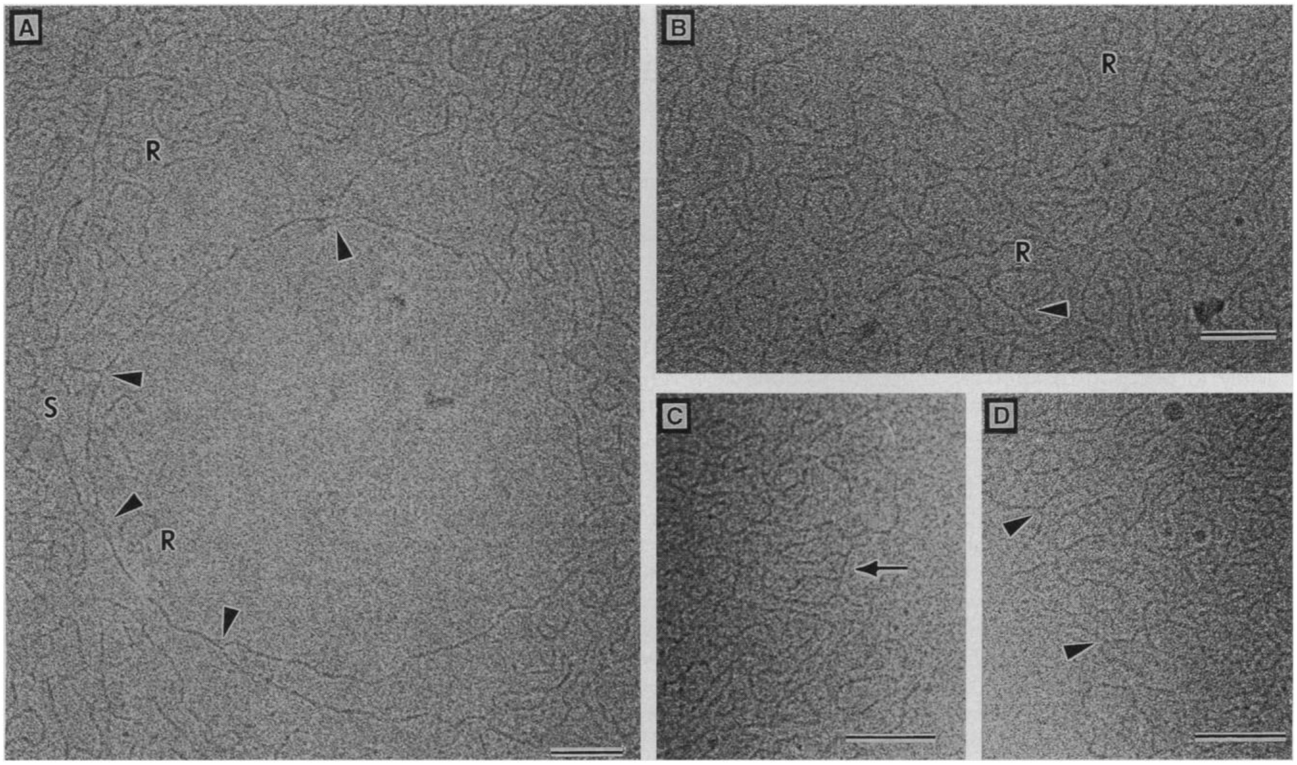


Fig. 1. Cryo-TEM images of 2% aqueous solution of the trimeric surfactant quenched from 50°C into liquid ethane at its freezing point. (**A**) A relatively thin area (less than 100 nm thick) of a specimen with a very long threadlike micelle in its center. Branching points are marked by arrow heads. Secondary branching is marked by S. More branching points can be seen in (**B**) to (**D**). (**C**) A micelle segment with at least four very closely located branches (arrow). Closed rings are denoted by R in (A) and (B). The ring in the lower part of (B) has an attached branch. Bars = 100 nm.

the micrographs of Fig. 1 are all the result of overlapping threads, as has been seen in other systems (*4*). Note the secondary branching in Fig. 1A (marked by the letter S), an indication that this feature may lead to three-dimensional network formation; this possibility is also suggested by the images in Fig. 1, B to D. Because transmission electron micrographs are projections on the photographic film of the structure in a relatively thin area, they appear as two-dimensional networks. Another feature of interest is seen in Fig. 1C: a micelle segment with at least four very closely located branches (arrow), indicating that branching in this system is a rather frequent phenomenon. Closed rings are also visible, as denoted by R in Fig. 1, A and B. Branching may take place off a ring, as seen in the lower part of Fig. 1B.

Direct experimental evidence for the existence of branched micelles has been discussed in the literature. Images by Vinson (*14*) suggest, but do not clearly demonstrate, the existence of branches. The branched micelles reported by Regev and co-workers (*15*) may in fact be intertwined micelles, similar to those previously observed in polysoap solutions (*16*). Well-developed network-forming branched micelles were observed recently in aqueous solutions of Habon G [$C_{16}H_{33}N^+(CH_3)_2(C_2H_4OH)$(3-OH-2-naphthoate)], a surfactant used in flow drag reduction (*17*). However, the 3-OH-2-naphthoate is an amphiphilic ion; thus, Habon G is in effect a surfactant mixture. Another possible example of branched elongated micelles has been observed in another mixed system of anionic and nonionic surfactants (*18*). "Y junctions" were also seen in cetyltrimethylammonium chloride (CTAC)–lecithin–NaCl and in CTAC–bile salt–salt systems (*19*). In surfactant mixtures local variations of composition, for example at the "seams," may help to compensate for the free energy penalty for forming a "seam." The notable aspect of the present study, in addition to the very clear images of the branching points, is that branching has been observed in a pure surfactant system. Perhaps rheological data will be soon available for systems that exhibit branched micelle formation, which could then be correlated with their microstructure.

REFERENCES AND NOTES

1. J. N. Israelachvili, J. D. Mitchell, B. W. Ninham, *J. Chem. Soc. Faraday Trans. II* **72**, 1525 (1976); E. McMullen, A. Ben Shaul, W. Gelbart, *J. Colloid Interface Sci.* **98**, 523 (1984); G. Taddei, *Colloid Polym. Sci.* **272**, 1300 (1994), and references therein.
2. G. Porte, R. Gomati, O. El Hataimy, J. Appell, J. Marignan, *J. Phys. Chem.* **90**, 5746 (1986).
3. P. K. Vinson, J. R. Bellare, H. T. Davis, W. G. Miller, L. E. Scriven, *J. Colloid Interface Sci.* **142**, 74 (1991).
4. P. K. Vinson and Y. Talmon, *ibid.* **133**, 288 (1989); T. M. Clausen *et al.*, *J. Phys. Chem.* **96**, 474 (1992).
5. J. Appell, G. Porte, A. Khatory, F. Kern, S. J. Candau, *J. Phys. (France)* **2**, 1045 (1992); A. Khatory *et al.*, *Langmuir* **9**, 993 (1993).
6. H. Hirata, M. Sato, Y. Sakaiguchi, Y. Katsube, *Colloid Polym. Sci.* **266**, 862 (1988).
7. L. Magid, J. Gee, Y. Talmon, *Langmuir* **6**, 1609 (1990); D. Danino and Y. Talmon, unpublished results; Z. Lin, L. E. Scriven, H. T. Davis, *Langmuir* **8**, 2200 (1992); K. Edwards, J. Gustafsson, M. Almgren, G. Karlsson, *J. Colloid Interface Sci.* **161**, 299 (1993), and references therein.
8. R. Zana and Y. Talmon, *Nature* **362**, 624 (1993); D. Danino, Y. Talmon, R. Zana, *Langmuir* **11**, 1448 (1995), and references therein.
9. A. Khatory, F. Lequeux, F. Kern, S. J. Candau, *Langmuir* **9**, 1456 (1993); F. Lequeux and S. J. Candau, *Structure and Flow in Surfactant Solutions* (*Am. Chem. Soc. Symp. Series* No. 578), C. Herb and R. Prud'homme, Eds. (American Chemical Society, Washington, DC, 1994), p. 51.
10. T. J. Drye and M. E. Cates, *J. Chem. Phys.* **96**, 1367 (1992).
11. S. Karaborni *et al.*, *Science* **266**, 254 (1994).
12. R. Zana, H. Levy, G. D. Papoutsi, G. Beinert, *Langmuir*, in press.
13. The full, proper name of this surfactant is 17-dodecyl-13,13,17,21,21-pentamethyl-13,17,21-triazoniatritriacontane tribromide.
14. P. K. Vinson, thesis, Minnesota University (1990).
15. I. Harwigsson, U. Söderman, O. Regev, *Langmuir* **10**, 4731 (1994).
16. D. Cochin, F. Candau, R. Zana, Y. Talmon, *Macromolecules* **25**, 4220 (1992).
17. X. Li, J. Zakin, Y. Talmon, in preparation.
18. Z. Lin, in preparation.
19. M. Silvander, G. Karlsson, K. Edwards, in preparation.

20. Supported in part by grants from the United States–Israel Binational Science Foundation (BSF), Jerusalem, and from the Fund for the Promotion of Research at the Technion.

10 May 1995; accepted 14 July 1995