Molecular conformations in surfactant micelles

DILL *et al.*¹ published recently a multi-coloured representation of a 38-chain decanoate micelle constructed according to their interphase theory, and they have implied that their model differs substantially from the one we have been advancing for some time^{2,3}. As the problem of micellar structure has been fraught with controversy and even 'outlandish hypotheses'⁴, some clarification of the subject is desirable. In fact, contrary to Dill *et al.*¹, there is surprising agreement between their calculations and our model based on physical organic data^{2,3}. Among the more important features of micellar structure that we have specified repeatedly are: (1) a rough micelle surface; (2) 'fatty patches' leading to an abundance of hydrocarbon-water contact where water-insoluble materials bind hydrophobically; (3) transient water-filled cavities; (4) chain bending and looping that place terminal methyls near the surface; (5) a water-free hydrocarbon core of <50% of the micellar volume. But the picture of Dill *et al.*¹ contains all these features. Thus, theory and experiment, although perhaps not in total accord, are at least in reasonable agreement.

Our recent paper² did indeed take strong issue with the Dill-Flory lattice model of micelles⁵ presented in 1981 and quoted widely since then⁶ (see figure). The

published picture possesses: (1) a smooth surface; (2) an absence of chain looping; (3) no terminal methyl groups at the surface; (4) a completely radial distribution of chains; (5) a crystalline interior (Dill and Flory write⁵: "Crowding of the chains near the core centre imposes a degree of order approaching that in a crystal.")—agreeing neither with our experimental data nor with the more recent model of Dill *et al.*¹. One cannot, however, charge Dill with inconsistency, because the Dill-Flory lattice model was not intended to represent a spherical micelle, but rather a cross-section of an infinitely-long cylinder. Unfortunately, as this picture was the only one appearing in an article devoted to micelles, many investigators mistook it for

a micelle⁷. Further use of this Dill-Flory 'micelle' will only perpetuate an irrelevant and totally unacceptable structure.

One final point of misunderstanding must be mentioned. In referring to our recent work, Dill *et al.*¹ write, 'it is claimed that micellar chains form 'loops' with termini 200 times more exposed to solvent than [are] internal segments'. But we made no such claim. Indeed, we specifically wrote², "All that can be stated with certainty is that internal olefin is less exposed to water than is the thoroughly-wet terminal olefin" and the value of 200 cited by Dill *et al.* was deduced incorrectly from our rate data. Incidentally, these rate data, pertain to the oxidation of double bonds at various locations along the surfactant chains. Comparisons of reactivity among the olefinic surfactants are legitimate because non-ideal mixing in the micelle, if it exists (it has been suggested⁸ that a "terminal double bond does not display a significant tendency to act as a second headgroup"), would remain constant in the series.

The recent model of Dill *et al.*¹ does not take into account head-group interactions, counter-ion binding, micellar water and deviations from spherical geometries. Yet even at this early stage of understanding, it is encouraging that theory and experiment are beginning to merge.

F. M. MENDER

Department of Chemistry,
Emory University,
Atlanta, Georgia 30322, USA

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DILL REPLIES—Although the present state of agreement between the theory of micellar organization and experiment is indeed most encouraging, it should be noted that many of the conceptual paradoxes, which have long plagued the subject of micellar structure, have not been resolved by intuitive models^{1,2}; more quantitative treatment has been required. In comparing his views to our interphase theory^{3,4}, Menger cites five points of agreement and five of disagreement. These comparisons, however, are inappropriate in two respects: (1) only our figures and diagrams are at issue, and not the underlying theory; (2) several of his claims are inaccurate.

For example, Menger has concluded from our Fig. 3 (ref. 3) that micelles should have rough surfaces, but from our Fig. 1 (ref. 4), that they are smooth. It is not the theory which is at issue here, for the underlying model is identical in that respect. Nor are the figures contradictory; it is simply that they are intended to serve two quite different purposes. In one figure, methylene groups are represented explicitly and in the other, schematically. In the latter, irrelevant details of chain structure are neglected explicitly to demonstrate the organization of viable chain conformations and, as such, to draw inferences about surface roughness from such a diagram is inappropriate.

In spite of the potential for misinterpretation, the figure with which Menger takes issue, and which is reproduced above, serves a most useful function, showing directly how chains can fully pack space and sustain disorder. That our figure represents cylindrical micelles as opposed to spherical ones is quite unimportant and, as Menger observes, it is appropriately labelled in any case. Indeed, his claim that others have mistaken its meaning is not supported by his reference to the work of Bendedouch *et al.*⁵. Although even the more realistic computer graphics Fig. 3 (ref. 3) oversimplifies significantly certain aspects of micellar structure (shape fluctuations of individual micelles undoubtedly occur on a rapid time scale), the assumption that micelles can be represented by averaged geometric shapes, such as spheres or cylinders, is of enormous utility, particularly for the description of properties which are averages over long times and over the large number of aggregates in solution.

Some of the implications of Menger's contribution are inaccurate. It is thus worth reiterating the principal features of micellar structure observed experimentally they are consistent with the premises and predictions of the interphase model. (1) The micellar core is virtually devoid of water^{3,5}. It is wrong to imply that there are significant amounts of 'water-filled cavities' and internal 'micellar water'. Moreover, 'transient cavities' is a term which has yet to benefit from definition and we are unaware of any experiments which have a bearing on their existence. (2) Micellar chains are highly disordered^{3,4,6}. Neither theory nor experiment can be construed to imply that the micellar core is crystalline or that the chains are radially aligned. (3) Chain bending and disorder are responsible for the distribution of chain ends near the micellar surface, but to varying degrees depending on chain length and micellar geometry. In general, the shorter the chains and the smaller the micelle, the greater the incidence of ends at the surface.