On the Structure of Micelles

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Prologue

Micelles have been the subject of over 2800 publications since 1970. Of these, 1938 are in English, 428 in Russian, 161 in Japanese, 123 in German, and 79 in French.[1] This worldwide interest in micelles originates from scientists with diverse specialties: organic chemistry, physical chemistry, biochemistry, pharmaceutical chemistry, polymer chemistry. Hundreds of patents on micelles and micelle-forming compounds testify to the commercial importance of the subject.[2] Micelles have been scrutinized by an unusually wide variety of techniques including X-rays, NMR, ESR, fluorescence, light scattering, and calorimetry. Despite all this attention, micelles have managed to elude detailed understanding. The multitude of publications has not resolved questions of micelle shape, water penetration, surface roughness, adsorption sites, interior viscosity, chain conformation, aggregation number, and ion binding. This account deals with these topics;[3] unpublished experimental data and molecular models of micelles assist the discussion. In order to place our ideas in proper context, I begin with an abbreviated history of micellar structure.

Decades ago McBain pondered the fact that surfactants (molecules possessing an ionic "head" coupled to a long paraffinic "tail") behave strangely in water.[4] Although a surfactant acts as a normal electrolyte below a fairly well-defined concentration, above this concentration abrupt changes take place in many solution properties (e.g., conductivity and osmotic activity). McBain pointed out in a lecture to the Royal Society of London that this behavior could be explained by surfactant aggregation above a critical micelle concentration (cmc). A leading physical chemist chairing the meeting responded to this idea with two words, "Nonsense, McBain".[5] Be that as it may, everyone today accepts the notion that about 30–150 surfactant units assemble into micelles so as to position the hydrocarbon chains near each other and away from the water. Apart from this, however, there seems to be

universal agreement on not a single structural feature of micelles. Even the concept of a sharp cmc below which surfactants are monomeric oversimplifies the situation.[6] I will focus here only on the uncertainties concerning surfactant solutions with concentrations 2- to 10-fold greater than the cmc; above that level micelles enlarge rapidly and ultimately create liquid crystalline phases.[7]

Early X-ray data[8] were thought to support a lamellar micelle structure[9] consisting of, in McBain's words,[10] "a double leaflet of soap molecules placed end to end and side by side" (Figure 1). Owing to the work of Hartley and others, this picture was later abandoned in favor of a roughly spherical micelle (Figure 1)[11] in which a shell of hydrated ions (termed the "Stern layer") encases a hydrocarbon core. The current popularity of spherical–ellipsoidal micelles stems from several factors (besides, of course, the ease with which these shapes lend themselves to theoretical calculations): (a) Reinterpreted X-ray data[12] do not demand the so-called "military hairbrush" micelle of McBain. (b) Critical micelle concentrations depend much more on the chain length of the surfactant tail than on the nature of the ionic head.[13] If the double leaflet were correct, one might have expected a greater sensitivity to the hydrophilic groups which lie closely in a flat bed

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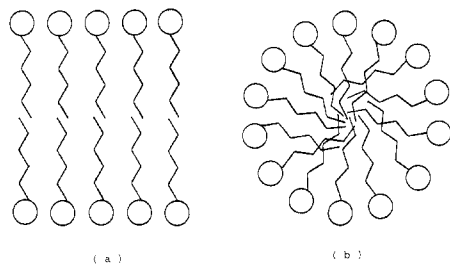
(1) These numbers, covering the time period from Jan 1, 1970, to May 31, 1978, were obtained using CA Condensates/CASIA. I thank Miss Pam Pickens for the information.

(2) Among other applications, surfactants are used in detergency, polymerization reactions, tertiary oil recovery, corrosion inhibition, lubrication, textile and paper processing, ore flotation, and preparation of emulsions for the food, cosmetic, and pharmaceutical industries.

(3) Only ionic surfactants in aqueous systems will be considered.

(4) J. W. McBain and H. E. Martin, J. Chem. Soc., 105, 957 (1914).

(5) J. W. McBain in "Colloid Chemistry", Vol. 5, J. Alexander, Ed., Reinhold, New York, 1944, p 102.

(6) J. S. Clunie, J. F. Goodman, and P. C. Symons, Trans. Faraday Soc., 63, 754 (1967).

(7) S. I. Ahmad and S. Friberg, J. Am. Chem. Soc., 94, 5196 (1972).

(8) K. Hess and J. Gundermann, Ber., 70, 1800 (1937).

(9) J. W. McBain and O. A. Hoffman, J. Phys. Colloid Chem., 53, 39 (1949); W. D. Harkins, J. Chem. Phys., 16, 156 (1948).

(10) E. W. Anacker in "Cationic Surfactants", Vol. 4, E. Jungermann, Ed., Marcel Dekker, New York, 1970, p 203.

(11) G. S. Hartley, Trans. Faraday Soc., 31, 31 (1935); G. S. Hartley, Q. Rev., Chem. Soc., 2, 152 (1948).

(12) F. Reiss-Husson and V. Luzzati, J. Phys. Chem., 68, 3504 (1964); M. L. Corrin, J. Chem. Phys., 16, 844 (1948).

(13) F. M. Menger in "Bioorganic Chemistry, Vol. III, Macro- and Multimolecular Systems", E. E. Van Tamelen, Ed., Academic Press, New York, 1977, p 137.

Figure 1. Schematically represented cross sections of a (a) McBain lamellar micelle and (b) Hartley spherical micelle.

of charge. (c) Double leaflets expose too much hydrocarbon to the external water. (d) Sedimentation, diffusion, and light-scattering data indicate spherical–ellipsoidal micelle shapes.[14] (e) Micelles are known to have rather fixed aggregation numbers;[12] double leaflets (which seem intuitively capable of accepting additional molecules one at a time) would probably not assume a distinct size. As a result of these considerations, the classical lamellar vs. spherical controversy is all but forgotten. Current discussions routinely depict the Hartley spherical–ellipsoidal micelle as a proven fact.[15-17]

Here and there throughout the chemical literature one finds dissenters who did not subscribe to the Hartley model.[18-20] Philippoff is a good example;[18] he believed that micelles consist of partially hydrated and ionized double layers. Debye also thought that surfactants form cylindrical double layers ("plates") in solutions of low ionic strength.[19] In order to explain the finite size of micelles in a plate configuration, one need only postulate that electrostatic repulsion among the head groups increases with aggregation number faster than the van der Waals and "hydrophobic" attraction of the tails.[21] As would be expected from this postulate, aggregation numbers increase with ionic strength.[22]

What of the data pointing to a spherical shape? Molecular models show that about 120 tightly packed dodecyltrimethylammonium ions can be fabricated into a cubical bilayer. (Fewer molecules are required if the molecules are not packed so closely.) No physical technique, whether it be sedimentation, diffusion, or light scattering, can differentiate a sphere from a cube or any other geometrical shape lacking appreciable dissymetry. It is apparent that none of the points favoring the Hartley micelle constitutes proof in the usual sense of the word. Despite good press, the Hartley micelle remains hypothetical. Experiments have still not differentiated beyond doubt the spherical micelle, with its ionic skin, from a lamellar micelle having a composite surface with *both* ionic and hydrophobic character.

Difficulties in devising a satisfactory micelle model originate not so much from a paucity of experimental data but rather from conflicting conclusions based on that data. Consider the viscosity of the micelle core. Shinitzky et al. measured the fluorescence depolarization of 2-methylanthracene adsorbed into micelles, and they found micellar viscosities of 17–50 cP.[23] (By way of comparison, the viscosities of water, dodecane, and 1-octanol are 1.0, 1.3, and 8.9 cP, respectively.) Thus, micelle interiors are liquid in nature but less fluid than hydrocarbon solvents of similar chain length. Ohnishi et al. showed that a spin-label adsorbed into a micelle experiences only a modest reduction in its tumbling rate (corresponding to a viscosity of about 17 cP).[24] Our own work with ^{13}C NMR spin–lattice relaxation times indicates a micellar viscosity of 8.3 cP.[25]

But many do not share this view of a fluid micelle. Pownall and Smith, using the relative intensities of monomer and excimer fluorescence of micelle-adsorbed pyrene, deduced a viscosity of 151 cP for hexadecyltrimethylammonium bromide.[26] Fluorescence data of Dorrance and Hunter are ostensibly consistent with a solidlike micelle core.[27] They used the words "extremely viscous" in describing the interior. Povich et al. go even further.[28] Their spin-label work supports a micellar environment similar to hexadecane at −22 °C (40 °C below the freezing point of the hydrocarbon!). Although the preceding citations represent only a fraction of the work on micellar viscosity, they suffice to demonstrate the confusion facing those interested in micellar structure.

The viscosity differences mentioned above derive from many problems: (a) Interpretating the data often requires tenuous assumptions. For example, fluorescence depolarization data yield reliable viscosities only if the micelle rotates much more slowly than does the probe molecule within the micelle. (b) Most microenvironmental studies use adsorbed probes whose locations inside the micelles are not known precisely. The possibility of several adsorption loci for a single probe and of a nonuniform micelle interior compounds the difficulties. (c) No doubt the disparate opinions with regard to micellar viscosity relates in part to structural differences among the probe molecules. A large fluorescence probe (pyrene) could well experience mobility problems within a micelle unlike those of a small spin-label (di-*tert*-butyl nitroxide). (d) Since micellar data are collected under an array of conditions (ionic strength, pH, surfactant concentration, etc.), comparisons are often muddled. (e) Probe molecules, especially large ones, can perturb the environment in which they are embedded. This last point hardly needs amplification.

Water penetration into the micelles, a critically important matter in micellar structure, suffers from the same bewildering array of opinions as micellar viscosity. Almost any conceivable hydration picture finds support somewhere in the literature. At one extreme lies the

(14) J. K. Backus and H. A. Scheraga, *J. Colloid Sci.*, 6, 508 (1951).
(15) J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Marcomolecular Systems", Academic Press, New York, 1975, p 31.
(16) L. R. Fisher and D. G. Oakenfull, *Chem. Soc. Rev.*, 6, 25 (1977).
(17) I am guilty too; see ref 13.
(18) W. Philippoff, *Discuss Faraday Soc.*, 11, 96 (1951).
(19) P. Debye, *Ann. N.Y. Acad. Sci.*, 51, 575 (1949).
(20) K. Shinoda, T. Nakagawa, B. Tamamushi, and T. Isemura, "Colloidal Surfactants", Academic Press, New York, 1963.
(21) G. D. Halsey, Jr., *J. Phys. Chem.*, 57, 87 (1953).
(22) L. Romsted, Ph.D. Thesis, Indiana University, Bloomington, 1975. This thesis contains a particularly thorough listing of micellar parameters as a function of surfactant structure and solution properties.

(23) M. Shinitzky, A.-C. Dianoux, C. Gitler, and G. Weber, *Biochemistry*, 10, 2106 (1971).
(24) S. Ohnishi, T. J. R. Cyr, and H. Fukushima, *Bull. Chem. Soc. Jpn.*, 43, 673 (1970).
(25) F. M. Menger and J. M. Jerkunica, *J. Am. Chem. Soc.*, 100, 688 (1978).
(26) H. J. Pownall and L. C. Smith, *J. Am. Chem. Soc.*, 95, 3136 (1973).
(27) R. C. Dorrance and T. F. Hunter, *J. Chem. Soc., Faraday Trans. 1*, 68, 1312 (1972).
(28) M. J. Povich, J. A. Mann, and A. Kawamoto, *J. Colloid Interface Sci.*, 41, 145 (1972).

"reef" model: water does not penetrate beyond the ionic head group. Stigter, a chief proponent of the reef model,[29] thinks that *all* methylenes of the tail endure a dielectric constant of 2. At the other extreme, one finds the "fjord" model in which water percolates nearly to the center of the micelle. Small-angle X-ray data of Svens and Rosenholm[30] and ^{19}F NMR work of Muller[31] lend credence to this particular description.

Intermediate schemes are also available. Corkill et al.[32] and Kurz[33] argue that the methylene groups adjacent to the ionic heads maintain an aqueous atmosphere. Kresheck writes, "Results from a variety of studies suggest that the first four to six carbons retain their hydration in the micellar state".[34] Not only do the data on water penetration appear ambiguous, the concept becomes difficult to define when applied to lamellar micelles and other aggregates having large hydrocarbon–water contact.

One property of micelles stands out above all others in importance: micelles solubilize organic compounds in water. Benzene, for example, dissolves in micellar solutions of sodium dodecyl sulfate ($NaDodSO_4$) to the extent of 0.90 mol/mol of surfactant. When 0.25 M $NaDodSO_4$ is added to water, the solubility of benzene increases 10-fold. The binding constant relating benzene and micelles of hexadecyltrimethylammonium bromide (HTAB) approaches 10^4 M^{-1}.[35] Of course, these numbers say nothing about the location and orientation of the benzene within the micelles. Differential UV spectroscopy investigations of Rehfeld suggest that benzene situates itself inside the hydrocarbon core of both cationic and anionic micelles.[36] On the other hand, NMR chemical shift data of Eriksson and Gillberg support benzene adsorption at the micelle–water interface.[37] Fendler and Patterson believe that the binding site for benzene varies with the surfactant: hydrocarbon core for $NaDodSO_4$ and micelle surface for HTAB.[38]

Spectroscopic sensors have not, as we have just seen with benzene, provided definitive information about micellar microenvironments. Part of the problem rests with the experimental approach: one compares the UV, NMR, ESR, or fluorescence spectra of a probe inside a micelle with those of the probe in a range of solvents. However, this procedure presupposes that solvents or solvent mixtures can simulate a micellar environment. Unfortunately, no solvent system yet developed solvates a benzene ring on one side with water and on the other side with hydrocarbon (as might well occur in a micelle). There is also doubt concerning the similarity of micellar water to bulk water.

Lack of suitable referencing solvents is not the only problem. Still another difficulty can be blamed on Hartley, and others who followed him, who perpetuated the "2-state" micelle consisting of an aqueous shell

surrounding a hydrocarbon core. Within the confines of the Hartley model, investigators have been forced to ascribe their probe data either to an aqueous site or to a nonpolar site. As I will demonstrate shortly, this represents a gross oversimplification; solubilized substances are undoubtedly distributed (and rapidly exchanging) among several micellar sites of varied character.

Assume for a moment that the Hartley "2-state" micelle is a fairly accurate picture. Then one must ask why many water-insoluble compounds (e.g., benzophenone, bromobenzene, butyronitrile) apparently prefer the highly aqueous micelle surface to the organic interior.[39] Few people other than Mukerjee have even addressed this puzzling question.[40] Mukerjee claims that benzene is surface active (albeit slightly), and that this fact combined with the extremely large surface area of micelles leads to effective interfacial adsorption near the water. "From a molecular point of view, the preference of benzene for the micelle–water interface can be attributed to the ability of the π-electron system to accept hydrogen bonds".[40] The model which I propose in this Account explains interfacial binding without resorting to hydrophilic properties of hydrophobic solubilizates.

Aggregation numbers (AN) should in principle reveal useful information about micellar packing. Once again, however, an undercurrent of doubt obscures the situation.[41] For example, dodecyltrimethylammonium bromide has been reported to have 45, 61, 73, and 84 molecules per micelle.[22] Even more perplexing, the aggregation number (whatever its actual value) represents only the most abundant of *many* micelle sizes in equilibrium with each other.[42] Presumably, a plot of frequency vs. number of surfactants per micelle would generate a Gaussian distribution centered at the so-called aggregation number, but no firm data can be found on the width of this curve. If forced to hazard a guess, one might state that AN ±10% includes the great majority of micelles.

"Monodispersity", claimed persistently for micellar systems, smacks of euphemism; translated, the word means that an experimental technique is not sufficiently sensitive to detect varying micelle sizes. Aniansson and Wall expressed it well:[43] "... the term "low-dispersity" should perhaps be used at present instead of "monodispersity"." In any event, neither AN data of others nor molecular models shown below demand an exclusive micelle size that is favored for some special steric or electostatic reason.

Aggregation numbers do depend on ionic strength: the AN for sodium dodecyl sulfate increases from 95 to 117 to 132 as the NaCl concentration is elevated from 0.00 to 0.10 to 0.40 M.[44] On the other hand, organic additives generally decrease the AN. Thus, micelles appear to be unfettered structures, held together in a delicate balance of forces, and able to contract or expand as solution conditions warrant. Kinetic data fit this "loose ball" picture; a monomer remains in a mi-

(29) D. Stigter, *J. Phys. Chem.*, 78, 2480 (1974).

(30) B. Svens and B. Rosenholm, *J. Colloid Interface Sci.*, 44, 495 (1973).

(31) N. Muller and R. H. Birkhahn, *J. Phys. Chem.*, 71, 957 (1967).

(32) J. M. Corkill, J. F. Goodman, and T. Walker, *Trans. Faraday Soc.*, 63, 768 (1967).

(33) J. L. Kurz, *J. Phys. Chem.*, 66, 2239 (1962).

(34) G. C. Kresheck in "Water, A Comprehensive Treatise", Vol. 4, F. Franks, Ed., Plenum Press, New York, 1975, p 95.

(35) K. M. Bansal, L. K. Patterson, E. J. Fendler, and J. H. Fendler, *Int. J. Radiat. Phys. Chem.*, 3, 321 (1971).

(36) S. J. Rehfeld, *J. Phys. Chem.*, 74, 117 (1970).

(37) J. C. Eriksson and G. Gillberg, *Acta Chem. Scand.*, 20, 2019 (1966).

(38) J. H. Fendler and L. K. Patterson, *J. Phys. Chem.*, 75, 3907 (1971).

(39) Reference 15, pp 76–81.

(40) P. Mukerjee, J. R. Cardinal, and N. R. Desai in "Micellization, Solubilization, and Microemulsions", Vol. 1, K. L. Mittal, Ed., Plenum Press, New York, 1977, p 241.

(41) N. J. Turro and A. Yekta, *J. Am. Chem. Soc.*, 100, 5951 (1978).

(42) M. J. Vold, *J. Colloid Sci.*, 5, 506 (1950).

(43) E. A. G. Aniansson and S. N. Wall, *J. Phys. Chem.*, 78, 1024 (1974).
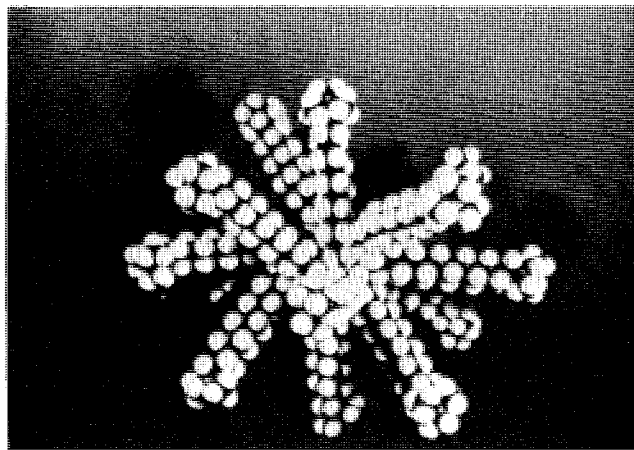
(44) K. J. Mysels, *J. Colloid Sci.*, 10, 507 (1955).

Figure 2. A dodecyltrimethylammonium ion micelle with an aggregation number of 14.

celle only 10^{-3} to 10^{-8} s depending on the chain length of the surfactant.[45]

The Model

I begin by describing micellar structures as deduced from CPK molecular models. Later on an attempt will be made to relate the structures to experimental data. Dodecyltrimethylammonium ions (DTA) were selected as building blocks for the model; the bromide salt of this surfactant has a cmc of 0.015 M and an AN near 60. Although water molecules and counterions were not included in the model, considerable attention was paid to the space available for these entities.

Three considerations dictated the construction of the model: (a) It was assembled about a point of symmetry. For example, the first six monomers were placed in three mutually perpendicular pairs about this point; the next eight were fitted symmetrically into each of the resulting octants. (b) Empty space within the core was held to a minimum.[46] Thus, the eight monomers just mentioned were inserted into the core until they could move no further without distorting the assemblage. (c) Chains were initially provided with all-trans (i.e., fully extended) configurations. Laser Raman scattering studies indicate that micelles contain chains having both all-trans and partially gauche conformations, but the former predominate.[47] As might be expected, micelle chains possess more kinks than chains in the crystalline state but fewer than those of surfactant monomers in solution. Since my constraints may underestimate the capriciousness of micelles, I will later consider a less bridled model.

The micelle models were constructed by suspending each molecule from two thin nylon threads attached to carbons 3 and 9 of the 12-carbon chain. A board, containing a grid of over 4500 holes spaced at 1-cm intervals, supported the molecules. Threads from a monomer were strung through two holes selected so as to place the molecule in more-or-less the desired location. After small adjustments in the hole position and/or thread length, the threads were permanently attached to the board. Most of the supporting threads sloped gently toward each other at the top, thereby holding the micelle in a compact form.

(45) Reference 15, pp 26–29.
(46) S. H. Yalkowsky and G. Zografi, *J. Pharm. Sci.*, 61, 793 (1972).
(47) K. Kalyanasundaram and J. K. Thomas, *J. Phys. Chem.*, 80, 1462 (1976); H. Okabayashi, M. Okuyama, and T. Kitagawa, *Bull. Chem. Soc. Jpn.*, 48, 2264 (1975).

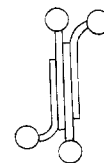**Figure 3.** A likely mode of association in a small aggregate.
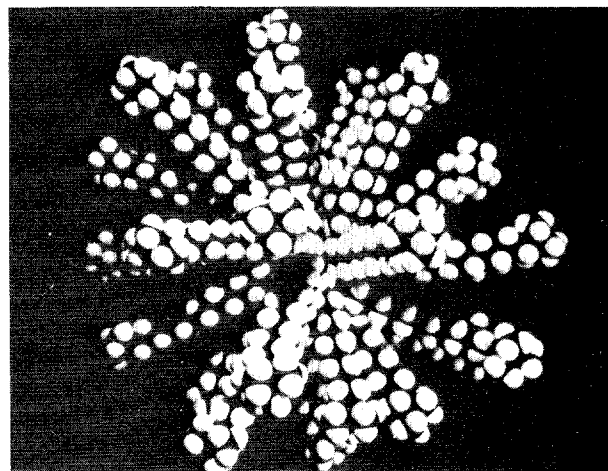

Figure 4. A dodecyltrimethylammonium ion micelle with an aggregation number of 30.

Figure 2 shows a photograph of a hypothetical DTA micelle having an AN = 14. The radius of this micelle is only slightly larger than the length of an extended DTA molecule (17.6 Å). The minimal hydrocarbon–hydrocarbon contact among the chains explains why linear surfactants resist forming small micelles. Hydrophobic interactions would be enhanced in a nonspherical geometry (Figure 3), but even here the majority of chains are exposed to water. Small aggregates (as might exist at low levels below the cmc) probably involve lateral association as in Figure 3.

Sixteen additional surfactant molecules were inserted into the aggregate to give an AN of 30 (Figure 4). This is roughly half the number believed to make up the actual micelle. The radius of the micelle increases by 10–20% over that in Figure 2. More importantly, direct chain-to-chain contact remains slight. Some of the chains touch the aggregate with only their terminal methyl groups; most chains have only 2–4 buried carbons. The result is an open structure with cavities 10–15 Å deep.

A micelle with a more realistic AN of 58 is shown in Figure 5. This spherical structure of radius = 23 ± 1.5 Å manifests the deep grooves seen in the smaller micelles. The great majority of chains have six or more "exposed" carbons outside the *nucleus* (the nucleus being defined here as the region of direct chain contact). With a few of the chains, water molecules could reach well beyond the first six carbons. Both the Hartley "2-state" micelle and the micelle in Figure 5 are approximately spherical, but the similarity ends there. Whereas the Hartley micelle has an ionic surface and hydrocarbon interior, it is not even clear what the words "surface" and "interior" mean with respect to Figure 5. Our micelle does have a nucleus which presumably contains no water and possesses a dielectric constant similar to that of pure hydrocarbon. However, a nucleus comprises only a fraction of the total micelle volume (perhaps 15–20% depending on where one locates the borders). Outside the nucleus lies a domain of hy-
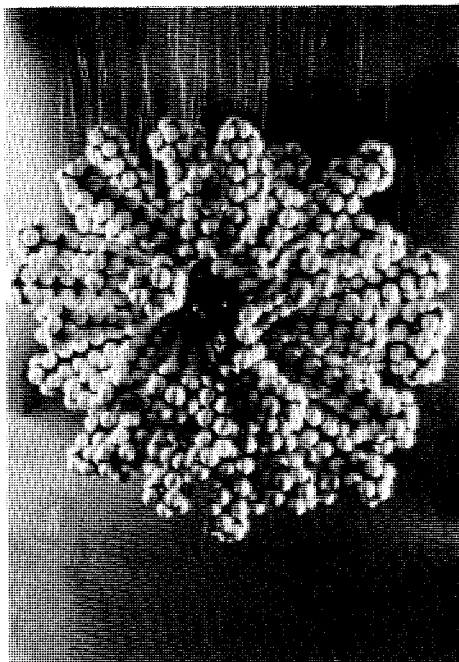
Figure 5. A dodecyltrimethylammonium ion micelle with an aggregation number of 58. All chains are fully extended. A pyrene molecule is situated among the chains close to the micelle surface.

drocarbon plus water, the proportion of the latter component increasing near the ionic heads. If Figure 5 is an approximately accurate picture, then the important Stern layer[48] should not really be called a "layer"; a better name would be *Stern region*. Stern regions penetrate effectively into micelles and occupy a large proportion of the micellar volume.

In the remainder of this Account, I interpret many observations, old and new, in terms of the revised model.

The diffuse "pincushion" configuration of the micelles explains their transient existence.[45] Self-association of surfactants stems primarily from hydrophobic bonding within a rather small nucleus; only short terminal sections of the chains cement the aggregate together. Consequently, the departure of a monomer from a micelle occurs rapidly and requires relaxation methods to detect.

Figure 5 accords with the ability of micelles to accumulate additional surfactant molecules when the ionic strength increases. As can be seen from the photograph, space is available between the crotches to accept many more surfactant molecules. The number of molecules in a sphere has limits, however, because tighter packing enhances electrostatic repulsion among the head groups. More importantly perhaps, any additional chains must reside between head groups already present (projecting to some extent further out into the solution). This embeds head groups in a hydrocarbon environment and destabilizes the micelle. Molecular models suggest that DTA micelles bearing over 90–100 molecules may have too many head groups fully buried in hydrocarbon to sustain an approximately spherical structure.[49] As is generally known, micelles do in fact elongate as their aggregation numbers in-

crease.[50] Actually, the much-discussed sphere vs. ellipsoid issue[51] has peripheral relevance here because there is no evidence that the two shapes differ fundamentally in their behavior.

The model in Figure 5 predicts deep penetration of water into micelles, and recent NMR work of ours supports this conclusion.[52] Solvent-sensitive ^{13}C NMR chemical shifts of carbonyls inserted into micelles were used to probe micellar microenvironments. It was found that octanal, 1-naphthaldehyde, and di-*n*-hexyl ketone solubilized in HTAB micelles display apparent polarities equivalet to those of 2-propanol, Me$_2$SO, and dioxane, respectively. Octanal can align itself with the surfactant molecules so as to place the carbonyl near the water-rich portion of the Stern region. Di-*n*-hexyl ketone, on the other hand, has a carbonyl flanked by two long alkyl groups which drag it closer to the nonaqueous nucleus. 1-Naphthaldehyde manifests an intermediate polarity. Thus, both the NMR data and the molecular models point to a complex and diverse micellar interior whose polarity covers a wide range. Since probe molecules move rapidly inside a micelle, an observed polarity depends on the fractional residence times at the various locales. Although di-*n*-hexyl ketone obviously spends a great percentage of its time near the nucleus, this does not preclude its fleeting presence in the more aqueous regions.

The depth of water penetration into a micelle can be determined only with probes of known location. For this reason we studied micelles composed of (8-ketohexadecyl)trimethylammonium bromide, a surfactant

$$CH_3(CH_2)_7CO(CH_2)_7\overset{+}{N}(CH_3)_3Br^-$$

bearing a carbonyl group but having a "normal" cmc. The ^{13}C NMR spectrum of this material above its cmc demonstrated that the carbonyl is bathed in a highly aqueous medium. The same conclusion was reached with mixed micelles comprised of the keto surfactant and excess HTAB. We do not believe that the carbonyl "pulls" water into a normally nonaqueous interior because, as mentioned above, di-*n*-hexyl ketone does not do likewise. The simplest rationale is that water penetrates the micelle until at least the first 7 of the 16 tail carbons. Figure 5 and the work of others[30,31] affirm the plausibility of this conclusion.

Parameters other than polarity should likewise vary with the distance from the center of the micelle. For example, we have shown by means of ^{13}C NMR spin–lattice relaxation times that phenyl rotation of C$_6$H$_5$-(CH$_2$)$_n$CO$_2^-$ in NaDodSO$_4$ micelles depends on n.[25] Phenyl groups of the $n = 3$ compound, positioned relatively near the micellar head groups, experience little impaired motion above that found in the free solution. When $n = 9$, the phenyl groups deep within the micelle rotate in a highly anisotropic manner. No doubt the widely divergent views about micellar viscosity originate in part from the different sizes and binding sites of the solubilized probes.

I now return to the question of why so many water-insoluble compounds appear to adsorb near the micelle surface. Recent unpublished experiments of

(48) Reference 15, pp 31–32.

(49) H. V. Tartar, *J. Phys. Chem.*, **59**, 1195 (1955); P. Ekwall, L. Mandell, and P. Solyom, *J. Colloid Interface Sci.*, **35**, 519 (1971); K. Kalyanasundaram, M. Gratzel, and J. K. Thomas, *J. Am. Chem. Soc.*, **97**, 3915 (1975).

(50) This is over twice the number arrived at theoretically by H. Schott, *J. Pharm. Sci.*, **60**, 1594 (1971).

(51) G. Zografi and S. H. Yalkowsky, *J. Pharm. Sci.*, **61**, 651 (1972).

(52) F. M. Menger, J. M. Jerkunica, and J. C. Johnston, *J. Am. Chem. Soc.*, **100**, 4676 (1978).

Table I
Relative Rates of Carbonyl
Reduction of Several Steroids Adsorbed in
Hexadecyltrimethylammonium Borohydride Micelles[a,b]

7.8					3.2

4.4					2.2

1.0					3.6
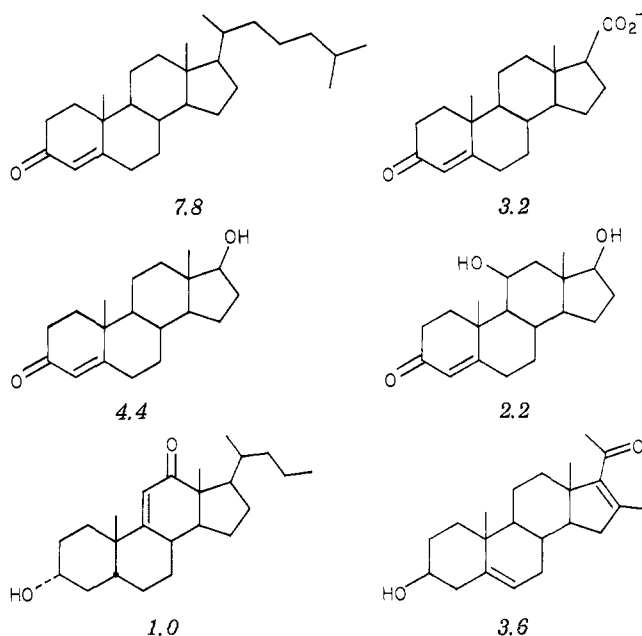
[a] The second-order rate constant for reduction of 3-methyl-2-cyclohexen-1-one by borohydride in bulk water at 25.0 °C was assigned a relative value of 1.0. [b] The top four compounds demonstrate the insensitivity of the rates to substituents in the C and D rings. The bottom two compounds demonstrate the insensitivity of the rates to the position of the carbonyl group.

ours suggest that even large hydrophobic molecules can situate themselves in the aqueous micellar regions.[53] These experiments were based on the idea that the location of a rigid molecule (drawn schematically below)

$$X- \boxed{} -Y$$
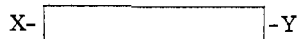
would be revealed if the position of substituents X and Y were established. For example, when X and Y are both near the micelle–water interface, the *entire* system must necessarily be there also.

Table I lists a group of steroids in which X is defined as the carbonyl in the A ring and Y as the group attached to the D ring. These steroids, adsorbed into hexadecyltrimethylammonium borohydride micelles, have their carbonyls reduced by borohydride counterions. Relative reduction rates are given beneath the structures in Table I. Two points are immediately obvious from the data: (a) Micelles cause small rate increases over the corresponding reaction in bulk water. This type of catalysis has literature precedent[54] and can be ascribed to favorable accumulation of the carbonyl and BH_4^- entities at the interface. (b) The reduction rates depend only slightly on the D-ring substituent (which varies from ionic to nonpolar). Apparently, the carbonyls of *all* the steroids in Table I are located at the micelle surface where they have similar access to borohydride. Now the steroid with X = carbonyl and Y = CO_2^- must, according to the above reasoning, reside in the aqueous Stern region if the two substituents do likewise. The trivial kinetic variations in Table I imply

(53) J. Bonicamp, unpublished results.
(54) F. M. Menger and C. E. Portnoy, *J. Am. Chem. Soc.*, **89**, 4698 (1967). This article develops the equations necessary to extract the rate constants for solubilized substrates from observed rate constants.
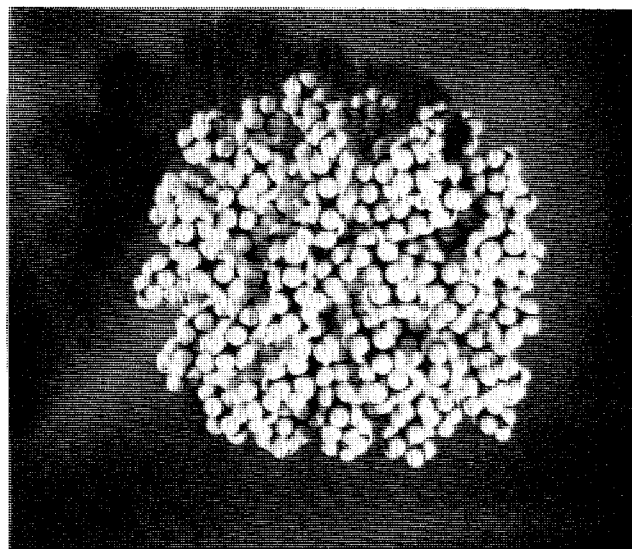

Figure 6. A dodecyltrimethylammonium ion micelle with an aggregation number of 58. Chains consist mainly of trans conformations but possess one or more "kinks" which shorten the chains.

that the other steroids, even the highly water-insoluble ones, also bind to the Stern region. Binding in the nonaqueous nucleus would have severely hampered the borohydride reductions.

The surprising "surface" binding of water-insoluble compounds is readily understood from the model in Figure 5. Large guest molecules, including steroids and pyrene, fit into the surface grooves without disrupting the micelle structure. Entry into the grooves is facilitated by ion-induced dipole forces and, more importantly, by hydrophobic interactions. When a solubilizate binds to the aqueous Stern region, water surrounding the chains is displaced,[37] an entropically favored process.[55] Contrast this situation with dissolution into the nonaqueous nucleus where electrostatic and hydrophobic factors give little assistance. Moreover, since the nucleus is a compact unit, adding to it a foreign substance requires reorganizing many surfactant molecules.

Note that the Stern region, as I have pictured it, is comprised of flexible chains free to move about. A hydrophobic guest molecule could quite possibly induce conformational changes in the chains to better accommodate solvation needs. In other words, a guest could create a fatty "lesion" near the micelle surface by surrounding itself with surfactant methylene groups.

Tanford has published a theoretical treatment for association of surfactants into micelles.[56] His interesting calculations involve two crucial assumptions not consistent with our model or experiments: (a) Only the CH_2 groups adjacent to the polar heads lie in water. (b) The radius of the hydrophobic core is limited by the length of the extended alkyl chain, precluding the possibility of small spherical micelles. According to Figure 5, the extreme roughness[57] of the micelle surface negates both assumptions.

(55) N. Muller in "Reaction Kinetics in Micelles", E. H. Cordes, Ed., Plenum Press, New York, 1973, pp 1–23.
(56) C. Tanford, *J. Phys. Chem.*, **76**, 3020 (1972); C. Tanford, *ibid.*, **78**, 2469 (1974).
(57) The term "rough micelle", coined by D. Stigter and K. J. Mysels, *J. Phys. Chem.*, **59**, 45 (1955), generally refers to a micelle with its first methylene outside the hydrophobic core. Such a micelle is rather smooth relative to our model.

The models discussed thus far were constructed with all chains in the micelle fully extended, but this is clearly an oversimplification. Figure 6 shows a DTA micelle with kinks in each of the 58 surfactant molecules. The radius of the compacted micelle is roughly 18 Å (close to the minimum possible and to the length of the all-trans DTA molecule). Folding the chains reduces the volume of the aqueous pockets at the cost of enhanced nonbonded interactions along the chains as well as electrostatic repulsion among the head groups. The micelle surface probably undulates between a multitude of configurations, Figures 5 and 6 being two extremes. In any event, folding certainly does not eliminate aqueous cavities within the micelle; space is still available to occlude benzene, p-nitrophenyl acetate, and other small probes. If a large molecule such as pyrene impinges on a contracted micelle, the chains could unfold and grasp the morsel much like the action of a hydra. Alternatively, pyrene could act as a template about which the micelle can organize. Both mechanisms reach the same end point: pyrene adsorbed in the Stern region.

Chain folding does reduce the hydrocarbon–water contact but less than one might think. When the chains arch to move the ionic head groups inward, portions of the chains are brought directly onto the micelle surface. Thus, hydrocarbon is exposed to water in *both* the extended and folded variations (Figures 5 and 6). In the former case, chains surround aqueous grooves; in the latter, chains intermingle with the head groups at the micelle–water boundary. Hydrocarbon–water contact more than any other feature distinguishes the micelles in Figures 5 and 6 from the Hartley "oil drop with a polar coat".[58]

The Hartley model places head groups in an aqueous shell of high ionic strength; accordingly, the Stern region should resemble a concentrated salt solution. On the other hand, the head groups in Figure 6 are immersed in a peculiar mixture of water, ions, and hydrocarbon. We have attempted to differentiate the two situations by examining the charge-transfer absorbance of the long-chain pyridinium iodide shown below.[59] Years ago Kosower used the solvent-sensitive UV absorption of a short-chain analogue of this compound to develop his "Z-value" solvent polarity scale.[60] Z values for our pyridinium salt above its cmc indicated a time-averaged

$$CH_3(CH_2)_9OC\text{—}\langle\text{—}\rangle\text{—}N^+\text{—}CH_3I^-$$
$$\overset{\|}{O}$$
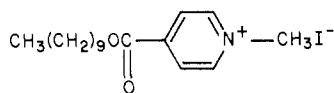
surface polarity equivalent to that of methanol[61] (*not* that of an aqueous salt solution predicted by the Hartley model). Enthalpy data support the Z-value results; Poland and Scheraga concluded from negative ΔH values of micellization that surfactant head groups change their solvation characteristics upon entering a micelle.[62]

Micelles have been investigated exhaustively by ki-

netic probe methods in which one determines the effect of solubilization on chemical reactivity.[63] We have derived an equation needed for analyzing the kinetics of pseudo-first-order micellar reactions,[13,54] and a Russian group later did the same for second-order processes in micelles.[64] Without going into details, the kinetics demonstrate clearly that most reactions within the Stern region are not radically affected by medium effects (a factor of 10 or less relative to bulk water). Bimolecular micellar reactions can sometimes experience a 10^2–10^3 catalysis, but this is largely the result of concentrating the reactants in a reduced volume.[64] The models in Figures 5 and 6 are consistent with the kinetic data. Solubilizing a compound in the grooves near the micelle surface (with an apparent polarity of methanol) should not greatly perturb reaction rates relative to those in bulk water, all other factors being equal. Only when a molecule is dragged into the inner recesses of the micelle can one expect a rate constant appreciably different from the water value.

Epilogue

Models are to be used, not believed. The structures in Figures 5 and 6 (or a hybrid thereof) appear to remove from serious consideration the classical Hartley 2-state micelle. But many other possibilities, including the old McBain lamellar micelle, remain viable. All of them feature considerable hydrocarbon–water contact rather than an ion double layer shielding a nonpolar core.

The model photographed in Figures 5 and 6 no longer exists. The molecules in it were irreversibly randomized into a "brush-heap" configuration. Interestingly, the diameter of the spongy aggregate expanded only 20%. In the absence of data to the contrary, chemists must not discount the chance that micelles are in fact rather disorganized assemblages of surfactant molecules. If this is a discordant note on which to end the Account, then let it also be a challenge, a challenge to introduce new ideas and methodology which will finally determine the structure of micelles. At the present time, our "porous cluster" must be considered a plausible model consistent with most available data.

Note Added in Proof

Theoretical calculations have just appeared which strongly support the model proposed in this account.[65]

(58) P. Mukerjee and J. R. Cardinol, *J. Phys. Chem.*, 82, 1620 (1978).
(59) T. E. Thanos, unpublished work.
(60) E. M. Kosower, *J. Am. Chem. Soc.*, 80, 3253 (1958).
(61) This conclusion agrees with that of P. Mukerjee and A. Ray, *J. Phys. Chem.*, 70, 2144 (1966). They used N-alkylated pyridinium salts which have a somewhat more buried quaternary nitrogen.
(62) D. C. Poland and H. A. Scheraga, *J. Colloid Interface Sci.*, 21, 273 (1966).

(63) E. H. Cordes, Ed., "Reaction Kinetics in Micelles", Plenum Press, New York, 1973.
(64) A. K. Yatsimirski, K. Martinek, and I. V. Berezin, *Tetrahedron*, 27, 2855 (1971).
(65) G. E. A. Aniansson, *J. Phys. Chem.*, 82, 2805 (1978).
(66) Several publications on micelles and interfaces by the author and co-workers were not cited in this Account: F. M. Menger and G. Saito, *J. Am. Chem. Soc.*, 100, 4376 (1978); F. M. Menger and J. M. Jerkunica, *Tetrahedron Lett.*, 4569 (1977); F. M. Menger, J. U. Rhee, and H. K. Rhee, *J. Org. Chem.*, 40, 3803 (1975); F. M. Menger and J. L. Lynn, *J. Am. Chem. Soc.*, 97, 948 (1975); F. M. Menger, G. Saito, G. V. Sanzero, and J. R. Dodd, *ibid.*, 97, 909 (1975); F. M. Menger and S. Wrenn, *J. Phys. Chem.*, 78, 1387 (1974); F. M. Menger and M. J. McCreery, *J. Am. Chem. Soc.*, 96, 121 (1974); F. M. Menger, J. U. Rhee, and L. Mandell, *J. Chem. Soc., Chem. Commun.*, 918 (1973); F. M. Menger, J. A. Donohue, and R. F. Williams, *J. Am. Chem. Soc.*, 95, 286 (1973); F. M. Menger, *Q. Rev., Chem. Soc.*, 1, 229 (1972); F. M. Menger, *J. Am. Chem. Soc.*, 92, 5965 (1970); F. M. Menger and C. E. Portnoy, *ibid.*, 90, 1875 (1968).