The Relationship between Domes and Foams: Application of Geodesic Mathematics to Micelles

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Abstract: With use of the principles of geodesic mathematics a model for a micelle is developed which succinctly describes a micelle in terms of symmetry, aggregation number (AN), and chirality. *Congeries* nomenclature is introduced for this purpose. To maintain a spherical aggregate with virtually equidistant head groups, certain AN's are more probable than others (e.g., 34, 38, 42, 52, 66, 74, 92, 100, 102, ...), these numbers being determined by symmetry considerations. Micelles are predicted to have a twisted internal structure as a consequence of tensegrity, and the generality of this concept and its application to membranes and similar complex structures is noted. The predictive power of this model is demonstrated by reconciling the differences between the Hartley micelle and modern experimental observations.

Beginning with the work of McBain,[1] micelle research has been known for its outlandish hypotheses. In keeping with this tradition of imaginative scientific thought, we wish to put forward the hypothesis that the detailed structure of a micelle can be described accurately in terms of the geodesic mathematics invented by Buckminster Fuller.[2] Such a hypothesis results in three predictions concerning micelles which are somewhat startling, albeit less remarkable than the micelle concept itself in 1913. The predictions, which apply to micelles or any other spherical or nearly spherical aggregate with approximately equidistant head groups located on its surface, are these: (1) micelles fall into three categories—tetrahedral, octahedral, or icosahedral—depending on the symmetry of the "perfect" solid amplified by geodesic subdivision to yield the geodesic structure; (2) the aggregation numbers (AN's) of micelles are "quantized", that is, certain numbers (4, 6, 10, 12, 18, 20, 34, 38, 42, 52, 66, 74, 92, 100, 102, 130, 146, 162, 164, 198, 202, etc.) are more probable than others; and (3) each individual micellar aggregate has a twisted core which is chiral as a consequence of *tensegrity*, the idea that in geodesic structures *tens*ion maintains structural int*egrity*. The chirality of micelles must be treated separately from the other two predictions, and while it is the most speculative prediction, it is the one with far-reaching implications. If geodesic mathematics proves to be a correct model for micelles and larger aggregates, then tensegrity could be invoked to explain the natural chirality of lipids in membranes and other systems of biological significance.

In this paper, we shall introduce the terms and concepts of geodesic mathematics and explain in some detail how these ideas can be applied to micelles. In the process, ideas will be developed which help to explain experimental observations and may help to reconcile the "Menger Micelle"[3] with the Hartley model[4] and that of Wennerström and Lindman.[5] The net result will be to place the concepts of Buckminster Fuller's geodesic mathematics at the disposal of the chemical community.[6]

Geodesic Mathematics and Micelles

Geodesic mathematics is used to describe spherical and nearly spherical objects which possess large numbers of points symmetrically dispersed on the surface of the sphere in a manner designed to minimize variations in the distances to nearest neighbors. In this way large numbers of points can be accommodated whereas if one requires a spherical structure and absolutely equidistant nearest neighbors the maximum number of points possible is 12. The process by which geodesic structures are built up is called geodesic subdivision,[2] and it is described below. The most important property of a geodesic structure is caused by the interplay of *tens*ion and compression which causes a geodesic object to maintain its structural int*egrity*, hence the word *tensegrity*.[2] Tensegrets exhibiting this property can be constructed from sticks (compression) and strings (tension) in which the sticks do not touch, being suspended in space by the tension on the strings. In a micelle the analogous elements of compression and tension are present. The elements of compression are the rigidity of the hydrocarbon tails and the electrostatic repulsion of the polar head groups, and the analogue of tension is the pressure exerted on the micelle by the water. Finally, the term geodesic multiplication[2] must be mentioned. Owing to the high symmetry of these structures a tensegret exhibits remarkable flexibility. All of these properties are compatible with the idea of micelles as "stable, disjoint, cooperative, closed equilibrium colloidal aggregates"[7] with a topological order (an inside and an outside), and yet they can readily be extended to the concept of a micelle as a dimensionally discordant fractal[8] which is surely more accurate. Geodesic concepts therefore constitute an appropriate context within which micelles can be discussed.

Table I. Congeries Nomenclature

designation	description
C_1-congeries	aspherical micelles which cannot be accurately described by any symmetry designation
K_h-congeries	spherical micelles of unknown or undefined symmetry and aggregation number
T_d-congeries	geodesic micelles of unspecified aggregation number, but possessing a tetrahedral arrangement of the head groups
O_h-congeries	geodesic micelles of unspecified aggregation number, but possessing an octahedral arrangement of the head groups
I_h-congeries	geodesic micelles of unspecified aggregation number, but possessing an icosahedral arrangement of the head groups
$C_{\infty v}$-congeries	cylindrical micelles of unknown or undefined aggregation number
$D_{\infty h}$-congeries	disk-shaped micelles or bilayers of unknown or undefined aggregation number

Congeries Nomenclature

Congeries are collections of things massed together without any organization. Since this word is not widely used we wish to appropriate it to describe micelles by using this term with a prefix to indicate the type and extent of organization present in the

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(2) Kenner, H. "Geodesic Math and How to Use It"; University of California Press: Berkeley and Los Angeles, 1976.
(3) (a) Menger, F. M. *Acc. Chem. Res.* **1979**, *12*, 111–117. (b) Menger, F. M.; Bonicamp, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 2140–2141.
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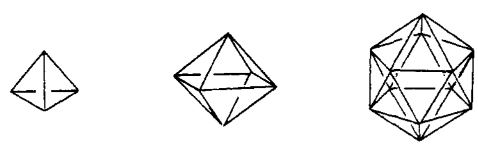

Figure 1. Platonic solids which are suitable generators for geodesic spheres: tetrahedron, octahedron, and icosahedron.

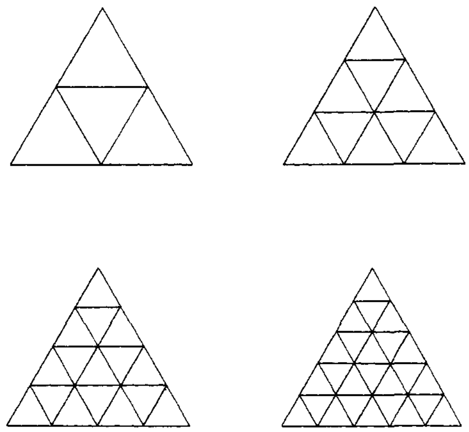

Figure 2. Geodesic subdivision of a triangular face: ν_1, ν_2, ν_3, and ν_4.

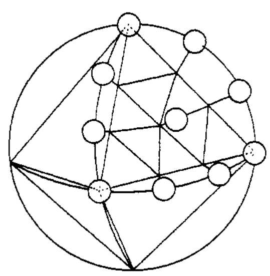

Figure 3. A geodesic sphere showing the placement of surface points and cut away to reveal the subdivided generator on which is is based.

structure. A C_1-congeries would then describe the nonsymmetrical and chaotic "Menger Micelle", K_h-congeries the spherical Hartley Micelle, and so forth (Table I). Congeries of all types[9] can be described in this way—$C_{\infty v}$-congeries are rods, $D_{\infty h}$-congeries bilayers, and so forth—but for our purposes only spheroidal congeries will be considered.

For the purpose of geodesic subdivision, only the Platonic solids with triangular faces are appropiate—the tetrahedron (T_d), octahedron (O_h), and icosahedron (I_h)—hence the prefixes in Table I. The Platonic solid is referred to as the generator and its vertex points are called generator points, and these points define the circumscribing sphere (Figure 1). The process of geodesic subdivision permits the development of a family of structures which maintain the symmetry of the Platonic solid and yet consist of a large number of "evenly spaced" points. In geodesic subdivision, the edges of each triangular face of the generator are interrupted at a frequency (ν_n) which divides the edge into $n + 1$ segments and the triangular face into $(n + 1)^2$ triangles, as illustrated in Figure 2. The vertices of the smaller triangles when projected onto the circumscribing sphere define a geodesic structure (Figure 3). The number of surface points in a geodesic structure determined in this manner constitutes a well-defined set which can be classified by the symmetry of the generator and ν_n. This is the source of the first two predictions given above. The numbers derived in this manner are given in Table II as aggregation numbers for the geodesic micelles: T_d-, O_h-, and I_h-congeries.

Conceptually, it is easiest to divide the face of the generator into equilateral triangles and project these points on the sphere. This procedure will give the correct number of points, but a more uniform distribution of points is obtained if instead of uniformly subdividing the edge of the generator (the chord) one uniformly subdivides the arc on the sphere. Coordinates for two geodesic structures of this type are given in Table III for a ν_1 octahedron with 18 surface points and a ν_2 tetrahedron with 20 surface points as examples of this technique.

(9) Kunitake, T.; Okahata, Y.; Shimomura, M.; Yasunami, S.; Takarabe, K. *J. Am. Chem. Soc.* **1981**, *103*, 5401–5413.

Table II. Geodesic Aggregation Numbers by Generator

ν	tetrahedral (T_d)	octahedral (O_h)	icosahedral (I_h)
0	4	6	12
1	10	18	42
2	20	38	92
3	34	66	162
4	52	102	252
5	74	146	362
6	100	198	492
7	130	258	642
8	164	326	812
9	202	402	1002
10	244	486	1212
11	290	578	1442
12	340	678	1692
13	394	786	1962
14	452	902	2252
15	514	1026	2562
16	580	1158	2892
17	650	1298	3242
18	724	1446	3612
19	802	1602	4002
20	884	1766	4412
21	970	1938	4842
22	1060	2118	5292
23	1154	2306	5762
24	1252	2502	6252
25	1354	2706	6762
26	1460	2918	7292
27	1570	3138	7842
28	1684	3366	8412
29	1802	3602	9002
30	1924	3846	9612
31	2050	4098	10242

Table III. Surface Coordinates for Two Geodesic Micelles in Spherical Coordinates

$\nu_2 T_d$-congeries (20 surface points)	$\nu_1 O_h$-congeries (18 surface points)
r, 0°, 0°	r, 0.0°, 0°
r, 0°, 36.49°	r, 0.0°, 45°
r, 0°, 72.98°	r, 0.0°, 90°
r, 0°, 109.47°	r, 90°, 45°
r, 120°, 36.49°	r, 90°, 90°
r, 120°, 72.98°	r, 180°, 45°
r, 120°, 109.47°	r, 180°, 90°
r, 240°, 36.49°	r, 270°, 45°
r, 240°, 72.98°	r, 270°, 90°
r, 240°, 109.47°	r, 45°, 90°
r, 60°, 70.51°	r, 135°, 90°
r, 180°, 70.51°	r, 225°, 90°
r, 300°, 70.51°	r, 315°, 90°
r, 0°, 180°	r, 0.0°, 135°
r, 40°, 122.88°	r, 90°, 135°
r, 80°, 122.88°	r, 180°, 135°
r, 160°, 122.88°	r, 270°, 135°
r, 200°, 122.88°	r, 0°, 180°
r, 280°, 122.88°	
r, 320°, 122.88°	

With use of frequency (ν_n) notation to modify the congeries terminology already presented, the aggregation number and symmetry of a geodesic micelle can be unambiguously specified. For example, $\nu_3 O_h$-congeries are spherical micelles in which 66 head groups are octahedrally arranged by geodesic subdivision of the arcs on the sphere (66 surface points = 6 generators + (3 × 12 edges) + (3 × 8 faces); a total of 16 triangles per face).

The detailed arrangement of the hydrocarbon portion of the detergent molecule in our model is quite arbitrary. However, if tensegrity is preserved and a twisted internal structure is main-

Table IV. Comparison of Tartar's Data with the Geodesic Hypothesis

detergent	solvent	exptl shape[a]	exptl	designation	(AN)[b]
$NaC_{10}H_{21}SO_4$	water	OS	50	ν_4T_d	52
$NaC_{12}H_{25}SO_4$	water	OS	71	ν_5T_d	74
$NaC_{14}H_{29}SO_4$	0.10 M NaCl	OS	138	$\nu_7T_d + \nu_5O_h$	138[c]
$NaC_8H_{17}SO_4$	water	S	27.7	$\nu_2T_d + \nu_3T_d$	27[d]
$NaC_{10}H_{21}SO_3$	water	S	40.5	ν_1I_h	42
$NaC_{12}H_{25}SO_3$	water	S	54	ν_4T_d	52
$NaC_{14}H_{29}SO_3$	water	S	80		?
$C_{10}H_{21}NMe_3Br$	water	S	36.4	ν_3T_d	34
$C_{12}H_{25}NMe_3Br$	water	S	50.3	ν_4T_d	52
$C_{14}H_{29}NMe_3Br$	water	S	75.2	ν_5T_d	74
$C_{16}H_{33}NMe_3Br$	0.013 M KBr	OS	169.3	ν_8T_d	164?
$[C_{12}H_{25}NMe_3]_2SO_4$	water	OS	64.7	ν_3O_h	66
$C_{12}H_{25}NH_3Cl$	water	S	55.5	ν_4T_d	52
$C_{12}H_{25}NH_3Cl$	0.015 M NaCl	OS	92.4	ν_2I_h	92
$C_{12}H_{25}NH_3Cl$	0.046 M NaCl	OS	141.6	ν_5O_h	146?
$Mg(C_8H_{17}SO_3)_2$	water	OS	50.6	ν_4T_d	52
$Mg(C_{10}H_{21}SO_3)_2$	water	OS	104	ν_4O_h	102
$Mg(C_{12}H_{25}SO_3)_2$	water	OS	107	ν_4O_h	102?
$(C_{12}H_{25})_2NMe_2Cl$	0.003 M NaCl	OS	209		?
$C_8H_{17}NMe_3SO_3C_8H_{17}$	water	OS	118	$\nu_4O_h + \nu_7T_d$	116[e]
$C_8H_{17}NMe_3SO_3C_{10}H_{21}$	water	OS	456	$\nu_{14}T_d$	452
$C_8H_{17}NMe_3SO_3C_{10}H_{21}$	0.18 M KCl	OS	701	$\nu_{12}O_h + \nu_{18}T_d$	701[f]

[a] OS = oblate spheroid; S = sphere. These are Tartar's assignments. [b] Taken from Table II. These are the geodesic predictions. [c] (130 + 146)/2 = 138. [d] (20 + 34)/2 = 27. [e] (102 + 130)/2 = 116. [f] (678 + 724)/2 = 701.

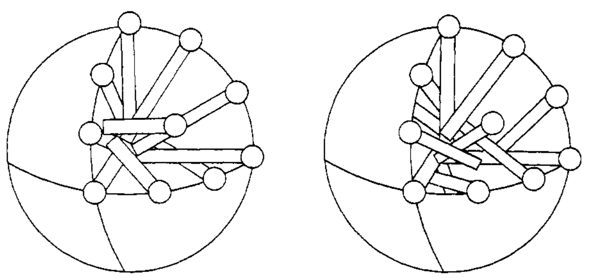

Figure 4. Geodesic congeries illustrating two methods for organizing the hydrocarbon tails while preserving tensegrity.

tained in all cases, the qualitative aspects of the geodesic congeries are quite similar. Two systems can be employed (Figure 4): In the first instance, the detergents located at the generator points penetrate as close to the center as possible. The first tail fills the central volume element and the subsequent tails press around the center and establish the basic chirality. The detergents which are nearest neighbors to the generator points are laid in pressing toward the center and yet preserving the chirality and so forth to the center of the face of the generator. Notice (Figure 4) that the tails rise closer to the surface as the heads get closer to the center of the face in this model and that the tail of the detergent located at the *center* of the face lies tangential to the spherical hydrocarbon core. In this model the orientation of the detergent located at the center of the face lying tangential to the spherical core is ambiguous, especially on the lower (z axis) face of the T_d-congeries.

In the second instance, detergents at the generator points are arranged to penetrate as close to the center as possible and establish the chirality. Then, beginning at the center of the face, detergent tails are pressed in close to the center, preserving the chirality. In this model, the detergents located closest to the generator points lie almost tangential to the sphere (Figure 5).

Regardless of the method used to stack the tails internally tensegrity can be preserved. The twisting of the head groups originating in a triangular face is illustrated in Figure 6, and it is independent of the generator being used. Furthermore, it is easy to demonstrate with models that on transition from a ν_6T_d-congeries (AN = 100) to a ν_4O_h-congeries (AN = 102) the generator points and face centers reverse roles while maintaining tensegrity. The concerted motion of the hydrocarbons about the generator points is compatible with the idea of geodesic multiplication and it accounts for the "liquid" nature of the hydrocarbon core.[10]

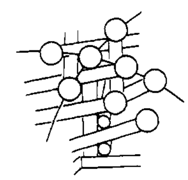

Figure 5. A detailed sketch illustrating that the hydrocarbon tails in a micelle must rise to the surface as the central volume element is filled.

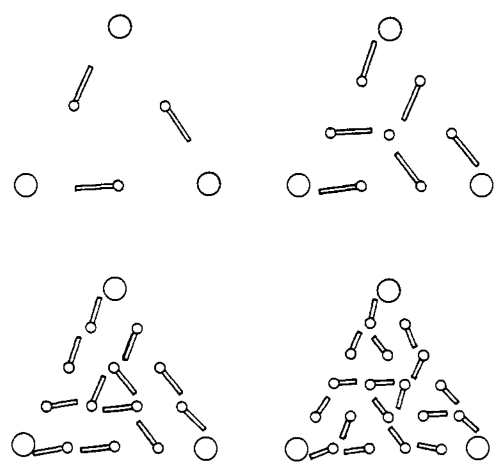

Figure 6. The twisted arrangement of the hydrocarbon tails as viewed from the triangular face of the generator. The two classes of tails shown in these figures complement each other, with one rising to the surface and the other penetrating toward the core depending on the system used to orient the tails.

Notice that because of their material bulk, the hydrocarbon portion of the detergent tails rises closer to the head groups as the micelle builds up and eventually even the terminal methyl group is in close proximity to the water. Thus the geodesic concept can explain the "deep penetration of water" into micelles observed by Menger, Whitten, and others.[3a,11] This geodesic treatment

(10) Riberio, A. A.; Dennis, E. A. *J. Phys. Chem.* **1977**, *81*, 957–963.

(11) (a) Tanford, C. "The Hydrophobic Effect: Formation of Micelles and Biological Membranes"; 2nd ed.; Wiley-Interscience: New York, 1980. (b) Menger, F. M.; Jerkunica, J. M.; Johnston, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4676–4678. (c) Menger, F. M.; Chow, J. F. *Ibid.* **1983**, *105*, 5501–5502. (d) Winkle, J. R.; Worsham, P. R.; Schanze, K. S.; Whitten, D. G. *Ibid.* **1983**, *105*, 3951–3956.

rigorously defines the "grooves where guest molecules bind in a mixed medium of water and hydrocarbon".[3,12] At the same time, the topological distinction of inside and outside advocated by Wennerström and Lindman[13] is preserved in this model. The concerted motion of detergent monomers allows each of the tails to rise to the micelle surface as required in Gruen's calculations.[14] Furthermore, the geodesic hypothesis improves on the Fromherz model[15] by providing a means for spacing the head groups without arbitrarily bending the detergent chain. Yet a geodesic micelle fulfills all of the Fromherz criteria and retains the attractive feature of having small aligned units present along the edge of the generator which are analogous to the groupings present in his model.

The significance of chirality in a geodesic micelle is such an important property that we further recommend adopting R^*, S^* terminology. Here R^* refers to a model in which clockwise rotation of the detergent located on the z axis turns it in the direction of the polar head group of the other generators when viewed from $(0,0+\infty)$. The mirror image would of course be S^*. A typical solution composed of micelles with an aggregation number of 74 would then be an equimolar mixture of (R^*)-ν_5T_d-congeries and (S^*)-ν_5T_d-congeries.

With the model clearly defined the detailed structure of micelles can now be tested and interpreted in specific terms of aggregation number, symmetry, and chirality.

The obvious failing of this mathematical model is that it treats a micelle as a static entity which is, of course, contrary to fact.[16] Furthermore, there is no reason a priori to assume that only one type of congeries will exist in a given solution. However, tensegrity should confer stability to the geodesic structures and on the basis of this notion we postulate that the majority of congeries present at a given time will possess a geodesic structure.

Comparison with Experimental Results

To our knowledge, the first work addressing the question of the spherical structure of micelles was done by Tartar[17] in 1955. He determined the molecular weight of the micelle aggregates by light scattering. By using bond lengths for calculating the length of the hydrocarbon tail and the density of a number of normal alkanes from available data, he could then calculate the shape of a micelle by treating it as an oblate spheroid in which the maximum length of the shorter diameter was no longer than the length of two hydrocarbon tails. Before comparing his data with the geodesic hypothesis, it should be pointed out that geodesic math applies to all objects in which spherical coordinates are appropriate.

The agreement (Table IV) between Tartar's data and the geodesic prediction is remarkably good if one is willing to believe that in cases where direct agreement is not obtained the solution is a 1:1 mixture of consecutive congeries (taken from Table I). Only in the case of AN = 80 does the hypothesis break down; in all other cases the aggregation numbers match (±2).

Significantly, the chirality of micelles is not predicted by previous models and as a result this aspect of micelle structure has only recently been observed.[18]

Conclusions

Geodesic mathematics provides a simple, direct approach to the description of micelles. The three important attributes of a micelle which must be stipulated are the symmetry, the aggregation number, and the chirality or twist of the structure. Congeries nomenclature has been introduced for this purpose. An example is an (R^*)-ν_4O_h-congeries which is a geodesic micelle with octahedrally dispersed head groups, an aggregation number of 102, and a hydrocarbon core twisted to the right. A comparison between experimental aggregation data and calculated numbers reveals a striking correspondence in many cases, and the need to consider more than one congeries in some cases is noted. It is hoped that this system will lessen the confusion surrounding micelle structure by providing an explicit framework from which to argue.

Work is presently underway in our laboratory to investigate the geodesic aspects of micelles through the use of whole micelle probes specially designed to produce knots as a consequence of tensegrity. Regardless of the validity of this approach, or the outcome of the research, geodesic mathematics provides a unique and detailed model for specifying micelle structure unambiguously. It is a basis for understanding and discussion of these aggregates.

Acknowledgment. We thank Dr. N. J. Turro for his advice and encouragement. We acknowlege Ohio University, Research Corporation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this project.

(12) Menger, F. M.; Boyer, B. J. *J. Am. Chem. Soc.* **1980**, *102*, 5936–5938.
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