

III. Micelle Size and Shape

A. Single Chain Amphiphiles

Micelles of simple ionic amphiphiles are spherical and remarkably homogeneous in size, with a radius is roughly equal to the length of the hydrocarbon chain of the amphiphile. For sodium dodecyl sulfate (SDS), this is approximately 17 Å. In a micelle of this size, there are on the order of 60 amphiphiles, and this number does not vary much from micelle to micelle. The reason that this is so remarkable is that the driving force for micelle formation is non-covalent and very non-specific in nature. What is it that regulates the size and geometry of the micelle? If the only forces operating were those favoring the aggregation of molecules, one would expect the micelle size to increase without limit, perhaps in the form of bilayer structures such as

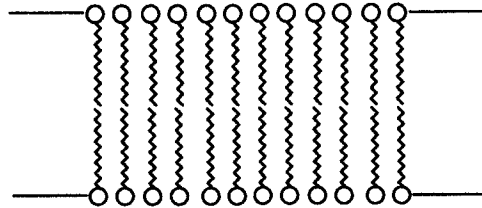


Fig 1

There must be repulsive forces limiting the micelle size as well as attractive forces favoring the micelle growth. These repulsive forces arise from electrostatic and/or steric interactions between the polar headgroups. In ionic amphiphiles, each amphiphile has a charged polar headgroup which strongly repels neighboring amphiphiles in the micelle tending to push the headgroups apart. This repulsion thus favors a curved surface over a planar one in which the headgroups are more closely spaced (Fig 2), and prevents unlimited growth in two dimensions. Sufficiently large repulsions lead to a spherical shape with a radius determined by the length of the alkyl chain.

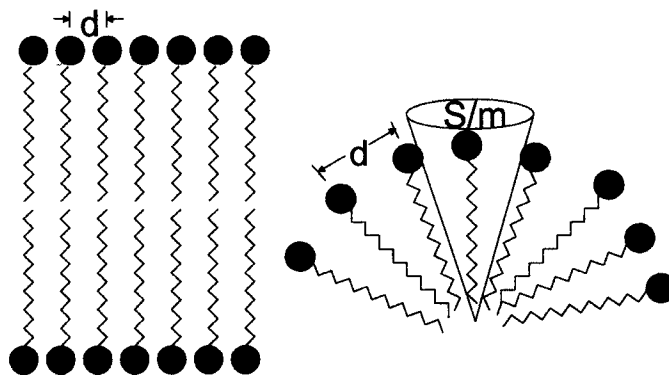


Fig 2

A quantitative analysis of micelle shape must consider both repulsive and attractive forces as well as geometrical constraints on micelle structure. The repulsive force between headgroups tends to push them apart. However, if they are pushed too far apart, water will be able to penetrate the interior of the micelle, increasing the free energy of the structure due to the hydrophobic effect. Thus, the hydrophobic effect will tend to keep the headgroups closely spaced, while the repulsive (electrostatic) forces tend to push them apart. The balance between these opposing forces will lead to an optimum head group spacing and determine the shape of the micelle. The area occupied per hydrophobic chain at the micelle surface is a quantitative measure of the headgroup spacing and is simply the total surface area of the micelle, S , divided by the number of amphiphiles in the micelle, m (Figure 2).

Repulsive forces tend to increase S/m while hydrophobic forces tend to reduce S/m . Thus, there is an optimum value for S/m which minimizes the overall free energy of the micelle for a given headgroup repulsion. The standard state chemical potential for a monomer in the micelle may be expressed by

$$\mu_{mic}^{\circ} = \gamma(S/m) + C(S/m)^{-1} + H$$

The first term increases the free energy with S/m and represents the hydrophobic effect tending to keep the headgroups together. The constant γ is proportional to the interfacial energy between hydrocarbon and water. The second term decreases the free energy with increasing S/m and represents the repulsive interaction between the headgroups. C is a constant that measures the strength of the repulsive interaction. The final term H represents all other interactions that do not depend strongly on S/m , such as the interaction between the hydrocarbon chains in the micelle interior. The optimal value of S/m occurs when

$$\left(\frac{\partial \mu_{mic}^{\circ}}{\partial (S/m)} \right) = 0$$

Thus,

$$S/m(\text{optimum}) = \sqrt{C/\gamma}$$

The larger the repulsive forces, the larger S/m (optimum).

The value of S/m for a micelle is determined by the micelle geometry, and can readily be computed by a very simple "oil drop" model of the micelle. This model and example calculations are given in the Appendix. A key point of this model is that the hydrophobic interior of micelle has the same density as pure liquid hydrocarbon of the same chain length. Thus a micelle of a given geometry can have no more chains packed in its interior than the number required to give the correct density.

Many ionic micelles have sizes and aggregation numbers consistent with an approximate spherical shape. Small distortions from a spherical shape into an oblate ellipsoid can account for others. In addition cylindrical micelles and planar bilayer micelles are observed. Table I shows values of S/m calculated according to the oil drop model for spherical, cylindrical and planar shapes (see Appendix). These values were obtained using a very simplified version of the model, but will serve to illustrate the principle.

Experimental studies of micelles of sodium dodecylsulfate (SDS) indicate that it has an aggregation number of around 60 and is roughly spherical in low ionic strength solutions. From the oil drop model, S/m is about 65 \AA^2 as indicated in Table I. Values in this range are also found for other ionic micelles in low ionic strengths. This apparently is the value of S/m (optimum) for a stable structure for ionic micelles at low ionic strength. It is clear then that cylindrical or planar bilayer structures could not form since the repulsive energy from the closely spaced head groups would be too great. What would happen if the ionic strength were increased? The electrostatic head group repulsions would be reduced, and lower values of S/m (optimum) would be preferred. Thus a structure change from spherical to cylindrical would be predicted to occur. Such changes are experimentally observed. If the repulsions are reduced far enough, bilayers of single chain amphiphiles could form.

B. Amphiphiles with Two Hydrocarbon Chains.

For single chain amphiphiles S/m is the surface area per hydrocarbon chain and per polar headgroup. However for two-chain amphiphiles, S/m for a given shape is twice as great (since there are only half as many head groups to cover the same surface area). Table I also gives values for S/m for double-chain amphiphiles. Since the repulsive force between headgroups should not be significantly affected by whether there are one or two alkyl chains attached to each group, the optimum area per head group for a two-chain ionic amphiphile should still be about 60 \AA^2 , and the table shows that such a small area can now be only be attained by a structure between the cylindrical and bilayer structures.

If we consider the two-chain amphiphiles that form biological membranes (phospholipids), it is clear that the bilayer is the preferred form, since the repulsion between the predominately zwitterionic head groups is far less than between charges amphiphiles, and the structure with the lowest S/m is preferred. The formation of bilayer structures by phospholipids can thus be accounted for on purely geometrical considerations, without new theoretical input.

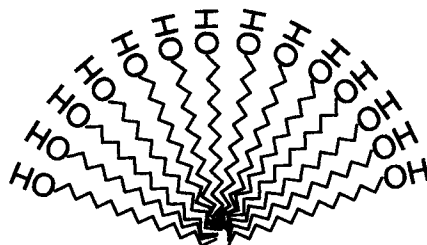
TABLE I

Shape	S/m-Single Chain (Å ² /amphiphile)	S/m-Two Chains (Å ² /amphiphile)
sphere	~65	~130
cylinder	~43	~ 86
bilayer	~22	~ 44

Again, it should be remembered that these data refer to strongly ionic amphiphiles.

C. Not All Amphiphiles Form Micelles

The long chain alcohols meet all requirements from amphiphiles, but do not form micelles. To see why, consider a portion of a hypothetical spherical micelle:



Since there are no large repulsive forces between the small, uncharged headgroups, **S/m** for a spherical micelle would be much too large, and this structure is unstable. If any micelle at all exists, it would have to be something like a bilayer with a small **S/m**. But this is really no more stable than a droplet of pure liquid alcohol in water, since the alcohol can hydrogen bond to itself as well as to water. Thus, the absence of strong headgroup repulsive forces favors the separation of a pure amphiphile phase rather than micelle formation.

In summary, we see that micelle stability can be accounted for totally on the basis of hydrophobic forces, but the size and shape of the micelles are determined by a balance between attractive and repulsive forces that depend on the structure of the individual amphiphile. Thus, an appropriate collection of, non-specific forces can give rise to stable entities of rather specific structure.

APPENDIX: THE "OIL DROP" MODEL OF THE MICELLE

We will assume the micelle interior to be a droplet of liquid hydrocarbon with the density of the corresponding hydrocarbon liquid. The surface of the droplet will be uniformly covered with the polar headgroups and of equal number to the chains in the droplet.

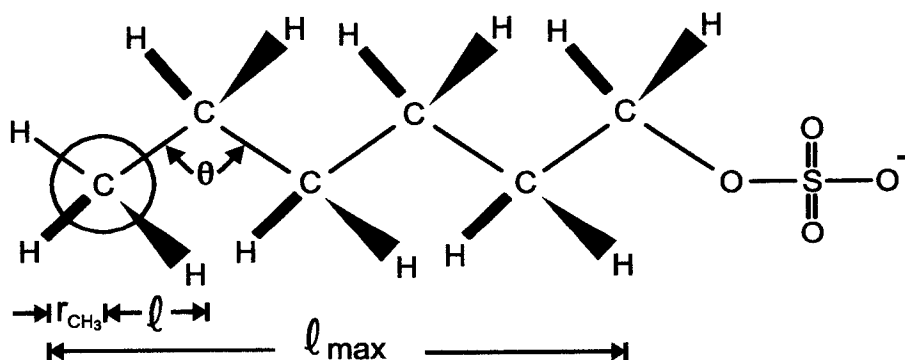
From the known densities of the alkanes as a function of N_C (Handbook of Chemistry and Physics), it is readily shown that the volume of a droplet of hydrocarbon containing m molecules is given by

$$V = (27.4 + 26.9N_C)m \quad (\text{Angstroms}^3) \quad \mathbf{A1}$$

The oil drop model assumes that this is the volume of the interior of a micelle containing m chains.

In the following equations, N_C will be taken as the number of carbon atoms in the chain which are actually in the micelle interior. This may be less than the total number of carbon atoms in the chain since the first carbon atom near the polar group is usually in contact with water. Thus, the chain length in the micelle interior is $(N_C - 1)$.

Since we require all polar headgroups to be at the micelle surface and do not allow holes in the micelle's interior, one dimension of the micelle is always restricted by the length of the hydrocarbon chain. The maximum length is calculated from the C-C bond length (1.54\AA) and the tetrahedral bonding angle ($109^\circ 54'$), and the radius of the terminal methyl group (r_{CH_3}).



The projection of the C-C bond length, l , along the chain axis is $l = 1.54 \sin(109^\circ 54'/2) = 1.26 \text{\AA}$. Thus $l_{\text{max}} = (N_C - 1)(1.26) + r_{\text{CH}_3}$, where $r_{\text{CH}_3} = 2.1 \text{\AA}$, the radius of the terminal -CH₃ group. Finally,

$$l_{\text{max}} = 1.26 N_C + 0.84, \text{ in } \text{\AA}. \quad \mathbf{A2}$$

1. Spherical Micelles

In this case, $\ell_{\max} = r$, where r is the radius of the sphere. For a sphere, $V = (4/3)\pi r^3 = (4/3)\pi \ell_{\max}^3$ but $V = (27.4 + 26.9 N_c)m$. Equating these independent expressions for V and rearranging:

$$m = \frac{(4/3)\pi \ell_{\max}^3}{(27.4 + 26.9 N_c)} = \frac{(4/3)\pi(1.26 N_c + 0.84)^3}{(27.4 + 26.9 N_c)} \quad \text{A3}$$

For a sphere, the number of monomers is thus completely determined by the length of a hydrocarbon chain. The surface area of a sphere, S , is $S = 4\pi r^2 = 4\pi \ell_{\max}^2$. Thus,

$$S/m = \frac{3(27.4 + 26.9 N_c)}{(1.26 N_c + 0.84)} \quad \text{A4}$$

For $N_c = 12$, $S/m = 65 \text{ \AA}^2/\text{amphiphile}$. For $N_c > 10$, the function S/m given by Eq A4 is essentially independent of N_c . For example, $\lim_{N_c \rightarrow \infty} S/m = 64 \text{ \AA}^2/\text{amphiphile}$ which is only slightly smaller than S/m for $N_c = 12$.

2. Cylindrical Micelles

For a cylindrical micelle, $V = \pi r^2 h$, where r = radius of cylinder and h = length of the cylinder. The radius r is restricted to ℓ_{\max} , and $V = \pi \ell_{\max}^2 h$. As before, we can determine m :

$$m = \frac{\pi \ell_{\max}^2 (h)}{(27.4 + 26.9 N_c)} = \frac{\pi(1.26 N_c + 0.84)^2 h}{(27.4 + 26.9 N_c)} \quad \text{A5}$$

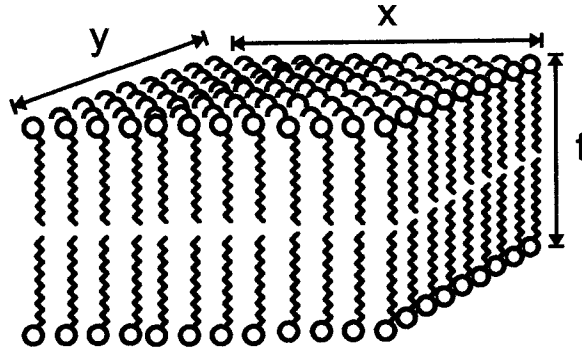
The surface area of a cylinder is just $S = 2\pi \ell_{\max} h = 2\pi(1.26 N_c + 0.84)$. Thus,

$$S/m = \frac{2(27.4 + 26.9 N_c)}{(1.26 N_c + 0.84)} = (2/3)(S/m)_{\text{sphere}} \quad \text{A6}$$

for $N_c = 12$, $S/m = 43.8$ and $\lim_{N_c \rightarrow \infty} S/m = 42.7$.

3. Bilayer Micelles

For a bilayer micelle, the volume is $v = (t)(x)(y)$.



The thickness, t , is restricted to $t = 2\ell_{\max}$. Thus, $v = 2(1.26N_c + 0.84)(x)(y)$. Calculation of m gives

$$m = 2 \frac{(1.26 N_c + 0.84)}{(27.4 + 26.9 N_c)} (x)(y) \quad \text{A7}$$

and

$$S/m = \frac{27.4 + 26.9 N_c}{1.26 N_c + 0.84} = (1/3)(S/m)_{\text{sphere}} \quad \text{A8}$$