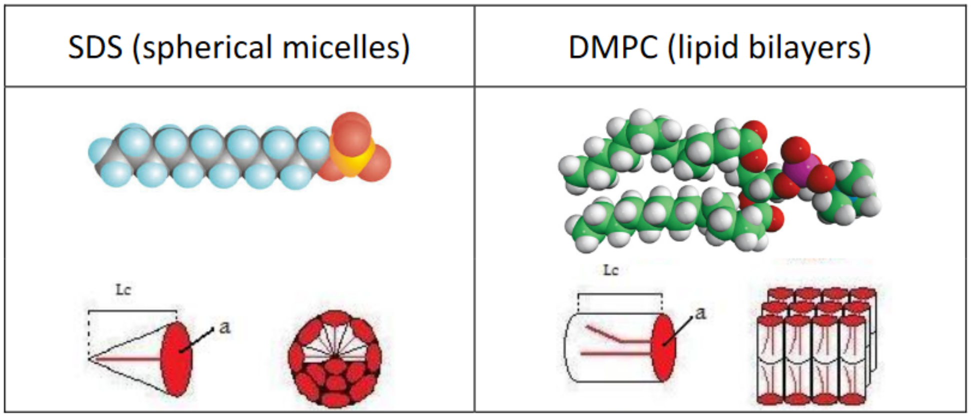
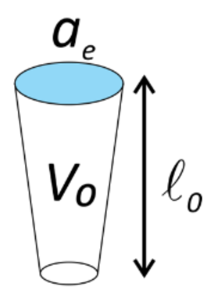
19.4: Shape of Self-Assembled Amphiphiles

Empirically it is observed that certain features of the molecular structure of amphiphilic molecules and surfactants are correlated with the shape of the larger structures that they self-assemble into. For instance, single long hydrocarbon tails with a sulfo- group (like SDS) tend to aggregate into spherical micelles, whereas phosopholipids with two hydrocarbon chains (like DMPC) prefer to form bilayers. Since structure formation is largely governed by the hydrophobic effect, condensing the hydrophobic tails and driving the charged groups to a water interfaces, this leads to the conclusion that the volume and packing of the hydrophobic tail plays a key role in shape. While the molecular volume and the head group size and charge are fixed, the fluid nature of the hydrocarbon chain allows the molecule to pack into different configurations.

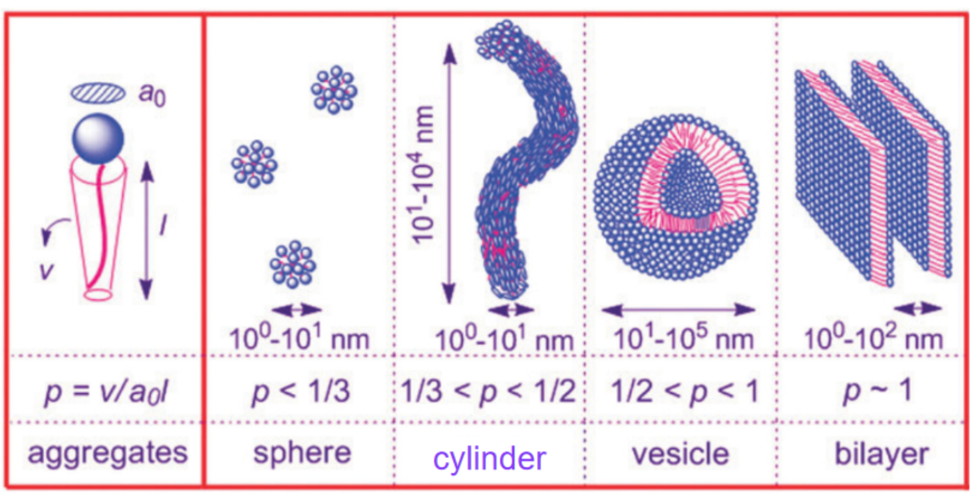


This structural variability is captured by the packing parameter:

$$p = \frac{V_0}{a_e \ell_0}$$



where V_0 and ℓ_0 are the volume and length of the hydrocarbon chain, and a_e is the average surface area per charged head group. V_0/ℓ_0 is relatively constant at ~0.2 nm^2, but the shape of the chain may vary from extended (cylindrical) to compact (conical), which will favor a particular packing.



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Empirically it is found that systems with p < ⅓ typically form micelles, for cylindrical structures for ⅓ < p < ½, and for bilayer structures for ½ < p < 1. Simple geometric arguments can be made to rationalize this observation. Taking a spherical aggregate with radius R and aggregation number n as an example, we expect the ratio of the volume to the surface area to be

$$\frac{V}{A} = \frac{nV_0}{na_e} = \frac{R}{3} \quad \rightarrow \quad V_0 = \frac{a_e R}{3} \tag{19.4.1}$$

Substituting into the packing parameter:

$$p=\frac{V_0}{a_e\ell_0}=\frac{R}{3\ell_0} \tag{19.4.2}$$

Now, even though the exact conformation of the hydrocarbon chain is not known, the length of the hydrocarbon tail will not be longer than the radius of the micelle, i.e., $\ell_0 \geq R$. Therefore

$$\therefore p \leq \frac{1}{3} \qquad (spheres) \tag{19.4.3}$$

Similar arguments can be used to explain why extended lipid bilayers have $p \approx 1$ and cylinders for p ≈ ½. In a more general sense, we note that the packing parameter is related to the curvature of the aggregate surface. As p decreases below one, the aggregate forms an increasingly curved surface. (Thus vesicles are expected to have ½ < p < 1). It is also possible to have p > 1. In this case, the curvature also increases with increasing p, although the sign of the curvature inverts (from convex to concave). Such conditions result in inverted structures, such as reverse micelles in which water is confined in a spherical pool in contact with the charged headgroups, and the hydrocarbon tails are project outward into a hydrophobic solvent.

Readings

J. N. Israelachvili, Intermolecular and Surface Forces, 3rd ed. (Academic Press, Burlington, MA, 2011).