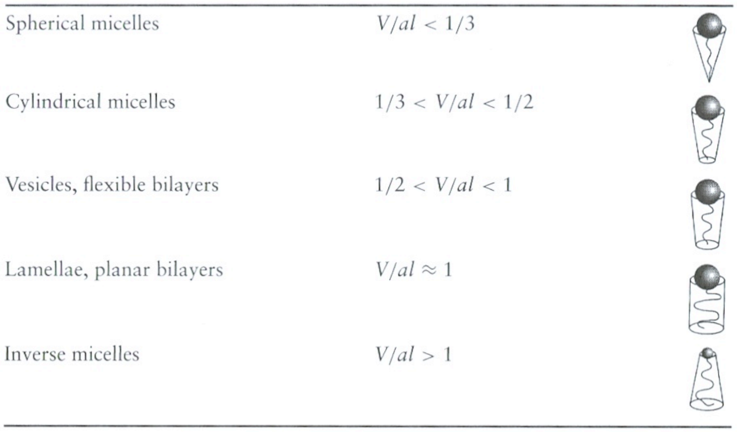
Aggregation of Amphiphiles [psl14]

Packing parameters:

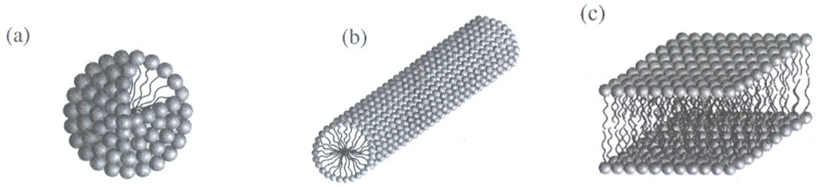
- l: length of fully extended tail
- V: effective volume of amphiphilic molecule
- a: effective area of headgroup

Range of packing parameters for specific amphiphilic aggregates:



Spherical micelles	$V/al < 1/3$
Cylindrical micelles	$1/3 < V/al < 1/2$
Vesicles, flexible bilayers	$1/2 < V/al < 1$
Lamellae, planar bilayers	$V/al \approx 1$
Inverse micelles	$V/al > 1$

Normal structures:



Inverse structures:

- possible occurrence if $V/al > 1$,
- common occurrence at large surfactant concentration, when the solvent is the minority phase.

[images from Hamley 2007]

Aggregation according to geometric argument:

Balancing two competing effects:

- short-range repulsion between particles with shapes,
- efficient separation between water and hydrophobic tails.

Predictions [pex39]:

- spherical micelles: $V/la \lesssim \frac{1}{3}$,
- cylindrical micelles: $V/la \lesssim \frac{1}{2}$,
- bilayers or vesicles: $V/la \lesssim 1$

Aggregation in thermal and chemical equilibrium:

- ϵ_m: activation energy of m-molecule aggregate
- μ: chemical potential
- X_m: volume fraction of m-molecule aggregates
- ϕ: overall volume fraction of amphiphiles

$$X_m = m \exp\left(\frac{m(\mu - \epsilon_m)}{k_{\rm B}T}\right), \quad \phi = \sum_{m=1}^{\infty} X_m. \tag{1}$$

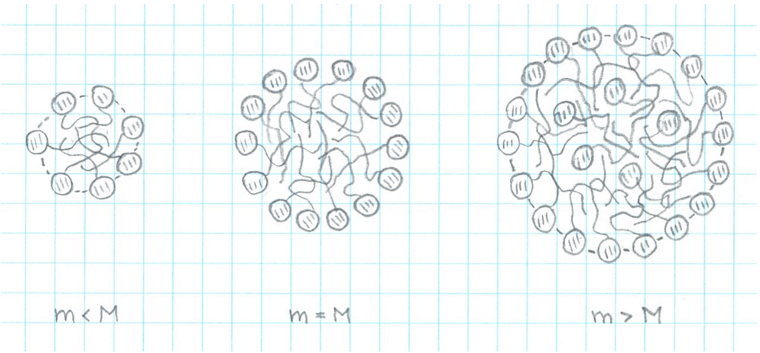
Eliminate μ from expressions for X_m (aggregates of size m) and X_1 (amphiphiles in solution):

$$\Rightarrow \; X_m = m\left[X_1 \exp\left(\frac{\epsilon_1 - \epsilon_m}{k_{\rm B}T}\right)\right]^m. \tag{2}$$

Aggregation is favored if $\epsilon_m < \epsilon_1$ for some $m > 0$. Aggregates of size m are favored if ϵ_m is a minimum.

Self-assembly of spherical micelles:

Mechanical stability optimized at size $m = M$:



- $m < M$: small radius; space for hydrocarbon tails too crowded; headgroups unable to form tight shield.
- $m > M$: large radius; space for hydrocarbons too large; mechanical stability requires some headgroups in the interior.

Model activation energies: $\epsilon_m = \epsilon_M + \Lambda(m-M)^2$.

Eliminate μ from expressions for X_m (arbitrary size) and X_M (optimal size):

$$X_m = m\left[\frac{X_M}{M}\exp\left(-\frac{M\Lambda(m-M)^2}{k_\mathrm{B}T}\right)\right]^{m/M}. \tag{3}$$

Size distribution is a narrow Gaussian with variance $\langle|m-M|^2\rangle = k_\mathrm{B}T/2M\Lambda$. This result justifies to continue the analysis for a single size of aggregates ($m = M$) in competition with amphiphiles in solution ($m = 1$).

This case is analyzed in [pex40] and predicts a sharp concentration threshold of amphiphiles at which spherical micelles of size $m = M$ begin to aggregate. This threshold is names critical micelle concentration (CMC).

Self-assembly of cylindrical micelles:

Unlike spherical micelles, cylindrical micelles can grow indefinitely (in length) without deviating from the optimized radius that provides mechanical stability and shielding. Therefore, a much broader size-distribution is to be expected.

Model activation energy of an amphiphile that is part of a size-m micelle:

$$\epsilon_m = \epsilon_\infty + \frac{\alpha k_\mathrm{B}T}{m}. \tag{4}$$

The endcap energy, $\alpha k_\mathrm{B}T$, favors long cylinders. Amphiphiles in solution ($m = 1$) have the highest activation energies.

In [pex41] we analyze the size distribution of cylindrical micelles, X_m versus m. This distribution is broad as expected. We identify the CMC as the value of ϕ_c where X_2 starts to exceed X_1. We also determine the size m^* for which the distribution has a maximum.

Critical aggregation of bilayers:

Model activation energy of amphiphiles that is part of a size-m bilayer:

$$\epsilon_m = \epsilon_\infty + \frac{\alpha k_\mathrm{B}T}{\sqrt{m}}. \tag{5}$$

The edge energy, $\alpha k_\mathrm{B}T$, favors wide bilayers. The highest activation energy pertains to amphiphiles in solution ($m = 1$).

In [pex42] we analyze the size distribution of bilayers along the same lines as carried out in [pex41] for cylindrical micelles. The distribution come out to be much more narrow. The critical aggregation concentration (CAC) is well defined by a kink in the curve of X_1 (amphiphiles in solution) versus ϕ overall volume fraction.

A similar model can be constructed for liposomes (vesicles). These are spherical bilayers with no boundaries. Here the perimeter energy is to be replaced by a sort of bending energy. The model must postulate a specific dependence of that bending energy on the size of the liposome.

Spherical aggregates of colloids:

The same modeling can be applied to the aggregation of colloids in a suspension. If the primary cause of aggregation is a an interfacial energy it can be reasoned that the the activation energy of a colloid that is part of a size-m aggregate has the form

$$\epsilon_m = \epsilon_\infty + \frac{\alpha k_\mathrm{B} T}{m^{1/3}}. \tag{6}$$

In [pex50] this reasoning is stated in more detail and the analysis carried out that determies the CAC.