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08. Amphiphiles I

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Amphiphiles Are Surfactants [p1n57]

The name *surfactant* is a contraction of “surface-active agent.” Surfactant molecules owe this function to their *amphiphilic* structure, typically with hydrophilic headgroup and hydrophobic tail. The prefix “amphi-” stands for “both” and the word “philia” for “affection”, both of Greek origin. Amphiphiles have two sides, one seeking polar, the other non-polar media.

Hydrophobic tails consist of one or several (non-polar) hydrocarbon chains.

Hydrophilic headgroups are classified as follows:

- uncharged (polar),
- anionic (negatively charged),
- cationic (positively charged),
- zwitterionic (containing equal positive and negative charges).

Anionic headgroups are common in detergents [psl13]. Cationic headgroups are useful as mild disinfectants due to anti-bacterial attributes.

Phospholipids are a major component of biological cell membranes. Their tails consist of two chains of linear hydrocarbons.

Amphiphiles have a propensity for self-assembly into hierarchical structures and (liquid crystalline) phases [tsl50].

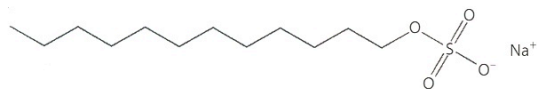
- *Spherical* micelles tend to order in a *cubic* phase.
- *Cylindrical* micelles tend to order in a *hexagonal* phase.
- *Bilayers* tend to order in a *lamellar* phase.
- *Vesicles* (liposomes) tend to order like micelles if they are monodisperse.

Onset of ordering is lyotropic, taking place at sufficiently high concentration of self-assembled structures.

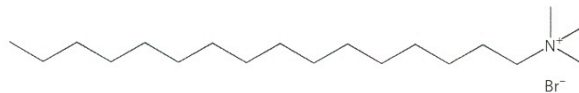
The size and shape of micelles depends on several factors:

- geometry and energetics of surfactant molecules,
- surfactant concentration,
- type of solvent,
- temperature.

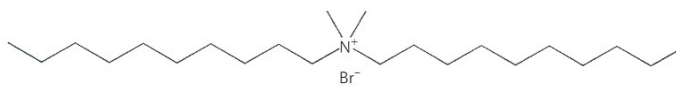
Five common surfactant molecules:



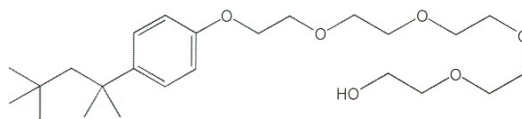
Sodium dodecyl sulphate (SDS)



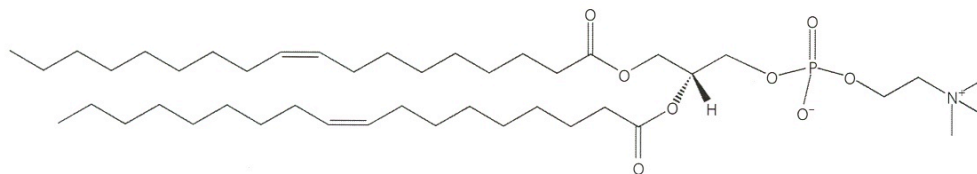
Hexadecyltrimethylammonium bromide (CTAB)



Didecyltrimethylammonium bromide (DDAB)



Triton X-100



1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC)

[image from Hirst 2013]

Ordering of surfactant molecules [ts150]

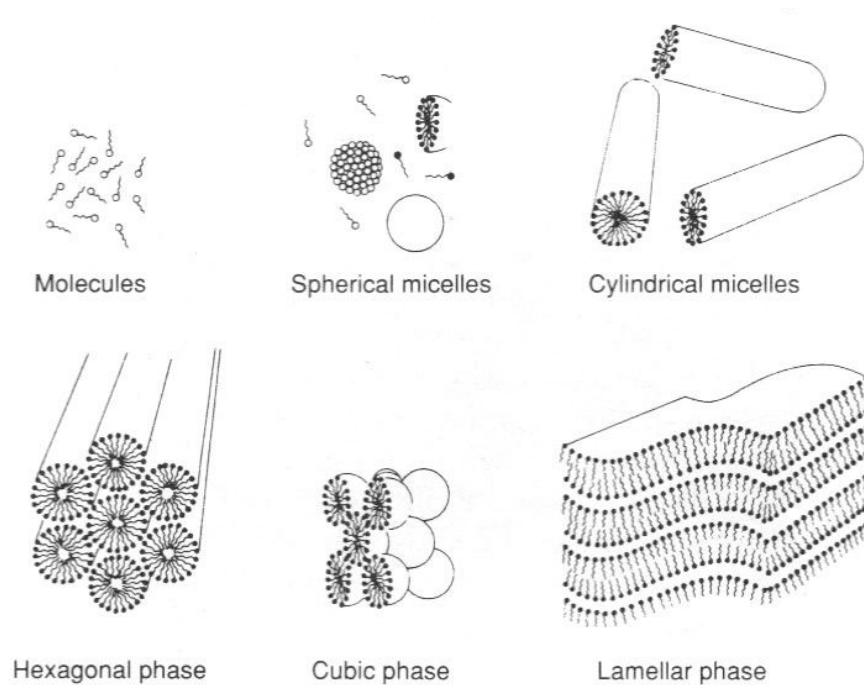
Surfactant molecules have highly soluble polar heads and barely soluble hydrocarbon tails. Increasing the surfactant concentration produces a succession of structures.

Cylindrical micelles have translational short-range order along the axis.
Amphiphilic bilayers have translational short-range order in the plane.

Hexagonal phase has 1D short-range order and 2D long-range order.

Lamellar phase has 2D short-range order and 1D long-range order.

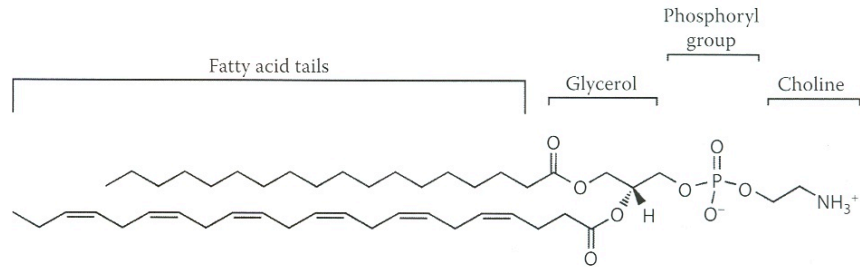
Cubic phase has 3D long-range order on mesoscopic scale.



[from Yeomans 1992]

Lipids [pln59]

Chemical structure of (zwitterionic) phospholipid:



[image from Hirst 2013]

Lyotropic phase behavior largely governed by shape of particular lipid (cone vs cylinder, see [psl14]). Thermotropic phase behavior in plane of bilayer somewhat akin to liquid crystals.

Sequence of common phases realized as T rises:

- Subgel phase L_c' is pseudo-crystalline with translational and rotational motion of lipid molecules severely restricted. Headgroups show hexagonal LRO.
- Gel phase L_{β}' allows for some rotational motion of lipid molecules. Headgroups show orthorhombic LRO. Tails may be tilted away from normal to plane of bilayer.
- Ripple phase P_{β}' features ripples perpendicular to plane of bilayer.
- Liquid crystal phase L_{α} is fluid-like. Headgroups are further apart and have positional SRO, similar to smectic-A liquid crystals. Lipid molecules are free to diffuse.

Lipid bilayers at room temperature typically are in phase L_{α} . Melting transition between β' and L_{α} is of first order with measurable latent heat.

[gleaned from Hirst 2013]

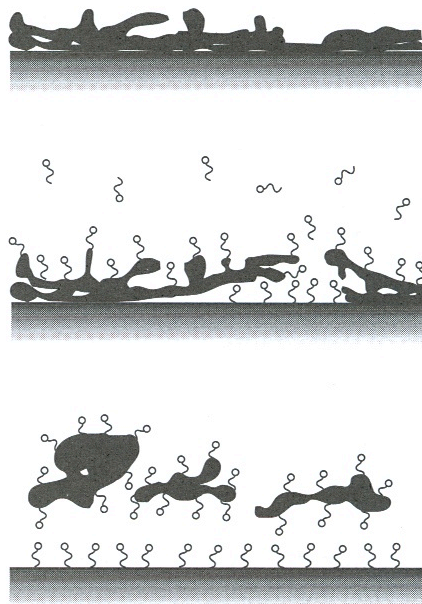
Detergency [ps113]

Detergents are surfactant molecules (amphiphiles) with special attributes:

- They wet fabric effectively (lower surface tension than water)
- Their hydrophobic tails are sufficiently long for high surface activity, yet sufficiently short for high mobility.

Detergency process:

- Detergent penetrates space between greasy particles and fabric.
- Contacts between grease and fabric are replaced by contacts to hydrophobic tails of surfactant molecules in solution.
- Adhesion of grease particles to fabric is reduced.
- Grease particles loosed into suspension by mechanical action of water.



[image from Hamley 2007]

The removal of dirt in the form of solid particles or liquid droplets from some surface in the presence of dissolved detergents has been observed to take place by different mechanism:

- *roll-up*: detachment into suspension of entire particles or droplets,
- *emulsification*: continual release into suspension of fragments,
- *solubilization*: continual release into solution of individual molecules.

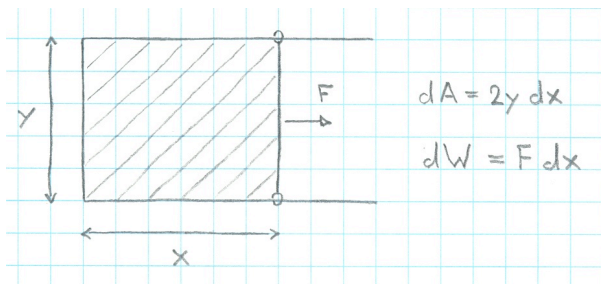
Surface Tension and Interfacial Tension [p1n60]

The key attribute that makes surfactants effective detergents (see [psl13]) is that they reduce surface tension and interfacial tensions.

Surface tension:

Cohesive forces between molecules become anisotropic at liquid-gas interface (liquid surface) due to sharp rise in intermolecular distance. Surface tension is defined as the surface free energy per unit surface area.

Application: stretching a soap film (with two sides) on a rectangular frame.



surface tension = excess energy per unit area [J/m^2]
= force per unit length [N/m]

$$\gamma = \frac{dW}{dA} = \frac{F}{2y}$$

Interfacial tension:

Consider two immiscible liquids a and b with surface tensions γ_a and γ_b , respectively, and interfacial tension γ_{ab} .

Removing a contact of area A between liquids a and b eliminates an interface and creates two surfaces. It costs work of *adhesion* $W_{ab} = Aw_{ab}$.

Separating two parts of liquid a creates two surfaces of area A . It costs work of *cohesion* $W_{aa} = Aw_{aa}$.

$$w_{ab} = \gamma_a + \gamma_b - \gamma_{ab}, \quad w_{aa} = 2\gamma_a.$$

Consider a drop of minority liquid a hitting the flat surface of a majority liquid b . The *spreading coefficient* S determines whether the interface tends to maximize ($S > 0$) and form a thin film of a or tends to minimize ($S < 0$) and form a compact lense of a .

$$S = w_{ab} - w_{aa} = \gamma_b - \gamma_a - \gamma_{ab}.$$






[gleaned from Hamley 2008]

Aggregation of Amphiphiles [ps114]

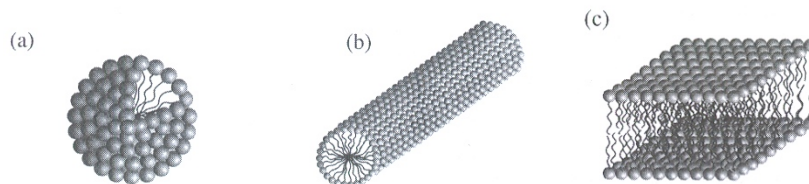
Packing parameters:

- 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:

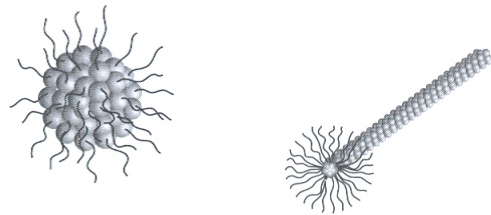
| | | |
|-----------------------------|--------------------|--------------------------------------------------------------------------------------|
| Spherical micelles | $V/al < 1/3$ |  |
| Cylindrical micelles | $1/3 < V/al < 1/2$ |  |
| Vesicles, flexible bilayers | $1/2 < V/al < 1$ |  |
| Lamellae, 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

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

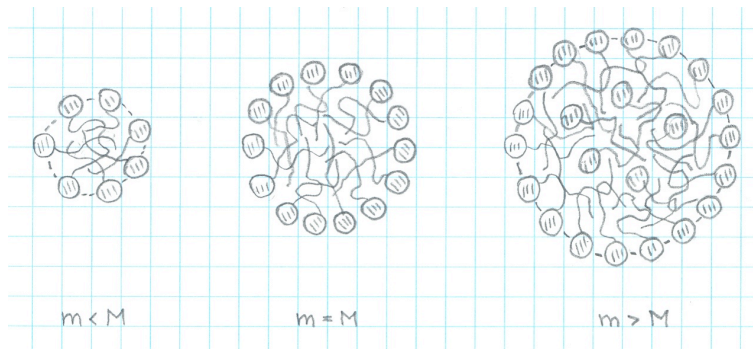
Eliminate μ from expressions for X_m (aggregates of size m) and X_1 (amphiphiles in solution):

$$\Rightarrow X_m = m \left[X_1 \exp\left(\frac{\epsilon_1 - \epsilon_m}{k_B T}\right) \right]^m. \quad (2)$$

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):

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

Size distribution is a narrow Gaussian with variance $\langle |m - M|^2 \rangle = k_B T / 2M\Lambda$. 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:

$$\epsilon_m = \epsilon_\infty + \frac{\alpha k_B T}{m}. \quad (4)$$

The endcap energy, $\alpha k_B T$, 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:

$$\epsilon_m = \epsilon_\infty + \frac{\alpha k_B T}{\sqrt{m}}. \quad (5)$$

The edge energy, $\alpha k_B T$, 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

$$\epsilon_m = \epsilon_\infty + \frac{\alpha k_B T}{m^{1/3}}. \quad (6)$$

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

[pex39] Self-assembly as predicted by geometric argument

Consider amphiphiles of (effective) volume V in aqueous solution with shapes as sketched in [psl14]. The effective area of their hydrophilic headgroups is a and the length of their hydrophobic tails is l when fully extended. The dimensionless quantity V/la is a convenient measure to characterize the shape of the amphiphilic molecule between cone-like and cylinder-like. The type of self-assembled structure is the result of balancing two competing agents: (i) the short-range repulsion between particles with shapes, (ii) the efficient shielding of the hydrophobic tails from contact with water. Present an argument that the spontaneous aggregation of amphiphiles into (a) spherical micelles, (b) cylindrical micelles, (c) flat bilayers or vesicles of radius $r \gg l$ is favorable from a pure packing point of view if (a) $V/la \lesssim \frac{1}{3}$, (b) $V/la \lesssim \frac{1}{2}$, (c) $V/la \lesssim 1$, respectively. For spherical and cylindrical micelles (of radius r) the criterion for efficient shielding and mechanical stability is $r \lesssim l$. In a bilayer of width d (flat or forming a vesicle) that same criterion is $d \lesssim 2l$.

Solution:

[pex40] Spherical micelles and CMC

Here we examine the coexistence of individual amphiphiles and spherical micelles containing M amphiphilic molecules in aqueous solution using an energetic argument. Thermodynamic equilibrium dictates that the concentration of micelles of size m have concentrations

$$X_m \propto m \exp\left(\frac{m(\mu - \epsilon_m)}{k_B T}\right), \quad m = 1, 2, \dots \quad (1)$$

where $\Delta\epsilon_m \doteq \epsilon_m - \epsilon_1$ is the change in free energy when an amphiphile from the solution joins a micelle of size $m - 1$ and μ is the chemical potential (common to aggregates of all sizes).

(a) In a scenario that justifies that we only consider free amphiphiles ($m = 1$) and micelles of size $m = M$, infer from (1) the relation

$$X_M = M \left[X_1 \exp\left(\frac{-\Delta\epsilon_M}{k_B T}\right) \right]^M. \quad (2)$$

(b) Now consider a situation where $e^{-\Delta\epsilon_M/k_B T} = 10$. Plot concentrations X_1 of free amphiphiles and X_M of spherical micelles of size M versus the total volume fraction $\phi = X_1 + X_M$ of amphiphiles for the cases $M = 50, 100, 500, 5000$. Combine one set of six curves representing X_1 and a second set of six curves representing X_M all in the same graph.

(c) Interpret your findings. Identify the critical micelle concentration (CMC), ϕ_c , where the concentration X_1 reaches a plateau and the concentration X_M begins to rise. What is different for small and large values of M ? How can these differences be interpreted?

[adapted from Jones 2002]

Solution:

[pex41] Cylindrical micelles and CMC

The energetic argument for the self-assembly of cylindrical micelles differs qualitatively from the that of spherical micelles [pex40]. Cylindrical micelles can grow with no change in curvatures, namely along the axis. The average change in free energy of an amphiphile when it joins a micelle has a much weaker dependence on the size of the micelle. This is reflected in the activation energy,

$$\epsilon_m = \epsilon_\infty + \frac{\alpha k_B T}{m}, \quad (1)$$

where α is an effective energy of the endcaps in units of the thermal energy. Similar to [pex40] we can write

$$X_m = m \exp\left(\frac{m(\mu - \epsilon_m)}{k_B T}\right), \quad m = 1, 2, \dots \quad (2)$$

(a) Infer from expressions (1) and (2) the relation

$$X_m = m [X_1 e^\alpha]^m e^{-\alpha}, \quad (3)$$

by eliminating the chemical potential μ . Then show that the volume fraction of amphiphiles, $\phi = \sum_m X_m$, is related to the volume fraction of individual amphiphiles in solution, X_1 , as follows:

$$\phi = \frac{X_1}{(1 - X_1 e^\alpha)^2}. \quad (4)$$

Solve this relation for X_1 and substitute it into (3) for a closed-form expression of the distribution of micelles, X_m , as a function of the amphiphile volume fraction ϕ and the parameter α that controls the longitudinal growth of cylindrical micelles. Show that for $\phi e^\alpha \gg 1$ that expression simplifies into the asymptotic form

$$X_m^{(as)} = m \left[1 - \frac{1}{\sqrt{\phi e^\alpha}}\right]^m e^{-\alpha}. \quad (5)$$

(b) Below the critical micelle concentration, $\phi < \phi_c$, we expect X_m to be a monotonically decreasing function of m . At $\phi > \phi_c$ we expect X_m to increase with m and reach a maximum for cylindrical micelles of a particular size, $m = m^*$. Infer ϕ_c for given α from the relation $X_1 = X_2$. Infer m^* from the asymptotic expression (5) and show that it approaches the value $\sqrt{\phi e^\alpha}$ for $\phi \gg \phi_c$.

(c) Plot X_m and $X_m^{(as)}$ versus m for $1 < m < 50$, $\phi = 0.05, 0.2, 0.5, 1.0$ (four solid curves and four dashed curves), and fixed $\alpha = 4$. Interpret your findings.

(d) Plot X_m and $X_m^{(as)}$ versus m for $1 < m < 400$, $\phi = 0.05, 0.1, 0.15, 0.2$ (four solid curves and four dashed curves), and fixed $\alpha = 10$. Interpret your findings.

(e) Predict the shape of the function $X_{m^*}^{(as)}(m^*)$ for large m^* and compare that prediction with the location of the maxima in the curves X_m versus m from parts (c) and (d).

[adapted from Jones 2002]

Solution:

[pex42] Critical aggregation of bilayers

As it turns out, the critical aggregation of amphiphile molecules into planar bilayers is more akin to the the CMC of spherical micelles [pex40] than to the CMC of cylindrical micelles [pex41]. Curvature is not an issue. The average change in free energy of an amphiphile when it joins an aggregation depends on the size of the bilayer via the typical perimeter effect:

$$\epsilon_m = \epsilon_\infty + \frac{\alpha k_B T}{\sqrt{m}}, \quad (1)$$

where α is an effective edge energy in units of the thermal energy. As in [pex40] we write

$$X_m = m \exp\left(\frac{m(\mu - \epsilon_m)}{k_B T}\right), \quad m = 1, 2, \dots \quad (2)$$

(a) Infer from expressions (1) and (2) the relation

$$X_m = m [X_1 e^\alpha]^m e^{-\alpha\sqrt{m}}, \quad (3)$$

by eliminating the chemical potential μ .

(b) Construct a Mathematica program that computes the concentration of size- m bilayers, X_m , and the total concentration of amphiphiles, $\phi \doteq \sum_m X_m$, as functions of the variable α and the parameter X_1 (the concentration of amphiphiles in solution). Use a cut-off m_{max} in the sum large enough that its effect on the results is negligible. The concentration of aggregated amphiphiles is $X_{agg} \doteq \phi - X_1$. Use the ParametricPlot option of Mathematica to produce curves of X_1 and X_{agg} versus ϕ . Use several values of the energy constant in the range $1 < \alpha < 7$. For each choice of α , zoom into the range of ϕ where interesting physical phenomena take place such as (more or less abrupt) changes in the concentrations of free and aggregated amphiphiles.

(c) Identify data points for the critical aggregation concentration (CAC) of planar micelles. Try to fit these data point to a model expression for $\phi_c(\alpha)$.

[adapted from Jones 2002]

Solution:

[pex50] Spherical aggregates of colloids

Consider a colloidal dispersion with a tendency for aggregation. The differential in mass density between colloids and dispersion medium is so small that any effects of gravity can be ignored. The colloids are monodisperse and have volume v . The interfacial energy $E_{int} = 4\pi r^2\gamma$ between aggregate and dispersion medium adds to the cost of aggregation. Therefore, if the energy of association for one colloid to an aggregate of infinite size is ϵ_∞ then the energy of association of m colloids to one spherical aggregate is $\epsilon_m = \epsilon_\infty + E_{int}/m$ for each of these colloids.

(a) Show that this energy of association can be written in the form

$$\epsilon_m = \epsilon_\infty + \frac{\alpha k_B T}{m^{1/3}}, \quad \alpha \doteq \frac{4\pi\gamma}{k_B T} \left(\frac{3v}{4\pi}\right)^{2/3}. \quad (1)$$

The parameter α decreases with increasing T not only because of the factor T in the denominator but also because the interface tension γ is expected to decrease. As in [pex40]-[pex42] we use the expression

$$X_m \propto m \exp\left(\frac{m(\mu - \epsilon_m)}{k_B T}\right), \quad m = 1, 2, \dots \quad (2)$$

for volume fractions of size- m aggregates at thermal equilibrium.

(b) Infer from expressions (1) and (2) the relation

$$X_m = m [X_1 e^\alpha]^m e^{-\alpha m^{2/3}}, \quad (3)$$

by eliminating the chemical potential μ .

(c) Construct a Mathematica program that computes the concentration of size- m aggregates, X_m , and the total concentration of colloids, $\phi \doteq \sum_m X_m$, as functions of the variable α and the parameter X_1 (the concentration of colloids in dispersion). Use a cut-off m_{max} in the sum large enough that its effect on the results is negligible. The concentration of aggregated colloids is $X_{agg} \doteq \phi - X_1$. Use the ParametricPlot option of Mathematica to produce curves of X_1 and X_{agg} versus ϕ . Use several values of the energy constant in the range $1 < \alpha < 7$. For each choice of α , zoom into the range of ϕ where interesting physical phenomena take place such as (more or less abrupt) changes in the concentrations of free and aggregated colloids.

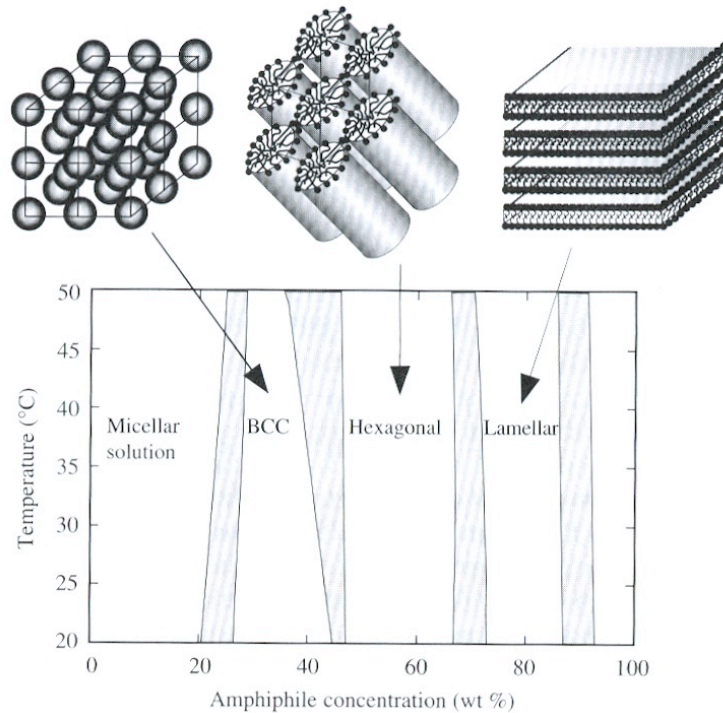
(d) Identify data points for the critical aggregation concentration (CAC). Try to fit these data point to a model expression for $\phi_c(\alpha)$.

[adapted from Jones 2002]

Solution:

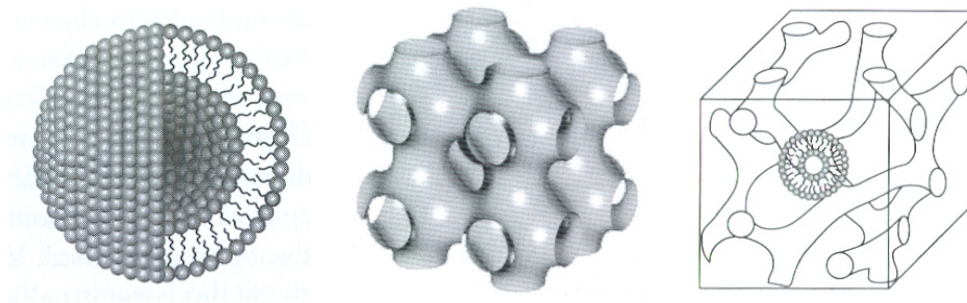
Hierarchical ordering of amphiphiles [ps115]

Phase diagram of amphiphilic copolymer in solution at high concentration:
interplay of enthalpic and entropic effects on the level of amphiphiles and on the level of aggregates.



Alternative structures at high concentrations:

vesicles (liposomes) [left] merging into bicontinuous cubic phase [center] or, with less symmetry, into gyroid phase [right].



[images from Jones 2002 and Hamley 2007]

Points of interest:

- Spherical micelles share attributes with colloids in suspension. Interactions: steric, (screened) electrostatic, elastic. Micelles are soft colloids with shapes that deform in crowded environment.
- BCC phase has 3D translational long-range order (LRO). Soft solid with gel properties. Typical lattice spacing: 20nm.
- Hexagonal phase has 2D translational LRO. Columnar liquid crystal phase. Cylindrical micelles have higher surface energy density than spherical micelles but the packing is more efficient: 91% vs 68%.
- Transition from BCC phase to hexagonal phase trades (steric and/or electrostatic) repulsive interactions for surface energy.
- Lamellar phase has 1D translational LRO. Smectic liquid crystal phase.
- In transition from hexagonal phase to lamellar phase a further increase in packing efficiency outweighs accompanying increase in surface energy density.
- Wrinkles in lamellar phase are suppressed by the (unilateral) constraints of boundaries and by a repulsive interaction between membranes of entropic origin (Helfrich force).
- More complex phases are common in ternary mixtures (e.g. water, oil, amphiphile):
 - micelles with hydrophobic interior swollen by non-polar fluid;
 - polar and non-polar fluids separated by amphiphilic monolayer;
 - lamellar phase (binary or ternary) may grow pores that establish a stable, bicontinuous, cubic structure;
 - sponge phase results when thermal fluctuations destroy the cubic symmetry but maintain the same topology.

[gleaned from Jones 2002]

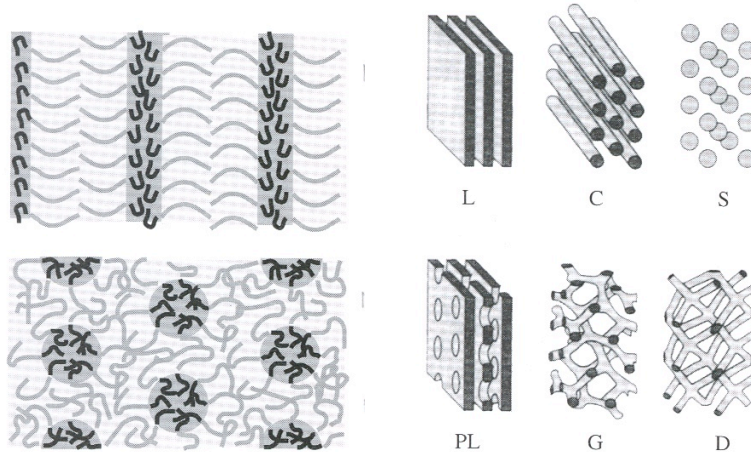
Self-Assembly in Polymers [pln58]

Blends of homopolymers have a strong tendency to phase separate as explained in [pln48]. The segregation is driven by an enthalpic gain $\Delta H < 0$ due to a lowering of interaction energies. The entropic cost $\Delta S < 0$ is reduced by the mobility constraints due to polymerization.

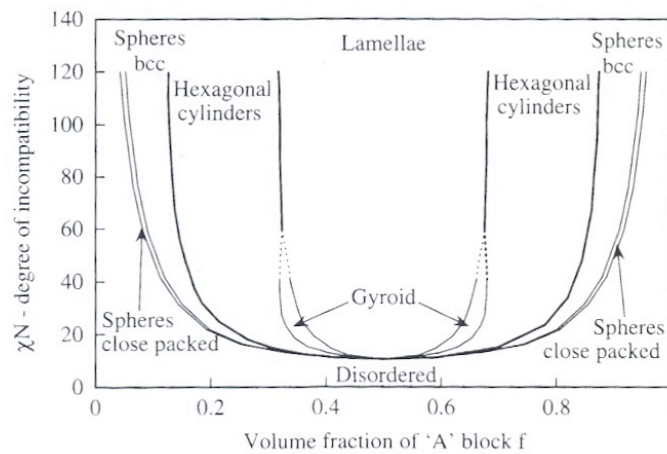
In ternary mixtures of homopolymers *A*, *B* and block copolymers *AB* the latter assumes a role akin to amphiphiles.

In the melt of a diblock copolymer where the two blocks have significantly different lengths, complex diagrams of microphase separation are realized.

Lamellar morphology has plane interfaces of optimized thickness [pex58]. There exist multiple morphologies with curved interfaces.



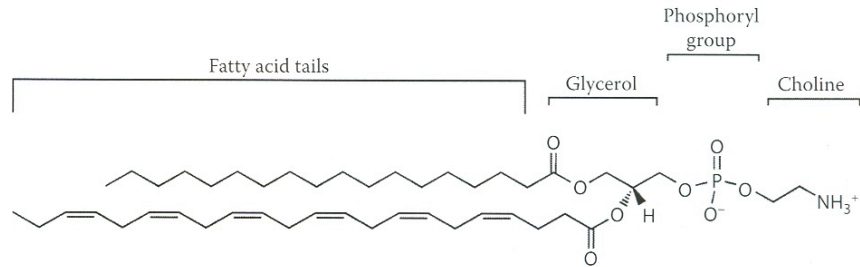
L: lamella, C: cylinders, S: spheres,
 PL: perforated lamellae, G: gyroid, D: double diamond.



[images from Jones 2002]

Lipids [pln59]

Chemical structure of (zwitterionic) phospholipid:



[image from Hirst 2013]

Lyotropic phase behavior largely governed by shape of particular lipid (cone vs cylinder, see [psl14]). Thermotropic phase behavior in plane of bilayer somewhat akin to liquid crystals.

Sequence of common phases realized as T rises:

- Subgel phase L_c' is pseudo-crystalline with translational and rotational motion of lipid molecules severely restricted. Headgroups show hexagonal LRO.
- Gel phase L_{β}' allows for some rotational motion of lipid molecules. Headgroups show orthorhombic LRO. Tails may be tilted away from normal to plane of bilayer.
- Ripple phase P_{β}' features ripples perpendicular to plane of bilayer.
- Liquid crystal phase L_{α} is fluid-like. Headgroups are further apart and have positional SRO, similar to smectic-A liquid crystals. Lipid molecules are free to diffuse.

Lipid bilayers at room temperature typically are in phase L_{α} . Melting transition between β' and L_{α} is of first order with measurable latent heat.

[gleaned from Hirst 2013]