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.
- Hexagoal 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 flutuations destroy the cubic symmetry but maintain the same topology.

[gleaned from Jones 2002]