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Interfacial architecture in surfactant–water mixtures: Beyond spheres, cylinders and planes

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Abstract
Geometric relations linking the (local) molecular shape of the aggregating surfactant molecules to the (global) composition of the surfactant-water mixture. The presence of cubic, tetragonal and rhombohedral phases is suggested to be due to the formation of hyperbolic interfaces, of minimum bending energy.

A CRUDE INVENTORY OF SURFACE SHAPES

An instructive example of the range of surfaces accessible in three-dimensional Euclidean space is offered by the following two-parameter cartesian equation:

$$\cos(x)+\cos(y)+1/a^2\cos(z/a) = b$$

If a single value of b is chosen, the level set in three-dimensional space describes a surface - or set of surfaces. The morphology of these surface varies as the parameters a and b are varied, and the surface shapes fall into the following classes:

(1) *Globules*. These are closed, compact objects, in general ellipsoidal in shape. They are classified topologically as genus one surfaces, which implies that their integral Gaussian curvature is positive; they fall within Riemann's ellipsoidal geometrical class.

(2) *Rods*. These shapes are open at two ends, the most familiar member is the cylinder. Their (integral) Gaussian curvature vanishes and they are classified as parabolic surfaces of genus one. Less familiar examples within this class include the Delaunay surfaces of revolution.

(3) *Sheets*. These are rippled planes, of zero Gaussian curvature, hence they too are parabolic surfaces.

(4) *Mesh*. These surfaces are less well known. They are saddle-shaped everywhere, thus their (integral) Gaussian curvature is negative, and their geometry is hyperbolic. They are confined between two planes, and can be described as porous lamellae. They can adopt constant mean curvature (ref. 1), although the Gaussian curvature varies over the surface. Mesh surfaces are not minimal surfaces, since their mean curvature cannot be identically zero. The surfaces generated by the equation above exhibit a square planar network of tunnels. The genus of a single "unit cell" of the surface (embedded in the three torus) is two - the simplest topology for doubly-periodic surfaces. Presumably, any two-dimensional mesh network can be realised. The other simple two-dimensional net - the hexagonal net - describes an alternative tunnel morphology. Parallel layers of these square and hexagonal mesh surfaces (with the nodes of one layer positioned over the holes of neighbouring layers) result in three-dimensional arrangements of rhombohedral and body-centred tetragonal symmetry respectively (space groups R3m and I422 resp.). Their tunnel geometries match those of the rod-structures proposed by Luzzati to describe the so-called T and R phases found in surfactant systems.

(5)*Strut*. This family corresponds to the class of bicontinuous structures: they carve space into two inter-penetrating sub-volumes, both continuous, and topologically identical. They are also hyperbolic and their genus per topological unit cell is at least three. Many examples have geometrically distinct networks on either side of the surface. The examples covered by the parametric equation above carve space into two interpenetrating simple cubic labyrinths. They are topologically identical to the P-surface, the simplest triply periodic minimal surface. Minimal surfaces are the simplest examples of hyperbolic surfaces forming bicontinuous space partitions, since they are curved equally towards both sub-volumes. They are able to be explicitly parametrised in many cases using equations from differential geometry, and many new triply periodic minimal surfaces have been uncovered in recent years (refs. 2-5). The tunnel geometries of the D-surface and the gyroid- consisting of interpenetrating diamond and oppositely handed Laves graphs respectively - match those of the structural proposals of Luzzati for bicontinuous cubic phases of space group symmetries Pn3m and Ia3d (Q^{224} and Q^{230} in Luzzati's notation)(ref. 6). In the case of direct (V_1 or I_1) phases, the tunnels are filled with paraffin moieties of the surfactant, while inverted phases (V_2, I_2) consist of bilayers lining these surfaces, with polar groups (including water) in the tunnels. The surface description is useful in that it offers a wide range of possible structures to describe these bicontinuous mesophases. A unique structural description of these phases must invoke topology as well as symmetry. For example, the space group Im3m (which has been detected in binary and ternary surfactant systems), can be realised by a number of triply periodic minimal surfaces, *viz*, the P-surface (genus three), the I-WP surface (genus four), the Neovius surface (genus nine) and the O,C-TO surface (genus ten). Luzzati's terminology therefore is incomplete, since it implies the existence of a single structure for a given symmetry - which need not be the case.

It is important to note here that a number of lower symmetry examples of triply periodic minimal surfaces can also be realised. These include tetragonal, hexagonal, orthorhombic, monoclinic, and (possibly) triclinic symmetry classes (refs. 5,7). Some of these examples are distortions of the surfaces mentioned above, others are of novel tunnel morphology. Important examples include the genus three H-surface - whose (identical) tunnels form a hexagonal rod-packing along the c-axis, linked by horizontal tunnels - and the tetragonal and rhombohedral distortions of the P and D surfaces (known as the tP, tD and rPD surfaces respectively).

MOLECULAR SHAPE AND SURFACE GEOMETRY

This brief catalogue of surface structure embraces the range of surface geometries - elliptic, parabolic and hyperbolic. How do we relate these forms to self-assembly?

The problem of self-assembly is essentially a thermodynamic one, involving a complex range of interactions governing the entropy of the system, and entropic terms. We shall subsume the former contributions within a phenomenological bending energy term, which assumes preferred curvatures at the polar-apolar interface. This approach involves a number of assumptions (e.g. small curvature deviations) and is itself the subject of some debate. However, some justification for the approach can be made in the case of an aggregating species of preferred molecular dimensions. As first enunciated by Israelachvili, Ninham and Mitchell (ref. 8), these dimensions are the result of a set of complex interactions. In this case, we can define a "surfactant parameter", v/al, where a is the preferred head group area,v the chain volume and l the preferred length ref. (Recent work by Ennis supports this approach (ref. 9)) To harmonic order, we can describe the deviations of the molecular dimensions away from these preferred values by the prescription:

$$F = k_1(a-a_0)^2 + k_2(l-l_0)^2$$

In our case, we further simplify the problem, and consider the situation where the two bending moduli are coupled, so that we can write the bending energy in terms of the actual surfactant parameter adopted by the aggregating chains in the phase, and the preferred value of the parameter:

$$F = \{(v/al) - (v/al)_0\}^2$$

If we assume that the chains lie normal to the polar-paraffin interface, the surfactant parameter can be determined from the Gaussian and mean curvatures of the interface at the head-groups (K and H resp.), *scaled by the chain length* (ref. 10):

$$v/al = 1 + Hl + Kl^2/3$$

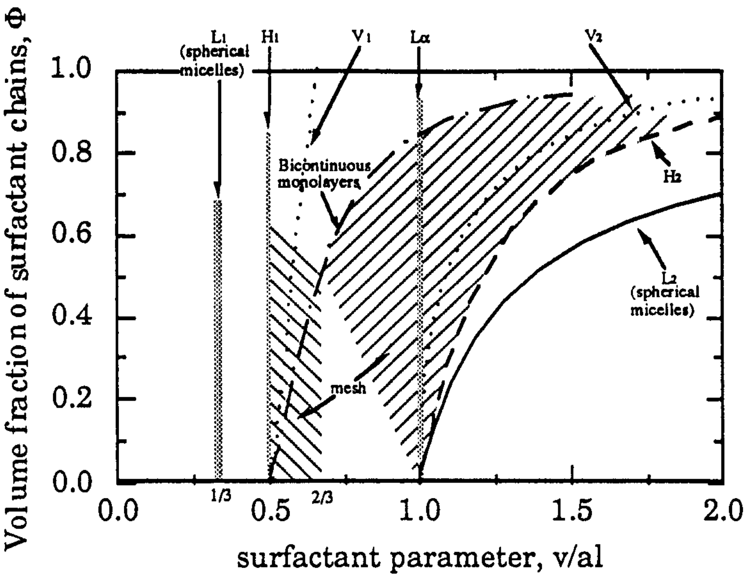

Figure 1: Relation between molecular shape (v/al) and composition (chain volume fraction, Φ) for as range of aggregation geometries.

This means that we can express the energy of deformation of the surfactant film in terms of deviations about the preferred curvatures, H_0 and K_0, which are set by the molecular dimensions by the previous equation. We implicitly assume local interactions only, set by the values of the (local) curvatures. Longer range interactions - for example between opposing sheets - are ignored.

Consider first some consequences of the model which can be obtained from considerations of the packing geometry as a function of surface morphology. Assume that the bending modulus is small, so that the aggregation geometry is set by the average value of the surfactant parameter alone. We require a map of the average value of the surfactant parameter as a function of the (global) composition of the molecular mixture, consisting here of surfactant and water only.

In general, there is no link between the (local) surfactant parameter - or the surface curvatures - and the compositional constraints (surface to volume ratio, volume fractions on either side of the surface). However, if we assume *homogeneity* - i.e. constant values of Hl and Kl^2, the volume fractions on either side of the interface determine the values of the curvatures,and hence the surfactant parameter (ref. 11)! This geometric assumption is equivalent to assuming small values of the bending energy, if the preferred value of the surfactant parameter is equal to the average value adopted in the geometry under consideration.

These calculations give plots of the average value of the surfactant parameter as a function of chain volume fraction for idealised homogeneous globular, rod, sheet and strut surfaces, shown in figure 1.

The results are only exact for parallel planes (L_α phases), and chain-filled spherical (L_1) and cylindrical (H_1) micelles. For reverse globular (L_2) or cylindrical (H_2) micelles they are approximate, since both curvatures and chain lengths cannot be fixed simultaneously. The paraffin volumes in these reverse phases are the Voronoi regions, set by the geometry of the micellar packing, which are most nearly homogeneous when the number of faces in the Voronoi cells is maximised. Thus, the data for globules and rods are most apposite to body centred cubic sphere packings, and hexagonal cylindrical packings (ref. 11). It is known that no hyperbolic strut surface can have constant mean and Gaussian curvatures (ref. 12). However, the data is an approximation to a single-sheeted (strut) interface, which - if the surface is decorated with surfactant monolayer - leads to bicontinuous structures, consisting of a labyrinth of polar moieties interpenetrated by a labyrinth of paraffin chains.

We have also calculated the local-global relation for symmetric bilayers and reverse bilayers lining triply periodic minimal surfaces (ref. 11). If the symmetry of the surface is cubic, the resulting structures consist of two intertwined polar strut networks separated by a bilayer for values of the surfactant parameter larger than unity (V_2 phases), and two interpenetrating paraffin strut labyrinths for values of the surfactant parameter between 1/2 and 2/3 (V_1 phases) - these structures are tricontinuous. (Note that the results for V_1 phases shown here differ from those shown in (ref. 11), due to an error in the latter calculations.)

The calculations for mesh structures are less quantifiable. Since these structures are of intermediate topological character to strut and rod surfaces, the regions of parameter space accessible to mesh_2 phases (with polar 2-d mesh networks in a paraffin continuum) are expected to lie between the curves for monolayer struts and reversed cylinders. (The lower limit of chain concentration in this mesh phase depends on the pore volume in the mesh structures). This morphology can only occur for values of the surfactant parameter exceeding 2/3. It is easy to demonstrate that mesh_1 phases (with 2-d paraffin networks embedded in a polar continuum) occur for values of the surfactant parameter between 1/2 and 2/3. In this case, the layer spacing (and consequent volume fraction) is independent of the surfactant parameter, and the upper limit of chain fraction is determined by the pore volume fraction.

RELATIVE STABILITY OF GLOBAL GEOMETRIES

In order to compare these data with actual molecular mixtures, we must compute relative values of the bending energies of actual surfaces, since the data so far offer average values of the surfactant parameter only. Such computations are not easy, since they require knowledge of the global surface geometry.

Consider the case of bilayers lining periodic minimal surfaces. Recent investigations of Nitsche support the claim that minimal surfaces minimise the bending energy with respect to deformations of these surfaces (ref. 13). The Gaussian curvature of minimal surfaces necessarily varies from point to point. For V_2 morphologies, if the chain length is constant (so that the bilayer is of constant thickness), the bending energy scales with the square of these curvature deviations (assuming the bending energy form given above). A relative estimate of these deviations is afforded by comparing the actual surface to volume ratios of periodic minimal surfaces to the ideal value, derived under the assumption of constant Gaussian curvature. Parallel surface theory gives the result for ideal homogeneous minimal surfaces: $\sqrt{[\sigma^3/2\pi(2-2g)]}=3/4$, where σ denotes the normalised surface to volume ratio ($=S/V^{2/3}$) and g is the genus per topological unit cell[*].

Actual values of this index for some triply periodic minimal surfaces are (in ascending order of bending energy):

surface	genus (per topological u.c.)	index
D	3	.7498
I-WP	4	.7425
gyroid	3	.7665
CLP ($c/a=\sqrt{2}$)	3	.7751
P	3	.7163
Neovius	9	.6640
F-RD	6	.6577

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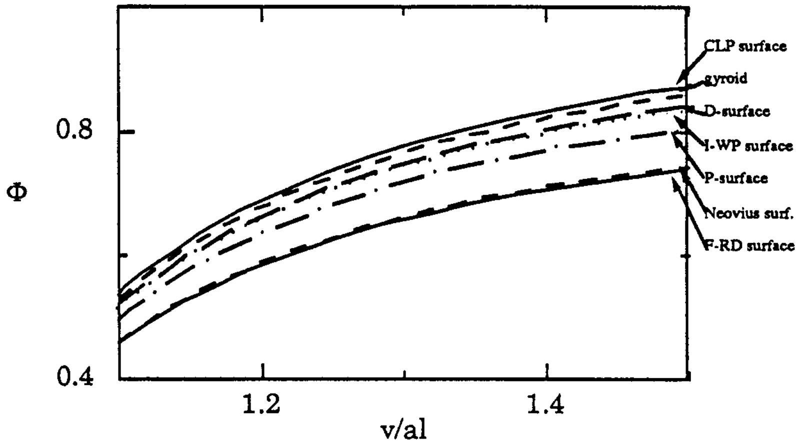
[*] In many cases the topological unit cell differs from the cell detected in X-ray measurements.

Since the local-global curves depend on the surface to volume ratio, we can utilise the actual values (rather than the "ideal" value), to plot the curves for a range of triply periodic minimal surfaces. These curves are shown below.



Thus, the symmetry of the bilayer must change upon dilution, in order to retain the preferred molecular shape. Particular mesostructures are only expected to occur over a few percent variation of chain volume fraction (for fixed molecular dimensions). The most favoured cubic mesophases (due to their low bending energy cost) are expected to be the gyroid (Ia3d)->D (Pn3m)->I-WP (Im3m)->P (Im3m) surfaces on water dilution. These symmetries are indeed most frequently observed in experimental studies of bicontinuous V_2 phases, having been seen in ionic and nonionic surfactants, soaps and lipids (refs. 6,14).

Note that the detection of a certain symmetry (by, for example, X-ray scattering) does not amount to a mesostructural determination. Other techniques must be used to determine the surface topology. One such technique requires only the measurement of lattice parameters as a function of the composition of the sample (ref. 15).

The experimental situation with regard to surfactant parameters less than unity, is less clear. Tiddy et al. have reported the preferred formation of "intermediate" anisotropic phases at the expense of cubic phases in numerous ionic as well as nonionic surfactant-water mixtures as the chain length is increased (ref. 16). This suggests that the film rigidity is indeed central to the stability of mesophases, a conclusion supported by the observation that less flexible, fluorocarbon chains form intermediate phases, while their hydrocarbon relatives form cubic phases (ref. 17). For other surfactant-water systems, both intermediate (anisotropic) and cubic mesophases occur. Thorough studies of the SDS-water system by Kékicheff have revealed the presence of tetragonal and rhombohedral as well as a cubic mesophase (ref. 18). Luzzati's group have also found tetragonal phases in dry long-chain calcium soaps (ref. 19).

We propose that these intermediate phases can be understood in terms of surfactant monolayers, just as cubic phases are a signature of curved bilayers. Explicit calculations of relative bending energies for monolayer geometries are difficult, however some trends can be deduced. An approximate trend of increasing bending energy with increasing genus for periodic minimal surfaces exists, with genus three and four surfaces being most favoured. Analogous behaviour for monolayers (which need not lie on minimal surfaces) suggests that mesh surfaces, of genus two, should be the most favourable hyperbolic geometry. Here too, maximisation of symmetry is expected in order to further decrease bending energy costs. On these tentative grounds, we expect the formation of square or hexagonal mesh structures, of both direct and reversed morphologies (with paraffin and polar groups in the mesh networks respectively). While periodic minimal surfaces exhibiting tetragonal and rhombohedral symmetries occur, in general they are expected to incur a higher bending energy cost than their cubic counterparts. Thus, the hypothesis that these intermediate phases are of similar topology to cubic phases is at odds with the fact that intermediate phases are preferred over cubic phases for higher film rigidities.)

These trends suggest that the presence of bicontinuous cubic phases, as well as rhombohedral or tetragonal intermediate phases, is indicative of the formation of homogeneous *hyperbolic* interfaces, just as hexagonal phases can be taken to be a signature of a parabolic interface. For example, the tetragonal ($\Phi \approx 65\%$) -> cubic (Im3m) -> rhombohedral ($\Phi \approx 60\%$) transitions seen in the SDS-water system (ref. 18) can occur with a variation of the value of the surfactant parameter between about 0.7 and 0.6 if the topologies are respectively $mesh_2$ -> V_1 -> $mesh_1$. The rhombohedral to cubic transition can occur by a simple intergrowth of neighbouring mesh networks, coupled with the formation of extra tunnels linking the mesh sheets. This process is analogous to the continuous topological changes seen in DDAB ternary microemulsions (ref. 20), and is a second order transition. The transition to the (reversed) tetragonal phase involves a more dramatic rearrangement and is expected to be first order, as measured.

DISCUSSION

This simple model requires more quantitative data to confirm its tentative conclusions. However, it is striking that the symmetries and topologies of the better characterised bicontinuous cubic phases, as well as the symmetries of intermediate phases can be understood.

Since the model assumes a single preferred value of the surfactant parameter, it is most applicable to "clean" systems. Extending the range of preferred surfactant parameters is expected to disfavour homogeneous geometries. For example, the V_2 phase in the lipid monoolein-water system disappears in less pure lipid mixtures. Indeed, the homogeneous D-surface is lost in the mixed lipid system, and the gyroid geometry extends through the V_2 phase region (ref. 21).

We expect the range of structures accessible to multicomponent systems to be larger, including the possibility of higher topology bicontinuous bicontinuous phases (not necessarily of cubic symmetry), due to the range of accessible molecular dimensions. However, in order for these ordered mesophases to form, the bending moduli and molecular dimensions must be reasonably constrained, to preclude melting.

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