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# Distinct Character of Surfactant Gels: A Smooth Progression from Micelles to Fibrillar Networks†

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Gel formation by surfactant molecules is argued to be a process similar to micellization rather than crystallization; it is controlled by thermodynamics rather than kinetics. The properties of surfactant-based gels are compared with those of gels with crystalline fibrillar networks, and questions associated with the nature of these gels are raised.



Numerous examples of liquid gelation by small organic molecules are detailed in the literature.[1−4] Considering the remarkable structural diversity of gelator molecules, it is likely that several mechanisms could be responsible for gelation. In this regard, it is useful to identify common principles that underlie whole classes of gelators, and this perspective is one attempt at doing so. The class of gels emphasized here consists of those in which one of the building blocks is a *surfactant* molecule. Surfactants often form gels under the inducement of a second additive (organic or inorganic);[5−8] in some cases, gels are formed even without other additives.[9] We will argue that surfactant gels are an entirely different class from prototypical molecular gels.

Many (in fact, most) gelators are amphiphilic, i.e., they have one portion that is hydrophilic or polar (e.g., capable of forming hydrogen bonds) and another portion that is considerably hydrophobic or nonpolar).[1,2] But not all amphiphiles are surfactants; on the other hand, all surfactants are amphiphiles. For the purpose of our discussion, we define surfactants as molecules with a hydrophilic headgroup and one or two hydrophobic tails (surfactants with two tails are often called lipids) that have the following key property: when added to water at concentrations above their critical micelle concentration (cmc), surfactants will form *micelles* (or in the case of lipids, *vesicles*).[10−12] Surfactants are thus molecules that have a spontaneous tendency to self-assemble into discrete nanoscale structures, regardless of their gelling abilities. In addition to water, surfactants may form micelles or other assemblies in nonpolar liquids as well.[11] Moreover, surfactants generally tend to emulsify a mixture of oil and water.[11,12]

To provide context for our discussion of surfactant-based gels, we first address the more general question: How or why do small molecules act as gelators? The conventional or dominant view, which has been elucidated in review articles,[1−3] is that gel formation is closely related to crystallization. That is, when a sol of the gelator is cooled, one set of conditions results in bulk crystals while a different set of conditions leads to a fibrillar gel. This picture emphasizes the kinetic aspects of gelation (i.e., nucleation and growth and path dependence); it suggests that the gel state may not be the thermodynamically stable one, and it also implies similarities between the crystalline form of the gelator and the fibrils of the gel. In this perspective, we will emphasize that surfactant-based gels fall into a different class where few of the above aspects seem to hold. Rather, the latter gels are more akin to micelles or similar assemblies, and gelation in surfactant systems appears to be a thermodynamically driven self-assembly process.

## Characteristics of Conventional Gels (Crystalline Assemblies)

Figure 1 depicts the development of a typical gel from small-molecule gelators under the "conventional" view expressed above. To begin, the gelator is dissolved in the solvent of interest at high temperature. The resulting sol (Figure 1a) is typically a clear, homogeneous solution of low viscosity. When the sol is cooled below a characteristic supersaturation temperature, nuclei of nano/microscale dimensions arise in the sample (Figure 1b). With time, these nuclei usually grow into straight or branched fibrils (Figure 1c), and the overlap or entanglement of these fibrils ultimately leads to gelation (Figure 1d). Studies on such gels using X-ray diffraction (XRD) usually reveal crystalline peak(s), indicating that the fibrils are crystalline.[13,14] Often, corresponding peaks are found in the powder XRD pattern of the gelator itself, which implies that the packing of gelator molecules in fibrils is analogous to that in its crystals.[13,14] The presence of fibrils/spherulites can also be directly detected in typical cases by optical microscopy, which means that the fibrils are quite large (diameters

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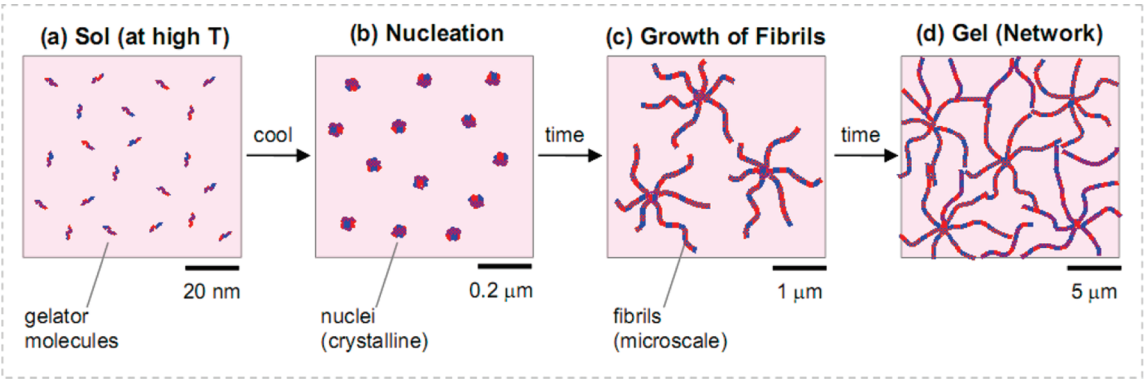


**Figure 1.** Schematic progression of gelation under the conventional view. A sol of the gelator at high temperatures (Figure 1a) is cooled, whereupon crystalline nuclei form (Figure 1b). These then nucleate the growth of crystalline fibrils, which tend to be large (microscale, Figure 1c), and the fibrils fill the volume to form a gel network (Figure 1d).

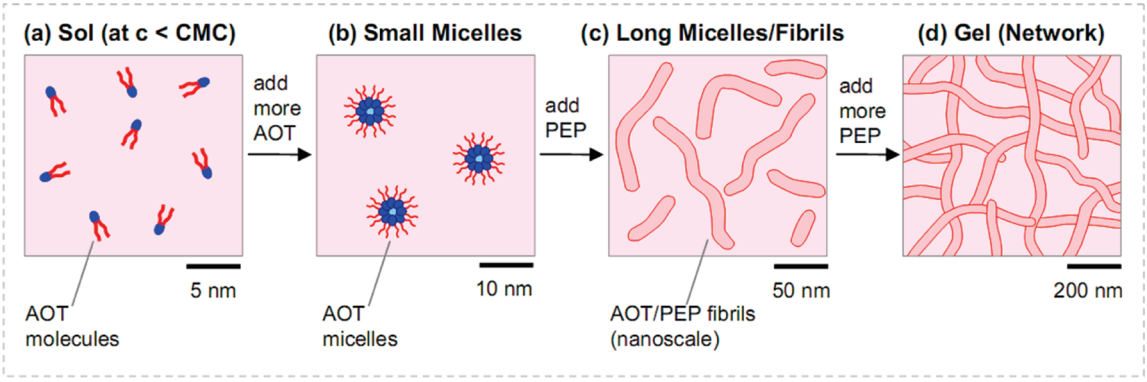


**Figure 2.** Schematic of gel formation in the case of surfactants, taking the system of AOT/PEP in isooctane as an example.[5] AOT is shown with a blue head and two red tails. At very low concentrations, AOT exists as individual molecules (Figure 2a). At a concentration above its CMC, AOT forms small reverse micelles, spherical or ellipsoidal in shape, and with a diameter < 10 nm (Figure 2b). Note that the micelle cores are formed by the AOT heads and the corona consists of the AOT tails. Upon addition of PEP to this sample, the micelles grow to form long fibrils whose diameter is on the nanoscale and comparable to the micelle diameter (Figure 2c). These fibrils overlap or entangle to form the gel network (Figure 2d).



on the order of hundreds of nanometers; lengths on the order of tens of micrometers).[13,15] Note that a gel composed of large fibrils (large compared to the wavelength of light, i.e., microscale) usually manifests as a turbid sample unless the refractive indices of the fibrils and solvent are nearly identical.

It is also useful to discuss the typical response of the above gels under rheology and scattering techniques. A gel is usually identified on the basis of its ability to withstand its weight under gravity in an inverted vial: this is the rheological property of yield stress.[16,17] Correspondingly, in dynamic rheology, a gel usually exhibits elastic ($G'$) and viscous ($G''$) moduli that are independent of frequency.[16,17] Whereas the yield stress and frequency-independent moduli are common to all gels, one striking feature of gels based on crystalline fibrils is that their strain limit tends to be very low—strains of ~1 to 2% are sufficient to disrupt the gel.[18] Additionally, when much larger strains or shear rates are applied, the gel is often irreversibly disrupted and converted to a sol (or in other cases, the gel recovers very slowly, over many hours).[19] Finally, under small-angle neutron or X-ray scattering (SANS or SAXS, respectively), gels formed by crystalline assemblies usually show a slope close to −4 on a plot of intensity $I$ versus wave vector $q$.[14,15] This slope reflects Porod's law, and it implies the presence of sharp interfaces in the sample, which effectively means that the fibrils are a distinct phase.

## Characteristics of Surfactant Gels (Amorphous Assemblies)

We can now discuss the characteristic features of surfactant gels and contrast them with those above. For this purpose, we will focus on a specific system involving the twin-tailed anionic surfactant Aerosol OT (AOT), shown in Figure 2a as a molecule with a hydrophilic head in blue and hydrophobic tails in red. In organic liquids such as isooctane at room temperature, AOT forms small reverse micelles (spherical or ellipsoidal), as shown in Figure 2b.[5,8] When an additive such as *p*-ethylphenol (PEP)[5] or the bile salt sodium deoxycholate (SDC)[8] is introduced into this micellar solution, the micelles transform in shape from spheres to cylinders (fibrils) (Figure 2c). Note that this shape transformation is driven by thermodynamics (free-energy minimization); it is not akin to the nucleation and growth discussed above. The average fibril length is thus a function only of concentration and temperature; it does not depend on the way in which the sample is prepared or whether a hot sample is cooled slowly or rapidly. At higher concentrations of the additive, the fibrils overlap and/or entangle to form a gel (Figure 2d). The gel itself is clear, homogeneous, and amorphous. No obvious features are visible under optical microscopy, indicating that the fibrils in the gel have

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sizes far below the wavelength of light, i.e., in the nanoscale (diameters on the order of tens of nanometers, lengths on the order of hundreds of nanometers). Direct visualization of the fibrils can be done only by atomic force microscopy (AFM) or transmission electron microscopy (TEM).

The above surfactant gels also show a yield stress and frequency-independent moduli in rheological experiments.[5,8] However, their strain limit is usually much higher (~20−100%) than those of crystalline gels (i.e., the gels are not easily disrupted).[8] The gels *can* be disrupted by large strains or shear rates, but they recover quickly (within seconds).[8] Both of these features are characteristic of micelles (see below) rather than crystalline gels. Under SANS or SAXS, surfactant gels usually show a slope close to −1 on a plot of intensity $I$ versus wave vector $q$, reflecting the presence of cylindrical assemblies or fibrils.[8] The lack of Porod behavior implies that the fibrils are molecular assemblies in solution rather than crystalline or lamellar fibers constituting a distinct phase.

Thus far, we have emphasized the differences between conventional and surfactant gels. However, it is important to state that Figures 1 and 2 represent extremes and many intermediate cases are possible. For example, fibrils in conventional gels can have nanoscale (rather than microscale) dimensions and yet be crystalline; such gels may be optically transparent or translucent.[20] Conversely, nanoscale fibrils in surfactant gels can show higher-order lateral aggregation into thicker bundles,[6,7] which in turn can be seen by optical microscopy[7] (in that case, the macroscopic gels are opaque). For instance, in the case of AOT-based systems, thick fibrils with diameters >100 nm are obtained if *p*-chlorophenol is used as the additive instead of PEP or SDC.[6,7] Interestingly, opaque surfactant gels can also show Porod behavior ($I \sim q^{-4}$) in SANS, much like conventional gels.[7] In other words, there are exceptions to every "rule" concerning gels! Nevertheless, understanding the typical responses of each type of gel can be instructive.

## Biological Connections

The connection between gels synthesized in the laboratory and those existing in biology (e.g., in normal or pathological cells) is a fascinating topic. Indeed, researchers on gels routinely make claims about the significance of their work with respect to biology and the understanding of disease. In this context, the classification scheme suggested by Figures 1 and 2 can be useful. We propose that gel formation in the conventional sense is related to the formation of *amyloid plaques* that are implicated in a number of neurodegenerative disorders such as Alzheimer's disease and Huntington's disease.[21] The plaques are formed by the aggregation of proteins (often partially denatured) into amyloid fibrils, which in turn further aggregate to form platelets; both fibrils and platelets may form networks. The plaques are typically crystalline and have a solid-like character, i.e., they are a distinct phase from the contents of the cytosol.[21]

On the other hand, we propose that gel formation by surfactants is akin to the assembly of gels of *cytoskeletal filaments* such as F-actin.[21−23] In the latter case, individual proteins (G-actin) self-assemble into filaments (F-actin), which in turn form a network. In vitro studies on F-actin usually lead to transparent, amorphous gels containing nanoscale filaments (~8 nm in diameter), with a slope of −1 being seen in SANS plots of $I$ versus $q$.[24] F-actin gel formation is well described within a thermodynamic (self-assembly) framework analogous to micelle formation.[21,25] Also, gels of F-actin are *not* broken down easily by shear; in fact, they show strain stiffening, which implies an increase in the gel modulus with strain amplitude.[26] The latter phenomenon has also recently been found in surfactant-based organogels, which is a further validation of the analogy indicated above.[8] To summarize this discussion, it should be clear that both types of gelation phenomena, as depicted in Figures 1 and 2, are important in their own way and both have biological implications.

## Wormlike Micelles versus Surfactant Gels

Historically, the word "gel" has been loosely defined. From a rheological perspective, the definition of a gel is quite strict, but in common parlance, the term is frequently used to describe materials that are "gel-like" but do not satisfy the rheological definition. One class of gel-like fluids that needs to be discussed in the context of surfactant systems is those containing "wormlike micelles" (worms for short; also called "living polymers").[27] The term refers to assemblies of surfactant molecules into long, cylindrical chains—the chains are entangled into a transient but not permanent network, i.e., their rheology is viscoelastic, not elastic (as always, exceptions do exist[9]). The rheological signature of worms is that they are viscoelastic Maxwell fluids with a single relaxation time.[27]

Worms can be formed both in water and in organic liquids.[27] In the case of organic liquids, addition of the lipid lecithin along with a small amount of water[28] or SDC[29] gives rise to long worms (reverse cylindrical micelles), much like the structures in Figure 2d. What distinguishes a wormlike micellar organosol (e.g., lecithin/SDC) from an organogel (AOT/SDC)? Both samples are optically clear, contain nanoscale fibrils, and recover quickly after shear, yet one is viscoelastic and the other elastic. In our estimation, a distinguishing factor is the temperature dependence of the rheology. Whereas worms tend to soften gradually upon heating, with their viscosity decreasing exponentially with temperature,[30] gels tend to melt; that is, they abruptly transform into a sol at a critical temperature.[8] Although the reasons for this distinction are not clear, it is worth noting that both conventional and surfactant gels exhibit similar responses (i.e., melting) as a function of temperature.[1,2]

## Future Directions

This perspective has attempted to show that surfactants give rise to a distinct class of molecular gels. Characteristics of surfactant gels and their differences from conventional crystalline gels have been highlighted. Many unanswered questions remain. In the context of surfactant gels, we mentioned that some systems form nanoscale fibrils (thickness on the order of individual micelles) whereas others show higher-order aggregation into

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bundles. What controls higher-order aggregation? Similarly, we mentioned the basic similarities between wormlike micelles and organogels, with subtle differences in sample composition being sufficient to tilt the system from one form to the other. What controls this? In a related context, an open question about surfactant-based gels is the issue of junction points. That is, one can easily understand the growth of long filaments or fibrils, but is mere entanglement of these sufficient to form a gel? Why would the filaments not be able to disentangle and thereby relax? Do specific interactions exist at junction points, or is the key issue simply one of time scale? These are a few of the questions that will continue to stimulate researchers interested in gels in the years to come.

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