

Theory of Micellar Stability in Isotropic and Nematic Phases[†]

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In this paper we present the basic ideas underlying the statistical thermodynamic theory of micellized solutions of soap in water. First we outline briefly the low concentration limit in which the micellar aggregates are essentially isolated from one another. Here the preferred shapes and sizes are determined by a delicate interplay between single-micelle free energies and solution entropies of mixing. Then we focus on higher concentration situations in which inter-aggregate forces become important. In isotropic suspensions of rod-like micelles, for example, it can be shown that the effect of excluded volume interactions between micelles is to enhance their length-to-width ratio. As the "rods" become longer and more concentrated they are eventually forced to align. Unlike in ordinary colloidal suspensions (lyotropics) and thermotropic systems, however, the aggregates reorganize themselves *internally* as they undergo the isotropic → nematic transition. We show in particular that the rods "grow" longer in the aligned phase. At still higher concentrations the coupling between growth and orientational ordering becomes so strong that finite aggregates can "explode" into the hexagonal phase. We conclude with a discussion of the effects of cosurfactant on micellar size and phase stability.

I. INTRODUCTION

In this paper we treat the phenomenological differences between "normal" and micellar lyotropic nematics. The term *lyotropic* is used

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here to refer to the long-range orientationally-ordered state brought about by an increase in concentration. The classic lyotropic nematic was treated by Onsager¹ who, in 1949, first explained the alignment of rigid rod-like macromolecules suspended in aqueous solution. We describe this situation as the "normal" one because the interacting particles maintain their integrity (i.e. their size and shape) as the system undergoes its isotropic(I)→nematic(N) phase transition. The only order parameter in the problem is η , the usual " P_2 " measure of the preference for molecular orientations to lie along the "director." For this reason the *phenomenology* of the I → N transition has long been regarded as straightforward.

In *micellar* solution, on the other hand, the interacting rod-like particles are no longer single molecules. Instead they are prolate *aggregates* (micelles) comprised of a large number of surfactant molecules. Furthermore, the equilibrium state of these systems involves a dynamic exchange of molecules between aggregates of all sizes. Consequently, the micellar size appears as a *new order parameter* which couples to the degree (η) of nematic alignment (as well as to thermodynamic variables such as the concentration). This coupling changes the nature of the long-range orientational-ordering transition and gives rise to new phenomenological features in both the isotropic and nematic phases.

In section **II** we present the basic ideas underlying the Onsager treatment of orientational order-disorder transitions in "normal" lyotropics. We also treat there the relatively straightforward complications due to polydispersity of the rod-like particles. Section **III** describes the micellar case, for which a new order parameter must be defined—it corresponds to the average size of anisotropic aggregates. This order parameter increases monotonically in the isotropic phase, due to several different mechanisms which contribute to the self-assembly process. In section **IV** we treat the coupling of micellar size to nematic order, focusing in particular on the growth of aggregates attendant upon their alignment: both mono- and poly-disperse situations are considered. Finally, section **V** discusses the role of "additives" (cosurfactant, salt, etc.) and outlines possibilities for generalizing the present treatment to more realistic physical situations.

II. I → N TRANSITION IN "NORMAL" LYOTROPICS

For purposes of phenomenological discussion it is useful to consider only *excluded-volume* interactions between the rod-like particles sus-

pended in isotropic solvent (e.g. an aqueous solution). Then the free energy per particle consists entirely of entropic contributions:

$$\frac{G}{N} \equiv \tilde{G} = -T(\tilde{S}_{orient} + \tilde{S}_{packing}). \quad (1)$$

Here \tilde{S}_{orient} is the loss of orientational entropy due to the long-range alignment. Writing $f(\Omega)$ for the fraction of molecules with orientation Ω , we have

$$-T\tilde{S}_{orient} = \int d\Omega f(\Omega) \ln 4\pi f(\Omega). \quad (2)$$

The packing entropy contribution is in general a complicated functional of f , depending furthermore on the density to all orders. To illustrate the basic physics of the situation, however, it suffices to describe the excluded volume interactions at the second-virial level:

$$-T\tilde{S}_{packing} \approx \rho \int d\Omega f(\Omega) \int d\Omega' f(\Omega') v_{pair}(\Omega, \Omega'). \quad (3)$$

Here ρ is the number density of rods, and $v_{pair}(\Omega, \Omega')$ is the pair excluded volume associated with rods having orientations Ω and Ω' . For spherocylinders of length L and width D , making an angle γ with respect to one another, say,

$$v_{pair} \approx L^2 D \sin \gamma(\Omega, \Omega') \quad (4)$$

for $L \gg D$. For an orientational distribution packed at $\theta = 0$, it is convenient to take¹

$$f(\Omega) \sim \cosh(\alpha \cos \theta) \quad (5)$$

where θ is the angle between the molecular axis and the local director. α describes the state of nematic alignment and is related to the usual “ P_2 ” order parameter via ($\alpha \gg 1$)

$$\eta \approx 1 - \frac{3}{\alpha}. \quad (6)$$

For large L/D and α it is straightforward to show that¹

$$-T\tilde{S}_{orient}^N \approx \ln \alpha, \quad -T\tilde{S}_{packing}^N \approx \phi \frac{L}{D} \frac{1}{\sqrt{\alpha}}. \quad (7)$$

Here $\phi = D^2LN/V$ is the dimensionless concentration (volume fraction) of rods. For the isotropic phase ($\alpha \equiv 0$), on the other hand,

$$-T\tilde{S}_{orient}^I = 0, \quad -T\tilde{S}_{packing}^I \approx \phi \frac{L}{D}. \quad (8)$$

At low concentration, then, the orientational entropy dominates the free energy and the isotropic phase is stable ($0 < \ln \alpha$). For larger ϕ , however, the packing contributions become overwhelming and the system's free energy is lowered by long-range alignment: $-T\tilde{S}_{packing}^N \sim \tilde{G} \sim 1/\sqrt{\alpha}$ according to Eq. (7). The I \rightarrow N transition is associated with the $\phi = \phi^*$ for which the sum of terms in Eq. (7) equals the sum of those in Eq. (8). A trivial algebraic manipulation of this equation shows that

$$\phi^* \frac{L}{D} = \mathcal{O}(1), \quad \text{or} \quad \phi^* \approx \frac{D}{L}. \quad (9)$$

Furthermore, the value of α in the nematic is given by

$$\alpha \approx \phi^2 \left(\frac{L}{D} \right)^2. \quad (10)$$

Figure 1a summarizes the above results for the "normal" lyotropic situation, accounting for the order-disorder phase transition at $\phi^* \approx D/L$ and the subsequent increase of η with ϕ in the aligned phase. Also shown is the dependence of rod size L on concentration. Here of course L is trivially constant since we have treated a *monodisperse* system of *true* particles, i.e. ones which are constrained to maintain their integrity. For a *polydisperse* suspension of such particles, the longer rods will simply partition preferentially into the ordered phase. Consequently the average size of the particles will be larger in the nematic state than in the isotropic phase with which it coexists: see Figure 1b. (This "fractionation" effect has been treated via lattice and virial theories by Flory² and Lekkerkerker³ and their coworkers.) It is important to remember, however, that this jump in L at the transition does not correspond to a *real* growth of particles but rather only to an *apparent* one due to the relative ease with which the nematic can accommodate the long rods in the distribution.

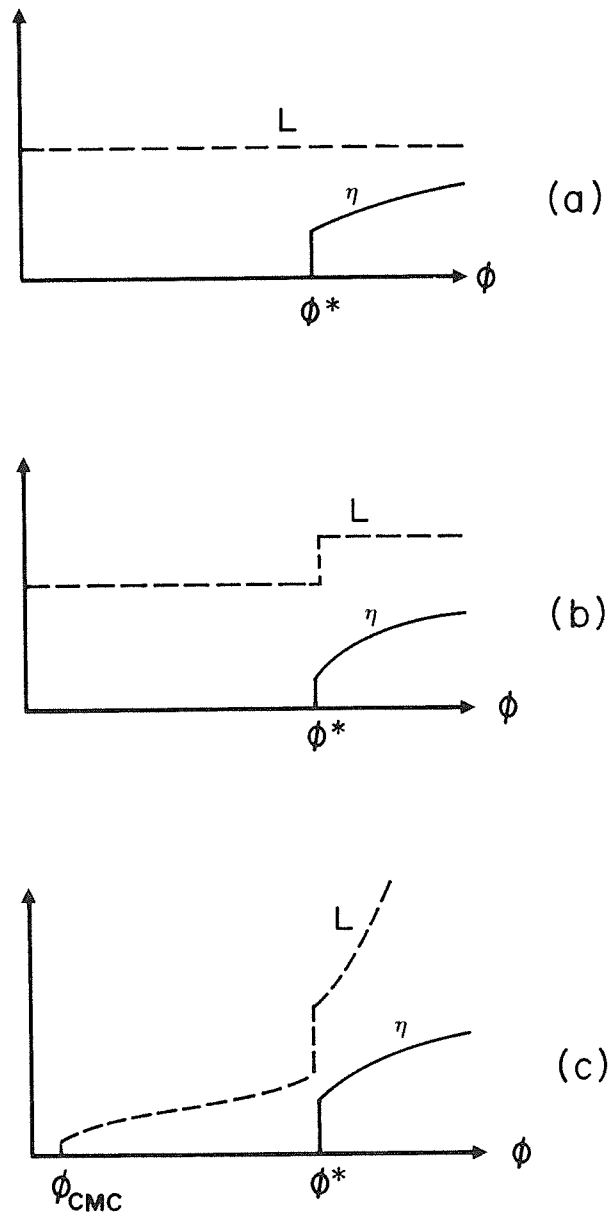


FIGURE 1: Schematic plots of the concentration dependence of size (L) and alignment (η) order parameters in suspensions of: (a) monodisperse rigid rods; (b) polydisperse rigid rods; and (c) micellar rods. ϕ is the volume fraction of suspended particles, the asterisk denoting its value at the isotropic-nematic transition.

III. MICELLAR SELF-ASSEMBLY AND ROD-GROWTH IN ISOTROPIC PHASES

The average size of micellar aggregates in isotropic phases depends sensitively on concentration as shown schematically in Figure 1c. For $\phi < \phi_{CMC}$ ($\ll 1$) the surfactant molecules go into aqueous solution as "monomers" ($\leftrightarrow "L = 0"$). At the critical micelle concentration (CMC) they have reached their solubility limit, essentially because of the hydrophobic moieties (often alkyl chains) which comprise their "tails." Their "heads," on the other hand, are hydrophilic groups (ionic or dipolar) which can be easily accommodated by aqueous solutions. Accordingly, for $\phi > \phi_{CMC}$, the soluble species become *aggregates* of surfactant (*amphiphilic*) molecules which allow the water to be shielded from the hydrophobic tails by a surface of hydrophilic heads.⁴ A typical such structure is shown schematically in Figure 2. Note that the particular size (and shape) of the micelle is of less importance than the fact that its aggregation number has exceeded a *minimum* value m which satisfies the hydrophobic effect via the formation of an interface of water-soluble heads.

Indeed, the free energy difference δ between surfactants in the (\approx spherical) "cap" and (\approx cylindrical) "body" portions of rod-like aggregate is generally less than kT . The free energy difference Δ between a "monomer" in solution and in the micelle, by contrast, is much larger. It is easy to show for example that the CMC is determined largely by Δ , according to

$$\phi_{CMC} \sim \exp^{-\Delta}. \quad (11)$$

($\phi_{CMC} \ll 1$ since Δ —measured in units of kT —is large compared to unity.) The magnitude, *and sign*, of δ depends sensitively on the

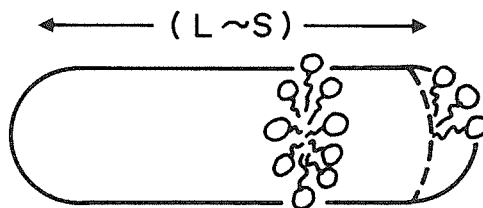


FIGURE 2: Schematic structure of a rod-like micellar aggregate composed of amphiphiles whose hydrophilic heads "sit" at the water surface and whose alkyl chains are found predominantly in the hydrophobic interior. L denotes the length of the micelle and s its aggregation number.

details of the particular surfactant and aqueous solution in question. More explicitly, the relative free energies of an amphiphile in different micellar geometries (e.g. spherical, cylindrical, planar, etc.) are determined by a delicate interplay between surface energies involving the “heads” and the splay/compressional elastic contributions from the “tails.”⁵ For our present purposes, where we wish to focus on the phenomenology of size/alignment coupling, it suffices to start with $\bar{\delta} \approx 1$ and positive.

As we show below, $\bar{\delta} > 0$ guarantees that the equilibrium micelles will become increasingly rod-like as the concentration is increased. For $\bar{\delta}$ *negative*, i.e. when the free energy of an amphiphile is lower in the “cap” than in the “body” of the prolate spherocylinder (Figure 2), we never observe anything but *spherical* aggregates: these *minimum micelles* would optimally satisfy the hydrophobic effect at the same time that they maximize the entropy of mixing of the micellized solution. $\bar{\delta} > 0$, on the other hand, “pushes” surfactants into the cylindrical body as soon as the caps have been “filled” (to assure that the aggregates are “closed”—“finite”).

Let $\tilde{G}(s)$ denote now the free energy *per molecule* in a micelle of size (i.e. aggregation number) s . Via many different (essentially dimensional) arguments it is straightforward to show⁵ that the “internal” contribution to $\tilde{G}(s)$ for a rod-like aggregate decreases with s according to

$$\tilde{G}_{micelle}(s) = \tilde{G}_x + \frac{\bar{\delta}}{s}. \quad (12)$$

Here $\bar{\delta} = m\delta$ and \tilde{G}_x is the free energy of a surfactant in the cylindrical (“body”) portion. Recall that $\bar{\delta}$ is the free energy “price paid” for each of the m molecules which must sit with spherical rather than cylindrical curvature. Clearly if $\tilde{G}_{micelle}$ were the *only* free energy contribution, $\tilde{G}(s)$ would decrease monotonically with s as in Eq. (12)—i.e. the rod-like aggregates would grow without bound in order to suppress the relative importance ($\sim 1/s$) of the “caps.” What stops this “explosion” into infinite aggregates is the ideal solution entropy of mixing:

$$\tilde{G}_{mixing} = -\frac{1}{s} \ln \frac{s}{\phi}. \quad (13)$$

This term, becoming *more positive* with increasing s , dominates $\tilde{G}_{micelle}$ at large s and confines thereby the equilibrium size to a finite

value. Note further that its magnitude decreases with ϕ , suggesting that the most probable s increases with concentration. Indeed, the minimum in the free energy $\tilde{G}_x + \delta/s - (1/s) \ln(s/\phi)$ occurs at $s \approx \phi \exp^{\delta+1}$, an increasing function of both δ and ϕ .

To complete our phenomenological analysis of micellar size in the isotropic phase we need to add the contribution to \tilde{G} from the "external" degrees of freedom.⁶

$$\tilde{G}_{rot/trans} = -\frac{1}{s} \ln q_{trans} q_{rot} \approx -\frac{1}{s} \ln s \left(\frac{3}{2} + \frac{7}{2} \right) - \frac{\delta^+}{s}. \quad (14)$$

Here the q 's are the translational and rotational partition functions for a "particle-in-a-box." For a long rod-like particle we have $q_{trans} \sim s^{3/2}$ and $q_{rot} \sim s^{7/2}$, giving rise to the "1/s ln s" terms in Eq. 14; multiplicative constants in the q 's yield the "1/s" term. Note that each of these contributions to $\tilde{G}_{rot/trans}$ has the same form as those in \tilde{G}_{mixing} and $\tilde{G}_{micelle}$: their negative signs imply that they act to *decrease* the aggregation size. Finally, to allow for corrections to ideal solution behavior of the micellar suspension, we must take into account the interactions *between* aggregates. In the case of excluded volume forces these can be shown to contribute terms of the form⁷

$$\tilde{G}_{excl. vol.} \approx (\phi/m) + \frac{\phi}{s}, \quad (15)$$

thereby enhancing micellar growth (the more so for higher volume fraction). That is, for any given ϕ , the packing entropy is optimized by a reorganization of the system into a smaller number of larger aggregates.

Defining \tilde{G}_{total} by the sum of Eqs. (12) through (15), and minimizing with respect to s we find

$$s \approx (\phi \exp^{\delta} \exp^{\delta-\delta^+})^{1/6}. \quad (16)$$

Thus we can understand the average aggregation number s as a balance between several free energy contributions involving "internal" and "external" degrees of freedom and entropies of "mixing" and "packing" (excluded volume). Noting that $L \sim s$ we obtain, in particular, a mean length which increases with concentration as shown schematically in the $\phi_{CMC} \leq \phi \leq \phi^*$ region of Figure 1c.

IV. COUPLING OF SIZE- AND ALIGNMENT- ORDER PARAMETERS

Consider again the \tilde{G}_{total} discussed above for the isotropic phase. Upon the onset of long-range orientational order, there are only two basic changes (both deriving from the qualitative arguments presented in section II): first the ϕ term from intermicellar excluded volume ($\tilde{S}_{packing}$) becomes $\frac{\phi}{m} (2/\sqrt{\alpha})$; and second the loss in orientational entropy (\tilde{S}_{orient}), contributing to \tilde{G} in the form $(1/s) \ln s$, must be taken into account. Accordingly, we have

$$\tilde{G}^I(s) = \tilde{G}_z + \frac{\phi}{m} - 6 \frac{1}{s} \ln s + \frac{1}{s} [\delta - \delta^+ + \ln \phi + \phi \quad] \quad (17A)$$

and

$$\tilde{G}^N(\alpha, s) = \dots \frac{\phi}{m\sqrt{\alpha}} \quad \dots \quad \ln \alpha \quad (17B)$$

Minimizing (17A) with respect to s and (17B) with respect to α and s , we obtain simple closed-form expressions for $\tilde{G}^I(\phi)$ and $\tilde{G}^N(\phi)$. Equating these two free energies and solving for ϕ gives directly the transition values of ϕ and hence α , s^N and s^I . ($s^I(\phi)$ follows from $\partial \tilde{G}^I / \partial s = 0$, and $\alpha(\phi)$ and $s^N(\phi)$ from $\partial \tilde{G}^N / \partial \alpha = 0 = \partial \tilde{G}^N / \partial s$.)

Within the simple phenomenological theory outlined above, many of the transition properties turn out to be universal. Specifically,

$$\alpha \approx 18 \quad (\leftrightarrow \eta \approx 0.8) \quad (18A)$$

and

$$\frac{s^N}{s^I} \approx 1.4, \quad (18B)$$

independent of the self-assembly parameters (e.g. δ) used to describe the micellization. Furthermore s^N is found to increase faster with concentration than s^I , varying as $(\phi^3 \exp \phi)^{1/4}$ rather than the $(\phi \exp \phi)^{1/6}$ implied by Eq. (16). These differences between s^I and s^N arise essentially from the orientational “entropy” (free energy) term $1/s \ln \alpha$ which couples size and alignment order parameters in the nematic phase. Note that, since

$$\alpha \approx s^2 \phi^2 / m^2 \quad (19)$$

(from $\partial\tilde{G}^N/\partial\alpha = 0$),

$$\tilde{G}_{orient} \sim \frac{\ln \alpha}{s} \sim \frac{\ln s}{s}, \quad (20)$$

decreasing with s . That is, with the onset of long-range order, the loss of orientational entropy is minimized by reorganization of the system into a smaller number of larger aggregates—fewer micelles need be aligned!

The estimate given by Eq. (18) for the ratio of micellar sizes in the coexisting nematic and isotropic phases is merely suggestive: its magnitude follows from Onsager theory, which is only *phenomenologically*—as opposed to quantitatively—valid for describing the order/disorder transition. The only firm conclusion we wish to draw is that

$$s^N > s^I, \quad (21)$$

due to the coupling between rod growth and alignment, i.e. between the size(s) and orientational order parameters ($\alpha \leftrightarrow \eta$). This same coupling gives rise to the stronger dependence of s^N (vs. s^I) on ϕ . Note that $s^N > s^I$ is not just a concentration effect—indeed in the simplified analysis given here we have specifically required both phases to have the same value of ϕ at the transition. Similarly, Eq. (21) is not just a consequence of the preferential partitioning of longer rods into the nematic, as mentioned at the end of section II—for we have explicitly suppressed polydispersity here, collapsing the full size distribution into the single (“most probable”) value s which minimizes \tilde{G} .

The effects of both density changes and polydispersity have been confronted directly elsewhere.⁸ We define a distribution

$$f(s, \Omega) = \{\text{fraction of surfactant incorporated in } s, \Omega\text{-rods.}$$

Using again the Onsager theory—i.e. the second-virial approximation applied to hard rods—we can explicitly express each thermodynamic property as a function of ϕ and $f(s, \Omega)$. Minimizing the Helmholtz free energy with respect to f guarantees *both* micellar equilibrium *and* the proper state of long-range orientational order in each phase. Having assured phase *stability* in this way, we then equate chemical potentials and osmotic pressures for the isotropic and ne-

matic states in order to establish *coexistence*. We determine thereby the coexisting concentrations (ϕ 's) and distributions (f 's) for a system of polydisperse rods which interact through their excluded volume and which exchange molecules in micellar equilibrium. The quantity

$$F(s) = \int d\Omega f(s, \Omega)$$

describes the fraction of surfactant incorporated into rod-like aggregates of size s (independent of their orientation).

For reasonable values of the micellar self-assembly parameters we find,⁸ for example, $\phi^I \approx 5.4\%$ and $\phi^N \approx 6.2\%$ (at the transition) with corresponding average aggregation numbers of $s^I \approx 1660$ and $s^N \approx 1910$. The associated polydispersities are significant: the widths at half-height of the $F(s)$'s are comparable in magnitude with the \bar{s} 's, being somewhat larger for the nematic than for the isotropic phase. As for the *orientational* ordering, we use $F(s)$ to define a new probability density $R(s, \Omega) \equiv f(s, \Omega)/F(s)$ which corresponds to the fraction of s -rods having orientation Ω . It is then easy to show that R has the form

$$R(s, \Omega) \sim \exp \left[\phi \frac{s}{m} \langle P_2 \rangle P_2(\cos\theta) \right]. \quad (22)$$

Here m is the minimum value of s —recall that a sphere is the smallest rod possible, so that the aggregation number m is related via trivial geometric constraints to the length and volume of a single molecule. That is, s/m scales with the length-to-width ratio, so that each micellar rod couples to the nematic field with a strength proportional to (the volume fraction ϕ and) its axial ratio L/D . Finally, the P_2 -order parameter for each size of aggregate—given by the average of $P_2(\cos\theta)$ over $R(s, \Omega)$ —is found⁸ to increase linearly with s for small s , saturating to unity at large s .

V. MORE REALISTIC CONSIDERATIONS

Our present discussion is a first, qualitative treatment of the phenomenon of size-alignment coupling which is unique to nematic phases of micellar (as opposed to “ordinary” lyotropic) systems. Nevertheless it is appropriate to consider here, in closing, some of the aspects of this problem which allow for contact with experiment.

First it is important to note that in the overwhelming majority of ionic-surfactant examples reported to date the observation of a *partially*-orientationally-ordered, *finite*-aggregate nematic phase has required the addition of alcohol or salt. This is commonly believed to be a consequence of the preferential partitioning of the additive into the region of lower curvature (smaller head-group area). In the case of an alcohol whose hydrophobic tail is the same as that of the primary surfactant, for example, the “headless” alcohol can interpose itself between the charged surfactants and decrease thereby the electrostatic strain at the micellar surface. This “strain” is greatest in the lowest curvature regions (where head groups are closest to one another) and the alcohol is thus most effective in these environments. Indeed, preliminary contrast-variation neutron scattering studies by Hendriks et al.⁹ indicate that, for example, decanol partitions preferentially into the “bodies” of rod- and disk-like sodium decyl sulphate micelles (rather than into their “caps” or “rims”). A similar surface-charge-dilution effect must be expected for added salts.

As a consequence of the above consideration it can be shown¹⁰ that $\bar{G}_{micelle}$ decreases faster with s than $1/s$. Specifically

$$\bar{G}_{micelle}(s)_{(12)} = \bar{G}_\infty + \frac{\delta}{s} \rightarrow \bar{G}'_\infty + \frac{\delta'}{s} + \frac{\delta''}{s^2} \quad (23)$$

with each (primed) constant depending on the same self-assembly parameters (as did \bar{G}_∞ and δ before) as well as on the alcohol-to-surfactant ratio. Accordingly, the isotropic→nematic transition occurs at smaller concentrations (ϕ), with larger average micellar sizes (s^I, s^N). Note, however, that the present discussion considers only an *intra*-micellar role for the cosurfactant. Clearly one should treat as well the effect of cosurfactant in interactions *between* micelles. For example, dilution of surface charge will affect the *inter*-aggregate electrostatic forces and hence the overall (concentration and) size dependence of \bar{G}_{total} . Similarly, the s -dependence of dispersive attractions between micelles must also be considered.

The possibility of biaxiality in micellar shape has been implicated in recent interpretations of structural data,¹¹ but is yet to be explored systematically.¹² It could well be, for example, that the role of added alcohol (or salt) is to “biaxialize” rod-like aggregates rather than to “stretch” them (see above). Still more importantly, it is necessary to understand the relative stability of “smectic” (e.g. hexagonal) phases vs. the nematic and isotropic states discussed in the present communication. As already mentioned, the addition of cosurfactant often

enhances the presence of a partially-orientationally-ordered, finite-aggregate intermediate. Is this because the additive serves to "push back" the hexagonal phase via intermicellar interactions in the "smectic?" Or is the otherwise-"buried" nematic "unearthed" simply by the size-alignment coupling outlined in section IV? These questions need to be pursued within the context of a single theory which includes simultaneously both finite *and* unbounded rod-like aggregates with accompanying partial *and* saturated orientational ordering.

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