

Effects of Interaggregate Forces on Micellar Size in Isotropic and Aligned Phases.

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1. - Introduction.

Colloidal suspensions of rodlike particles have been studied for many years. On the one hand, they provide important examples of « real » (vs. « ideal ») solution behavior, with the rich literature on virial coefficients and equations of state being applied to account for osmotic pressures and other thermodynamic properties [1]. On the other hand, the transition from *isotropic* to long-range-orientational-order (LRO) *nematic* states of these suspensions has been treated explicitly in terms of the anisotropic interactions between particles [2]. At the same time a great deal of effort has been devoted to the special case of colloidal solutions whose « particles » consist of *aggregates* (micelles) of amphiphilic molecules [3]. Here, unlike the case of rigid macromolecules or metallic grains, the solute species do not maintain their integrity. Instead they vary their size and shape upon changes in temperature or concentration. As a result, the usual statistical mechanical prescription—proceeding from a fixed interparticle potential to a calculation of bulk properties—is not applicable. Rather, because the interaction forces change with thermodynamic state, there is a coupling between single- and many-micelle organization. This phenomenon is the subject of the present lecture; to our knowledge it has not yet been treated within the context of the isotropic and nematic phases of soap solutions.

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To introduce the basic concepts and notation, and to emphasize from the outset the fundamental sense in which micellized systems differ from « ordinary » colloidal suspensions, we begin with a brief statement of the relevant ideal solution theory. For rodlike aggregates, say, we write

$$(1) \quad \tilde{\mu}_s = \tilde{\mu}_{\text{cyl}}^0 + \frac{1}{s} \delta_{\text{rod}} + \frac{1}{s} \ln \frac{X_s}{s}$$

for the chemical potential per soap molecule in a micelle of size s [4]. $\tilde{\mu}_{\text{cyl}}^0$ is the chemical potential of an amphiphile in the cylindrical « body » of the rodlike aggregate (assumed to be spherocylindrical). $\delta_{\text{rod}} \equiv m(\tilde{\mu}_{\text{sph}}^0 - \tilde{\mu}_{\text{cyl}}^0)$, where $\tilde{\mu}_{\text{sph}}^0$ is the chemical potential in the (half-) spherical « caps » which contain $m = 4\pi l^3/3v_1$ of the s molecules; l is the radius of both the cylindrical and spherical portions, and v_1 is the volume of a single amphiphilic chain (« tail »). The first two terms in (1) comprise the *standard*, or single-micelle, free-energy contribution. The third term adds the translational entropy associated with *mixing* the aggregates: X_s is the mole fraction of soap molecules incorporated into s -aggregates. (The $1/s$ factor derives from our looking at chemical potentials *per amphiphile*, and the usual kT factor is dropped since we measure all energies in units of kT .) Writing

$$(2) \quad \tilde{\mu}_1 = \tilde{\mu}_1^0 + \ln X_1$$

for the monomer, and imposing the molecular exchange (« chemical ») equilibrium condition

$$(3) \quad \tilde{\mu}_s = \tilde{\mu}_1, \quad \text{all } s,$$

one obtains immediately the size distribution

$$(4) \quad \frac{X_s}{s} = (X_1 \exp[\tilde{\mu}_1^0 - \tilde{\mu}_{\text{cyl}}^0])^s \exp[-\delta_{\text{rod}}].$$

Furthermore, it is straightforward to show that the critical micelle concentration X_{CMC} is well approximated by $[\exp[\tilde{\mu}_1^0 - \tilde{\mu}_{\text{cyl}}^0]]^{-1}$ —consistent with $\tilde{\mu}_1^0 - \tilde{\mu}_{\text{cyl}}^0$ being the driving force for micellization—and that

$$(5) \quad \frac{\sum_s s X_s}{\sum_s X_s} \equiv \bar{s}_{\text{weight}} \simeq (X \exp[\delta_{\text{rod}}])^{\frac{1}{2}}.$$

(Here $X \equiv \sum_s X_s$ is the total mole fraction of soap.)

Note from (5) that the average aggregation size increases strongly with δ_{rod} , as can be understood qualitatively from the following argument. Rodlike aggregates will not « grow » from the (minimum-micelle) spheres unless the

amphiphilic species prefer cylindrical rather than spherical geometry for their packing [4]: we must have $\delta_{\text{rod}} \sim \tilde{\mu}_{\text{cap}}^0 - \tilde{\mu}_{\text{cyl}}^0 > 0$. The larger the value of δ_{rod} , the more the average free energy per molecule is lowered by increasing the micellar size, *i.e.* by minimizing the importance of the « cap » contributions ($m/s \rightarrow 0$). Note further that \bar{s} increases also with total concentration X . This is because, for higher mole fractions of soap, the entropy of mixing $(1/s) \ln (X_s/s)$ becomes relatively less important. And it is this term which « puts the brakes » on the micellar growth induced by $(1/s) \delta_{\text{rod}}$ —bigger aggregates imply fewer ones, and hence less entropy of mixing.

The above « picture » has been pioneered by many groups of investigators over the past decade, notably by TANFORD [4a] and by ISRAELACHVILI [4b], who are both lecturing at this School. We shall be focussing instead on a different aspect of these isotropic suspensions of micelles, namely the extent to which they cease to behave as ideal solutions. In sect. 2, then, we outline a simple treatment of the effect of interaction between aggregates on their equilibrium size distribution. To illustrate the basic idea we start with the dilute-solution case in which second-virial corrections to ideal solution behavior are dominant. Via simple scaling arguments, based on the one- and two-dimensional character of rodlike and disklike growth, we shall show that micellar size is enhanced by interaction for both shapes of aggregates. This conclusion is then generalized to arbitrarily high concentrations by summing the virial-series corrections to all orders. Finally, in sect. 3 we consider the special nature of the isotropic to nematic phase transition in these micellized solutions. Again the key point is that—unlike in « ordinary » colloidal suspensions—the interacting particles do not maintain their integrity. Instead, with the onset of long-range orientational order the rodlike aggregates must be expected to grow beyond what would obtain for their isotropic state at the same concentration; in turn, this increase in axial ratio leads to an enhancement of the nematic alignment. This coupling must, of course, be treated self-consistently and thereby requires a theory which is more general than those developed to describe ordinary thermo- and lyo-tropic liquid crystals [5]. In particular, we need to allow explicitly for the possibility that the aligned rods can grow *without bound*, *i.e.* can form a *hexagonal* (rather than nematic) phase. As an introduction to this problem we present first a simple phenomenological analysis (subsect. 3'1) and then an outline of further work which is in progress.

2. — Excluded-volume effects in isotropic solutions.

2'1. *Second-virial contributions.* — Consider the following generalization of eq. (1):

$$(6) \quad \tilde{\mu}_s = \tilde{\mu}_{\text{body}} + \frac{1}{s^2} \delta + \frac{1}{s} \ln \frac{X_s}{s} + \chi_s.$$

Here $p = 1$ for rods and $p = \frac{1}{2}$ (asymptotically, $s \rightarrow \infty$) for disks [4]. χ_s is the correction arising from the free energy of intermicelle interactions; in the second-virial approximation, and in the case where excluded-volume forces are dominant, it has the form

$$(7) \quad \chi_s = \frac{1}{s} \varrho \sum_r v_{sr} \frac{X_r}{r}.$$

ϱ is the total (water + soap) number density, and v_{sr} is the pair excluded volume associated with a s - and a r -aggregate. For both rodlike and disklike micelles v_{sr} is known explicitly as a function of s and r (and of the geometric parameters l and v_1). In this way it can be shown [6] that χ_s decreases with s according to

$$(8) \quad \chi_s \simeq \chi_0 + \frac{1}{s^2} \chi,$$

with again $p = 1$ and $p \simeq \frac{1}{2}$ for rods and disks, respectively.

This result can also be obtained from an elementary dimensional analysis. Recall that for hard-core steric forces, which serve simply to distinguish between unallowed configurations and those with zero energy, the χ_s correction consists wholly of « packing entropy », S_{packing} , which in turn is proportional to the total available volume, $V - V^{\text{excluded}}$:

$$(9) \quad \begin{aligned} \chi_s &\sim -S_{\text{packing}} \sim V^{\text{excluded}} \sim \\ &\sim (\text{no. of pairs}) v_{\text{pair}}, \end{aligned}$$

the last line following from the second-virial approximation. Consider first the case of large disks of diameter D . We know that the leading term in $v_{\text{pair}}^{\text{disk}}$, i.e. the highest order in D/l (where l is both the half-thickness of the « bilayer » body and the radius of the half-toroidal « rim »), involves D to the third power. Since $D \sim s^{\frac{1}{2}}$ for large s (the body area goes as the aggregation number, s), we have $v_{\text{pair}}^{\text{disk}} = \mathcal{O}(s^{\frac{3}{2}})$. With no. of pairs $\sim 1/s^2$ it follows from (9) that χ_s^{disk} decreases as $1/s^{\frac{1}{2}}$. For large rods of length L , on the other hand, $v_{\text{pair}}^{\text{rod}}$ has highest-order terms in L/l which vary as L^2 and L . Furthermore, from the one-dimensional nature of the growth involved here (as opposed to 2-D in the disk case), $L \sim s$, implying immediately that χ_s^{rod} has the form (8) with $p = 1$.

Combining (8) with (6), we see that the intramicellar « growth » parameter δ is enhanced additively by the interaction excluded-volume coefficient χ . Inspection of (5) with $\delta \rightarrow \delta + \chi$ (> 0) suggests that the average aggregation size is increased by intermicellar interactions. That is, for any given amount (X) of soap, the packing entropy (interaction free energy) is maximized (minimized) by a reorganization into a smaller number of larger aggregates. And, of course, the relative importance of the χ contributions (compared to δ)

increases monotonically with overall concentration. These qualitative considerations are born out by a more detailed analysis [6] in which eqs. (6) and (7) are treated explicitly within the context of the chemical-equilibrium condition (3).

2'2. *Higher-order terms.* — Note from the above discussion that the average micellar size is increased approximately by a factor of $(\exp [\chi])^{\frac{1}{2}}$. Furthermore, within the same second-virial (pair) approximation, it is easy to show that $\chi = \mathcal{O}(\varphi)$, where $\varphi \equiv \varrho v_1 X$ is the volume fraction of soap. Accordingly, for volume fractions up to a few percent—above which higher-order virial corrections become important—it follows that average aggregation numbers are enhanced by at most a few percent over what would obtain in the absence of intermicellar interaction effects. To describe the real solution behavior through arbitrarily high concentrations (*i.e.* φ no longer much less than unity), then, it becomes necessary to avoid the virial expansion, or—equivalently—to sum it to all orders.

In our earlier work on thermotropic liquid crystals [5] we were led naturally to develop hard-particle equations of state whose validity extended over the full liquid range and reasonable values of axial ratios for both rods and disks. Our approach [7] is based on obtaining systematically better infinite-order resummations of the virial series by considering successively higher-order truncations of an expansion in (not the volume fraction φ but) the new variable $y \equiv \varphi/(1 - \varphi)$. More explicitly, for the one-component case appropriate to a polydisperse solution of micelles, we write $y_s = (\varrho/(1 - \varphi))(X_s/s)$ for X_s/s in (6) and represent χ_s as a power series in the $\{y_s\}$, retaining all terms up to $\mathcal{O}(y^3)$. This level of truncation had been shown by previous theory [7] to give pressure equations of state for *monodisperse* hard particles which are accurate to within a few percent. In the case of spheres, for example, this approximation yields exactly the same result as that obtained from analytic solutions to the Percus-Yevick [8] and scaled-particle [9] theories; for *anisotropic shapes* (*e.g.* « dumbbells », fused spheres, spherocylinders ...) it agrees closely with Monte Carlo simulations.

With the resummation of the virial series sketched above—see ref. [6b, 7]— χ_s still has the form $\chi_0 + (1/s)\chi$ (we confine our discussion to rods again), even though each of the coefficients is now a complicated function of v_1 , l and the three moments $\nu \equiv \sum_r y_r$, $\bar{r} \equiv (1/\nu) \sum_r r y_r$ ($\equiv \bar{s}_{\text{number}}$) and $\bar{r}^2 \equiv (1/\nu) \sum_r r^2 y_r$ ($\equiv \bar{s}_{\text{number}}/\bar{s}_{\text{weight}}$). These latter three quantities, and hence the micellar-size distribution, are then determined from the chemical-equilibrium condition (3) and the fixed (arbitrary) mole fraction X . Typical results for \bar{s}_{weight} vs. X are shown in fig. 1, where we have taken $v_1 = 360 \text{ \AA}^3$, $l = 12 \text{ \AA}$, $\tilde{\mu}_1^0 = 15(kT)$, $\tilde{\mu}_{\text{cy1}}^0 = 5.5$ and $\delta_{\text{rod}} = 13.2$ [6b]. The solid curve includes the effects of excluded-volume interactions as described above, while the dashed curve neglects them completely. Note that the CMC for this system ($X_{\text{CMC}} \simeq 8 \cdot 10^{-5}$) corresponds to zero on

the scale of this figure and that intermicellar interaction effects only begin to be significant a couple of decades of concentration higher than this ($X \geq 8 \cdot 10^{-3}$). This vindicates the analyses of light scattering experiments which are confined to $X/X_{\text{CMC}} < 100$ and in which intermicellar effects on size are not considered; these studies have been discussed in detail by MAZER and BENEDEK [10] and CORTI and DEGIORGIO [11] and will be presented by them at the present School.

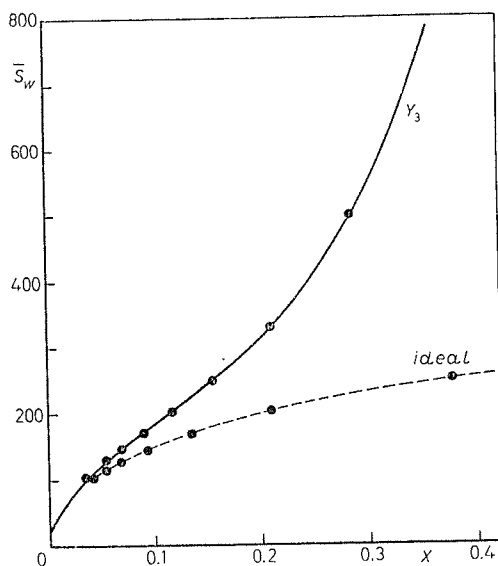


Fig. 1. — We plot here the weight-average aggregation number (\bar{s}_w) vs. total mole fraction (X) of soap. The dashed curve shows the behavior for an ideal solution of micelles, whereas the solid curve includes effects of excluded-volume interactions through third order in the γ -expansion.

For higher concentrations, on the other hand, it is clear from fig. 1 that the effect of intermicellar interactions on average aggregation number can no longer be neglected. At $X \approx 0.035$, for example, corresponding to a volume fraction of $\approx 30\%$, \bar{s}_{weight} is enhanced by as much as a factor of three. It is also precisely in this concentration range that one observes a transition from isotropic to nematic states of the micellized solution [12]. One must expect, then, an additional increase in aggregate size due to the onset of long-range orientational order. First there will be a fractionation effect, such as that observed in polydisperse suspensions of *rigid* rods [13], arising from the preference of the longer rods to go into the nematic phase. Second, because the micelles do not maintain their integrity, we should see also a *real* growth effect associated with the coupling between self-assembly and alignment. As this phenomenon has not yet been treated in the theoretical literature, we devote the remainder of our present discussion to it.

3. - Growth-alignment coupling in the nematic state.

3'1. *Phenomenological analysis.* - Consider again the chemical potential per soap molecule, now generalized to include the possibility of long-range orientational ordering (LROO):

$$(10) \quad \tilde{\mu}_s = \tilde{\mu}_{sv1}^0 + \frac{1}{s} \delta_{rod} + \frac{1}{s} \ln \frac{X_s}{s} + \chi_s + \frac{1}{s} \sigma_s.$$

Here $\sigma_s \equiv \int d\Omega f_s(\Omega) \ln 4\pi f_s(\Omega)$ is the loss of orientational entropy associated with ordering the s -micelles according to the distribution $f_s(\Omega)$; $f_s(\Omega)$ is the fraction of s -aggregates having orientation Ω . Similarly, the interaction term χ_s now involves an average of the angle-dependent pair excluded volume over both $f_s(\Omega)$ and $f_r(\Omega)$: $s\chi_s \approx \varrho \sum_r \int d\Omega \int d\Omega' v_{sr}(\Omega, \Omega') f_s(\Omega) f_r(\Omega') (X_r/r)$. For purposes of illustration it is convenient here to take the Onsager form [2] for the orientational distribution, *i.e.* $f_s(\Omega) \sim \cosh(\alpha_s \cos \theta)$, where α is related to the usual « P_2 »-order parameter via $\eta \simeq 1 - 3/\alpha$. Furthermore, we temporarily suppress all details of polydispersity and put $X_s = X \delta_{s\bar{s}}$. Finally, recalling the form $\chi_0 + (1/s)\chi$ for χ_s , and neglecting the explicit dependence of χ_s and σ_s on s (*i.e.* allowing only for their variations with α_s), we write

$$(11) \quad \tilde{\mu}(\bar{s}, \alpha) \approx \tilde{\mu}_{sv1}^0 + \chi_0(\alpha) + \frac{1}{\bar{s}} \left[\delta_{rod} + \ln \frac{X}{\bar{s}} + \chi(\alpha) + \sigma(\alpha) \right].$$

We can then use the definitions of σ_s and χ_s given above, in conjunction with $f_s \sim \cosh(\alpha \cos \theta)$, to show that [2]

$$(11a) \quad \sigma \simeq \ln \alpha - 1 \quad \text{and} \quad \left. \begin{array}{l} \chi_0 \\ \chi \end{array} \right\} \simeq \begin{cases} 2 \frac{\varphi}{\sqrt{\alpha}} \\ \varphi \end{cases}$$

in the nematic ($\alpha \gg 1$) phase; otherwise ($\alpha = 0$), $\sigma = 0$ and χ_0 and χ are *both* $\approx \varphi$.

Equations (11), (11a) provide a free energy per molecule which can be minimized with respect to the «order parameters» \bar{s} (size) and α (alignment). That is, we solve simultaneously

$$(12) \quad \frac{\partial \tilde{\mu}}{\partial \bar{s}} = 0 \quad \text{and} \quad \frac{\partial \tilde{\mu}}{\partial \alpha} = 0.$$

Consider first the isotropic (I) solution according to which $\alpha \equiv 0$, *i.e.* $f_s(\cos \theta) = 1/4\pi$ and $\sigma \equiv 0$. Here the $\partial \tilde{\mu} / \partial \alpha \leq 0$ condition never arises, leaving $\tilde{\mu}(\bar{s}, \alpha \equiv 0)$ to take on its minimum ($\partial^2 \tilde{\mu} / \partial \bar{s}^2 > 0$) for

$$(13) \quad \bar{s} = X \exp[\delta + 1] \exp[\varphi].$$

Thus, consistent with the more honest (« chemical equilibrium ») analysis described earlier, the average size of aggregates in the isotropic solution is seen to increase (linearly rather than via the $\frac{1}{2}$ power) with overall mole fraction, X , and exponentially with the intramicellar chemical-potential difference, $\delta \equiv m(\bar{\mu}_{\text{cap}} - \bar{\mu}_{\text{cyl}})$. Further, the multiplicative factor $\exp[\varphi]$ includes the enhancement of rod growth due to excluded-volume interactions.

If now we look for a nematic (N)—*i.e.* nonzero, but finite, α and \bar{s} —solution to eqs. (12), we only find one which corresponds to an *unstable* state. There *does* exist a *minimum* extremum associated with an anisotropic solution to (12)—namely at \bar{s} , $\alpha = \infty$, ∞ —but this describes the infinite-rod, perfectly aligned, *hexagonal* (H) phase (which can be shown to give a lower value of $\bar{\mu}$ than the isotropic (I) solution as soon as the concentration becomes high enough). It appears that *the coupling between rod growth and orientational ordering is so strong that a (finite \bar{s} and α) nematic phase of micelles cannot be stabilized: the I→H transition occurs directly*. As stressed earlier, there exists no analogue to this phenomenon in suspensions of *real* particles, *i.e.* ones which maintain their integrity upon changes in concentration.

To understand phenomenologically the « explosion » from small rods to infinite cylinders upon the onset of nematic order, it is sufficient to introduce s -dependence into the chemical-potential difference δ . In this way we can allow for « negative feedback » in the coupling between the growth and alignment of micelles. Since $s \gg 1$, it is natural to expand δ in powers of $1/s$ and to keep only the lowest-order term:

$$(14) \quad \delta_{\text{rod}} \rightarrow \delta(\bar{s}) \simeq \delta_1 + \frac{1}{s} \delta_2.$$

(The s^{-1} decrease of δ with s means that, as the rod gets bigger, it has less « push » to grow further!) $\bar{\mu}(\bar{s}, \alpha)$ still has I and H solutions which are qualitatively similar to those in the $\delta_2 = 0$ case, but now a new nematic solution appears which does indeed correspond to a *minimum* value of $\bar{\mu}$. This solution has the property that \bar{s} increases with φ throughout the range where the nematic is more stable than the hexagonal phase, taking on a maximum value of δ_2 at the transition; α goes as $\varphi^2 \bar{s}^2$. Thus we have the sequence I → N → H upon raising the concentration ($\varphi \simeq \rho v_1 X$). For $\delta_1, \delta_2 = 1, 50$, for example (and $\rho v_1 \approx \rho_{\text{water}} v_{\text{ads}} \approx 10$), the two successive phase transitions occur at $\varphi \simeq 0.15$ and 0.20, respectively.

3'2. Microscopic considerations. — In the above we have introduced a « negative feedback » which « tames » the coupling between the growth and alignment of prolate aggregates. We have done so phenomenologically by allowing the chemical-potential difference between « cap » and « body » to decrease with size, thereby stabilizing the nematic phase against « explosion »

into the hexagonal. These effects of intermicellar forces on average aggregation number are dramatically more important than those discussed earlier (sect. 2) for the isotropic phases. It remains then to offer some comments on the more microscopic considerations underlying our treatment of the long-range orientational ordering.

First we mention that the form (14) for $\delta(s)$ can be derived from a specific model for the partitioning of cosurfactant (*e.g.* alcohol) between « cap » and « body » environments, namely one in which the cosurfactant is assumed to interpose itself between ionic soap molecules and to dilute thereby the surface charge density. This picture provides the order-of-magnitude estimates for δ_1 and δ_2 quoted above. A similar analysis of the « partitioning » of added salt should also be explored, since nematic phases are known to be stabilized (over hexagonal) states upon the addition of electrolyte as well as cosurfactant. But binary (*i.e.* « just » surfactant and water) systems are also believed to show finite-rod nematic phases. Preliminary calculations suggest that free-energy contributions from overall rotation and translation of individual micelles are sufficient to stabilize nematic states in these cases.

Second we note that the treatment of LROO in sect. 3 suppressed the explicit role of molecular exchange (« chemical ») equilibrium, replacing intrinsic polydispersity by an effective size; we also neglected the concentration differences between coexisting phases. By returning to the analyses of sect. 2, but including the new free-energy contributions arising from nematic order, it will be possible to pursue a more complete description of the $I \rightarrow N \rightarrow H$ transitions and of the changes in aggregation numbers as we move along different paths in soap/water/alcohol (or salt) phase diagrams. By determining the size distributions in each of the coexisting solutions, for example, we can obtain the relative sizes and polydispersities as functions of the self-assembly parameters δ_1 , δ_2 , $\bar{\mu}_1^0$, $\bar{\mu}_{cap}^0$ and $\bar{\mu}_{cy1}^0$. Recall that for polydisperse *rigid* rods the increase in \bar{s} corresponds only to an *apparent* growth, *i.e.* to the preferential partitioning of the longer rods into the nematic phase. In the micellized soap solution case, however, this fractionation effect is enhanced by a *real* growth of *all* the rods.

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