# ON THE THEORY OF MICELLAR SIZE IN

# ISOTROPIC AND NEMATIC SURFACTANT SOLUTIONS

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In this paper we outline a simple statistical thermo-
dynamic treatment of those portions of amphiphilic-solution
phase diagrams which involve finite aggregates, i.e. iso-
tropic phases of micelles of all shapes and sizes, and
orientationally-aligned (nematic) states of rods and disks.
In accounting for the equilibrium distribution of sizes we
focus on several aspects of surfactant self-association
which have not been treated in previous theories.

   (i)   In the dilute-solution limit, the suspension of
micelles behaves like an ideal gas of molecules and hence
can include translational and rotational contributions as
well as the usual entropy of mixing.  These "new" terms can
be shown to favor smaller aggregates (via decreased mass and
moments of inertia).

   (ii)   At higher concentrations the solution no longer
behaves ideally, i.e. forces between the aggregates begin to
significantly affect the system free energy.  In the parti-
cular case of excluded-volume interactions, it is possible
to show that these "activity" corrections can enchance
micellar size by easily-observable factors.

   (iii)   Upon the onset of long-range orientational order
there is a coupling between growth and alignment of aniso-
tropic aggregates which results again in bigger micelles.
This coupling quickly becomes so strong, in fact, that the
namatic phases can be unstable against "explosion" into
hexagonal and lamellar states.

## INTRODUCTION

   In this paper we want to develop a brief outline of the major
factors which determine the size and shape of micellar aggregates in
simple surfactant solutions.  In doing so we shall assume that the
reader is familiar with the basic background literature on self-
assembly in amphiphilic systems, such as is presented by Tanford[1] in
his recent monograph and by Israelachvili et al[2] in their series of

review articles. Our emphasis will be on rod-like (prolate) aggregates, although mention will be made of other micellar symmetries as well. Details of the relevant theoretical calculations have been or will be published elsewhere: here we concentrate instead on collecting the key mechanisms for aggregate growth and on providing simple physical interpretations for them.

Sections 1 and 2 describe the free-energy contributions arising from "mixing entropy" and local geometry effects associated with different environments in a single micelle. These ingredients are already well-known and suffice to account for the existence of stable but polydisperse rod-like aggregates in dilute solution. Section 3 presents a "new" contribution, arising directly from the translational and rotational degrees of freedom corresponding to the overall micelle being treated as a rigid body. These terms are of course familiar from elementary statistical thermodynamics, and are treated here for the first time as a mechanism for controlling the growth of aggregates. In Section 4 we discuss real (vs. ideal) solution effects, i.e. the role of forces between micelles in determining their equilibrium size distribution. These interactions have been studied extensively within the context of interpreting light scattering and other transport and thermodynamic data, but not with an eye to the structure and stability of the aggregates themselves. Finally, in Section 5, we show how the alignment of micellar "rods" in nematic phases can further enhance their growth in concentrated solution.

1. Local Geometry ("Intra"-Micellar Effects)

The fundamental thermodynamic quantity of interest is the standard chemical potential per molecule, $\tilde{\mu}_N^\circ$, of an amphiphile in an aggregate of size N. With $\mu_N^\circ$ the standard chemical potential of a spherocylindrical ("rod-like") micelle containing N molecules, say, we can write

$$\tilde{\mu}_{N,rod}^\circ = \mu_N^\circ/N = (N_{cap}/N)\tilde{\mu}_{cap}^\circ + ((N-N_{cap})/N)\tilde{\mu}_{cyl}^\circ. \qquad (1)$$

Here it has been implicitly assumed that the micelle behaves like a macroscopic phase consisting of the two components "cap" and "cyl." That is, $\tilde{\mu}_N^\circ$ is simply a weighted average of $\tilde{\mu}_{cap}^\circ$ and $\tilde{\mu}_{cyl}^\circ$, the chemical potentials for amphiphiles in the (hemispherical) caps and (cylindrical) body respectively. $N_{cap}$ and $N-N_{cap}$ are the corresponding numbers of molecules in these two environments. Note that $N_{cap}$ is independent of N, being determined wholly by single-molecule geometry: $N_{cap} = 4\pi\ell^3/3\nu$ where $\ell$ and $\nu$ denote the length and volume of the (hydrophobic) "tail" of each amphiphile. A trivial rewriting of eq. (1) gives

$$\tilde{\mu}_{N,rod}^\circ = \tilde{\mu}_{cyl}^\circ + (1/N)\delta_{rod} \qquad (2)$$

where $\delta_{rod} = N_{cap} (\tilde{\mu}_{cap}^\circ - \tilde{\mu}_{cyl}^\circ)$ is the free energy "price" paid for keeping the cylinders finite, i.e. for capping the rods.

A similar analysis for disk-like aggregates leads to (for large N)

$$\tilde{\mu}_{N,disk}^\circ \cong \tilde{\mu}_{bil}^\circ + (1/N^{1/2})\delta_{disk}. \qquad (3)$$

Here the "bil" refers to the bilayer environment comprising the body of a disk. But now, unlike the rod case, the micelle is capped by a (hemi-toroidal) rim whose size ($N_{rim}$) is not independent of aggregation number N. More explicitly, instead of having $N_{cap}$ = constant ($=4\pi\ell^3/3\nu$) we have $N_{rim} = N_{rim}(N) \sim N^{1/2}$ for large N. That is, $\delta_{disk}$ in eq. (3) is a decreasing function of N which behaves as a constant only in the asymptotic limit of large ($N \to \infty$) micelles. Note that the

$1/N^{1/2}$ vs. $1/N$ fall-off of $\mu_N$ follows directly from the dimensionality of the problem, i.e. disks "grow" in two dimensions and rods only in one.

The fact that $\tilde{\mu}_N^{\circ}$, the chemical potential per molecule, decreases monotonically with N would seem to imply that the rod-and disk-like micellar aggregates should grow without bound. (Only in the case where $\tilde{\mu}_{sph}^{\circ} < \tilde{\mu}_{cyl}^{\circ}$, $\tilde{\mu}_{bil}^{\circ}$ would this not be true). But the zero superscript indicates that only the standard contribution to the chemical potential has been considered. One must add to this quantity the free-energy contribution associated with the ideal-solution mixing entropy: $\mu_N^{\circ} \rightarrow \mu_N^{\circ} + kT \ln\rho_N/\rho$. Here $\rho_N = \rho X_N/N$ is the number density of N-aggregates (with $\rho$ the total -- surfactant plus water -- number density and $X_N$ the mole fraction of surfactant molecules incorporated into micelles of size N).

## 2. "Mixing Entropy" Contribution

We now write $\mu_N$ as

$$\tilde{\mu}_N = \mu_N/N = \tilde{\mu}_N^{\circ} + (kT/N) \ln(X_N/N) \tag{4}$$

and consider the mechanism whereby the mixing entropy term serves to resist micellar growth, i.e. to offset the monotonic decrease of $\tilde{\mu}_N^{\circ}$ with N. Qualitatively it is clear that the mixing entropy term is optimized when the fixed amount ($X = \Sigma X_N$ = total mole fraction) of surfactant is organized into as many (hence, as small) aggregates as possible. Accordingly, this term favors minimum--spherical--micelles in contrast to $\tilde{\mu}_N^{\circ}$ which is optimized by growth in one- (rod) or two- (disk) dimensions. The compromise between these competing demands gives rise to a polydisperse distribution of aggregates in which at least one dimension exceeds the molecular length. This balance must be expected to depend on overall concentration X as well as on the intramicellar "growth" parameter $\delta$. Note that $\delta$ is generally on the order of tens of kT.

More explicity, for purpose of illustration, consider the case in which polydispersity is suppressed and we focus attention directly on the optimal size $\bar{N}$. That is, we put $X_N = X\delta_{N\bar{N}}$ and ask for the value of $\bar{N}$ which minimizes

$$\tilde{\mu}_{\bar{N}} = \tilde{\mu}_{\bar{N}}^{\circ} + (kT/\bar{N})\ln(X_{\bar{N}}/\bar{N}) = \tilde{\mu}_{cyl}^{\circ} + (1/\bar{N})((\delta+kT\ln X) - kT\ln\bar{N}). \tag{4'}$$

It is trivial to show that the $\bar{N}$ satisfying $\partial\mu_{\bar{N}}/\partial\bar{N} = 0$ is given by

$$\bar{N} = X\exp(\delta). \tag{5}$$

$\bar{N}$ increasing with X reflects the fact that the balance between $\tilde{\mu}_{\bar{N}}^{\circ}$ and $-(kT/\bar{N})\ln(\bar{N}/X)$ is being shifted increasingly towards larger $\bar{N}$ for bigger X. Equivalently, the loss of mixing entropy (associated with organization of surfactant into a smaller number of larger aggregates) becomes less important as the system becomes more concentrated. Similarly, $\bar{N}$ increases with $\delta$ because the intra micellar growth mechanism begins to dominate in this limit.

A full treatment of the equilibrium size distribution (polydispersity) shows the same effects of competition between the two terms in eq. (4). The simplest way to see this is by invoking the law of mass action appropriate to the set of "reactions" described by $NA_1 \rightleftharpoons A_N$. Here $A_N$ denotes an aggregate of size N. ($A_1$ corresponds to the monomer

[i.e. a single amphiphile in solution] and it is assumed that $N \geq N_{cap}$, the minimum micelle number.) "Chemical" equilibrium is then specified by $\mu_N = N\mu_1$ which -- in conjunction with eq. (4) -- leads directly to

$$X_N/N = X_1^N \exp(N(\mu_1^\bullet - \tilde{\mu}_N^\bullet)/kT).\qquad(6)$$

Recalling eq. (2) for $\tilde{\mu}_{N,rod}^\bullet$, say, we see immediately that the size distribution is completely determined by the two chemical potential differences $\Delta = (\mu_1^\bullet - \tilde{\mu}_{cyl}^\bullet)$ and $\delta = N_{cap}(\tilde{\mu}_{cap}^\bullet - \tilde{\mu}_{cyl}^\bullet)$. $\Delta$ is the free energy difference between an amphiphile in solution and one which is packed (optimally in the cylindrical body) in a micelle. This quantity is expected to determine the concentration at which aggregates become the dominant "home" for surfactant in solution: indeed it is easy to show that

$$X_{CMC} \cong \exp(-\Delta/kT).\qquad(7)$$

Similarly, $\delta$--the free-energy "price" paid for capping the rods-- is the controlling factor in shaping the equilibrium distribution. One finds, for example, that

$$\bar{N} = \sum NX_N / \sum X_N \sim (X\exp(\delta))^{1/2}\qquad(5')$$

as anticipated qualitatively by the crude argument leading to eq. (5).

The above results are well-known. There are in particular many studies of how a sphere "grows" into a rod upon increasing the overall concentration.[3] Similarly the sphere to disk transition has been extensively discussed[1,2], as well as the relative stability of prolate and oblate aggregates.[4] From this point on, then, we concentrate on free-energy contributions whose effects on micellar size distributions have not previously been treated.


3. Rotational and Translational Degrees of Freedom

Recall that $\mu_N^\bullet$ is the standard chemical potential of an N-aggregate, i.e. it is equal to $-kT \ln(q_N/v)$ where $q_N$ is the partition function of a micelle of size N. Treating the micelle as a finite rather than macroscopic system it is clear that--in addition to being a sum of cap (rim) and body $\tilde{\mu}^\circ$'s [see, for example, eq. (1) for rods]--$\mu_N^\bullet$ should include contributions from the overall translational and rotational degrees of freedom. In fact, the factor from integration over center-of-mass coordinates has been taken into account: it gives rise to the kT $\ln$ ($\rho_N/\rho$) term, the free energy of mixing. Integrations over center-of-mass momenta and overall rotational degrees of freedom result directly in additional terms of the form

$$\mu_N^\bullet = kT \ln(\Lambda^3 N\rho/q_{rot,N}).\qquad(8)$$

Here $\Lambda_N = (h^2/2\pi NmkT)^{1/2}$ is the usual thermal (de Broglie) wavelength associated with the N-aggregate (mass Nm), and $q_{rot,N}$ is its rotational (symmetric-top) partition function. Clearly $\Lambda_N \sim N^{-3/2}$, while for a rigid rod (vs. disk) it can be shown that $q_{rot,N} \sim N^{7/2}$. Thus we can write

$$\tilde{\mu}_N^\bullet = \mu_N^\bullet/N = (-(\delta^+) - kT(3/2 + 7/2)\ln N)(1/N)\qquad(9)$$

the $\delta^+$ term arising from the multiplicative constants in the argument of the logarithm in eq. (8).


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Eqs. (8) and (9) follow from treating the micellar aggregate as a quantum mechanical "chunk" of solid. If, on the other hand, the center-of-mass motion of the individual molecules is described classically, the translational momenta do not contribute. Even in this case, however, one is left with $(\ln N)(1/N)$ terms in $\overset{\sim}{\mu}_N$--from$(\ln q_{rot})(1/N)$ --which add to the $\overset{\sim\bullet}{\mu}_N$ discussed earlier. (Their coefficients will be of order unity but not necessarily 7/2, say, as in eq. (9)). In general the question of how to best treat the translational and rotational contributions to $\mu_N$ is a highly complicated one which deserves further study in its own right. In this connection we mention that similar questions in the theory of nucleation clusters have still not been completely resolved.[5] We note also that the role of translational/ rotational degrees of freedom in determining CMC's has been treated several times in the past few decades.[6] Our discussion of these effects in the context of micellar growth, however, appears to be new.

It is clear from inspection of eq. (9) that these new con- tributions to $\overset{\sim}{\mu}_N$ will all serve to restrict the size of micellar aggregates. First, $\delta^+$ (which can be estimated to be of the order of 10 kT) enters with a minus sign, thereby offsetting partially the $+\delta$ $(1/N)$ term in $\overset{\sim\bullet}{\mu}_N$ -- see eq. (2). Second, the $(\ln N)1/N$ terms also enter with negative coefficients, further working against the decrease of $\overset{\sim\bullet}{\mu}_N$ with N. In fact, these latter terms can be thought of as enhancing directly the "braking" effect of the mixing entropy contributions discussed in the previous section. We showed in particular there that $X_N - X\delta_{N\overline{N}}$ gave rise to $+(kT \ln X)$ $(1/\overline{N}) - (kT [1] \ln \overline{N})$ $(1/\overline{N})$ terms in the mixing free energy and that this N-dependence accounted qualitatively for the existence of finite rods and for the variation of their size with concentration. Now we see that the "1" in square brackets is augmented by additive factors of 3/2 and 7/2 from the translational and rotational contributions.

Again, a full treatment of the equilibrium size distribution (polydispersity) confirms these simple predictions of the $X_N \cong X\delta_{N\overline{N}}$ model. More explicitly, allowing for the "chemical reaction" $(NA_1 \rightleftharpoons A_N)$ balance embodied by eq. (6), and adding the above-described $\overset{\sim}{\mu}_N$ terms to $\overset{\sim\bullet}{\mu}_N$ in the exponent, we have solved for the relative amounts of both rod and disk micelles of different sizes.[7] The rod-like aggre- gates are indeed found to be smaller and less broadly dispersed than predicted without the $\overset{\sim\bullet}{\mu}_N$ contributions. Also, the disks are seen to be more competitive in the intermediate concentration range where they appear. Furthermore, smaller (more realistic) values of the micellar interfacial tension suffice to account for the large rod-like aggre- gates which are believed to be present in dilute solution.

## 4. Inter-Aggregate Interaction Effects

Up until now we have assumed that the aqueous suspension of micelles is behaving ideally, i.e. forces between the aggregates make no contribution to the free energy of the system. Real solution (e.g. activity coefficient) effects have of course been extensively con- sidered throughout the recent history of colloidal suspension theories. In the case of micellar systems, however, we are confronted by a fundamental complication: the interacting particles are aggregates, and -- via molecular exchange $(NA_1 \rightleftharpoons A_N)$ -- do not maintain their integrity. Accordingly, interactions between the micelles give rise to a new size distribution and hence to new interactions.

To illustrate this point most simply it is useful to consider

interaggregate forces of the excluded-volume type. In this case the free-energy term which we add to $\tilde{\mu}_N$ is purely entropic, proportional to the number of ways of packing a $\{X_N/N\}$ - distribution of rod-like particles:

$$\tilde{\mu}_N = \tilde{\mu}_N^{\bullet} + (kT/N)\ln(X_N/N) + \tilde{\mu}_N^{\bullet\bullet} + (1/N)X_N \qquad (10)$$

with

$$\sum_N X_N(X_N/N) = -T(\text{packing entropy}). \qquad (11)$$

This interaction free energy is, in turn, proportional to the total excluded volume, $V^{ex}$. For a sufficiently dilute system, for which the second-virial approximation suffices to describe the effects of inter-action, $V^{ex}$ can be expressed as

$$V^{ex} = (\# \text{ of pairs})v^{ex} \qquad (12)$$

with $v^{ex}$ denoting the excluded volume associated with a pair of interacting micelles. (Here we again start by suppressing polydispersity via $X_N \cong X\delta_{N\bar{N}}$.) For large disks, for example, $v^{ex} \sim D^3$, where $D(\gg\ell)$ is their diameter. Recall that it is the area ($\sim D^2$) of the disks which varies linearly with aggregation number, thereby implying $D \sim N^{1/2}$. Furthermore, since ($\#$ of pairs) goes as $1/N^2$, it follows that

$$v^{ex}_{\text{disks}} (\sim X_N/N) \sim 1/N^{1/2}. \qquad (13)$$

Similarly, for large rods of length $L(\gg\ell)$ we have that the leading terms in $v^{ex}$ go as $L^2$ and $L$ -- with $L \sim N$, and recalling ($\#$ of pairs) $\sim 1/N^2$, this translates into a $1/N$ decrease for $V^{ex}$:

$$(X_N/N)_{\text{rod}} \sim 1/N \qquad (14)$$

Note that the N-dependence of the interaction contributions to $\tilde{\mu}_N$ are identical to those from $\tilde{\mu}_N^{\bullet}$ for both rods and disks. This again follows from dimensional considerations, as seen from the above scaling arguments ($D \sim N^{1/2}$, $L \sim N$) which can be regarded as being analogous to the ($N_{rim} N \sim N^{3/2}$ and $N_{cap} N \sim N$) asymptotics described earlier for the intra micellar case. It is clear from the monotonic decreases of $X_N/N$ with N that the interaction free energy is lowered by growth of the aggregates. Equivalently, the packing entropy--for a given mole fraction X--is maximized by reorganization of surfactant into bigger micelles: a small number of large rods takes up less room than a larger number of smaller ones (comprising the same volume fraction of amphiphilic material) and thereby can realize a lower interaction free energy.

The intermicellar growth mechanism described above becomes in-creasingly important at higher concentration. In this latter regime the virial contributions must be summed to all orders and are expected to affect significantly the average micellar size. Using techniques developed earlier[8] for hard particle equations of state appropriate to simple liquids (i.e. consisting of real rod-like particles rather than molecular aggregates), we have studied the effects of intermicellar interactions on equilibrium size distributions via systematically better, infinite-order resummations of the virial series. In particular we have used successively higher-order, finite truncations of expansions in powers of $y_N = \rho_N/(1-\phi)$ where $\phi = \rho vX$ is the (dimension-

less) volume fraction of surfactant: recall from Section 1 that $\rho_N = \rho\, X_N/N$ where $\rho$ is the total number density and $X_N$ is the mole fraction of amphiphile incorporated into N-aggregates. In this way we show that the intermicellar growth mechanism illustrated above at the second-virial level persists to all orders in the density.[9]

## 5. Growth-Alignment Coupling in Nematics

Reviewing the above discussion we have the following scenario. At sufficiently low concentrations -- indeed up to hundreds of times $X_{CMC}$ -- the micellar suspension behaves like an ideal solution of aggregates. If $\tilde{\mu}^{\circ}_{cyl} < \tilde{\mu}^{\circ}_{sph}$, for example, the micelles will undergo a sphere → cylinder transition, growing monotonically with concentration. The increase in size is driven by a shifting balance between the "push" from $\tilde{\mu}_N$ and the "pull" from $(kT/N)\ln(X_N/N)$. At higher concentrations the free energy contributions from <u>intermicellar</u> interactions become non-negligible and serve to enhance the growth of aggregates. Thus, with increasing mole fraction of surfactant, the micelles become both larger and more numerous, as is indeed observed experimentally[1,2,3]. Clearly there comes a point where there is no longer sufficient packing room for the rod-shaped aggregates. That is, they are forced to align -- long range orientational order (LROO) -- in order to keep out of one another's way at high volume fraction.

To treat this alignment effect it is most illustrative to employ the simple excluded volume picture suggested originally by Onsager in his theory of isotropic → nematic transitions in simple colloidal suspensions of rigid rod-like (macro-)molecules.[10] First we need to generalize the second-virial interaction term, $(1/N)_{X_N}$, to include the possibility of LROO. More explicitly, we replace the pair excluded volume $v_{NN'}$, in

$$X_N/N = (\rho/N)\sum_{N'} v^{ex}_{NN'} X_{N'}/N' \tag{15}$$

by

$$v^{ex}_{NN'} \longrightarrow \int d\Omega \int d\Omega' f_N(\Omega) f_{N'}(\Omega') v^{ex}_{NN'}(\Omega,\Omega') \tag{15A}$$

where $f_N(\Omega)$ is the fraction of N-aggregates having orientation $\Omega$ and $v_{NN'}(\Omega,\Omega')$ is the excluded volume associated with a pair of N- and N'-rods having orientations $\Omega$ and $\Omega'$. We also need to add a new term $\sigma_N$ to $\tilde{\mu}_N$ which represents the loss of orientational entropy (per amphiphile) attendant upon the alignment of an N-aggregate:

$$\sigma_N = (1/N))\int d\Omega f_N(\Omega)\ln 4\pi f_N(\Omega). \tag{16}$$

Note that $\sigma_N = 0$ for $f_N(\Omega) = 1/4\pi$, i.e. there is <u>no</u> loss of orientational entropy in the isotropic phase (for which all $\Omega$ are equally likely).

The N-dependence of $(1/N)_{X_N}$ can be easily evaluated in the case of sufficiently long rods. In this limit the pair excluded volume can be approximated by[10]

$$v^{ex}_{NN'} \cong L\, L'\, \ell\, \sin\gamma(\Omega,\Omega') \tag{17}$$

where $\gamma(\Omega,\Omega')$ is the angle between directions $\Omega$ and $\Omega'$ and the

alignment is sufficiently strong to express all free energies as asymptotic expansions in an inverse LROO parameter ($\alpha_N$, say). More explicitly we can choose

$$f_N(\Omega) \sim \cosh(\alpha_N \cos\vartheta) \tag{18}$$

where $\sigma$ denotes the polar angle between the rod axis and a space-fixed direction. (This choice for $f$ has the right form and symmetry for an orientational distribution function and will not qualitatively affect any of our conclusions.) It is then straightforward to show that

$$X_N/N \simeq X_0 + (1/N)\chi \tag{19}$$

with $\chi \simeq \phi$ in both isotropic ($\alpha = 0$) and nematic ($\alpha \gg 1$) phases and

$$X_0 \sim \begin{cases} \phi, & \text{isotropic} \\ \phi/\alpha^{1/2}, & \text{nematic} \end{cases} \tag{19A}$$

Thus the isotropic-phase form for $(1/N)X_N$--see previous section-- perseveres into the nematic state: the <u>intramicellar growth co-efficient $\delta$ is enhanced additively by an interaction contribution</u> which grows with concentration (volume fraction $\phi$).

Similarly, with the choice of $f$ given by eq. (18) we can write

$$\sigma_N \simeq (\ln\alpha)/N \tag{20}$$

for $\alpha \gg 1$. Note that both here and in eqs. (19, 19A) we have suppressed the explicit dependence of the LROO parameter $\alpha$ on N. The key point is that the orientational entropy loss $\sigma_N$ decreases with N for large N. From the equilibrium condition $\partial\tilde{\mu}_N/\partial\alpha = 0$, for example, we find that $m^2\alpha = N^2\phi^2$ in the nematic state. Thus $\ln\alpha \approx \ln N$ and

$$\sigma_N \simeq (\ln N)/N \tag{20A}$$

i.e. the $\sigma_N$ term in the free-energy $\tilde{\mu}_N$ is lowered by a reorganization of the system (at fixed $\phi = \rho\nu x$) into a smaller number of larger aggregates. In other words, the micellized solution conspires to align as few rods as possible. This coupling between size and LROO, of course, is not possible in "ordinary" suspensions whose anisotropic particles are constrained to maintain their integrity.

Once again, a full treatment[11] of the polydisperse size distribution including properly all of the exchange equilibria ($NA_1 \rightleftharpoons A_N$) leads to the same conclusion. The average size of micelles in a nematic phase is significantly larger than that in the isotropic phases with which it coexists. This is because of at least three reasons: (1) the overall concentration (X) is higher in the nematic, (2) the longer rods partition preferentially into the LROO phase, and (3) micellar rods tend to grow as a response to being aligned. It is this last reason which is phenomenologically new and which is unique to liquid crystallinity in surfactant systems.

## 6. Summary

We have discussed above the several physical considerations ("mechanisms") which control the size of micellar aggregates in aqueous solution. Clearly, much work remains to be done. In particular, the contributions of <u>flexibility</u>[12] and <u>biaxiality</u>[13] must be included in treatments of the <u>intramicellar</u> free energies. Similarly, intermicell-

ar interactions involving <u>dispersional</u> (attractive) and <u>electrostatic</u>[14] (repulsive) forces need to be considered. Also, it will be important to provide a theoretical framework for understanding the role of additives such as cosurfactants, alcohols and salts in determining the preferred shapes and sizes of micellar aggregates. Finally, all of these treatments must be extended to include the more highly-ordered, liquid-crystalline states such as the hexagonal (infinite-cylinder) and lamellar (∞-disk) phases. It is well-known that experimental determinations of micellar shapes and sizes are fraught with fundamental difficulties, again because the aggregates do not maintain their integrity as one passes from one thermodynamic state to the next. However, it is hoped that theoretical analyses of the type described here will encourage further measurements.

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