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# Micellar Growth Due to Interaggregate Interactions

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In a recent Letter we sketched a theory which takes into account the leading, second-virial corrections to ideal solution behavior in micellar suspensions. Allowing for excluded volume interactions between aggregates, we showed how the chemical potential of a soap molecule is modified by intermicellar packing entropy and how this can lead to enhancement of average size. In the present communication we generalize this idea to (arbitrarily) high concentrations and provide numerical estimates for the case of spherocylindrical rods. For overall soap concentrations more than two orders of magnitude above the cmc, the average aggregation number is shown to be significantly increased by intermicelle interactions of the excluded-volume type.

## I. Introduction

Micellization phenomena in dilute soap solutions have attracted renewed interest in recent years.[1] Apart from differences in detail, most workers agree on the nature of the microphase separation which occurs at the "critical micelle concentration" (cmc). The aggregates initially formed are spherical, often "growing" into rods and/or disks as the overall concentration of soap molecules is increased further. Controversy remains as to whether the "natural" shape is prolate,[2] or oblate,[3] or both.[4] But common to all thermodynamic analyses is the supposition that the suspension of micelles behaves as an ideal solution.[5]

In a recent Letter[6] we suggested the importance of taking into account the leading corrections to ideal solution behavior. We introduced there the notion of intermicellar contributions to the chemical potential of an aggregate and discussed the effects of these terms on the size distributions of *large* rods and disks. In the present paper, we provide a more quantitative study of these effects, applicable to *arbitrary* size and concentration of micelles. We find that, at overall concentrations more than two orders of magnitude higher than the cmc, average aggregation numbers are significantly enhanced by *inter*micelle forces of the excluded volume type: the interaction free energy (packing entropy) is minimized (maximized) by reorganization of the soap molecules into a smaller number of larger aggregates.

To illustrate this point most simply we outline in section II the elementary ideas involved in treating the leading, second-virial corrections to ideal solution behavior in micellar suspensions. Generalization to higher concentrations and numerical estimates are presented in sections III and IV, respectively, for the case of rodlike aggregates interacting via excluded volume forces. We discuss these results in the context of our earlier phenomenological arguments, recent experiments, and possibilities for further theoretical study.

## II. Excluded Volume Analysis: Low Concentration

For a rodlike micelle (e.g., right-circular cylinder plus half-spherical caps) containing $s$ molecules we write (in units of $kT$)

$$\tilde{\mu}_s = \tilde{\mu}_\infty{}^0 + \frac{1}{s}\alpha + \frac{1}{s}\ln\frac{\rho_s}{\rho_0} + \chi_s \tag{1}$$

for the chemical potential per surfactant. The first two terms comprise the *standard* chemical potential[7] contributions: $\tilde{\mu}^0{}_\infty$ is the free energy of an amphiphile in the cylindrical part of the aggregate, and $\alpha$ is proportional (via $m$) to the difference between $\tilde{\mu}_\infty{}^0$ and the chemical potential of a molecule in the spherical caps. $s$ is assumed to exceed $m = 4\pi l^3/3v_1$, the aggregation number of a spherical ("minimum") micelle of radius $l$; $v_1$ is the volume of a single molecule. The third term in (1) describes the ideal solution "entropy of mixing": $\rho_s = \rho X_s(1/s)$, where $X_s$ is the fraction of soap molecules incorporated into $s$ aggregates and $\rho$ ($\rho_0$) is the total (water) number density ($\rho \lesssim \rho_0$ for dilute solutions). Finally, $\chi_s$ includes the corrections to ideal solution behavior arising from intermicelle forces.

In the second-virial approximation, and allowing only for steric ("hard-core") interactions, we have[6]

$$\chi_s \simeq \chi_s{}^{B_2} = \frac{1}{s}\rho\sum_r v_{sr}\frac{X_r}{r} \tag{2}$$

where $v_{sr}$ is the pair-excluded volume associated with $s$ and $r$ aggregates. (The "$B_2$" superscript refers to the second-virial level of approximation.) In Appendix A we provide explicit expressions for $\tilde{\mu}_\infty{}^0$ and $\alpha$ in terms of surfactant–water interfacial tension $\gamma$, the optimum area per head group $a_0$, the single molecule volume $v_1$, and the cylinder radius $l$. We also show there that

$$\chi_1{}^{B_2} - \chi_s{}^{B_2} = \chi_0{}^{B_2} - \frac{1}{s}\chi^{*B_2} \tag{3}$$

with both $\chi_0{}^{B_2}$ and $\chi^{*B_2}$ on the order of the volume fraction $\rho v_1 X$, $X = \sum_s X_s$ being the total concentration of soap. From the re-

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(1) For recent review of the current literature, see, for example, B. Lindman and H. Wennerström, *Top. Current Chem.*, **87**, 1 (1980).

(2) J. N. Israelachvili, D. J. Mitchell, and B. W. Ninham, *J. Chem. Soc., Faraday Trans. 2*, **72**, 1525 (1976).

(3) C. Tanford, "The Hydrophobic Effect: Formation of Micelles and Biological Membranes", 2nd ed, Wiley, New York, 1980.

(4) W. E. McMullen, A. Ben-Shaul, and W. M. Gelbart, *J. Colloid Interface Sci.*, in press.

(5) Several investigators (see, for example, C. A. J. Hoeve and G. C. Benson, *J. Phys. Chem.*, **61**, 1149 (1957); A. Wulf, *ibid.*, **82**, 804 (1978)) have described micellar suspensions within the formal context of real solution theory, but without the explicit aim of accounting for the effects of interactions on average aggregation sizes.

(6) A. Ben-Shaul and W. M. Gelbart, *J. Phys. Chem.*, **86**, 316 (1982).

(7) A. Ben-Naim, "Hydrophobic Interactions", Plenum, New York, 1980.

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quirement of chemical equilibrium

$$\tilde{\mu}_s = \tilde{\mu}_1 \equiv \mu_1{}^0 + \ln \frac{\rho_1}{\rho_0} + \chi_1 \qquad s \geq m \tag{4}$$

($\rho_1 = \rho x_1$, where $x_1$ is the monomer mole fraction), it follows that the micellar size distribution is given by

$$\frac{\rho_s}{\rho_0} = \left(\frac{\rho_1}{\rho_0}\right)^s \exp(s(\mu_1{}^0 - \tilde{\mu}_s{}^0)) \exp(s(\chi_1 - \chi_s)) = \left(\frac{\rho_1}{\rho_0}A^*\right)^s \exp(-\alpha^*) \tag{5}$$

Here

$$A^* \equiv \exp(\mu_1{}^0 - \tilde{\mu}_\infty{}^0) \exp \chi_0{}^{\mathrm{B}_2} \tag{5a}$$

and

$$\alpha^* \equiv \alpha + \chi^{*\mathrm{B}_2} \tag{5b}$$

Note that eq 5 has the same form as the "usual", ideal-solution, size distribution for rodlike aggregates:[2] $A^* \rightarrow A \equiv \exp(\mu_1{}^0 - \tilde{\mu}_\infty{}^0)$ and $\alpha^* \rightarrow \alpha$ as the amphiphilic volume fraction $\rho v_1 X$ becomes negligible compared to unity. (Recall that both $\chi_0{}^{\mathrm{B}_2}$ and $\chi^{*\mathrm{B}_2}$ are $\mathcal{O}(\rho v_1 X)$ whereas both $\mu_1{}^0 - \tilde{\mu}_\infty{}^0$ and $\alpha$ are $\mathcal{O}(10)$.) It is instructive, in fact, to return to eq 1 and rewrite it in the ideal solution form

$$\tilde{\mu}_s = \tilde{\mu}_\infty{}^{0*} + \frac{1}{s}\alpha^* + \frac{1}{s} \ln \frac{\rho_s}{\rho_0} \tag{$\bar{1}$}$$

where $\mu_\infty{}^{0*} \equiv \tilde{\mu}_\infty{}^0 + \chi_1{}^{\mathrm{B}_2} - \chi_0{}^{\mathrm{B}_2}$ (and $\alpha^* = \alpha + \chi^*$, as before). As is well-appreciated, the "energy" term $(1/s)\alpha^*$ drives the micelles to be as big as possible: $\alpha$ is proportional (via $m$) to $\tilde{\mu}_{\mathrm{cap}}{}^0 - \tilde{\mu}_\infty{}^0$, and hence increasing $s$ (i.e., "growing") lowers $\tilde{\mu}_s$ by decreasing the relative number of amphiphiles in the "high-energy" caps. This growth would continue to lower the micellar free energy without bound were it not for the price paid in the entropy-of-mixing term.

More explicitly, suppose for the moment that we neglect all of the polydispersity details implied by the size distribution (5), and consider instead a monodisperse suspension of $N$ aggregates. Then, assuming a negligible monomer concentration, we can put $X_s \simeq X\delta_{S,N}$ and write (neglecting $\ln \rho/\rho_0$)

$$\tilde{\mu}_N \simeq \tilde{\mu}_\infty{}^{0*} + \left(\alpha^* - \ln \frac{N}{X}\right)\frac{1}{N} \tag{6}$$

for the free energy of the micellar solution per amphiphile. ($N$ can be thought of as an average aggregation number $\bar{s}$.) Note that $\ln (N/x) > 0$ since $N >> 1$ and $X << 1$; furthermore the coefficient $\ln (N/X)$ increases with $N$. Thus, eq 6 tells us that $\tilde{\mu}_N$ first decreases with $N$, and then increases for $N > N^+ = X \exp(\alpha^* + 1)$. That is, the solution free energy is minimized for an average aggregation number ($N^+$) which increases with both $X$ and $\alpha^*$. The fact that $\ln (N/X)$ *de*creases with $X$ means that the "entropy-of-mixing" term becomes less important at higher concentrations. Furthermore, its minus sign causes it to work against the (positive) "growth" coeffcient $\alpha^*$. That is, the mixing entropy arrests the rod growth induced by the cap/cyl chemical potential difference ($\alpha$), with this "braking" effect weakening at higher concentrations.

Of course, we should take into account all of the polydispersity effects, as described below. The idea of the crude analysis offered above is just to expose the way in which micellar size increases with concentration even in the absence of interactions. Recall that eq $\bar{1}$ and the approximate eq 6 retain their same form in the $\rho v_1 X \rightarrow 0$ limit; we simply need to drop the *'s from all quantities. A more careful analysis, i.e., dealing directly with the asymptotics of eq $\bar{1}$, leads to $\bar{s} \sim (X \exp \alpha^*)^{1/2}$ rather than the $N^+ \sim X \exp \alpha^*$ from above. In any case, we have average aggregation numbers increasing with $X$ and $\alpha^*$, and $\alpha^*$ increasing further with $X$ due to interaction effects.

The fact that micellar growth is enhanced by interactions can be appreciated via rather simple "scaling" arguments. Again, to simplify things, we consider a monodisperse suspension of $N$ aggregates. Let there be $n_N$ of them in a volume large enough so that the second-virial approximation is adequate. Then the *total* excluded volume is given by

$$V^{\mathrm{ex}} = \frac{(n_N)^2}{2} v_{N,N} \tag{7}$$

where $v_{N,N}$ is the volume excluded to one $N$ aggregate by another. For spherocylinders with $N >> m$[8]

$$v_{N,N} \simeq \frac{4}{3} m v_1 \left[\left(\frac{N}{m}\right)^2 + 6\left(\frac{N}{m}\right)\right] \tag{7a}$$

Thus $v_{N,N}$ increases significantly slower than $N^2$, even for $N/m$ as large as 100 (i.e. for length-to-width ratios as large as 65). That is, for reasonable values of $N$ the linear ($\sim N$) term in $v_{N,N}$ remains important; since $(n_N)^2$ goes *exactly* as $1/N^2$, the *total* excluded volume $V^{\mathrm{ex}}$ decreases with $N$ as $1/N$. Accordingly, the interaction free energy is lowered upon reorganization of the fixed amount ($X$) of soap into larger aggregates.

For $N/m \rightarrow \infty$, of course, $v_{N,N} \sim N^2$ and $V^{\mathrm{ex}}$ becomes independent of rod size. This was the limit considered in our earlier Letter,[6] in which we concluded that—within the second-virial approximation—the growth of large rods is not affected by their excluded volume interactions. Keeping only the $N^2$ term in $v_{N,N}$, then, leads to $\chi^{*\mathrm{B}_2} \rightarrow 0$ and hence to $\alpha^* \rightarrow \alpha$, i.e., no micellar growth beyond that due to the "internal" (*intra*aggregate) "energy" ($\tilde{\mu}_N{}^0$) term. Note that even in the large rod ($N/m \rightarrow \infty$) limit, $\chi_0{}^{\mathrm{B}_2}$ does *not* vanish identically; instead, $\chi_0{}^{\mathrm{B}_2} \rightarrow \rho v_1 X$. But it is easy to show from eq 5 for the size distribution $\{\rho_s/\rho_0\}$ that the weight average aggregation number $\bar{s}_{\mathrm{W}} = \sum s^2\rho_s/\sum s\rho_s$ depends on $X$ and $\alpha^*$ only—not on $A^*$. Similarly, as discussed earlier,[6] the "equilibrium constant"

$$K_{sr} \equiv \frac{(X_s/s)^r}{(X_r/r)^s} = \exp[-\alpha^*(r-s)] \underset{r,s>>m}{\rightarrow} \exp[-\alpha(r-s)] \equiv K_{sr}{}^{\rho\rightarrow 0}$$

also becomes independent of $A^*$—and hence of interaction effects—in the large rod limit.

For large disks, on the other hand, $K_{sr}$ remains dependent on overall concentration even as $s,r \rightarrow \infty$. In the language of the monodisperse case treated above, this is because $v_{N,N}$ goes as $N^{3/2}$ for large disks—rather than like $N^2$, as for rods. Recall that[8] $v_{\mathrm{pair}}^{\mathrm{disks}} = \mathcal{O}(D^3)$, where $D$ is the disk diameter, and that $D^2 \sim$ area $\sim N$. This is to be compared with $v_{\mathrm{pair}}^{\mathrm{rods}} = \mathcal{O}(L^2)$, where $L$ is the rod length, and $L \sim N$.

Thus the excluded volume correction $\chi_N$ goes as $N^{3/2}/N^2 = 1/N^{1/2}$ for disks and as $N/N^2 = 1/N$ for rods (see the $\mathcal{O}(N)$ term in (7a)). Just as in the $1/N^{1/2}$ and $1/N$ contributions to the *intra*micellar $\tilde{\mu}_N{}^0$'s[2], these power laws follow from the two- vs. one-dimensional growths associated with disks and rods.

With polydispersity included, these scaling arguments are only a little less straightforward, as shown earlier.[6] In any event, as suggested above and demonstrated explicitly below, the effects of interactions on the size of *small* micelles in *concentrated* solutions have little to do with the $N$-asymptotic behavior cited here for dilute systems.

## III. Packing Entropy Effects at Higher Concentration

The preceding discussion, based on eq 1 with only second-virial corrections included in $\chi_s$, is of course only valid at low concentrations. More explicitly, we have shown that the effect of the pair-excluded-volume contributions is primarily to add an intermicellar term to the "growth" parameter $\alpha$: $\alpha \rightarrow \alpha + \chi^*$, where $\chi^* = \mathcal{O}(\rho v_1 X)$. Thus the average aggregation number is increased approximately by a factor of $(\exp \chi^*)^{1/2} = \mathcal{O}(\exp (\nu/2))$ where $\nu = \rho v_1 X$. For volume fractions up to a few per cent—above which higher-order virial corrections contribute (see below)—it follows

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(8) L. Onsager, *Ann. N.Y. Acad. Sci.*, **51**, 627 (1949).

that micellar sizes are enhanced by at most a few percent.

To describe the real solution effects through ***arbitrarily high*** concentration (i.e., $\nu$ no longer much less than unity) it becomes necessary to avoid the virial expansion, or—equivalently—to sum it to all orders. In our earlier work on thermotropic liquid crystals,[9] specifically in our efforts to generalize the Onsager theory[8] of the isotropic → nematic transition to liquid densities, we have shown[10] that it is possible to obtain systematically better infinite-order resummations of the virial series by considering successively higher-order truncations of an expansion in (not the density $\rho_s$ but) the new variable

$$y_s \equiv \frac{\rho_s}{1 - \sum_r v_r \rho_r} = \frac{\rho_s}{1 - \rho v_1 X} \tag{8}$$

(Here $v_r = rv_1$ is the volume of an $r$ aggregate.) Thus, instead of (see eq 1)

$$\tilde{\mu}_s = \tilde{\mu}_s{}^0 + \frac{1}{s} \ln \frac{\rho_s}{\rho_0} + \chi_s$$

we write

$$\tilde{\mu}_s = \tilde{\mu}_s{}^0 + \frac{1}{s} \ln \frac{y_s}{\rho_0} + \chi_s{}^{(y)} \tag{1*}$$

The "chemical" equilibrium condition $\tilde{\mu}_s = \mu_1$ then leads again to a size distribution (compare with eq 5):

$$\frac{y_s}{\rho_0} = \left(\frac{y_1}{\rho_0}\right)^s \exp[s(\mu_1^0 - \tilde{\mu}_s{}^0)] \exp[s(\chi_1{}^{(y)} - \chi_s{}^{(y)})] \tag{9}$$

In Appendix B we derive explicit expressions for $\chi_1 - \chi_s$ using the $y$ representation of the thermodynamic functions.[10] We show in particular that a three-term ("$y_3$") truncation for the pressure gives

$$s(\chi_1{}^{(y)} - \chi_s{}^{(y)}) \simeq s\chi_0{}^{y_3} - \chi^{*y_3} \tag{10}$$

where $\chi_0$ and $\chi^*$ are explicit functions only of the first three and two moments, respectively, of the micellar size distribution:

$$\chi_0{}^{y_3} = \chi_0{}^{y_3}(\nu, r, \overline{r^2}) \tag{10a}$$

and

$$\chi^{*y_3} = \chi^{*y_3}(\nu, \bar{r}) \tag{10b}$$

with

$$\nu \equiv \sum_{r \geq m} y_r = \frac{\rho}{1 - \rho v_1 X} \sum_{s \geq m} \frac{X_s}{s} \tag{11a}$$

$$\bar{r} \equiv \frac{\sum r y_r}{\nu} = \frac{\sum X_s}{\sum \frac{1}{s} X_s} \equiv \bar{s}_N \tag{11b}$$

$$\overline{r^2} \equiv \frac{\sum r^2 y_r}{\nu} = \frac{\sum s X_s}{\sum \frac{1}{s} X_s} \equiv \bar{s}_N \bar{s}_W \tag{11c}$$

Substituting from (10) into (9) gives—again, compare with eq 5—

$$\frac{y_s}{\rho_0} = \left(\frac{y_1}{\rho_0} A'\right)^s \exp(-\alpha') \tag{9'}$$

with

$$A' = \exp(\mu_1{}^0 - \tilde{\mu}_\infty{}^0) \exp \chi_0{}^{y_3} \equiv A \exp \chi_0{}^{y_3}$$

and

$$\alpha' = \alpha + \chi^{*y_3}$$

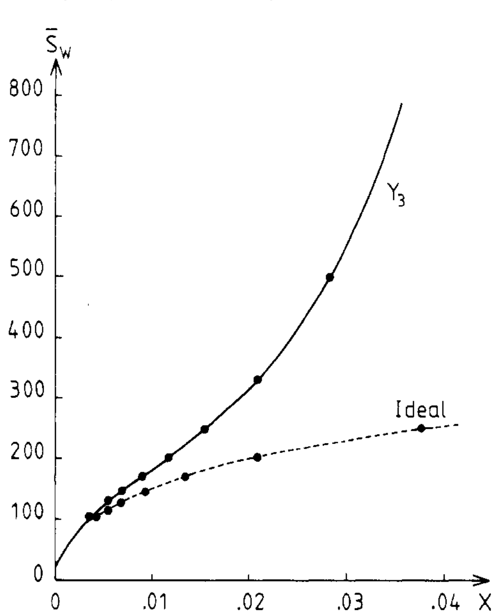

**Figure 1.** We plot here the weight-average aggregation number ($\bar{s}_W$) vs. total mole fraction ($X$) of soap. The dashed curve shows the behavior for an ideal solution of micelles, whereas the solid curve includes effects of excluded volume interactions through third-order in the $y$ expansion.

Equivalently, and more suggestively for the numerical analysis which follows, we write

$$\frac{y_s}{\rho_0} = B(C)^s \tag{12}$$

where

$$B = \exp[-\alpha - \chi^{*y_3}(\nu, \bar{r})] \tag{12a}$$

and

$$C = (y_1/\rho_0) \exp[\mu_1{}^0 - \tilde{\mu}_\infty{}^0 + \chi_0{}^{y_3}(\nu, r, \overline{r^2})] \tag{12b}$$

$\alpha$ and $\tilde{\mu}_\infty{}^0$ are determined by $\gamma$, $a_0$, l, and $v_1$—as in the preceding section—according to eq A.1.4 and A.1.6–7. Similarly, $\chi^{*y_3}$, $\chi_0{}^{y_3}$ are known for arbitrary $\nu$, $\bar{r}$, $\overline{r^2}$ (see eq B10a,b) as soon as these same parameters ($\gamma$, $a_0$, $l$, $v_1$; implying $m$ and hence $a_1$, $a_2$, $a_3$) are specified.

## IV. Results and Discussion

To obtain the size distributions $\{y_s/\rho_0\}$, we start by choosing a value for $C$. This implies both $\bar{r}$ and $\overline{r^2}$ via

$$\bar{r} = \frac{I_1(C)}{I_0(c)} \quad \text{and} \quad \overline{r^2} = \frac{I_2(C)}{I_0(C)} \tag{13}$$

where the $I_n(C)$'s are defined by $I_n(C) = \sum_{r \geq m} r^n C^r$. The relation (definition—see eq 11a and 12)

$$\nu = \rho_0 B(\nu, \bar{r}) I_0(C) \tag{14}$$

is then solved iteratively for $\nu$, from which eq 12b yields $y_1$: the size distribution follows immediately from eq 12a,b. In this way we generate $\{y_s/\rho_0\}$'s— and hence $\bar{s}$'s—for different values of $X = (\nu\bar{r}/\rho_0)(1 - X)$.

Typical results are shown in Figure 1, for the choice[3]

$$\gamma = 1/20\ kT/\text{Å}^2 \qquad v_1 = 360\ \text{Å}^3$$

$$a_0 = 55\ \text{Å}^2 \qquad \mu_1{}^0 = 15\ kT$$

$$l = 12\ \text{Å} \qquad \rho_0 = 0.033/\text{Å}^3$$

(hence $m = 20$ and $\tilde{\mu}_\infty{}^0 = 4.9\ kT$). The solid curve shows the weight average aggregation number

$$\bar{s}_W \equiv \frac{\sum s X_s}{\sum X_s} = \frac{\sum s^2 y_s}{\sum s y_s} \tag{15}$$

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(9) W. M. Gelbart, *J. Phys. Chem.*, **86**, 4298 (1982), and references contained therein.

(10) B. Barboy and W. M. Gelbart, *J. Stat. Phys.* **22**, 709 (1979).

vs. concentration $X$, in the $y_3$ level of approximation outlined above; it describes the effect of excluded-volume interactions between micelles on the mean size. The dashed curve was obtained by repeating the same calculation, but with "$\rho \equiv 0$", i.e., neglecting all interaggregate forces; more explicitly it is what we would find by setting $y_s$, $y_1 \rightarrow \rho(x_s/s)$, $\rho x_1$ and $\chi_0^{y_3}$, $\chi^{*y_3} \rightarrow 0$ in eq 12a,b.

We note several points of interest in Figure 1:

(i) The cmc for this system occurs at $X \simeq 8 \times 10^{-5}$ (i.e., $X_{\text{cmc}} \approx 0$ on the scale of our figure).

(ii) Interactions between micelles begin to have nonnegligible effect on $\bar{s}_W$ (greater than 20%, say) only for $X \gtrsim 8 \times 10^{-3}$.

(iii) $\bar{s}_W$ is enhanced (by these excluded-volume forces) by as much as a factor of three at $X \simeq 0.035$.

From (i) and (ii) we conclude that the effect of interaggregate repulsions on micellar size distributions can indeed be neglected for concentrations up to two orders of magnitude above the cmc. This vindicates the usual analyses of static and dynamic light scattering experiments which are confined to $X/X_{\text{cmc}} \leq 100$. Missel et al.,[11] for example, study SDS at concentrations varying from 3 to 185 times the cmc, for different temperatures and salt contents; their integrated intensities (average aggregation numbers $\bar{s}$) and hydrodynamic radii (rod lengths $L$) are interpreted via an *intra*micellar growth theory which neglects the effect of *non*ideal solution behavior on the distribution $\{X_s/s\}$ of micelle sizes. Corti and Degiorgio[12] have reported quasielastic light scattering data for SDS under comparable conditions of temperature, salt, and mole fraction of soap ($X/X_{\text{cmc}} \leq 100$). They account for the concentration dependence of the apparent molecular weight $M$ ($\sim\bar{s}$) and diffusion coefficient $D$ ($\sim 1/L$) by considering the corrections to $M$ and $D$ due to interparticle interactions, rather than by allowing actual growth of the aggregates; the size of the rodlike micelles is still assumed to be independent of the forces between them. Similarly, Cheng and Gulari[13] have treated *both* the ideal-solution description of micellar growth *and* the interacting particle model for static scattering and translational diffusion, to account for the variation with concentration of the integrated intensities and hydrodynamic radii in aqueous solutions of SDBS and NaCl—again, though, the size distributions are determined wholly by the *intra*aggregate chemical potential.

Observations (ii) and (iii) indicate, on the other hand, that for higher mole fractions of amphiphile the measured properties of soap solutions can no longer be analyzed in terms of theories which neglect the effect of intermicelle forces on aggregation size. $X \simeq 0.035$, for example, corresponds to a volume fraction

$$\nu \equiv \rho v_1 X = \frac{X}{\dfrac{v_0}{v_1} + \left(1 - \dfrac{v_0}{v_1}\right)X} \tag{16}$$

of $\simeq$30% in the case of SDS ($v_1 = v_{\text{SDS}} = 360$ Å$^3$ and $v_0 = v_{\text{H}_2\text{O}} = 30$ Å$^3$). This is precisely the concentration range characterizing the isotropic (I) solution in equilibrium with nematic (N: "discotic" and "calamatic") phases of SDS/decanol/water[14] and many other systems showing lyotropic liquid crystallinity.[15] In these cases a theory of micellar size must properly include the effects of interaggregate forces, to all orders in the density. Furthermore, the two-phase (I/N) coexistence leads to a preferential partitioning of the larger rods into the nematic solution. This "fractionation" effect, intrinsic to polydisperse systems, is complicated by the fact that the particles involved do not maintain their integrity, their size distribution being determined instead by the chemical equilibria treated earlier. To describe micellar growth at the I → N transition, then, it is necessary to couple the self-assembly and long-range orientational ordering in a fully self-consistent way, i.e., to satisfy simultaneously the conditions of chemical and phase equilibria. We are presently attempting to do so by extending the $y$ theory outlined above to the nematic state.

We close with a few remarks about the effects of intermicellar *attractions* on the size of rods in the isotropic phase. Let $u_{sr}(\tau_s, \tau_r)$ denote the potential energy of attraction between $s$ and $r$ aggregates described by the (positional and angular) coordinates $\tau_s$ and $\tau_r$. Then, in the spirit of the generalized van der Waals theory,[9] we rewrite eq 1* as

$$\tilde{\mu}_s = \tilde{\mu}_s^{\,0} + \frac{1}{s}\ln\frac{y_s}{\rho_0} + \chi_s + \frac{1}{2}\sum_r W_2(s,r)\rho_r \tag{1$'$}$$

where

$$W_2(s,r) = \int \mathrm{d}\tau_s \int \mathrm{d}\tau_r \exp(-\beta u_{\text{hard core}}(s,r,\tau_s,\tau_r))u_{sr}(\tau_s, \tau_r) \tag{17}$$

The Boltzmann factor in the integrand vanishes for $\tau_s$, $\tau_r$ such that the $s$ and $r$ rods overlap, and is unity otherwise; accordingly, it defines the mean field $W_2(s,r)$ as an unweighted average of the attraction $u_{sr}(\tau_s,\tau_r)$ over all "allowed" configurations.

To proceed with a crude qualitative analysis we assume that the integral in (17) is dominated by configurations in which the rodlike particles are "crossed" ("perpendicular"). We note further that the corresponding dispersion energy $u_{sr}$ is negligible whenever the particles are separated by more than a few Å and that otherwise it is slowly varying. Let $\zeta$ denote this "maximum separation" distance and let $-\bar{u}$ be the average attraction. Then it follows that the mean field (17) can be approximated by

$$W_2(s,r) \simeq -\bar{u}[v(L_s, l + \zeta; L_r, l + \zeta) - v(L_s,l;L_r,l)] \tag{18}$$

where $v(L_s,l;L_r,l)$ is the pair excluded volume $v_{sr}$ given by eq A.2.2 and $v(L_s,l+\zeta; L_r,l+\zeta)$ is the same but with the rod-radius $l$ replaced by $l + \zeta$.

With a similar approximation for $W_2(1,r)$ it is straightforward to show that the corrections (arising from *attractions*) to $\chi^*$—see eq 10 and B.10.8—have a sign *opposite* to those from excluded-volume repulsions. But for $\zeta$ on the order of a few Å and for $\bar{u} = \mathcal{O}(kT)$, we find $\bar{s}_W$ vs. $X$ plots which are qualitatively the same as that shown in Figure 1. Clearly, however, a more careful analysis is required to properly investigate the possibility that macroscopic dispersion interactions might overwhelm the size enhancement described above for forces of the excluded-volume type. At the same time, the effects of rod *flexibility* on the *intra*- and *inter*micellar growth mechanisms must also be considered. Finally, in the spirit of Onsager,[8] the role of counterion layers (or more generally, the screened Coulomb repulsions) can be included by appropriately "padding" the excluded-volume dimensions.

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## Appendix A

*(1) Size Dependence of Chemical Potential for Single Micelles.* For a spherocylindrical rod we have

$$\tilde{\mu}_s^{\,0} = \frac{s_{\text{cyl}}}{s}\tilde{\mu}^0(a_{\text{cyl}}) + \frac{s_{\text{cap}}}{s}\tilde{\mu}^0(a_{\text{cap}}) \tag{A.1.1}$$

where "cyl" and "cap" refer to the right-circular cylindrical body and the half-spherical caps, respectively. $\tilde{\mu}^0(a)$ is the free energy of a surfactant with micellar head group area $a$; as discussed often elsewhere[2-4] it can be approximated by

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(11) P. J. Missel, N. A. Mazer, G. B. Benedek, C. Y. Young, and M. C. Carey, *J. Phys. Chem.*, **84**, 1044 (1980).

(12) M. Corti and V. Degiorgio, *J. Phys. Chem.*, **85**, 711 (1981).

(13) D. C. H. Cheng and E. Gulari, *J. Colloid Interface Sci.*, **90**, 410 (1982).

(14) Y. Hendrikx and J. Charvolin, *J. Phys.*, **42**, 1427 (1981).

(15) G. J. T. Tiddy, *Phys. Rep.*, **57**, 1 (1980).

$$\tilde{\mu}^0(a) = 2\gamma a_0 + \gamma a\left(1 - \frac{a_0}{a}\right)^2 \qquad \text{(A.1.2)}$$

From the requirement that the hydrophobic core be completely filled by the hydrocarbon chains ("tails"), straightforward surface/volume ratios give[2-4]

$$a_{\text{cyl}} = 2v_1/l \quad \text{and} \quad a_{\text{cap}} = 3v_1/l \qquad \text{(A.1.3)}$$

Allowing for intermediate optimization of head-group packing (between "cyl" and "bilayer"—$a_{\text{bil}} = v_1/l$—ideals) we write[4]

$$a_0 \equiv \frac{v_1}{l}(1 + y) \qquad \text{(A.1.4)}$$

Finally, recognizing that $s_{\text{cyl}} \equiv s - s_{\text{cap}}$ where $s_{\text{cap}} \equiv m \equiv 4\pi l^3/3v_1$ is the minimum micelle aggregation number, it follows directly from substitution of (A1.2–1.4) into (A1.1) that $\tilde{\mu}_s{}^0$ has the form of eq 1 in the text:

$$\tilde{\mu}_s{}^0 = \tilde{\mu}_\infty{}^0 + \frac{1}{s}\alpha \qquad \text{(A.1.5)}$$

with

$$\tilde{\mu}_\infty{}^0 = 2\gamma a_0\left[1 + \frac{(1 - y)^2}{4(1 + y)}\right] \qquad \text{(A.1.6)}$$

and

$$\alpha = \frac{m}{6}\gamma a_0 \frac{(5 - 2y - y^2)}{(1 + y)} \qquad \text{(A.1.7)}$$

(2) *Second-Virial Micellar-Interaction Correction.* From eq 2 in the text we can write

$$\chi_1{}^{\mathrm{B}_2} - \chi_s{}^{\mathrm{B}_2} = \rho\sum_r\left[v_{1,r} - \frac{1}{s}v_{sr}\right]\frac{X_r}{r} = \rho\left[v_{1,1} - \frac{1}{s}v_{s,1}\right]X_1 + \rho\sum_{r>m}\left[v_{1,r} - \frac{1}{s}v_{sr}\right]\frac{X_r}{r} \qquad \text{(A.2.1)}$$

Since $m >> 1$ and $X_1 << \sum_{r\geq m}(X_r/r)$ in all micellized solutions of interest, we drop the first term in the last line of equation above. The *sr*-pair excluded volume is known[6,8] to have the form

$$v_{sr} = \frac{32}{3}\pi l^3 + 4\pi l^2(L_s + L_r) + \pi l L_s L_r \qquad \text{(A.2.2)}$$

where $L_s$ is the rod-length of a *s*-spherocylindrical aggregate of radius $l$

$$(\pi l^2)L_s = (s - m)v_1 \qquad \text{(A.2.3)}$$

(Note that use of (A.2.3) in (A.2.2), with $s = r = N$ gives directly eq 7a in the text; the length to width ratio, $L_s/2l + 1$, is given by $2/3(s/m + 1/2)$). Substituting (A.2.2) and (A.2.3) for $v_{sr}$ in the second term of (A.2.1), and recognizing that $v_{1,r} \simeq rv_1$, leads to

$$(\chi_1 - \chi_s)^{\mathrm{B}_2} = \rho v_1\left[\sum_{r\geq m}X_r - \frac{8}{3}\sum\frac{1}{r}X_r - \frac{4}{3}\,\frac{1}{m}\sum X_r - \frac{8}{3}\,\frac{1}{s}\sum X_r - \frac{4}{3}\,\frac{m}{s}\sum\frac{1}{r}X_r\right] \qquad \text{(A.2.4)}$$

or

$$(\chi_1 - \chi_s)^{\mathrm{B}_2} = \chi_0{}^{\mathrm{B}_2} - \frac{1}{s}\chi^{*\mathrm{B}_2} \qquad \text{(A.2.5)}$$

as in eq 3 of the text, with

$$\chi_0{}^{\mathrm{B}_2} \equiv \rho v_1 X\left[1 - \frac{8}{3}\left\langle\frac{1}{r}\right\rangle - \frac{4}{3}\,\frac{1}{m}\right] \qquad \text{(A.2.5a)}$$

and

$$\chi^{*\mathrm{B}_2} \equiv \rho v_1 X\left[\frac{8}{3} + \frac{4}{3}m\left\langle\frac{1}{r}\right\rangle\right] \qquad \text{(A.2.5b)}$$

$X \equiv \sum_s X_s$ is defined in the text, and $\langle 1/r\rangle$ by

$$\left\langle\frac{1}{r}\right\rangle \equiv \frac{1}{X}\sum_{r\geq m}\frac{1}{r}X_r \quad (\equiv \bar{s}_N{}^{-1})$$

## Appendix B

$y_3$ *Micellar Interaction Correction.* Consider the $y$ expansion form for the chemical potential of an $s$ aggregate:

$$s\tilde{\mu}_s \equiv \mu_s = \mu_s{}^0 + \ln\frac{y_s}{\rho_0} + s\chi_s{}^{(y)} \qquad \text{(B.1)}$$

From the definition given by Barboy and Gelbart[10]—i.e., the isotropic-phase limit of their general eq 18—we have

$$s\chi_s{}^{(y)} = v_s P + 2\sum_r \bar{C}_{sr}y_r + {}^3\!/_2\sum_r\sum_{r'}\bar{C}_{srr'}y_r y_{r'} + \ldots \qquad \text{(B.2)}$$

Here $v_s$, the volume of the *s*th hard-"particle" species, corresponds in the present case to $sv_1$, the volume of an aggregate containing $s$ molecules. The pressure $P$ is given by[10]

$$P = \sum_r y_r + \sum_r\sum_{r'}\bar{C}_{rr'}y_r y_{r'} + \ldots \qquad \text{(B.3)}$$

and the $\bar{C}$'s by[10]

$$\bar{C}_{rr'} = \bar{B}_{rr'} - \frac{v_1}{2}(v + r') \qquad \text{(B.4)}$$

and

$$\bar{C}_{srr'} = \bar{B}_{srr'} - (2/3)v_1(\bar{C}_{sr}r' + \bar{C}_{sr'}r + \bar{C}_{rr'}s) - (1/3)v_1{}^2(sr + sr' + rr') \qquad \text{(B.4b)}$$

$\bar{B}_{rr'}$ and $\bar{B}_{srr'}$ are the usual[16] second and third virial coefficients for a multicomponent mixture. For example, $B_{rr'}$ for hard particles is equal to $(1/2)v_{rr'}$ where $v_{rr'}$ is the $r$–$r'$ pair excluded volume discussed in the text.

In writing eq B.2–B.3 we have implicitly anticipated that terms $\mathcal{O}(y^3)$ in the chemical potential are not of qualitative importance. Indeed, in our earlier work[9,10] we demonstrated directly that this level of approximation ("$y_3$") leads to pressure equations of state for monodisperse hard particles which are accurate to within a few percent over the full liquid (and gas) range. In the case of spheres, for example, $y_3$ gives[17] exactly the same result as that obtained from analytic solutions to the Percus–Yevick[18] and scaled particle theories;[19] for anisotropic particles ("dumbells", spherocyclinders, fused spheres, etc. ...) $y_3$ agrees[17] closely with full Monte Carlo simulations of the pressure.

The sums in eq B.2–B.3 run over the values $r = 1$ (monomer) and $r \geq m$ (minimum micelle). It is easy to show, however, that the $r = 1$ contributions are negligible compared to the $r \geq m$ terms: this follows directly from the fact that $v_{1r'} << v_{rr'}$ $(r \geq m)$ and that $X_1 << \sum_{r\geq m}(X_r/r)$ for concentrations $(X)$ sufficiently above the micellization threshold $(X_{\text{cmc}})$. We can then write $\chi_s{}^{(y)}$ in the form (using relations (B.4a–B.4b) for the $\bar{C}$'s):

$$s\chi_s{}^{(y)} = -v_1\bar{r}\nu + \frac{v_1{}^3}{2}\bar{r}^2\nu^2 + 2\sum_{r\geq m}\bar{B}_{sr}y_r - 2v_1\sum_{r,r'\geq m}\bar{B}_{sr}r'y_r y_{r'} + (3/2)\sum_{r,r'\geq m}\bar{B}_{srr'}y_r y_{r'} \qquad \text{(B.5)}$$

where the moments $\nu$ and $\bar{r}$ are defined by eq 11a–b in the text.

It remains only to introduce expressions for the second and third virial coefficients appropriate to hard spherocylinders. For $\bar{B}_{sr}$ the well-known result of Onsager[8] (see eq A.2.2.) gives

$$2\bar{B}_{sr} = a_1 sr + a_2(s + r) + a_3 \qquad \text{(B.6)}$$

where $a_1$, $a_2$, and $a_3$ are ${}^4\!/_3(v_1/m)$, ${}^8\!/_3 v_1$, and ${}^1\!/_3 m v_1$, respectively. For the *third* virial coefficient, we use

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(16) J. E. Mayer, "Theory of Real Gases" in "Handbuch der Physik", Vol. 12, S. Flügge, Ed., Springer, Berlin, 1958.

(17) B. Barboy and W. M. Gelbart, *J. Chem. Phys.*, **71**, 3053 (1979).

(18) J. K. Percus and G. J. Yevick, *Phys. Rev.*, **110**, 1 (1958); E. Thiele, *J. Chem. Phys.*, **39**, 474 (1963); M. S. Wertheim, *Phys. Rev. Lett.*, **10**, 321 (1963).

(19) See review by H. Reiss in "Statistical Mechanics and Statistical Methods: Theory and Application", U. Landmann, Ed.; Plenum, New York, 1977.

$$\bar{B}_{srr'} \simeq (64/3)L_sL_rL_{r'}l^3 + 10(\tfrac{4}{3}\pi l^3)^2 \qquad \text{(B.7)}$$

The first term in (B.7) corresponds to the asymptotic ($L >> l$) result suggested by Straley[20] for rods whose length $L$ greatly exceeds their radius $l$; the second term is the hard-sphere ($L \rightarrow 0$) result for $\bar{B}_3$.[21] The length $L_s$ can be expressed simply—see eq A.2.3—as $L_s = (v_1^3/\pi l^2)(s - m)$, and similarly for $L_r$ and $L_{r'}$.

An expression identical with (B.5) but with $s \rightarrow 1$ can be written for $\chi_1^{(y)}$, the "real solution" correction to the chemical potential $\mu_1$ of a monomer. We need only choose a form for the second and third virial coefficients in the case where one of the particles is the monomer. For $v_{1r}$ it is natural to take the volume of an $r$ aggregate

$$2\bar{B}_{1r} \simeq v_r = rv_1 \qquad \text{(B.8)}$$

while for the three-body excluded volume we write

$$\bar{B}_{1rr'} \simeq \tfrac{1}{3}(v_r + v_{r'})\bar{B}_{rr'} \qquad \text{(B.9)}$$

It follows immediately from eq B.5–B.9 that the difference $\chi_1 - \chi_s$ can be expressed as in eq 10 of the text, with

$$\chi_0^{y_3} = -\nu(a_2 + a_1\bar{r}) + \nu^2\left\{-\frac{v_1^2}{2}\overline{r^2} + v_1\bar{r}(a_2 + a_1\bar{r}) - \frac{32}{\pi^3 l^3}v_1^3(\bar{r} - m)^2 + \frac{v_1}{2}[a_1\overline{r^2}\bar{r} + a_2(\overline{r^2} + \bar{r}^2) + a_3\bar{r}]\right\} \qquad \text{(B.10a)}$$

and

$$\chi^{y_3} = -\nu(\nu_1\bar{r} - a_2\bar{r} - a_3) - \nu^2\left\{-\frac{v_1^2}{2}\overline{r^2} + v_1\bar{r}(a_3 + a_2\bar{r}) + \frac{32}{\pi^3 l^3}mv_1^3(\bar{r} - m)^2 - \frac{80}{3}\pi^2 l^6\right\} \qquad \text{(B.10b)}$$

Note that, in the limit where $\sum_s v_s\rho_s \equiv \rho v_1 X \equiv \nu << 1$, i.e., where the volume fraction of soap is small compared to unity, $y_s \rightarrow \rho_s(1 + \rho v_1 X)$, $v_1\bar{r}\nu \rightarrow \rho v_1 X + \mathcal{O}(\nu^2)$, and $v_1\nu \rightarrow \rho v_1 X\langle 1/r\rangle + \mathcal{O}(\nu^2)$. Then, neglecting the $\mathcal{O}(\nu^2)$ terms in eq 10a,b, we have

$$\chi_0 \simeq -\nu(a_2 + a_1\bar{r}) = \rho v_1 X\left(-\frac{8}{3}\left\langle\frac{1}{r}\right\rangle - \frac{4}{3}\frac{1}{m}\right) \qquad \text{(B.11a)}$$

and

$$\chi^* \simeq -\nu(v_1\bar{r} - a_2\bar{r} - a_3) = \rho v_1 X\left(\frac{5}{3} + \frac{4}{3}m\left\langle\frac{1}{r}\right\rangle\right) \qquad \text{(B.11b)}$$

Recognizing that $y_s/\rho_0 = (\rho_s/\rho_0)e^{\rho v_1 X}$ and $(y_1/\rho_0)^s = (\rho_1/\rho_0)^s e^{s\rho v_1 X}$, eq 3, 5, and A.2.5a,b are seen to be identical with eq 9, 10, and B.11a,b. That is, the second virial approximation falls out naturally as the low-volume fraction limit of the $y$ theory.

In the above analyses we have, for purpose of simplicity, neglected all the $r = s = 1$ contributions to $\chi_s^{B_2}$ (see Appendix A.2) and $\chi_s^{(y)}$ (Appendix B). We have checked, however, that retaining them leads to only negligible changes in the calculated $\bar{s}_W$ vs. $X$ plots. Similarly, we have approximated $2\bar{B}_{1r}$ by $v_r = rv_1$, whereas in fact it is easy to show that $2\bar{B}_{1r} - rv_1$ is itself on the order of $rv_1$. But, again, allowing for this correction changes imperceptibly the calculated dependence of average micellar size on overall soap concentration.

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(20) J. P. Straley, *Mol. Cryst. Liq. Cryst.*, **24**, 7 (1973).

(21) K. W. Kratky, *Ann. Phys. (N.Y.)*, **87A**, 584 (1977).

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# Hydrogen Isotope Exchange between Fluoroform and Water. 5. Equilibrium Deuterium Distribution. The Temperature Dependence of $\alpha$[1]

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A knowledge of the equilibrium deuterium distribution between water and fluoroform is useful for design of the redeuteration stage of a heavy water production process based on IR laser-activated decomposition of $CF_3D$ in excess $CF_3H$. The first *measured* fractionation factor data are presented for the temperature range 70–130 °C. The deuterium is favored in the fluoroform ($\alpha = 1.139$ at 130 °C, 1.215 at 70 °C, and 1.287 at 25 °C (extrapolated)). These values are approximately 10–20% higher than various reported theoretical estimates calculated by using isotopic reduced partition function ratios based on molecular vibrational frequencies (with harmonic oscillator approximation). $\Delta H° = -1.23$ kJ/mol was calculated from the temperature dependence of ln $\alpha$.

## Introduction

Any deuterium isotope separation process based on laser-activated selective dissociation of $CF_3D$ molecules in the presence of a large excess of $CF_3H$ will include a stage for catalyzed redeuteration of the depleted fluoroform by contact with an inexpensive deuterium source like water.[2-6] An important element in the design of such a process stage is the isotopic fractionation factor, $\alpha$, for equilibrium distribution of deuterium between gaseous fluoroform and liquid water (eq 1); $\alpha$ is defined by eq 2.[7] Values of $\alpha$ have been measured over the temperature range 70–130 °C.

$$CF_3H + HOD \xrightleftharpoons{\alpha = 2K_{eq}} CF_3D + HOH \qquad (1)$$

$$\alpha = \frac{(D/H)_{\text{fluoroform}}}{(D/H)_{\text{water}}} \qquad (2)$$

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(1) AECL Report 8275.

(2) Marling, J. B.; Herman, I. P. *J. Chem. Phys.* **1980**, *72*, 5603–5634.

(3) Evans, D. K.; McAlpine, R. D.; Adams, H. M. *J. Chem. Phys.* **1982**, *77*, 3551–3558.

(4) Symons, E. A.; Clermont, M. J. *J. Am. Chem. Soc.* **1981**, *103*, 3127–3130.

(5) Symons, E. A.; Clermont, M. J.; Coderre, L. A. *J. Am. Chem. Soc.* **1981**, *103*, 3131–3135.

(6) Bigeleisen, J.; Hammond, W. B.; Tuccio, S. *Nucl. Sci. Eng.* **1983**, *83*, 473–481.

(7) Weston, R. E., Jr. *Z. Naturforsch. A* **1973**, *28A*, 177–184.

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