Effect of Interaggregate Forces on the Size Distribution of Micelles

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The size distributions of given shapes of micelles, in aqueous solutions of soap molecules, are believed to be determined primarily by amphiphile geometry and hydrophobicity. Accordingly, direct forces between the aggregates have generally been neglected. In the present paper we extend the Onsager–McMillan–Mayer theory of dilute colloidal suspensions to allow for the exchange of molecules between aggregates. By so doing we are able to describe the effects of intermicelle interactions on the size distribution of aggregates. We conclude, from simple excluded volume considerations, that these effects depend upon the shape of micelle involved, e.g., they are more important for "disks" than for "rods". It is also possible, with the same formalism, to treat the effects of interaggregate forces on the formation of orientationally ordered (nematic) phases.

Introduction

The effects of particle size and shape on the thermodynamic properties of colloidal solutions, particularly the role of hard-core (excluded volume) interactions as the driving force for long-range orientational ordering, were studied by Onsager some 30 years ago.[1] His theory was formulated for a fixed ("frozen") size distribution of particles of a given shape, e.g., rods or disks. In this Letter we extend and apply some aspects of Onsager's theory to the case where the particles are (not rigid bodies but rather) aggregates of many molecules; molecules, or groups of them, can detach from one aggregate and join another. The size and shape distributions of the aggregates are determined accordingly by a chemical-like equilibrium condition. Interaggregate interactions, especially at high concentrations, may affect the size distribution and play a role in determining the thermodynamically preferred shapes. This coupling between the stabilization of many-molecule aggregates and the interactions between them is our concern in this Letter.

The above question is of particular interest for understanding the thermodynamics of aqueous solutions of amphiphile ("soap") molecules.[2] Due to hydrophobic interactions the amphiphile molecules assemble into aggregates of various shapes (e.g., spherical, rodlike, or disklike micelles). Packing constraints implied by the geometrical properties of the amphiphilic molecules seem to play the major role in determining the preferred micellar shapes.[3] At low concentrations the size distribution is mainly controlled by the overall concentration and by the binding forces between the molecules within the aggregates. Interactions between aggregates are expected to be important only at higher concentrations, where they may affect the size distribution and play a role (together with other factors, such as curvature effects) in determining the thermodynamically preferred shape. Such interactions are particularly important near the isotropic–nematic phase transition, where orientational ordering of anisotropic micelles is observed over a limited range of concentration.[4]

Interaggregate interactions have not been considered previously in models for the self-assembly of amphiphile molecules. The discussion below, based largely on the theories of Onsager[1] and McMillan–Mayer,[5] is intended as a first step in this direction. As such, we shall keep it as simple as possible. In particular we shall limit it to the

leading ("second virial") correction to dilute solution theory. Also, following Onsager we shall only treat hard-core (excluded volume) interactions. Furthermore, we shall consider only isotropic (as opposed to orientationally ordered) solutions. Finally, we shall discuss the effects of interactions on the size distribution, but not on the relative stability of different shapes.

The Chemical Potential and Size Distribution

Consider an aqueous solution of N amphiphile molecules at volume V and temperature T. The molecules assemble into aggregates of different sizes. We assume that all aggregates have the same shape, e.g., rods or plates. Let n_s denote the number of aggregates made up from s molecules ("s aggregate"). Then

$$N = \sum_{s \geq 1} s n_s = \sum_{s \geq 1} N_s \qquad (1)$$

where $N_s = s n_s$ is the number of molecules incorporated into s aggregates. The system is in a state of chemical equilibrium with respect to the passage of molecules between aggregates. Thus, if A_s denotes an s aggregate, all chemical reactions of the form

$$s A_r \rightleftharpoons r A_s \qquad (2)$$

are in equilibrium. (Note that, via linear combination, this set includes processes like $A_s \rightleftharpoons A_{s-1} + A_1$, etc.) Therefore, the chemical potential per molecule, $\tilde{\mu}_s = \mu_s/s$, must be the same in all aggregates, i.e., $\tilde{\mu}_s$ must be independent of s:

$$\tilde{\mu}_s = \tilde{\mu}_r = \mu_1 \qquad (3)$$

The chemical potential is given by

$$\tilde{\mu}_s = \tilde{\mu}_s^{\,0} + (kT/s) \ln \rho_s + \chi_s \qquad (4)$$

where $\rho_s = n_s/V$ is the number density of s aggregates. The

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standard chemical potential $\bar{\mu}_s^0$ depends on the properties of an isolated s aggregate in the solvent.[2,3] The second term involves the usual "entropy of mixing", and the last term accounts for interaggregate interactions. $\chi_s = (kT/s) \ln \gamma_s$ where γ_s is the activity coefficient of an s aggregate. (As $\rho = \sum \rho_r \to 0$, $\gamma_s \to 1$ and $\chi_s \to 0$.) Combining (3) and (4) we obtain the density quotient corresponding to (2):

$$(\rho_s)^r/(\rho_r)^s = \exp\left[-\frac{sr}{kT}(\bar{\mu}_s^0 - \bar{\mu}_r^0)\right]\exp\left[-\frac{sr}{kT}(\chi_s - \chi_r)\right]$$
$$\equiv K_{sr}^0 \psi_{sr}$$
$$(5)$$

Here K_{sr}^0 is the equilibrium constant of (2) for highly dilute solutions. The quotient of activity coefficients, $\psi_{sr} = (\gamma_r)^s/(\gamma_s)^r$, measures the effects of interaggregate interactions. $\psi_{sr} > 1$ for $s > r$ means that the interactions favor the formation of larger aggregates. (Note that the size distribution, defined either as $n_s/\sum n_s$ or as $N_s/\sum N_s$, is determined by (5) and (1).)

The leading term in the expansion of $\chi_s = (kT/s) \ln \gamma_s$ as a power series in the aggregate densities is given by

$$\chi_s = -(kT/s)\sum_r \beta_1(s,r)\rho_r \qquad (6)$$

where $\beta_1(s,r)$ is the cluster integral[1,5]

$$\beta_1(s,r) = \frac{1}{V}\int f_{rs}\, d\tau_r\, d\tau_s =$$
$$\frac{1}{V}\int [\exp(-w_{rs}/kT) - 1]\, d\tau_r\, d\tau_s \quad (7)$$

Here f_{rs} is the Mayer function, and w_{rs} is the potential of mean force acting between an r and an s aggregate in the solution. The integrations are over the translational and orientational coordinates of the aggregates. From (5) and (6) we note that if $\beta_1(s,r) \propto s$ then $\psi_{sr} = 1$ and interaggregate interactions will have no effect on the size distribution.

As mentioned above we shall only consider hard-core (hc) interactions. Thus $w_{rs} = w_{rs}^{hc}$ where $w_{rs}^{hc} = 0$ for configurations where the two aggregates do not touch each other and $w_{rs}^{hc} = \infty$ when they overlap. Correspondingly $f_{rs} = 0$ and -1 for the nonoverlapping and overlapping configurations, respectively. Consequently $\beta_1(s,r) < 0$ and $\chi_s > 0$. The precise value of the integral in (7) depends on the size and shape of the particles; $-\beta_1(s,r)$ is the (orientational) average of the volume excluded to the s aggregate by the r aggregate (or vice versa). (In this paper we shall consider only isotropic systems where all orientations are equally likely.)

Excluded Volume Effects

The amphiphile molecules in the aggregates are arranged such that their polar (or ionic) headgroups face the aqueous solution while their alkyl chains form a liquidlike hydrocarbon phase in the interior of the aggregates. Packing considerations then imply that there is some large, $m \gg 1$, lower limit on the number of molecules per aggregate.[2,3] This corresponds to $(\bar{\mu}_s^0 - \bar{\mu}_m^0)/kT \gg 1$ for $s < m$—see eq 5 for K_{sr}^0. It can be argued further that for $s > m$ it is reasonable to write $\bar{\mu}_s^0 = \bar{\mu}_\infty^0 + \alpha/s^p$ where p ($\sim$1) depends on the shape of the aggregates. The size distribution then depends on α, p, and the overall concentration of amphiphiles, N/V. At low concentration the N/V dependence enters through the translational entropy terms ($kT \ln \rho_s$) in $\bar{\mu}_s$, cf. (4). At higher concentrations the interaction term in (4), χ_s, introduces an additional density dependence. With hard-core repulsions as the only interactions, χ_s can be interpreted as a translational entropy contribution resulting from the finite volume occupied by

the particles. We consider these contributions for two special but common cases, rodlike and disklike micelles.

Rodlike Micelles. Model calculations[3] suggest that rodlike micelles are spherocylinders (cylinders capped by hemispheres at both ends) whose diameter, d, is somewhat larger than twice the length of the constituent amphiphile molecules. Even at low and moderate concentrations these micelles are polydisperse in size with $\langle l_s \rangle \gg d$; l_s denotes the length of the cylindrical part of an s aggregate. As first shown by Onsager[1] for two spherocylinders of the same diameter d and cylindrical parts of lengths l_s and l_r

$$-\beta_1(s,r) = (4\pi/3)d^3 + \pi d^2(l_s + l_r) + (\pi/2)dl_s l_r$$
$$\simeq (\pi/2)dl_s l_r \qquad (l_s, l_r \gg d) \qquad (8)$$

The last equality in (8) is valid only for a system containing predominantly long rods, $\langle l_s \rangle \gg d$. In this case most of the molecules comprising an s aggregate lie in the cylindrical part, so that $\pi d l_s \simeq a_0 s$ where a_0 is the average area per head group in the aggregate. Thus $l_s \propto s$. But, according to (6) and the last line of (8), χ_s is independent of s if $l_s \propto s$. Hence $\psi_{sr} \simeq 1$ and excluded volume interactions are expected to have very little effect (via the neglected terms in (8)) on the size distribution of a polydisperse system of long rods.

More explicitly, as far as excluded volume effects are concerned, the free energy corresponding to n_s rodlike aggregates of length l_s ($\gg d$) is the same as that of a system containing $2n_s$ aggregates of length $l_s/2$. This is because for $l_s \gg d$, the excluded volume per s aggregate is proportional to l_s ($\propto s$) while the overall contribution to the free energy should be multiplied by the number of s aggregates ($\propto 1/s$). This argument can be generalized to arbitrary variations in the size distribution.

Disklike Micelles. Packing considerations suggest that disklike micelles have the shape of a very flat cylinder with a hemicylindrical rim surrounding its edges.[3] The flat part of the disk is a bilayer of amphiphile molecules, so that its width, h, is again about twice the molecular length. We consider a polydisperse mixture of large disklike micelles, i.e., $\langle d_s \rangle \gg h$, where d_s is the diameter of an s-disklike aggregate. Then the major contribution to $\beta_1(s,r)$ is due to the interaction between the flat parts of the disk. For two particles with d_s, $d_r \gg h$ we have[1]

$$-\beta_1(s,r) \simeq (\pi/4)^2 d_s d_r(d_s + d_r) = \kappa(sr^{1/2} + rs^{1/2}) \quad (9)$$

where the second line follows from the fact that $d_s \propto s^{1/2}$. More precisely $\pi(d_s/2)^2 = a_0(s/2)$; thus $d_s = (2a_0/\pi)^{1/2}s^{1/2}$ and the proportionality constant in (9) is $\kappa = (\pi/32)^{1/2}a_0^{3/2}$.

Substituting (9) into (6) and using (1) we obtain

$$\chi_s = a + b(N/V)/s^{1/2} \qquad (10)$$

where a and b are constants independent of s, with $b = kT\kappa$. Using (10) in (5) we find that the activity quotient ψ_{sr} is given by

$$\psi_{sr} = \exp[\kappa(N/V)(sr^{1/2} - rs^{1/2})] \qquad (11)$$

From this result it follows directly then that $\psi_{sr} > 1$ for $s > r$. That is, excluded volume effects favor the formation of larger disklike aggregates. Furthermore, these effects can be significant, i.e., $\psi_{sr} \gg 1$.

As an example, consider $\psi_{s,s/2}$ corresponding to $A_s \rightleftharpoons 2A_{s/2}$. From (11) we have that $\psi_{s,s/2} = \exp[c(N/V)(a_0 s)^{3/2}]$ where $c = (\pi/32)^{1/2}(1/\sqrt{2} - 1/2) \lesssim 1$. But the total volume fraction of amphiphile molecules is $y \sim N(a_0 h/2)/V$, where h (about twice the molecular length) is the width of each disk. Thus $\psi_{s,s/2} = \exp[c'y(a_0 s)^{3/2}/a_0 h]$ with $c' \sim 1$. But $(a_0 s)^{1/2}/h \gg 1$ since $s \gg 1$ and $(a_0 s)^{1/2}/h \gg 1$. Hence, even at relatively small total amphiphile concen-

tration ($y \ll 1$), $\psi_{s,s/2}$ may be significant.

An analysis of the type presented above can be easily applied to the case of spherical micelles. However, this case is of less interest since geometric packing considerations require that the size distribution is nearly monodisperse, i.e., even small variations in the number of molecules per micelle imply a change of shape.

Discussion and Summary

The micellar aggregates formed in soap solutions usually have well-defined shapes due to the relatively strong binding between the molecules comprising them. These clusterings are accounted for by the $\tilde{\mu}_s{}^0$ term in the chemical potential, cf. (4) and (5). Interaggregate interactions represent perturbations whose effects on the self-assembly mechanism depends on the relative magnitudes of χ_s and $\tilde{\mu}_s{}^0$. (Note the analogy to the problem of interacting "physical clusters" in classical nucleation theory.[5,6]) In particular the effects on the size distribution of aggregates of a given shape depend on the relative magnitudes of the s dependent contributions to χ_s and $\tilde{\mu}_s{}^0$. $\tilde{\mu}_s{}^0$ is often of the form $\tilde{\mu}_s{}^0 = \tilde{\mu}_\infty{}^0 + \alpha k T / s^p$ where p depends on the shape;[3] e.g., for rods $p = 1$ while for disklike micelles $p = 1/2$. The parameter α measures (in units of kT) the difference between the average binding energies of molecules in the hemispherical caps and cylindrical parts, respectively, of a spherocylindrical aggregate. Based on model calculations using (4) without the χ_s term, and comparisons to some available experimental data, it has been concluded[3] that α is typically ~ 10. If this is indeed the case then interaggregate interactions are expected to be of significance in determining the size distribution only at high concentrations.

More explicitly, recall from eq 10 that for disks the s dependent part of χ_s is $b(N/V)/s^{1/2}$, or $a_0{}^{3/2}(N/V)kT/s^{1/2} = [2(a_0{}^{1/2}/h)y]kT/s^{1/2}$. This is to be compared with the s dependent part of $\tilde{\mu}_s{}^0$: $[\alpha]kT/s^{1/2}$. Since $y < 1$ for all concentrations, and $2a_0{}^{1/2}/h \lesssim 1$, $[2(a_0{}^{1/2}/h)y]$ will be small compared to α if needed α is as large as 10. It follows from eq 5, where $\tilde{\mu}^0$ and χ contribute additively to $\ln (\rho_s)^r/(\rho_r)^s$, that interaction effects will make only small corrections to the size distribution. This is not inconsistent with the possibility discussed earlier that $\psi_{sr} \gg 1$. It simply means that the "equilibrium constant" $K_{sr}{}^0$, see eq 5, is still larger than ψ_{sr}, i.e., $K_{sr}{}^0 \gg \psi_{sr} \gg 1$.

Even if $\alpha > 1$ and interaggregate interactions have little effect on the size distribution, they may still play a decisive role in discriminating between different shapes. Suppose, for example, that two micellar shapes have nearly (but not exactly) the same $\tilde{\mu}_s{}^0$ values. Since χ_s is concentration

dependent the micellar shape which was less stable at the lower concentration can have a lower chemical potential as the concentration (N/V) is increased. In this connection it should be mentioned that relatively secondary effects, e.g., those associated with the different curvatures of different shapes, have been argued to be important in determining the thermodynamically most stable shape.[3d]

At high enough concentrations, interaggregate interactions become the driving force for the transition from an isotropic to an ordered solution of micelles. A variety of such order–disorder transitions has been observed in aqueous surfactant systems. Depending upon the precise conditions of concentration and temperature, lyotropic nematic phases are found[4] which are uniaxial with positive or negative character, or biaxial (many lamellar and other kinds of positionally ordered phases are also seen). To study the properties of these systems one must generalize the chemical potential $\tilde{\mu}_s$ to allow explicitly for an anisotropic distribution of aggregate orientations. Also, the Onsager–McMillan–Mayer virial expansion must be abandoned in favor of a representation which involves summing the density to all orders (see, for example, the y expansion proposed in earlier work[7] on the statistical thermodynamics of *neat* liquid crystals). Note that in the case of nematic ordering our primary concern is no longer with the effects of intermicelle interactions on the *size* distribution, as reflected by the s dependent part of χ_s, but rather with the *total* (s dependent *and* independent) contribution of χ_s. Finally, it is interesting to extend the above considerations to include the effects of different shapes coexisting in a single soap solution and the role of interaggregate forces on their relative stability. For example, in the case of coexisting "rods" and "plates", these forces probably account for the biaxial properties observed in potassium laurate systems.[4b] In *thermotropic* (*neat* liquid) samples of rod–plate mixtures, biaxiality can be explained[8] by invoking interactions between the prolate and oblate axially symmetric particles. In the *lyotropic* soap solutions, on the other hand, the interacting anisotropic particles do not maintain their integrity. Instead, as described above, they change their size (and shape) with concentration and temperature. Also there is often present more than one amphiphilic species (e.g., decanol is added to potassium laurate[4]), so that real chemical mixture effects must be treated. These phenomena are presently under study.

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