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LETTERS

Flow Effects on Micellar Size Distribution

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We consider for the first time the consequence of flow fields on the size of micellar aggregates. In the case of extensional flow, we incorporate directly an effective potential into the conditions for self-assembly equilibrium. While the perpendicular component of the viscous forces serves mainly to align the rodlike micelles, the parallel contribution results in a deformation energy. This latter term imposes on the size distribution an upper cutoff which is a strongly decreasing function of velocity gradient.

Micellized solutions of surfactant molecules present many conceptual challenges arising from the coupling of self-assembly and thermodynamics. Even in dilute solution, for example, the size of rodlike aggregates is known to increase significantly upon raising the surfactant concentration.¹ At higher concentrations, where interactions between the micelles become important, the average aggregation number is further affected by adding surfactant.² The onset of long-range orientational or positional ordering is also observed to change the micellar size.³

In attempting to measure directly via X-ray and neutron scattering the size of micelles in concentrated, isotropic solutions, weak shear flows have been used to align the rodlike aggregates.⁴ These studies assume implicitly that neither flow nor alignment has any sensible effect on the average aggregation number. Similarly, in analogy with polymer solutions and colloidal suspensions whose particles have a fixed molecular weight, mea-

surements of intrinsic viscosities have commonly been pursued as a means for determining micellar shapes and dimensions.⁵ Here too the data are interpreted under the assumption that the aggregates maintain their integrity under the imposed conditions of shear, even as concentration effects on micellar size are shown to be significant.⁶ Finally, recent studies^{7,8} of the dynamics of

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stress relaxation in solutions of "wormlike" micelles have treated nonlinear viscoelasticity effects, but not yet those arising from dependence of aggregate size on flow rate.

In the present Letter we consider for the first time the direct effect of viscous forces on the micellar self-assembly process. This phenomenon is of interest in its own right, since it has no counterpart in the case of "ordinary" colloidal solutions whose particles can at most be deformed/aligned (as in the case of flexible polymers⁹) or positionally ordered (as, say, in latex sphere suspensions¹⁰). In these latter situations, the structural changes imposed by the flow give rise to dramatic nonlinear features for the viscosity. In the case of micelles, on the other hand, the "particles" undergo in addition a change in their average aggregation number ("molecular weight"). We expose in particular here the direction and extent to which the self-assembly equilibrium is shifted in response to the viscous forces associated with elongational flow.

Consider first the torques exerted on a rigid rodlike object which is suspended in a solvent whose velocity field has the form $\mathbf{v}(\mathbf{r}) = \gamma z \hat{\mathbf{z}} - (\gamma/2)r\hat{\mathbf{r}}$. This is the case of uniaxially converging, extensional flow in the z direction: $\hat{\mathbf{r}}$ is the unit vector along the radial normal and γ the velocity gradient. As argued in the context of polymer solutions by Kramers,¹¹ the case of extensional flow is special since, unlike the shear situation where the velocity field has nonvanishing curl, the role of the viscous forces can be described by an effective potential. Modeling the rod by a linear, rigid string of point masses, each separated from the next by a distance a , and assuming that their center of mass moves with the solvent, it is straightforward to show¹² that the total torque on the rod, when it makes an angle of θ with respect to the flow, is $(\gamma\xi a^2/8)M^3 \sin\theta \cos\theta$. Here, ξ is the bead friction coefficient and M is the number of beads in a rod of length $L = Ma$. It follows that

$$U_{\perp}(\theta) = (\gamma\xi/16a)L^3 \sin^2\theta \quad (1)$$

is the work (integrated torque) required to bring the rod from 0 angle to θ . The \perp subscript refers to the fact that the relevant viscous forces act perpendicular to the rod axis. In addition to the above mechanical analysis, it is also possible to obtain the effective potential (1) from consideration of the steady-state solution to a Smoluchowski-type equation for rotational diffusion in the presence of elongational flow.¹³

Now what about the frictional forces which act parallel to the rod axes? Using similar analysis as for torques above, we find that the axial force on the bead at a distance s from the center of mass is $\gamma\xi s P_2(\cos\theta)$. Integrating this result from s out to $L/2$ then gives $F_{\parallel}(s) = (\gamma\xi/a)P_2(\cos\theta)[(L/2)^2 - s^2]$ for the total parallel component (tension!) at position s . The local stretching deformation is proportional to $F_{\parallel}(s)$, according to $\delta(s) = F_{\parallel}(s)/K$, where K is an intrinsic elastic constant characterizing the rod. Writing the corresponding deformation energy as $1/2 K \delta^2(s)$ and integrating over the length of the rod, we find

$$U_{\parallel}(\theta) = (\gamma^2\xi^2/60Ka^3)L^5(P_2(\cos\theta))^2 \quad (2)$$

Note that for an undeformable rod ($K \rightarrow \infty$) $U_{\parallel} \rightarrow 0$ and the only effect of the viscous forces is to exert a reorienting torque ($\leftrightarrow U_{\perp}$).

To incorporate the effect of flow into the self-assembly process, we consider the "slow reaction limit" in which changes in micellar size occur on a time scale that is long compared to orientational diffusion of the rods in presence of flow. In this regime we assert

that the potentials (1) and (2) can be added to the micellar free energy which appears in the excess (over pure solvent) Helmholtz function ΔA of the overall surfactant solution.¹⁴ More explicitly, we write

$$\frac{\beta\Delta A}{N_w} = \sum_n \int d\Omega \frac{X_n(\Omega)}{n} \left\{ \beta\mu_n^{\circ} + \ln \frac{X_n(\Omega)}{n} - 1 + \beta U(\Omega) \right\} \quad (3)$$

(In writing eq 3 it has been assumed that the micellar solution is dilute enough to behave ideally; i.e., no interaggregate force effects are significant.²) Here $\beta = 1/kT$, N_w is the number of water molecules, $X_n(\Omega)/n$ is the mole fraction of micelles of size (aggregation number) n and orientation Ω , $\beta\mu_n^{\circ}$ is the standard chemical potential of an n -micelle,¹ and $U(\Omega) = U_{\perp} + U_{\parallel}$ is the effective potential due to flow discussed above. Minimization of (3) with respect to $X_n(\Omega)$, subject to the conservation condition

$$x_1 + \sum_{n \geq m} \int d\Omega X_n(\Omega) = X \quad (4)$$

where X is the total mole fraction of surfactant in water, leads to the size/orientation distribution

$$4\pi X_n(\gamma = \cos\theta) = ne^{-\beta\delta}(x_1 e^{\beta\Delta})^n e^{-\beta U(\gamma)} \quad (5)$$

In deriving the above, we have used the fact that $X_n(\Omega)$ depends only on $\cos\theta$ for elongational alignment and that $\mu_n^{\circ}/n = \bar{\mu}_n^{\circ} = \bar{\mu}_{\infty}^{\circ} + \delta/n$ for rodlike micelles with $n \geq m$, where m is a minimum aggregation number (of order 50). The energy $\delta \equiv m(\bar{\mu}_s^{\circ} - \bar{\mu}_{\infty}^{\circ})$ is proportional, through m , to the difference in standard chemical potentials (per molecule) for the "cap" ($\bar{\mu}_s^{\circ}$) and "body" ($\bar{\mu}_{\infty}^{\circ}$) portions of the rod. Similarly, $\Delta \equiv \bar{\mu}_1^{\circ} - \bar{\mu}_{\infty}^{\circ}$ is the standard free energy difference for isolated surfactants ("monomer") in solution and molecules in the rod body. (x_1 is the mole fraction of monomer.) Note that the dimensionless quantity $\beta\Delta$ determines the overall tendency for micellization to occur (e.g., the critical micelle concentration $X_{cmc} \approx e^{-\beta\Delta}$), whereas $\beta\delta$ controls the average aggregation number ($\langle n \rangle_0 \approx (Xe^{\beta\delta})^{1/2}$) in the absence of flow.

Since $U(\theta)$ is given by the sum of (1) and (2), its n dependence is seen to follow directly from that of the rod length, i.e., from $L \approx [(n-m)/m]a \approx (a/m)n$. Furthermore, to estimate the elastic constant K , we set the maximum deformation energy Ka^2 equal to αkT and take α of order 20, corresponding to the typical binding strength for a micelle. Finally, we replace the bead friction coefficient ξ by $6\pi\eta a$, where η is the solvent viscosity. Thus, the coefficient of $\sin^2\theta$ in U_{\perp} (see eq 1) can be expressed as $(3\pi/8m^3)(\eta\gamma a^3)(n-m)^3$, while that of $(P_2(\cos\theta))^2$ in U_{\parallel} (see eq 2) assumes the form $(3\pi^2/5m^5\alpha kT)(\eta\gamma a^3)^2(n-m)^5$. For the results discussed below, we take $e^{-\beta\delta} = 2 \times 10^{-10}$, $e^{\beta\Delta} = 10^5$, $m = 20$, $\eta = 10^{-2}$ P, $a = 10$ Å, $T = 300$ K, and $\alpha = 20$. For $\gamma = 10^3$ s⁻¹, then, the dimensionless flow potential becomes ($n \gg m$)

$$\beta U_n(\gamma) = a_{\perp}(1 - \gamma^2)n^3 + a_{\parallel}(P_2(\gamma))^2 n^5 \quad (6)$$

with $a_{\perp} \approx 3.6 \times 10^{-11}$ and $a_{\parallel} \approx 5.4 \times 10^{-21}$. To generate the micellar size distribution for an arbitrary overall concentration X , we solve for the monomer mole fraction x_1 which allows the $X_n = 4\pi \int_0^{\pi} d\gamma X_n(\gamma)$ from eq 5 to sum to X according to (4): $x_1 + \sum_{n \geq m} X_n = X$.

The effects of viscous forces on micellar size distribution $\{X_n\}$ are demonstrated in Figure 1 A and B, for total surfactant concentrations $X \approx 6.0 \times 10^{-3}$ and 6.0×10^{-2} , respectively. Each figure contrasts the distribution corresponding to zero flow (i.e., $\beta U_n = 0$) with that for finite flow with $\gamma = 10^3$ s⁻¹. These results can be understood by considering the roles played by the two terms in the effective potential (6). Clearly their effects on $X_n(\gamma)$, and hence on X_n , will only be significant for those values of n that allow $a_{\perp}(1 - \gamma^2)n^3$ and/or $a_{\parallel}(P_2(\gamma))^2 n^5$ to exceed unity. Using the numerical estimates of a_{\perp} and a_{\parallel} given above, it is easily seen that—except for $\theta \approx 0$ (where $U_{\perp} \approx 0$)—the first term in βU will become important at smaller values of n than the second. Spe-

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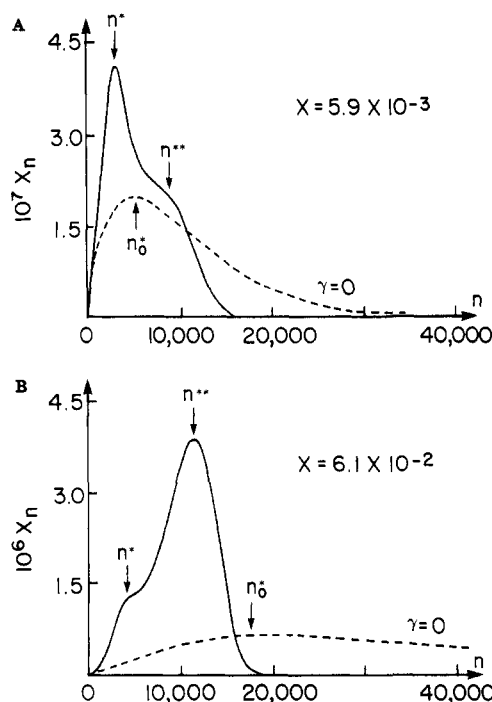


Figure 1. (A) Size distributions, at a total surfactant mole fraction of 5.9×10^{-3} , in the presence of velocity gradients of 10^3 s^{-1} (solid curve) and zero (dashed). (B) Same as in (A), but for $X = 6.1 \times 10^{-2}$.

cifically, $U_{\perp}(y)$ will suppress all $X_n(y)$ for which n is greater than $n_{\perp}(y) \approx [1/a_{\perp}(1-y^2)]^{1/3}$. $y \approx 0.5$, for example, gives $n_{\perp} \approx 3500$, implying that no micelles larger than this can survive at an off-axis angle of $\theta \approx \cos^{-1}(0.5)$: bigger aggregates can remain only if they are aligned closer to the flow axis ($\theta = 0$, $y = 1$). For $y \approx 0.95$, for example, n_{\perp} is as large as 7800, and so on.

Even though U_{\perp} allows large micelles to survive along the flow axis,¹⁵ their size is limited even in this preferred direction. This is because $X_n(y \approx 1)$ is eventually suppressed (i.e., the size distribution is truncated) by the influence of the *parallel* component U_{\parallel} of the flow potential. More explicitly, for $y \approx 1$ ($P_2(y) \approx 1$) a sharp decrease in X_n will occur for $n > n_{\parallel}(y \approx 1) \approx (1/a_{\parallel})^{1/5} \approx 11\,400$. (Recall that all of the above estimates refer to $\gamma = 10^3 \text{ s}^{-1}$.) Since micelles in *off-axis* directions cannot attain such high n values due to the action of U_{\perp} , this n_{\parallel} limit heralds the onset of a sharp falloff in $X_n \sim \int dy X_n(y)$ as well.

Thus, it appears that the aligning (U_{\perp}) potential acts as a "funneling filter", suppressing micellar size (beyond n_{\perp}) in off-axis orientations, so that the larger aggregates can only survive if they are aligned near parallel to the flow. The size of micelles along this axis, however, is eventually limited by the deformation term (U_{\parallel}), which presents a barrier to aggregation numbers exceeding n_{\parallel} . The effect of parallel viscous forces is seen, then, to enter as a *cutoff* in micellar size, as if the aggregates were *breaking* upon reaching a critical length in the presence of flow. This phenomenon can be understood by reexamining the axial component, F_{\parallel} , of the viscous forces. Recall that its maximum occurs at the center

($s = 0$) of the micelle, where $F_{\parallel} = (\gamma\xi/a)L^2$. The maximum deformation $\delta = F_{\parallel}/K$ is then given by $(\gamma\xi a)L^2/\alpha kT$, where we have used $K = \alpha kT/a^2$ as before. Clearly, the micelle "breaks" when $\delta = \mathcal{O}(a)$, i.e., when $L^2\gamma$ exceeds $\alpha kT/\xi$, implying $L_{\text{max}} (\propto n_{\text{max}}) \propto 1/\gamma^{1/2}$.¹⁶ For the α and $\xi = 6\pi\eta a$ values mentioned earlier, n_{max} turns out to be of order 10^4 – 10^5 for $\gamma = 10^3 \text{ s}^{-1}$.

In order that the effects of flow will be nonnegligibly reflected in X_n , the $\gamma \equiv 0$ distribution X_n^0 should of course give rise to micelles of size $n > n_{\parallel}$. Since $\langle n \rangle_0$ —and, similarly, the most probable size n^*_0 —increases with total concentration X (roughly as $X^{1/2}$), the size reduction due to flow will *also* increase with X . In Figure 1A, where $n^*_0 \approx 5500$, we note the appearance of a shoulder in $\{X_n\}$ around $n^{**} \approx 9000$, followed by a sharp cutoff at $n \approx 16000$, the latter effect being due to the U_{\parallel} barrier. The sharpness of the peak at $n^* \approx 3200$ arises from the (alignment, n_{\perp}) suppression of $X_n(y)$ for $n \geq 5000$ for $y \leq 0.9$. In addition, the shoulder at n^{**} reflects a high- n preference which anticipates the limit n_{\parallel} imposed by the U_{\parallel} potential: this feature is due entirely to $y \approx 1$ micelles, whereas the first peak (n^*) corresponds to aggregates which are small enough not to be significantly affected by the flow; their angular distribution is very nearly isotropic. The fact that the micelles want to be as big as possible (large n^*_0) and yet still respect the U_{\parallel} cutoff ($n < n_{\text{max}} < n^*_0$) implies that the size distribution will be narrower than in the absence of flow.

As X increases, we expect that the n^{**} feature will become more and more pronounced, as a large number of big micelles appear, and shift out to bigger n (see Figure 1B). These aggregates will necessarily be more narrowly confined to the flow axis, simply because big micelles in other directions cannot survive. Note that the large- n cutoff still lies around 17000, as in Figure 1A, since this maximum size is determined essentially by the imposed velocity gradient ($n_{\text{max}} \propto \gamma^{1/2}$) rather than by concentration.

To test experimentally the predictions displayed in Figures 1A,B, it will be important to work with a surfactant that is known to form sufficiently large ($n > 10^3$) and rigid rodlike aggregates in dilute isotropic solution and then to measure directly the size distributions over a wide range of overall concentration and elongational flow strength. Alternatively, one could probe the effect of size reduction via tension by looking for a maximum in the plot of induced birefringence vs velocity gradient;¹⁷ the initial increase is due to flow alignment with the subsequent decrease arising from the "breaking" of the micelles into smaller lengths.¹⁸ Indeed, numerical evaluation of $\langle n \rangle$ over the full range of velocity gradients ($0 < \gamma < 10^3 \text{ s}^{-1}$) shows a weak variation at small γ followed by a dramatic decrease at large γ .

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(15) In fact, keeping only the perpendicular contribution to U in eqs 4 and 5 leads to an average aggregation number which first varies only weakly with γ and then becomes infinite at a critical value, with γ_{crit} a strongly decreasing function of concentration.