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Hydrodynamic Theory of Micellar Solutions: Suppression of Micellar Growth by Interactions

S. Q. Wang

Departments of Macromolecular Science and Physics, Case Western Reserve University, Cleveland, Ohio 44106

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ABSTRACT: A hydrodynamic theory of rigid-rod micellar solutions is presented. The previously omitted intermicelle interactions are incorporated by generalizing the Onsager theory for nematic liquid crystals to account for polydispersity and self-assembly in the presence of flow. The micellar size distribution is derived as a function of shear rate in the form of a highly nonlinear integral equation. A numerical iteration procedure has been developed to simulate the solution to this integral equation. It is found that intermicellar repulsion postpones the micellar growth (*Macromolecules* **1991**, *24*, 3004) in flow to higher shear rates.

I. Introduction

Hydrodynamics of self-assembling micellar solutions is a relatively new subject and is not well understood despite its fundamental importance to practical applications. Over the past decade several experimental papers have appeared, some discussing the viscoelastic behavior of rodlike micelles in surfactant solutions,[2] some reporting light scattering measurements of the diffusion coefficient,[3] some addressing drag reduction in turbulence (DRT) by surfactant aggregates,[4,5] and others dealing with so-called flow-induced supramolecular structures (SIS) in sheared micellar solution.[6,7] There seems to be a connection between DRT and SIS based on the view that SIS should also form in turbulent flow and may be responsible for the drag reduction. In order to probe such a connection, one needs to study SIS in detail both experimentally and theoretically. If there were SIS, what are they? How are they formed? How can one experimentally probe them directly rather than infer them from rheological measurements? One crucial question is whether formation of supramolecular structures in shear flow is the only explanation for the viscosity increase with shear rate or whether other uncovered flow effects can account for the shear-thickening behaviors observed in many ionic surfactant solutions.[6,7]

Two approaches have been proposed to provide a theoretical interpretation of the shear-thickening behavior of micellar solutions.[8,9] By formulating a kinetic reaction-rate equation for micellar distribution and considering collinear collisions between micelles, Cates and Turner find that elongational flow is more effective in inducing micellar growth than a simple shear flow. One reason for why this conclusion is reached is that the association and dissociation rates for micelle formation and scission are assumed to remain the same in both quiescence and flow. Along a different line where the steady-state shear-rate-dependent micellar size distribution is derived, it was demonstrated in contrast to the conclusions of ref 9 that the average micellar size becomes significantly bigger upon increasing shear rate Γ while the micelles shrink in size under a uniaxial extensional flow field. Furthermore, for a dilute surfactant solution containing rodlike micelles, we showed that the micellar growth in the absence of intermicellar interactions does not contribute to the viscosity buildup with shear rate.[11]

Although the prediction of increasing micellar size with shear rate is an important one (and needs to be experimentally verified) and may help understand the drag reduction by surfactant aggregates, it does not explain the experimental data on the SIS-forming systems.[6,7] Most importantly, we have completely omitted[8] in our formulation the intermicellar repulsive interactions which become more and more nonnegligible as the micelles grow with Γ.

In this paper we recognize that a reliable model of rheological properties of micellar solutions should include intermicellar (electrostatic or steric) interactions. It is expected that the excluded-volume interaction will prohibit significant micellar growth in shear flow. It remains to be seen what the rheological implications are when the interaction is taken into account. In section II we introduce our hydrodynamic theory for micellar solutions which incorporates micelle–micelle interactions for the first time, and in section III numerical results are presented.

II. Dynamics of Interacting Micelles

A. Excluded-Volume Interactions. Steric repulsion between rodlike particles, either charged or neutral, can be described in terms of the particle orientational distribution.[12] If the particles are uniformly distributed in space, then the leading term of the excluded-volume interaction is linearly proportional to the particle density with higher order terms negligible for $d/L \ll 1$ where d and L are the diameter and length of the rodlike particle. It is straightforward to generalize the Onsager theory to a polydisperse and self-assembling system such as rigid-rod micelles. Suppose the distribution function $\chi_n(\mathbf{u})$ is the mole fraction of surfactants forming micelles with aggregation number n and orientation $\mathbf{u}$ and ρ_s designates the surfactant number density in the solution. Then the concentration of n-sized micelles with orientation $\mathbf{u}$ is given by $[\rho_s\chi_n(\mathbf{u})/n]$. A rodlike micelle of size (aggregation number) n in the solution has the following excluded-volume interaction potential (in units of $k_BT = 1$)

$$U_n(\mathbf{u},\{\chi_n\}) = \sum_{n'}\int d\mathbf{u}'\ \rho_s[\chi_{n'}(\mathbf{u}')/n']\ \beta(\mathbf{u},\mathbf{u}') \qquad (2.1a)$$

where the excluded-volume function $\beta(\mathbf{u},\mathbf{u}')$ is given by

$$\beta(\mathbf{u},\mathbf{u}') = 2L_nL_{n'}d_{\text{eff}} \sin\gamma \qquad (2.1b)$$

Here γ is the angle between $\mathbf{u}$ and $\mathbf{u}'$; L_n and $L_{n'}$ are the lengths of two micelles: $L_n = (n/m)d$ where m = minimum aggregation number of a (spherical) micelle and d = diameter of the micelles. The effective micellar diameter $d_{\text{eff}} > d$ is introduced to incorporate the electric double-layer interaction which is on the order of the double-layer thickness. By definition, the mole fraction function $\chi_n(\mathbf{u})$ normalizes to unity through summation over n and

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integration over **u**

$$\sum_n \int \mathrm{d}\mathbf{u}\, \chi_n(\mathbf{u}) = 1 \qquad (2.2)$$

In equilibrium (absence of a macroscopic flow field), the distribution $\chi_n^{\mathrm{eq}}(\mathbf{u})$ assumes the following form of an integral equation[13]

$$\chi_n^{\mathrm{eq}}(\mathbf{u}) = \mathrm{const} \times n\lambda_0^{\,n} \exp[-U_n(\mathbf{u},\{\chi_n^{\mathrm{eq}}\})] \qquad (2.3a)$$

where const is determined through the normalization condition (2.2), namely

$$\mathrm{const} = [\sum_n n\lambda_0^{\,n} \exp[-U_n(\mathbf{u},\{\chi_n^{\mathrm{eq}}\})]]^{-1} \qquad (2.3b)$$

λ_0 is a phenomenological quantity controlling the micellar sizes in the equilibrium solution. The highly nonlinear integral equation (2.3a) with (2.3b) has the same structure as that of Onsager's for nematic liquid crystals,[12] except for being complicated by the additional variable n which leads to polydispersity. Here we choose to solve the integral equation (2.3a) and the one below in (2.6) via numerical iteration instead of by spherical-harmonic expansion.[13,14]

B. Micelle Orientation in Shear Flow. When both Brownian rotational motion and flow alignment are important, the nonequilibrium statistical mechanical description of rodlike particles in shear becomes difficult. This is mainly due to the rotational component in a simple shear flow and therefore to the absence of a stable position associated with a "potential" minimum. Unable to treat the effects of shear flow as a potential, one resorts to the standard formulation of Brownian motion in the presence of an external field and writes down a Smoluchowski type diffusion equation (SDE) for the orientational distribution. This partial differential equation cannot be analytically solved even in the steady-state limit, making the analysis rather complicated. In dealing with the rheology of lyotropic liquid-crystalline polymer solutions, Marrucci and Maffettone[15] were the first to simplify the SDE to an ordinary differential equation by considering a two-dimensional analogue. Their approach was later justified by a three-dimensional calculation.[16] We have adopted this simplified picture and formulated a hydrodynamic treatment of flow behaviors of dilute micellar solutions.[8] It was found that in the absence of intermicellar interactions micelles can get longer in shear than in the quiescent state. Of course, we only expected the single-particle approximation[8] to be applicable in the extremely dilute limit: It is possible that excluded-volume effects will work against micellar growth and invalidate our previous results.

In this paper, we neglect any flexibility of the cylindrical micelles and take the two-dimensional version of the Smoluchowski equation for the orientational (angular) dependence of the mole fraction $\chi_n(\theta)$. For a simple shear flow $\mathbf{v}_0 = \Gamma y\hat{x}$, we have

$$\partial\chi_n(\theta,t)/\partial t = D_r(n)(\partial/\partial\theta)[\partial\chi_n/\partial\theta + \chi_n\partial U_n/\partial\theta + (\Gamma/D_r)(\sin\theta)^2\chi_n] \qquad (2.4)$$

where $D_r(n) = 4k_BT/\pi\eta_s L_n^{\,3}$ is the rotational diffusion coefficient of the n micelle which scales as n^{-3} with n the aggregation number and U_n in (2.1a,b). The steady-state $\chi_n(\Gamma,\theta)$ can be derived by integrating (2.4) with $\partial\chi_n/\partial t$ = 0:

$$\chi_n(\Gamma,\theta) = C(\Gamma,n)e^{-G[\theta-1/2\sin(2\theta)]-U_n(\theta,\{\chi_n\})} \times x[B(\Gamma,n)\int_0^\theta \mathrm{d}\alpha\, e^{G[\alpha-1/2\sin(2\alpha)]+U_n(\alpha,\{\chi_n\})} + 1] \qquad (2.5)$$

where B and C are integration constants which may depend on n and shear rate Γ. The dimensionless constant $G = \Gamma/2D_r(n)$. Constant B can be determined by using the boundary condition $\chi_n(\Gamma,\theta{=}0) = \chi_n(\Gamma,\theta{=}\pi)$. Constant C is obtained by comparison between (2.5) and the equilibrium function (2.3a). Finally the explicit expression for the mole fraction distribution $\chi_n(\Gamma,\theta)$ is given by

$$\chi_n(\Gamma,\theta) = \mathrm{const} \times n\lambda^n e^{-G[\theta-(1/2)\sin(2\theta)]-U_n(\theta,\{\chi_n\})} \times [(e^{\pi G}-1)\int_0^\theta \mathrm{d}\alpha\, e^{G[\alpha-(1/2)\sin(2\alpha)]+U_n(\alpha,\{\chi_n\})} / \int_0^\pi \mathrm{d}\alpha\, e^{G[\alpha-(1/2)\sin(2\alpha)]+U_n(\alpha,\{\chi_n\})} + 1] \qquad (2.6)$$

where const is similarly defined as in (2.3b). The parameter λ is now so chosen that the normalization condition is satisfied by (2.6). Equation 2.6 represents a set of highly complex nonlinear integral equations labeled by n since U_n depends on $\{\chi_n(\theta)\}$. At first glance, solution of (2.6) appears formidable. Below we will apply our newly developed direct simulation method[14] to the present situation.

III. Results

We begin our evaluation of (2.6) by writing the excluded-volume potential U_n in a more explicit form

$$U_n(\theta,\{\chi_n\}) = [2\rho_T\chi(d/m)^2 d_{\mathrm{eff}}]n\sum_{n'}\int_0^\pi \mathrm{d}\theta'\, \sin(|\theta-\theta'|)\chi_{n'}(\theta') \qquad (3.1)$$

where $L_n = n(d/m)$ is written into (2.1b) and ρ_s by definition is given by the product of the total number density of molecules ρ_T and the total molar fraction χ of surfactant molecules in solution. Let us take d = 20 Å, m = 20, and $\rho_T = \rho_w(1+\chi) \approx (6.023 \times 10^{23}/18)$ cm^{-3} = 0.033 Å^{-3} as that of water for $\chi \ll 1$. Thus the value in square brackets in front of (3.1) is $1.338\chi'$ where $\chi' = \chi(d_{\mathrm{eff}}/d)$. So the quantity (d_{eff}/d) can be regarded as the second phenomenological variable. In the expression (2.6) this parameter appears together with the total surfactant molar fraction χ as a product and therefore different sets of values for χ and (d_{eff}/d) may correspond to the same value of χ'.

First consider a micellar solution in quiescence. For a given value of χ', i.e., a given surfactant molar fraction $\chi = \chi'(d/d_{\mathrm{eff}})$, the parameter λ_0 in (2.3) can be freely varied to match the experimental situation. As λ_0 increases, the solution of (2.3a,b) transforms from the isotropic state where $\chi_n^{\mathrm{eq}}(\mathbf{u})$ is independent of $\mathbf{u}$ to the nematic state where micelles are uniaxially oriented around a particular direction with longer ones better oriented. In this paper, we choose to consider an isotropic dilute solution in equilibrium. Let us take χ' (defined in the previous paragraph) to be $\chi' = 10^{-4}$ and pick $\lambda_0 = 0.9996$ so that the peak of the micellar size distribution is around n = 2000. Once these two variables χ' and λ_0 are chosen, the solution of (2.3a,b) with (3.1) simply amounts to an iteration beginning with an initial trial function $\chi_n^0 = n\lambda_0^{\,n}/\Sigma_n n\lambda_0^{\,n}$. At every iterative step, the normalized $\chi_n^{(i)}$ is inserted into U_n on the right-hand side of (2.3a), and the normalized $\chi_n^{(i+1)}$ on the left-hand side is obtained once the const is computed according to (2.3b): const(i) = $[\Sigma_n n\lambda_0^{\,n} \exp[-U_n(\mathbf{u}, \{\chi_n^{(i+1)}\})]^{-1}$. The final solution is reached when this iterative procedure converges to a fixed $\chi_n^* = \chi_n^{\mathrm{eq}}$ where const is

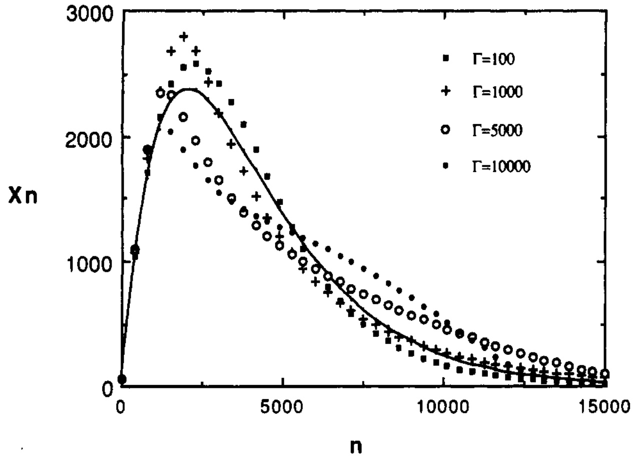

Figure 1. Micellar size distribution. The thin line represents the equilibrium distribution.

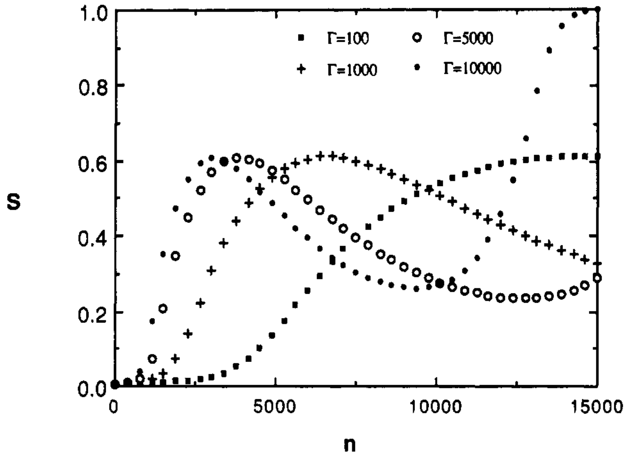

Figure 2. Orientational order parameter S for micelles of all sizes in the solution.

found to be const = 7.5×10^{-8}.

When the micellar solution is subjected to a simple shear flow with shear rate Γ, we need to solve the more complex integral equation (2.6). The same $\chi' = 10^{-4}$ is inserted into (3.1) and (2.6). Now in addition to the numerical iteration described above, the value for the adjustable parameter λ is selected so that the const in (2.6), which is the reciprocal of the summations of the right-hand side of (2.6) over n and θ, equals 7.5×10^{-8}. For example, for the shear rates $\Gamma = 100, 10^3, 5 \times 10^3$, and 10^4 s^{-1}, the values of λ are respectively 0.999 64, 0.999 72, 0.999 78, and 0.999 82. We plot the micellar size distribution $\chi_n(\Gamma) = \int_0^\pi d\theta\, \chi_n(\Gamma,\theta)$ for these values of Γ in Figure 1. As expected, the micelles do not grow substantially; rather, the populations of different sizes are simply redistributed among themselves. It is not clear to us how to observe these changes in the size distribution with shear rates in a micelle-flow experiment. At still higher shear rates than considered here, a tail may start to develop in $\chi_n(\Gamma)$ versus n where micellar growth is no longer prevented by intermicellar interactions since the interactions are diminishing upon increasing flow alignment.

It is instructive to calculate the order parameter for alignment $S(n,\Gamma)$ as a function of micellar size n for different shear rates Γ. This parameter in two dimensions is defined as

$$S(n,\Gamma) = \int_0^\pi d\theta\, [2(\cos\theta)^2 - 1]\chi_n(\Gamma,\theta) \Big/ \int_0^\pi d\theta\, \chi_n(\Gamma,\theta) \qquad (3.2)$$

It indicates the degree of orientation of an n micelle along the shear flow direction X at a given shear rate Γ. In the absence of intermicelle interactions, $S(n,\Gamma)$ increases with micellar size n for a fixed Γ; i.e., the longer the micelle, the better it is aligned by the flow.[8] However, our present results according to (3.2) and (2.6) are a bit surprising in that at high shear rates S does not monotonously increase with n, as shown in Figure 2. This is due to the coupling of the anisotropic intermicellar interaction to the shear flow. At high enough shear rates, the long micelles find themselves in an environment similar to a nematic phase. It is known that shear flow can reduce the orientational order of polymeric liquid crystals, resulting in a negative normal stress difference. We have shown elsewhere[17] that for a lyotropic nematic liquid-crystalline polymer solution at a given shear rate the alignment order parameter S is *not* a monotonously increasing function of the polymer concentration which determines the strength of the Onsager excluded-volume interaction. This decrease of orientational ordering with increasing concentration is the prelude to the onset of a flow instability where the nematic director tumbles. Since the interaction strength is directly proportional to the particle size (the aggregation number n for micelles), our finding in Figure 2 is consistent with the recent results[17] for liquid-crystalline polymers. It is also interesting to see that for different values of Γ the order parameters $S(n,\Gamma)$ all reach the same maximum value as a function of the aggregation number n, with the position of the peak shifting toward smaller n for larger Γ. At present, we do not know how to explore the implication of this behavior nor is it obvious how the decrease of S with n is manifested in the experiment.

In summary, we have developed a tentative molecular-level hydrodynamic theory for rodlike micellar solutions. With the intermicelle interactions incorporated, this theory is, in principle, applicable to micellar solutions up to their nematic phase. In the present study, only one concentration was considered. The effect of concentration comes in through U_n of (3.1) in (2.6). At a higher concentration than considered here, the effect of flow is enhanced and similar curves as shown in Figures 1 and 2 can be seen at smaller shear rates. To describe columnar/hexagonal and lamellar phases of surfactant solutions in flow will require considerable modification of the present theory to account for spatial orderings. In comparison to the noninteracting systems, the intermicellar interaction is found to work against a significant micellar growth simply because larger micelles imply large excluded-volume repulsion. Our work demonstrates that although the interparticle interaction does not play an important role in certain regions of the equilibrium phase diagram it is crucial in dictating the dynamic response of self-assembling micelles to flow.

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