

Low Shear Viscosity of a Dense Ionic Micellar Solution

Ying-Chun Liu¹ and Eric Y. Sheu^{2,*}

¹Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

²Texaco R&D, P.O. Box 509, Beacon, New York 12508

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We present a method for evaluating the low shear viscosity of a strongly interacting nonspherical micellar solution. The contribution from hydrodynamic interaction was calculated according to the Batchelor-Green equation with the effect of micellar shape and the hydration taken into account. The Brownian contribution was calculated by modifying the method of de Schepper, Smorenburg, and Cohen [Phys. Rev. Lett. **70**, 2178 (1993)] with the structure factor extracted from a small angle neutron scattering experiment. The low shear viscosity agrees with the experimental results for hydrated micellar volume fraction ϕ_m up to 0.4.

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The theoretical calculation of the steady shear viscosity of suspensions has attracted rheologists since Einstein derived the equation for the dilute case [1], which is generally accepted as being accurate to first order in the solute volume fraction ϕ . Following Einstein's work a number of equations were developed [2], and several neglected effects, such as solvation, polydispersity, particle shapes, particle viscosity, and agglomeration, were taken into account [3]. As extensions of Einstein's formula, most of the expressions are for dilute suspensions.

Recently the calculation for concentrated hard sphere systems started drawing rheologists' attention. In a concentrated system, one has to accurately evaluate the contributions both from the hydrodynamic interaction and from the Brownian forces. Several authors have computed the pairwise or many-body hydrodynamic interaction [4] to estimate the zero shear viscosity. The results are comparable to experimental data up to $\phi \sim 0.3$. The Brownian contribution was also estimated based either on the Smoluchowski equation or on the Fokker-Planck kinetic equation [5]. Again, most of the results are good for $\phi < 0.3$ only, except Brady's work [5], which agrees with experimental data reasonably well for ϕ up to ~ 0.6 . Although Brady's work is based on the first principles and shows reasonable agreement with the experimental results, it was incomplete. The author used the short time diffusion coefficient to replace D_0 , the dilute limit diffusion coefficient, but then applied Phung's simulation result [5] in the quantitative calculation. Additionally, the formalism developed for hydrodynamic interactions was not used in the calculation (the Batchelor-Green equation was used) and the three-body collision was neglected (the Smoluchowski equation was within the pair space).

de Schepper *et al.* took a different approach [6]. They calculated the Brownian contribution based on the analogy of the linewidth of the intermediate scattering function between a colloidal system and a dense atomic fluid. The Brownian force is directly related to the linewidth which is a function of D_0 , the structure factor $S(Q)$, or its

Fourier transform, the pair correlation function. By evaluating $S(Q)$ with Percus-Yevick's method, de Schepper *et al.* obtained a surprisingly good estimate of zero shear viscosity of a hard sphere system for ϕ from 0.3 to 0.6.

The Brownian contribution to the steady shear viscosity can be written as [6-9]

$$\eta_B(\nu, \phi, \omega) = \frac{n^2}{2\nu} \int dr g(r, \nu, \omega) y \frac{\partial V(r)}{\partial r}, \quad (1)$$

where $g(r, \nu, \omega)$ is the pair distribution function, ω the frequency, ν the shear rate, ϕ the volume fraction, and $V(r)$ the pairwise potential. At zero shear limit and under the condition of mean spherical approximation (MSA), Eq. (1) can be expressed in terms of $S(Q)$ and its derivative $S'(Q)$,

$$\eta_B(\phi, \omega) = \frac{k_B T}{60\pi^2} \int_0^\infty dQ Q^4 \left[\frac{S'(Q)}{S(Q)} \right]^2 \frac{1}{2\omega_H(Q) - i\omega}, \quad (2)$$

where k_B is the Boltzmann constant, T the absolute temperature, and $\omega_H(Q)$ the linewidth of the intermediate scattering function $S(Q, \omega)$. At low frequency limit, $\omega_H(Q)$ is a function of $S(Q)$ and the Enskog self-diffusion coefficient D_E by $\omega_H(Q) = [D_E Q^2 / S(Q)] d(Q)$. This expression is true for a dense fluid of spherical molecules or a hard sphere system [10]. The correction function $d(Q)$ accounts for the effect of the binary collisions on the self-diffusion process at different Q . An approximate form of ω_H [6] is

$$\omega_H(Q) = \frac{D_0 Q^2}{\chi S(Q) [1 - j_0(Q\sigma) + 2j_2(Q\sigma)]}, \quad (3)$$

$$\chi = \frac{1 + \phi/2}{(1 - \phi)^2}. \quad (4)$$

$D_0 = k_B T / 6\eta_0 R_h$ (η_0 is the solvent viscosity and R_h the hydrodynamic radius) is the Stoke-Einstein diffusion coefficient, χ is the value of the pair correlation function

at contact when the system is at equilibrium, and $j_i(x)$ is the spherical Bessel function of i th order.

The advantage of this approach is that the essential quantity in the Brownian contribution, $S(Q)$, is experimentally obtainable. In fact, for many complex fluids systems, $S(Q)$ and its corresponding pair correlation function can be reliably obtained through scattering experiments, as opposed to hard sphere system where $S(Q)$ can be calculated *a priori*. This method provides an opportunity to extend the viscosity calculation beyond the hard sphere limit.

We adopt this approach, with some modification, to evaluate the zero shear viscosity of a strongly interacting ionic micellar system. Since we deal with a wide concentration range, it is essential to take into account both the hydrodynamic interaction and the Brownian forces. de Schepper *et al.* neglected the hydrodynamic contribution completely, nevertheless, their calculation is valid for high volume fraction, where the Brownian effect dominates the low shear viscosity [11].

The system we study is an ionic micellar solution. It represents a class of fluids of great practical importance. The micellar solutions were made by dissolving lithium dodecyl sulfate [$\text{LiSO}_4(\text{CH}_2)_{11}\text{CH}_3$] surfactant (LDS) in water. A LDS surfactant molecule consists of a hydrophobic chain, a polar sulfate headgroup, and a Li^+ counterion. As the concentration exceeds critical micellization concentration (8.9 mM at room temperature), LDS molecules aggregate to form quasispherical micelles. As concentration increases, LDS micelles grow and gradually transfer into ellipsoids [12,13]. The micelle is composed of a hydrophobic core made of dodecyl chains and a hydrophilic outer layer made of polar headgroups and undissociated counterions. The micelle is often hydrated by a substantial amount of solvent molecules in the outer layer. The concentration range studied is from 1 to 28 g dL^{-1} , equivalent to hydrated micellar volume fraction ϕ_m from 0.01 to 0.4, determined from small angle neutron scattering (SANS) experiments. (ϕ_m will be used from what followed as the hydrated volume fraction, in order to be distinguished from ϕ , the volume fraction of the solute).

SANS measurements were performed for LDS in deuterated water (D_2O). Pure D_2O was used in order to enhance the scattering contrast against the protonated alkyl micellar core. The scattering intensity distribution function $I(Q)$ always shows a characteristic peak, signifying strong intermicellar interactions. The intensity $I(Q)$ can be formulated as [13]

$$I(Q) = CN \left(\sum b_i - \rho_s V_m \right)^2 P(Q) S(Q), \quad (5)$$

where C is the molar concentration of LDS, N the aggregation number, b_i the scattering length of the i th nucleus, ρ_s the scattering length density of the solvent, and V_m the dry volume of a LDS molecule ($V_m = 410 \text{ \AA}^3$). The normalized intraparticle structure factor $P(Q)$ is a function of the micellar size, shape, and the scattering lengths density profile. A two-shell ellipsoid

model was used to derive $P(Q)$ [12]. The inner region is an ellipsoid with a minor radius b , equal to the fully stretched length of the dodecyl chain ($b = 16.7 \text{ \AA}$ [14]). The major radius a , determined by the core volume under compact packing constraints, increases with LDS concentration. The outer layer of the micelle has a thickness t . The degree of aggregation N (number of LDS chains in a micelle) and the degree of hydration (number of water molecules per LDS molecule) can be extracted from SANS data fitting. From these two parameters, the average micellar diameter σ ($= 2[(a+t)(b+t)^2]^{1/3}$), micellar shape a/b , and the hydrated volume ϕ_m can be determined.

To evaluate $S(Q)$ we employed the generalized mean spherical approximation (GMSA) theory reported previously [13]. The Ornstein-Zernike equation can be solved within the MSA limit to obtain $S(Q)$. One adjustable parameter, the effective micellar surface charge, is involved. This charge defines the strength of the intermicellar potential $V(r)$. The role of counterions has been neglected except for their contribution to the ionic strength.

Figure 1 shows a typical scattering intensity distribution functions $I(Q)$ and extracted $P(Q)$ and $S(Q)$ for 5 g dL^{-1} LDS in D_2O . At this concentration the aggregation number is 80, the average diameter 49 \AA , the effective charge 26, the a/b ratio 1.47, and the number of hydrated D_2O molecules 10.

These structural parameters can be extracted from SANS data analysis at each LDS concentration. As

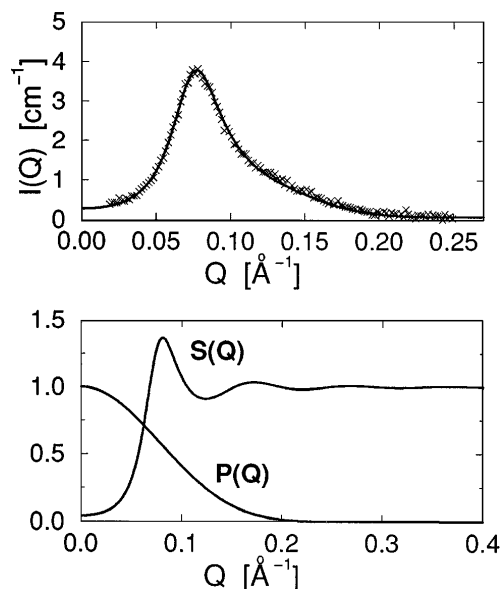


FIG. 1. SANS spectrum and extracted structure factors in an ionic micellar solution made of lithium dodecyl sulfate in deuterated water at room temperature. Top: SANS intensity profile $I(Q)$ data (crosses) and fitted curve (solid line) for 5 g dL^{-1} LDS in D_2O . Bottom: Particle structure factor $P(Q)$ calculated based on a two-shell model, and intermicellar structure factor $S(Q)$ evaluated from GMSA theory.

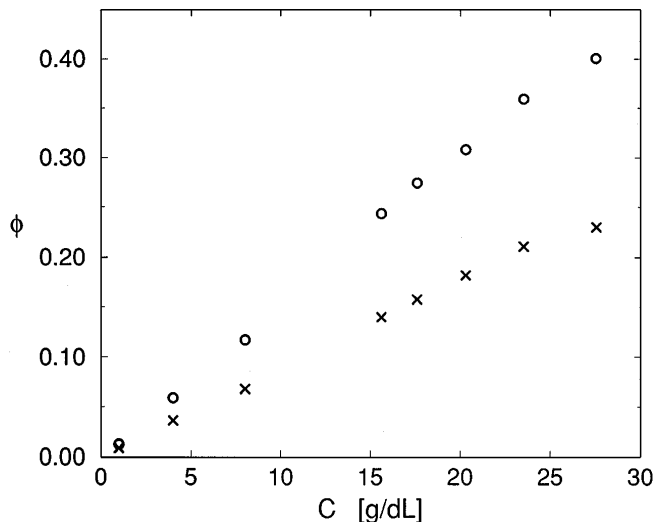


FIG. 2. Hydrated volume fraction ϕ_m (circles) and “dry” volume fraction ϕ (crosses) of ionic micelles as function of LDS surfactant concentration C .

concentration increases from 1 to 28 g dL⁻¹, aggregation number N increases from 62 to 100, corresponding to a/b ratios from 1.1 to 1.8, average micellar diameters σ from 45 to 51 Å, and $\kappa\sigma$ from 1.8 to 6.2 (κ is the inverse Debye screening length). The hydration number remains approximately 10 throughout the concentration range. Figure 2 illustrates the significance of hydration by comparing the hydrated volume fraction ϕ_m and solute (dry) volume fraction ϕ .

Having obtained $S(Q)$ and ϕ_m , we determine the parameter χ in Eq. (4) using an equivalent hard sphere

method. The physical basis of the equivalent hard sphere is established through the second virial coefficient, $2B_2$. We write B_2 of an interacting system as [15]

$$2B_2 = 6\pi\sigma^3(C_{HS} + C_i), \quad (6)$$

where $C_{HS} = 8$ represents the hard sphere contribution and C_i the contribution from long range interaction. The parameter C_i can be written as

$$C_i = 24 \int_1^\infty \left[1 - \exp\left(-\frac{V(x)}{k_B T}\right) \right] x^2 dx, \quad (7)$$

where $x = r/\sigma$ is the reduced distance. C_i can be calculated using $V(r)$ extracted from SANS data analysis. Substituting C_i into Eq. (6) and imposing it into a hard sphere form ($2B_2 = 6\pi\sigma_{eq}^3$), the equivalent hard sphere diameter σ_{eq} can be obtained. Thus, χ can be obtained from Eq. (4) using the equivalent hard sphere volume fraction ϕ_{eq} . Once $S(Q)$ and χ are known, the Brownian contribution can be calculated using Eqs. (2) and (3).

We next calculate the hydrodynamic contribution η_H using the Batchelor-Green equation [4],

$$\eta_H = \eta_0(1 + 2.5\phi_m + 5.2\phi_m^2). \quad (8)$$

This equation is valid for spherical suspensions. For nonspherical suspensions, viscosity increases with axial ratio. To account for the shape effect, we replace the coefficient 2.5 by the intrinsic viscosity, $[\eta] = (\eta - \eta_0)/\eta_0\phi_m$, using the Jeffery equation [16],

$$[\eta] = \frac{4\beta^2}{15} \left[\frac{14}{p^2(4p^2 - 10 + 3\alpha)} + \frac{3\beta}{p^2(p^2 + 1)[(2p^2 - 1)\alpha - 2]} + \frac{6}{(p^2 + 1)(2p^2 + 4 - 3p^2\alpha)} + \frac{4p^2 + 2 - (4p^2 - 1)\alpha}{p^2(4p^2 - 10 + 3\alpha)[(2p^2 + 1)\alpha - 6]} \right], \quad (9)$$

with $\beta = p^2 - 1$ and $\alpha = \ln[(p + \sqrt{\beta})/(p - \sqrt{\beta})]/p\sqrt{\beta}$ for axial ratio $p > 1$. We calculate $[\eta]$ at each concentration using the axial ratios extracted from SANS data.

Combining the Brownian and the hydrodynamic contributions, we obtain the relative viscosity as

$$\eta_r = \frac{\eta_B + \eta_H}{\eta_0}. \quad (10)$$

Figure 3 shows the measured and calculated low shear viscosity of the LDS/water system as a function of hydrated micellar volume fraction ϕ_m . The calculation for a hard sphere system is also shown. The effect of the long range interaction on rheological properties is significant. We restrict the upper limit of LDS concentration

to 28 g dL⁻¹, which corresponds to a hydrated micellar volume fraction of 0.4. Beyond this concentration, the structure factor can no longer be accurately evaluated due to a high axial ratio of micelle and due to a liquid crystal phase transition (~ 35 g dL⁻¹).

In an ionic system, the idea of equivalent hard sphere may be jeopardized if $\kappa\sigma$ is less than 1, since the double layer may subject to distortion under shear. In our case, $\kappa\sigma$ values are greater than 1, which makes the calculation of χ possible. As for using the Batchelor-Green equation to calculate the hydrodynamic contribution, inaccuracy may arise from the second order term which is derived based on a mean field theory. Another factor that may affect the calculation is the polydispersity. It alters the system compressibility leading to a slow down of the

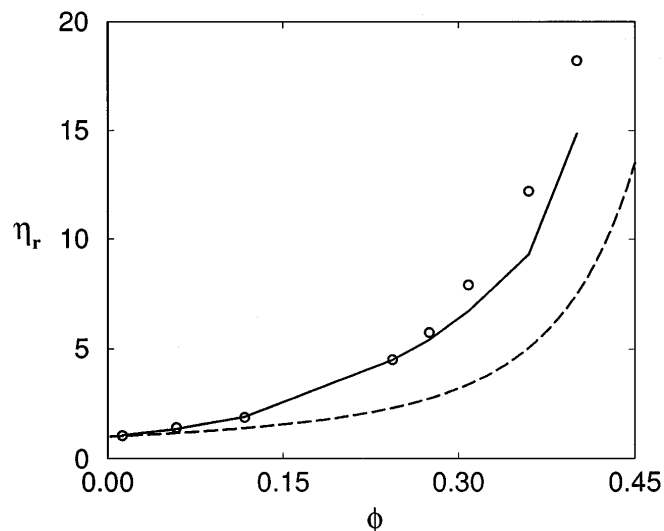


FIG. 3. Relative viscosity η_r at low shear as a function of hydrated micellar volume fractions ϕ_m . The open circles are experimental data, and the solid line is theoretical calculation. The dashed line is a theoretical prediction for a hard sphere system.

particle diffusion at the short time limit [17]. Since we are dealing with the low shear viscosity, which is in the long time limit, the polydispersity effect can be neglected.

In comparison with the work of de Schepper *et al.* on hard sphere systems, this work aims at a much broader class of fluids in a wide concentration range. Both Brownian force and hydrodynamic interaction are calculated, which is necessary for an interacting system [18]. The Brownian force is calculated with the structure factor determined from a scattering experiment. An equivalent hard sphere concept is introduced to calculate the linewidth of the intermediate scattering function. The hydrodynamic interaction is estimated using the Batchelor-Green equation with the particle shape factor taken into account. This methodology, validated through the LDS system, has laid a foundation for studying the rheological properties of a complex fluid.

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*To whom all correspondence should be addressed.

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