Rheology of wormlike micellar fluids from Brownian and molecular dynamics simulations

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J T Padding[1,2,4]**, E S Boek**[1,2] **and W J Briels**[3]

[1] Schlumberger Cambridge Research, High Cross, Madingley Road, Cambridge, UK
[2] Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK
[3] Department of Science and Technology, University of Twente, Enschede, The Netherlands

E-mail: boek@cambridge.oilfield.slb.com

Abstract
There is a great need for understanding the link between the detailed chemistry of surfactants, forming wormlike micelles, and their macroscopic rheological properties. In this paper we show how this link may be explored through particle simulations. First we review an existing bead–spring model. We find that shear flow enhances the formation of rings at the expense of linear chains. The shear viscosity of this model is dominated by solvent contributions, however, and the link with the chemistry of the surfactants is missing. We introduce a more realistic Brownian dynamics model, the parameters of which are measured from atomistic molecular dynamics simulations.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Surfactant molecules self-assemble reversibly into micelles with a variety of morphologies [1]. In aqueous salt solutions, they may assemble into wormlike micelles. Above the overlap concentration, the viscosity increases steeply with increasing surfactant concentration [2]. This creates highly viscous, shear thinning fluids with viscoelastic behaviour [3, 4]. In the presence of oil, the wormlike micelles disassemble, resulting in a low viscosity Newtonian fluid. This responsive behaviour makes viscoelastic surfactant (VES) solutions, operating in the wormlike micellar regime, ideal for many industrial applications, such as in hydraulic fracturing operations in the oilfield [5].

One of our goals is to explain the flow of wormlike micellar fluids in porous media. It is observed that the apparent viscosity (pressure drop) in porous media does not decrease

[4] Present address: Department of Science and Technology, University of Twente, Enschede, The Netherlands.

monotonically with apparent shear (flow) rate [6]. A possible explanation is that elongational effects lead to an increased extensional viscosity. Bautista and Manero [7] have proposed a rheological equation of state (REoS) for wormlike micellar fluids. However, for this REoS, all solutions for the steady state extensional viscosity η_E were found to be unstable when the elongational rates $\dot{\epsilon}$ exceed some critical value [6]. This problem can be cured by a slight modification of the original equations [6]. However, this REoS has not yet been sufficiently validated. Moreover, and this applies to *all* REoS, the parameters depend in an unknown fashion on the particular chemistry of the surfactants, concentration and temperature. Therefore, despite the large amount of experimental data on particular surfactant systems, there is no systematic way to design fluids with a particular desired rheology. In this paper we will show how particulate simulation methods can be used to predict rheology from first principles.

It is impossible to reach large enough scales of length and time to determine the macroscopic rheology using atomistic molecular dynamics (MD) simulation methods; therefore a mesoscopic approach is required. In the past [8, 9] we have considered an existing generic simulation model for wormlike micelles [10]. In this so-called FENE-C model the wormlike micelle is represented by beads connected by springs which can reversibly break. The solvent is represented by similar, but unconnected, beads. The essential physics of a wormlike micelle is therefore captured without making any reference to the actual chemistry. This can sometimes be an advantage. For example, we have studied the influence of shear flow on the formation of micelles forming closed loops (rings) [9]. Ring formation has been used to explain the shear thickening effects observed in certain wormlike micellar solutions [11] but has never been directly observed in experiments [12]. For the FENE-C model, rings dominate in dilute solutions, while linear chains dominate in concentrated solutions. Interestingly, we found that shear flow induces a net shift of micellar mass from linear chains to rings. At the same time, the average size of rings is increasing at the expense of linear chains. We showed that the increased abundance and size of rings are caused by a decreased entropy gain associated with ring opening under shear flow. This can provide a positive feedback between strain and ring connectivity. It may contribute to shear thickening behaviour, observed in micellar solutions near the overlap concentration [9].

A disadvantage of any generic model is that the details of the interactions between the wormlike micelles may not be very realistic. For example, for FENE-C wormlike micellar solutions at high concentrations, we found that the recombination kinetics are diffusion controlled and dominated by self-recombination events, contrary to most real wormlike micelles whose recombination kinetics are reaction limited [8, 13]. More seriously, the shear viscosity is dominated by the contribution of the (unrealistically) similarly sized solvent. In real micelles, the stress is dominated by the micellar bonds and entanglements.

To overcome these difficulties, we have developed a Brownian dynamics (BD) model. The input parameters for this BD model are derived from atomistic molecular dynamics (MD) simulations. The aim of the BD model is to realistically calculate the dynamics and rheology of an entangled solution of wormlike micelles. Such a simulation can offer new insights because the theory available for the dynamics of wormlike micelles [14] makes assumptions that cannot be directly validated by experiments. For example, the average break-up time per unit length of worm is assumed to be constant and independent of stress or shear rate. Another approximation in the theory is that no fusions occur at entanglements, as has been suggested by Briels *et al* [15]. A mesoscopic simulation approach can check and go beyond these assumptions.

In the next section we will describe how the parameters that go into the BD model, which are mainly the mechanical properties of a wormlike micelle, can be measured from MD simulations. Then we will give an introduction to the BD model, the details of which will be published elsewhere.
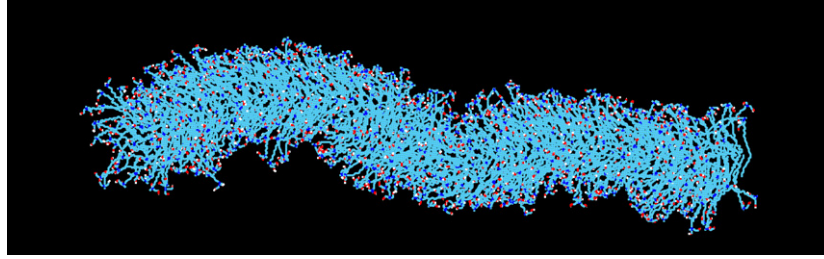
Figure 1. Snapshot of an MD simulation of an EHAC wormlike micelle in a 3% NaCl solution. Only the surfactant molecules are shown: carbon (light blue), oxygen (red), nitrogen (dark blue) and hydrogen (white).

2. Mechanical properties from molecular dynamics simulations

Using atomistic MD simulations, we can find relationships between the chemistry and mechanical properties of a wormlike micelle. To this end, we carry out simulations of a small segment of a wormlike micelle, consisting of a limited number of surfactant molecules, in this example EHAC [5]. The worm is immersed in water containing the required concentration of salt (NaCl) ions. Typically, the MD simulation box has dimensions of the order of 10 nm and contains $\mathcal{O}(10^5)$ atoms. Periodic boundary conditions are applied in three dimensions, so effectively we are considering an infinite segment of a wormlike micelle. Typically, the simulations require of the order of 10 ns of simulation time to obtain statistically meaningful ensemble averages. A simulation snapshot is shown in figure 1. This system contains 640 surfactant and 40 000 water molecules together with Na^+ and Cl^- ions corresponding to a 3% (by weight) NaCl solution. Coulomb interactions are treated using Ewald summations.

First, we calculate radial distribution functions as ensemble averages over the particle coordinate trajectories. From these functions, we find a radius of the worm $r = 2.3$ nm. Then, we determine the tensionless state. This is achieved by a series of MD simulations, where we compress/stretch the worm at constant volume [16]. We observe that the surface tension ΔP decreases linearly with the length of the worm segment L_z. The elastic modulus K_L is then calculated from

$$-\Delta P \frac{V}{L_z} = \frac{K_L}{L_{z0}}(L_z - L_{z0}) \tag{1}$$

where L_{z0} is the box z dimension in the tensionless state. Both K_L and L_{z0} have been determined [16] from a graph of $-\Delta PV/L_z$ as a function of L_z. From a linear fit of all data points, we find $L_{z0} = 15.10$ nm and $K_L = 1.9$ nJ m^{-1}. Note that it is difficult to determine the elastic modulus of a single wormlike micelle experimentally.

The persistence length l_p of the worm in the tensionless state is calculated from the position fluctuation spectrum perpendicular to the worm (z-)axis, as shown in figure 2:

$$S_\alpha(n) = \langle c_{\alpha,n}c_{\alpha,n}^* \rangle = \frac{1}{L_z l_p}q_n^{-4}, \qquad \text{where } q_n = \frac{2\pi}{L_z}n; \quad \alpha = x, y \tag{2}$$

where $c_{\alpha,n}$ are the coefficients of the Fourier decomposition [17].

Qualitatively, we find that the low q modes follow a q^{-4} scaling behaviour, as expected [17]. We try to fit the low q modes to the fluctuation spectrum of a coarse-grained worm simulation [17], in which each surfactant is represented by one head bead and four tail beads of diameter σ. We find quantitative agreement for $\sigma = 0.6$ nm. Note that the radius of the coarse-grained worm is 4σ. This agrees very well with our previous measurement of 2.3 nm
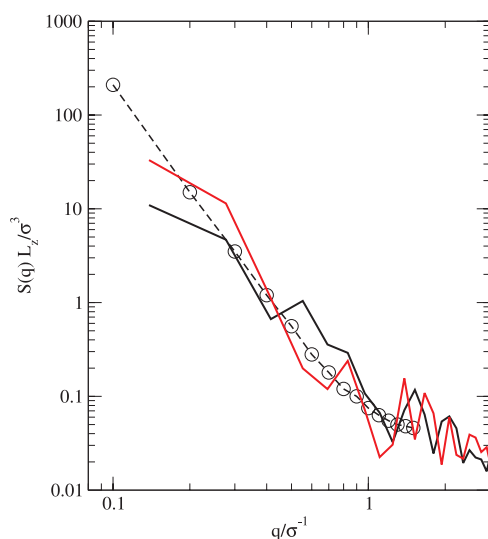
Figure 2. Structure factors $S_\alpha(q)$ of a tensionless EHAC worm; $\alpha = x, y$ in black and red respectively. The dashed line shows the $S(q)$ for a coarse-grained worm simulation [17], using $\sigma = 0.6$ nm.
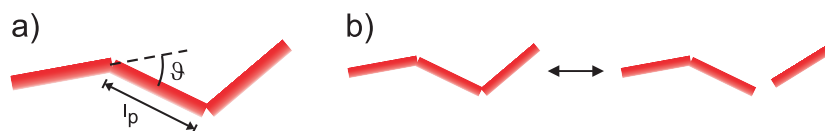

Figure 3. (a) Mesoscopic model of a wormlike micelle. (b) The dynamics of break-up and recombination of a wormlike micelle.

from the radial distribution function. The persistence length is calculated to be of the order of $38\sigma = 23$ nm. This value is in agreement with experimental values for wormlike micellar persistence lengths reported in the literature [18]. We are currently developing methods for calculating the scission energy required to break a worm, as well as the activation barrier associated.

3. Rheology from Brownian dynamics simulations

We have developed a Brownian dynamics (BD) model with the aim of calculating the dynamics and rheology of an entangled solution of wormlike micelles. The simulation method is based on Brownian dynamics of coarse-grained wormlike micellar units (see figure 3(a)). Each unit represents one persistence length l_p. The mechanical properties are calculated from atomistic MD simulations. In the BD simulation, the ends of wormlike micelles can approach each other and, if a certain activation barrier is overcome, fuse to form elastic bonds (see figure 3(b)). The dynamics of break-up and recombination of a wormlike micelle are determined by the scission energy (the difference in free energy between a broken and an unbroken wormlike micelle), activation energy and compressibility of the worm. The break-up rates may change as a function of temperature, concentration (entanglement effects) and deformation rates.

Entanglements are very important for the rheology of a concentrated solution of wormlike micelles. In fact, the average mass M_e between active entanglements is directly related to
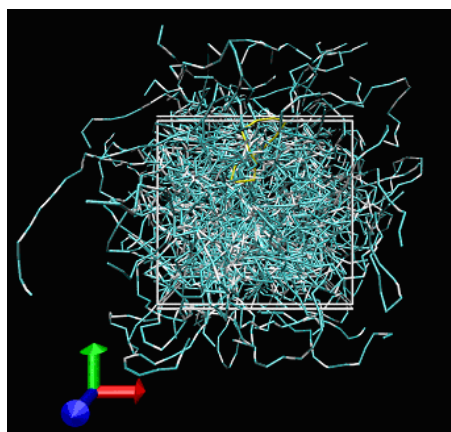
Figure 4. Snapshot of a typical Brownian dynamics simulation box. Wormlike micelles (blue) which penetrate the periodic planes are displayed entirely. Entanglement points are coloured white. One ring is present, which is coloured yellow.
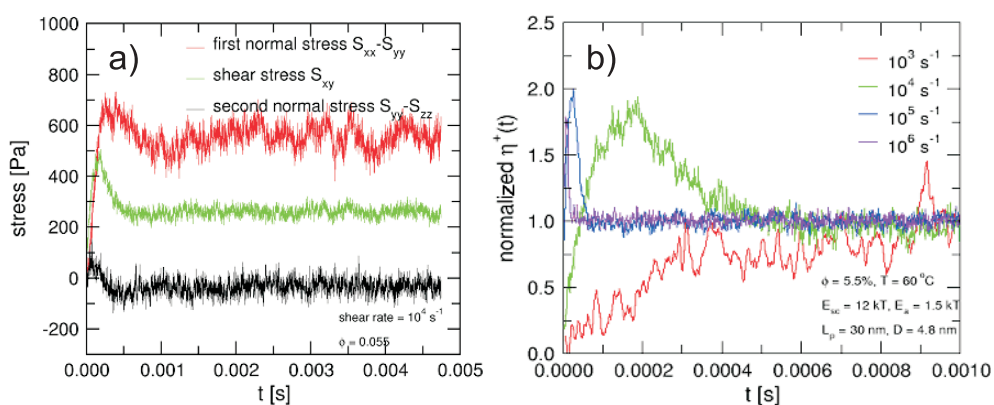

Figure 5. (a) Transient shear stress and normal stress differences as measured from a mesoscopic simulation. (b) Normalized transient shear stress. The amount and location of the maximum stress overshoot depends on the shear rate and mechanical properties of the wormlike micelles.

the plateau modulus G_0 through the relation $G_0 = \rho k_B T / M_e$ [19]. Entanglements emerge naturally when two wormlike micelles try to cross. In the simulation, these crossings are monitored, and entanglement points are inserted when a crossing is imminent [20]. A snapshot of a typical simulation box is given in figure 4.

In the simulations, the zero-shear relaxation modulus $G(t)$ can be calculated as the ensemble average over time autocorrelations of off-diagonal elements of the stress tensor **S**. The zero-shear viscosity then is simply the infinite time integral over the relaxation modulus [21]. The non-linear shear rheology, on the other hand, can be measured by applying a shear to the simulation box. When starting from an equilibrated configuration, the transient shear rheology can first be investigated. An example is given in figure 5(a). The transient rheology can be studied for different mechanical properties of the wormlike micelles, different concentrations, temperatures and shear rates. An example of the latter is given in figure 5(b). Note that the amount of shear stress overshoot is in qualitative agreement with recent experimental observations [23].
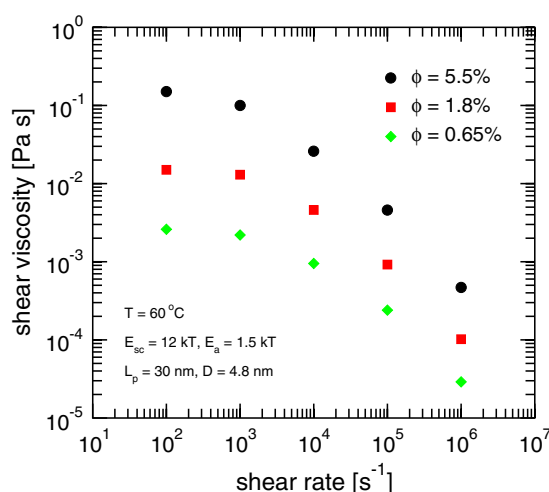
Figure 6. Steady state shear viscosity as a function of shear rate for various surfactant concentrations ϕ.

After some time, the transient behaviour has evolved into steady state behaviour. The steady state shear viscosity is then given by the ratio of the shear stress and shear rate:

$$\eta(\dot{\gamma}) = \lim_{t \to \infty} \frac{\langle S_{xy}(\dot{\gamma}) \rangle}{\dot{\gamma}}. \tag{3}$$

An example of how the steady state shear viscosity changes with the shear rate and concentration is given in figure 6. Note that the zero-shear viscosity increases rapidly with increasing surfactant concentration, in agreement with experimental observations. Moreover, the observed shear thinning is much stronger than in the corresponding case of unbreakable polymers [22]. A more surprising observation is that the critical shear rate, where shear thinning starts, is found to be very weakly dependent on the surfactant concentration. Recent experiments seem to confirm this [23].

4. Conclusion

In this paper we have introduced a BD model, with which we can find trends and relationships between mechanical properties of an individual wormlike micelle and the (transient) rheology of a solution of wormlike micelles. When combined with atomistic MD simulations, giving relationships between the chemistry and mechanical properties of the worm, this will enable a more rational design of new surfactant systems.

Acknowledgments

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