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Viscoelasticity of model surfactant solutions determined by magnetic rotation spectroscopy

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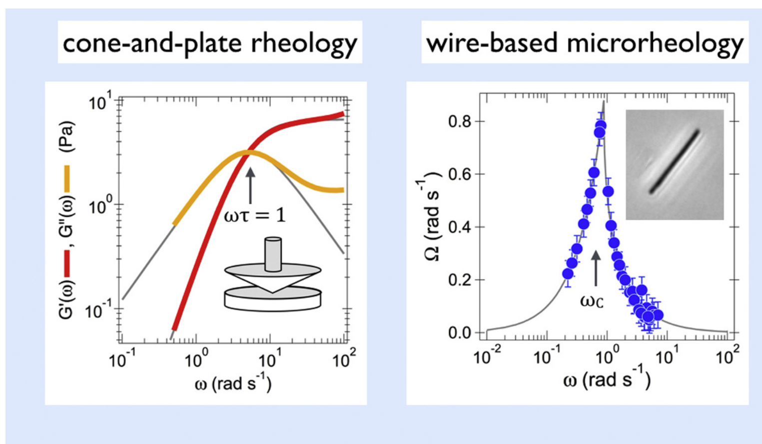
HIGHLIGHTS

- Microrheology is implemented using micron size magnetic wires.
- Motion predictions are made for wires embedded in viscoelastic fluid.
- The technique is assessed on wormlike micellar solutions and compared to conventional rheometry.

GRAPHICAL ABSTRACT



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ABSTRACT

Being able to reduce the size of a rheometer down to the micron scale is a unique opportunity to explore the mechanical response of expensive and/or confined liquids and gels. To this aim, we synthesize micron size wires with magnetic properties and examine the possibility of using them as microrheology probes. In this work, we exploit the technique of magnetic rotation spectroscopy by placing a wire in a rotating magnetic field and monitor its temporal evolution by time-lapse microscopy. The wire-based microrheology technique is tested on wormlike micellar surfactant solutions showing very different relaxation dynamics and viscosities. A model for the wire rotation is also developed and used to predict the wire behavior. It is shown that the rheological parameters of the surfactant solutions including the static shear viscosity, the entangled micellar network relaxation time and the elastic modulus are in good agreement with those of conventional rheometry.

1. Introduction

Rheology is the study of how complex fluids flow and deform under stress [1,2]. Traditional rheometers measure the frequency-dependent linear viscoelastic relationship between strain and stress on milliliter scale samples. Microrheology in contrast measures these quantities using colloidal probes directly embedded in

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the fluid [3,4]. Fluids produced in tiny amounts or confined in small volumes, down to 1 picoliter can be examined by this technique. The past 20 years have seen significant advances in the field, both theoretically and experimentally [5].

In microrheology, the objective is to translate the motion of a probe particle into the relevant rheological quantities such as the elastic complex modulus or the creep response function [6,7]. Following the work by Crick and Hughes [8], recent studies have shown that microrheology based on the use of anisotropic probes, such as wires, rods or needles could bring notable contributions to the field [5,9–20]. Anisotropic probes present many advantages compared to spherical ones, in particular these probes behave like conventional stress rheometer when subjected to an external field. It has been found for instance that the static viscosity of a Newtonian fluid can be determined from the motion of micro-actuators submitted to rotating electric or magnetic fields [21–23]. In these studies, the response of the probe over a broad spectral range appears as a resonance peak similar to that found in mechanical systems [24]. This technique was thereafter described as a spectroscopic method for probing fluid viscosity, and dubbed electric or magnetic rotation spectroscopy [25,26]. Here, we combine this steady rotation technique along with micromechanical response modeling to examine complex fluids displaying both viscosity and elasticity effects. The method is based on the tracking of magnetic wires submitted to a magnetic rotation field at increasing frequencies, and on the analysis of their temporal trajectories [10,11,14,17,19,21,26–29].

In this work, we first introduce a mechanical model for the magnetic wire rotation in Maxwell fluids. Magnetic rotational spectroscopy is thereafter implemented on surfactant wormlike micellar solutions. The solutions investigated are a mixture of cetylpyridinium chloride (CPCl) and sodium salicylate (NaSal) and a mixture of cetyltrimethylammonium bromide (CTAB) and NaSal. Following the work by Rehage and Hoffman [30,31] CPCl/NaSal and CTAB/NaSal are known to self-assemble spontaneously into micrometer long wormlike micelles and to build semi-dilute entangled networks [32–34]. This network confers to the solution a Maxwell-type viscoelastic behavior [1]. In this study, we compare surfactant solutions that are characterized by different relaxation dynamics and viscosities. It is shown that in such conditions the wire motion exhibit a wide variety of behaviors as a function of the time, including steady rotation, oscillations, continuous and discontinuous back motions. These behaviors depend on a newly defined parameter expressed as the product of the Maxwell relaxation time and critical frequency. The rheological parameters of the surfactant solutions studied are in good agreement with those of conventional rheometry.

2. Materials and methods

2.1. Iron oxide nanowires

Iron oxide nanoparticles were synthesized by co-precipitation of iron(II) and iron(III) salts in aqueous media and by further oxidation of the magnetite (Fe_3O_4) into maghemite (γ-Fe_2O_3) [35,36]. The particle size and dispersity were determined from transmission electron microscopy (Jeol-100 CX) at D_{TEM} = 13.2 nm and s_{TEM} = 0.23, whereas the maghemite structure was assessed by electron beam diffraction [37]. Light scattering (NanoZS, Malvern) was used to measure the weight-average molecular weight ($M_w = 12 \times 10^3$ kDa) and the hydrodynamic diameter (D_H = 27 nm) of the uncoated particles [35,36]. The wires were made according to a bottom-up co-assembly process using the γ-Fe_2O_3 particles coated with poly(acrylic) acid together with cationic polymers [37,38]. The polymer used was poly(diallyldimethylammonium chloride) (PDADMAC, Sigma Aldrich) of molecular weight M_w = 26.8 kDa. Determined by size exclusion chromatography, the degree of polymerization and the dispersity $Đ$ were found equal to 50 and to 3.5 respectively. The wires dispersion was autoclaved at 120 °C and atmospheric pressure during 20 min to prevent bacterial contamination and stored at 4 °C.

2.2. Maxwell viscoelastic solutions

The surfactant solutions investigated were a mixture of cetylpyridinium chloride and sodium salicylate at a concentration of 2 wt.% in 0.5 M NaCl [30,33,34] and a mixture of cetyltrimethylammonium bromide and sodium salicylate at c = 1 wt.% [31]. At the concentration of 1–2 wt.%, the network mesh size is of the order of 30 nm, *i.e.* much smaller than the wire diameter [33]. A cone-and-plate and controlled shear rate rheometer (diameter 50 mm, MCR 500 Physica) was used to determine the frequency dependence of the elastic complex modulus $G^*(\omega) = G'(\omega) + iG''(\omega)$. At the temperature T = 27 °C, the two wormlike micellar fluids studied are almost perfect Maxwell fluids, *i.e.* characterized by a unique relaxation time. CPCl/NaSal at 2 wt.% is associated with a static viscosity $\eta_0 = 1.0 \pm 0.1$ Pa s, a relaxation time $\tau = 0.14 \pm 0.01$ s and an elastic modulus $G = 7.1 \pm 0.1$ Pa, whereas CTAB/NaSal 1 wt.% is given with $\eta_0 = 40 \pm 4$ Pa s, $\tau = 23 \pm 3$ s and an elastic modulus $G = 1.7 \pm 0.2$ Pa. The two fluids have hence a similar entangled network structure, but differ in their micellar network dynamics. The breaking and recombination time τ for CTAB/NaSal is around 160 times larger than that of CPCl/NaSal.

2.3. Microrheology and electromagnetic coils device

Bright field microscopy was used to monitor the wire actuation as a function of time. Stacks of images were acquired on an IX73 inverted microscope (Olympus) equipped with a 100× objective. For magnetic rotation spectroscopy experiments, 65 µl of surfactant solution were deposited on a glass plate and sealed into to a Gene Frame® (Abgene/Advanced Biotech) dual adhesive system. The glass plate was introduced into a homemade device generating a magnetic rotation field, thanks to two pairs of coils (23 Ω) working with a 90°-phase shift (Fig. 1a). An electronic set-up allowed measurements in the frequency range 10^{-2}–100 rad s^{-1} and at magnetic fields B = 0–20 mT. Fig. 1b displays the magnetic field distributions between the poles of the electromagnetic coils in the X- and Y-directions. The image acquisition system consisted of an EXi Blue CCD camera (QImaging) working with Metaview (Universal Imaging). Images were digitized and treated by the ImageJ software and plugins. Fig. 1c shows snapshots of a rotating 10 µm wire in a 85 wt.% water-glycerol (Aldrich) mixture at fixed time interval during a 180° rotation. For the wire magnetic property calibration, experiments were performed on a 85 wt.% water-glycerol mixture of static viscosity η_0 = 0.062 Pa s (T = 32 °C).

3. Results and discussion

3.1. Modeling wire rotation in Newtonian and Maxwell fluids

3.1.1. Newtonian liquid

In continuum mechanics, a Newtonian fluid of viscosity η_0 is described by a dashpot [2]. In such a fluid, a wire submitted to a rotating field experiences a restoring torque that slows down its motion. With increasing frequency, the wire undergoes a transition between a synchronous and an asynchronous regime. The critical frequency ω_C between these two regimes reads [21–23]:

$$\omega_C = \frac{3}{8}\frac{\mu_0 \Delta\chi}{\eta_0} g\left(\frac{L}{D}\right)\frac{D^2}{L^2}H^2 \quad (1)$$