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DYNAMICS AND MICRORHEOLOGY OF WORM-LIKE MICELLES.

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GENERAL ABSTRACT

Utilization of wormlike micelles covers a wide spectrum of applications ranging from fracture fluids to drag reducing agents. The response of a fluid with wormlike aggregates to mechanical perturbation is viscoelastic. In the semidilute regime. The relaxation modulus *G(t)* measured in stress relaxation experiments follows a Maxwellian behavior $G(t)=G_o exp(\tau_R)$. Here, G_o is the plateau modulus related to the entanglement density of the micellar mesh and τ_R is a relaxation time equal to the geometric mean of τ_{rep} and t_b. This behavior is indeed so general that it is now admitted that a single relaxation time in the linear mechanical response is a strong indication of the wormlike character of self-assembled structures. In the last fifteen years, different techniques have been developed determine $G*(\omega)$, usually named micro-rheology techniques, where micron-sized probe particles are embedded into the fluid to locally measure the viscoelastic response of the soft material. The response can be measured either by actively manipulating the probe particles or by passively measuring the mean square displacement of the particles $<r^2(t)>$, where the bulk mechanical susceptibility of the fluid determines the response of the probe particles excited by the thermal stochastic forces which lead to Brownian motion. $<r^2(t)>$ can be related to $G*(\omega)$ by describing the motion of the particles with a generalized Langevin equation incorporating a memory function to take into account the viscoelasticity of the fluid.

TECHNICAL ABSTRACT

We have studied the microrheological behavior of a micro-emulsion made of hexadecyltrimetylamonium bromide (CTAB)/Sodium Salicilate/water, which forms very long flexible cylindrical micelles. The viscoelastic behavior of this mixtures depends on molar concentration of CTAB, molar number ratio of NaSal to CTAB, R = [NaSal]/[CTAB], and temperature. We have measured the viscoelastic properties of the mixture with a light scattering technique (diffusing wave spectroscopy, DWS.) Prior obtaining the intensity autocorrelation function, we obtain the mean square displacement of the particles embedded in the sample. Using the generalized Langevin equation, the mean square displacement is related to the viscoelastic modulus, G'(w) and G''(w) of the mixture. We compare our results with that obtained by standard rheology measurements.

MULTIPLE SCATTERING

Phase Shift

$$\left\langle \Delta\Phi(\tau)^2 \right\rangle \cong \tfrac{2}{3} k_o^2 \left\langle \Delta r(\tau)^2 \right\rangle \frac{s}{l^*}$$

Scattered Field

$$E_S(r,t) = E_o(r)\exp\{-i\omega_o t\}\sum_{i=1}^{N}\exp\{i[q\bullet \vec{R}_i(t)]\}$$

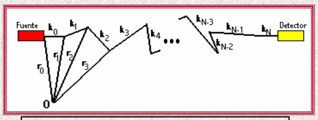


Fig. 1.- Photon light path trough a scattering sample.

Field Autocorrelation Function

$$g_{(1)}(t) = \int_0^\infty P(s)\exp\{-\frac{k_o^2\langle\Delta r^2(t)\rangle}{3}\frac{s}{l^*}\}ds$$

Siegert relation

$$\left[\frac{\langle E(0)E^*(t)\rangle_E}{\langle |E(0)|^2\rangle_E}\right]^2 = |g_{(1)}(t)|^2 = \frac{1}{\beta}[g_{(2)}(t)-1] = \frac{1}{\beta}\left[\frac{\langle I(0)I(t)\rangle_T}{\langle I(0)\rangle_T^2}-1\right]$$

TRANSMISSION GEOMETRY

Multiple scattered light emerges from the sample in all directions, almost with the same intensity. For this reason, there are only two geometries of interest in the experiment of difusing wave spectroscopy, transmission and backscattering. In this work, Transmission was the principal geometry used.

The problem of light traveling through slab of transverse extension much bigger than its thickness, *L*, can be solved exactly for the fiel autocorrelation function using the diffusion aproximation for the transport of photons. In transmission geometry, it is found, for an incident plane wave:

$$g_1(\tau) = \frac{\frac{L/l^*+4/3}{\alpha+2/3}\left[\sinh[\alpha x]+\frac{2}{3}x\cosh[\alpha x]\right]}{\left(1+\frac{4}{9}x^2\right)\sinh\left[\frac{L}{l^*}x\right]+\frac{4}{3}\sqrt{k_0^2\langle\Delta r^2(\tau)\rangle}\cosh\left[\frac{L}{l^*}x\right]}$$

$$x = [k_0^2\langle\Delta r^2(\tau)\rangle]^{1/2}$$

MICRORHEOLOGY

Generalized Langevin equation:

$$m\frac{\partial v}{\partial t} = f_R(t) - \int_0^t \zeta(t-\tau)v(\tau)d\tau$$

$f_R(t)$ Random Forces

$\zeta(t)$ Memory function

Solving this equation in the Laplace space and using the equipartition energy theorem

$$m\langle \tilde{v}(0)v(0)\rangle = m\langle \tilde{v}(t)v(t)\rangle = 3k_BT$$

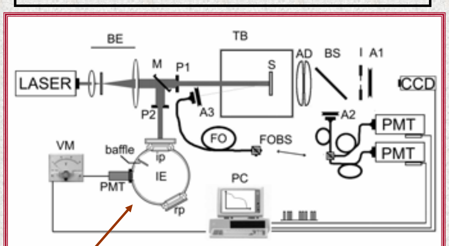
The relation between the mean square displacent and the complex viscoelastic modulus is found.

$$\tilde{G}(s) = s\tilde{\eta}(s) = \frac{s}{6\pi a}\left[\frac{6k_BT}{s^2\langle\Delta\tilde{r}^2(s)\rangle} - ms\right]$$

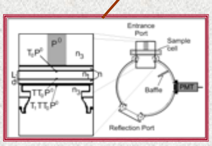
Here, we have supposed that the relation between viscosity and the memory fuction, which is exact for the case of pure viscous fluids, holds for viscoelastics fluids.

$$\tilde{\eta}(s) = \frac{\tilde{\zeta}(s)}{6\pi a}$$

EXPERIMENTAL SETUP



TRANSPORT MEAN FREE PATH, *l**



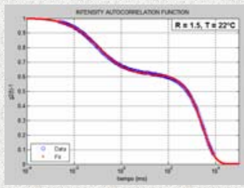
Transport mean free path is the distance a photon travels before its trajectory becomes random. Using the diffusion equation for the transport of photons inside the sample, l* can be related to the the total transmitted light

$$l^* = \frac{(3C_0+2)T_{cd}}{(C_0+\alpha)(3C_L+2)(T_l T_0 - T_{cd}) + (C_L-\alpha)(3C_0+2)T_{cd}}L$$

In this experiment, the transmitance and reflectance of the sample are measured to calculate the total difuse light transmitted, T_{cd}. The constants C_o and C_L depend on the reflection coeficients of the sample cell and integrating sphere. T_l and T_o are the transmitances of the cell walls as shown in the figure.

MEAN SQUARE DISPLACEMENT

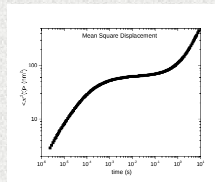
Prior obtaining the Intensity Autocorrelation Function, we obtain the Mean Square Displacement of the probe particles immersed in the micro-emulsion using the transmission formula and the Siegert relation.



$$\left[\frac{\langle E(0)E^*(t)\rangle_E}{\langle |E(0)|^2\rangle_E}\right]^2 = |g_{(1)}(t)|^2 = \frac{1}{\beta}[g_{(2)}(t)-1] = \frac{1}{\beta}\left[\frac{\langle I(0)I(t)\rangle_T}{\langle I(0)\rangle_T^2}-1\right]$$

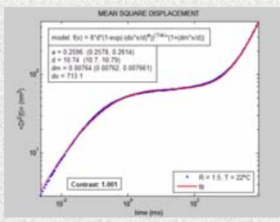
Numerical Inversion

$$g_1(t) \approx \frac{\frac{L/l^*+4/3}{1+2/3}\left\{\sinh\left(\sqrt{\frac{6t}{\tau_o}}\right)+\frac{2}{3}\sqrt{\frac{6t}{\tau_o}}\cosh\left(\sqrt{\frac{6t}{\tau_o}}\right)\right\}}{\left(1+\frac{8t}{3\tau_o}\right)\sinh\left(\frac{L}{l^*}\sqrt{\frac{6t}{\tau_o}}\right)+\frac{4}{3}\sqrt{\frac{6t}{\tau_o}}\cosh\left(\frac{L}{l^*}\sqrt{\frac{6t}{\tau_o}}\right)}$$



The mean square displacement (msd) was obtained for different temperatures and NaSal/CTAB concentration ratios, R= [NaSal]/[CTAB].

In order to obtain the viscoelastic modulus from the msd data, we made a fit with a model proposed by Bellour, *et al*. This model takes into account three different regimes for the motion of the tracer particles.



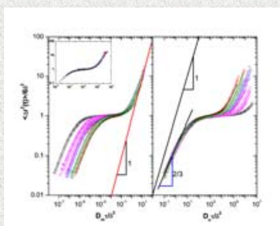
At short times, the dynamics is Brownian: $\langle\Delta r^2(t)\rangle = 6D_o t$

Then, the msd reaches a plateau at intermediate times because the articles are trapped by the micelles. And

At long times, the msd becomes diffusive again, with a diffusion coefficient, D_m corresponding with the macroscopic viscosity of the solution. The particles moves from their caged position because of the diffusion of the micellar solution.

The expression proposed for the msd is:

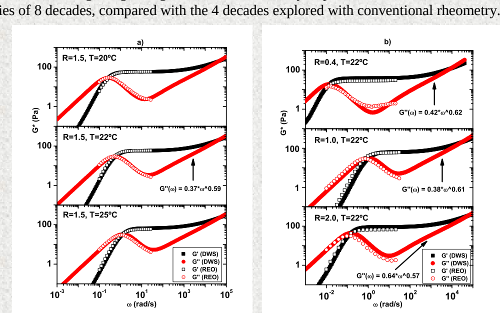
$$\langle\Delta r^2(t)\rangle = 6\delta^2\left(1-e^{-\left(D_o t/\delta^2\right)^\alpha}\right)^{1/\alpha}\left(1+\frac{D_m t}{\delta^2}\right)$$



In a plot of <Dr2(t)> vs. a) D_m/δ^2 it is found that all systems behave in the same manner at long times, and b) Dm/δ^2 also for short times.

THE VISCOELASTIC MODULUS

Comparison with rheometric data gives good agreement. It is necessary to point out that measurements with DWS gives a range of frequencies of 8 decades, compared with the 4 decades explored with conventional rheometry.



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