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Microscopic observation of magnetodeformational effects in magnetic nanocomposite micelles

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Abstract

Magnetically induced elongation of magnetic nanocomposite micelles is observed microscopically. The superparamagnetic particles of double-surfacted water based ferrofluid are incorporated in spherical micelles of cetyltrimethyl ammonium bromide (CTABr) mixed with sodium salicylate salt (NaSal). Under the application of an external magnetic field these spherical magnetic micelles deformed to ellipsoids. The shape distortion occurs instantaneously and disappears when the external field is removed. This magnetodeformational effect is analyzed using linear magnetization and Hookean elasticity.

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

1. Introduction

Ferrogels belong to a challenging class of novel magneto-controlled elastic materials, which are chemically cross-linked polymer networks swollen with a ferrofluid. Coupling the elastic medium with the magnetic properties of the superparamagnetic particles allows us to manipulate the elastic behavior of ferrogels using external magnetic fields and/or field gradients. This smart behavior ensures for ferrogels wide technological prospects, e.g., use in soft actuators, micromanipulators, artificial muscles (Zrinyi and Horkay 1993). Heating of these materials in an alternating magnetic field is a promising approach in cancer therapy (Babincova *et al* 2001). These field sensitive gels can also be used in an apparatus for immuno-blotting (Uritani and Hamada 1999). The shape transitions of giant liposomes filled with a magnetic colloid were also studied by Sandre *et al* (2000); they have studied the shape transition of giant magnetic liposomes induced by the ionic strength. Recently a complete set of macroscopic dynamic equations for ferrogels under an external magnetic field, including the magnetization as an independent dynamic degree of freedom, were derived (Jarkova *et al* 2003). Magnetodeformational effects in ferrogel objects and ferrovesicles were theoretically studied by Raikher *et al* (Stolbov and Raikher 2006, Raikher Yu and Stolbov 2005). The small angle neutron scattering technique was also used to study magnetic nanocomposite micelles and vesicles recently (Lecommandoux *et al* 2005). In this context, the introduction of inorganic nano-objects into self-organized structures is still a challenge for chemists as well as for physicists, although Nature produces and frequently uses these types of hybrids. The pioneering work on the entrapment of inorganic particles in vesicles was carried out by Fendler and Tundo (1984) and Herve *et al* (1984). Here, we are interested in the inclusion of magnetic nanoparticles in mesoscopic micelles/vesicles in order to study microscopically the effect of externally applied moderate magnetic field. In this experiment, we have prepared a novel type of hybrid colloid, based on the association of micellar solution and ferrofluids. The organic part of this hybrid colloid is prepared using cetyltrimethyl ammonium bromide (CTABr) mixed with sodium salicylate salt (NaSal). The reason behind using these compounds is their striking viscoelastic behavior upon additions of small amounts of salt solution like NaSal, KBr, etc (Aswal and Goyal 1998). The inorganic part is magnetic nanoparticles in ferrofluids, which are colloidal suspensions of nanometric magnetic grains stabilized by appropriate tensioactives in organic solvent (Rosensweig 1985). The ferrofluid used in this experiment is a double-surfacted (both the surfactants were oleic acid) aqueous ferrofluid.

2. Magnetism in magnetic nanocomposite micelles

Elongation of a magnetoelastic material under the action of an external magnetic field can be discussed assuming linear

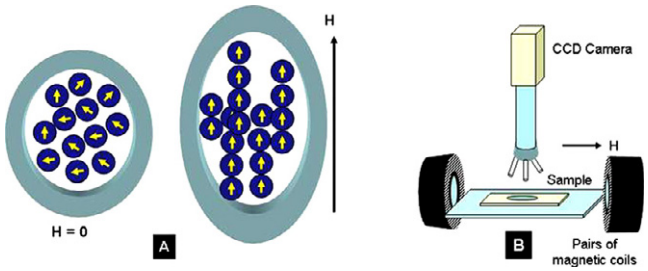

Figure 1. (A) Schematic of the encapsulation of magnetic particles in hollow micelles. When the field is zero the net magnetization of the magnetoelast is zero. Upon applying the magnetic field the elongation of the micelle is shown. (B) Schematic of the microscopic arrangement.

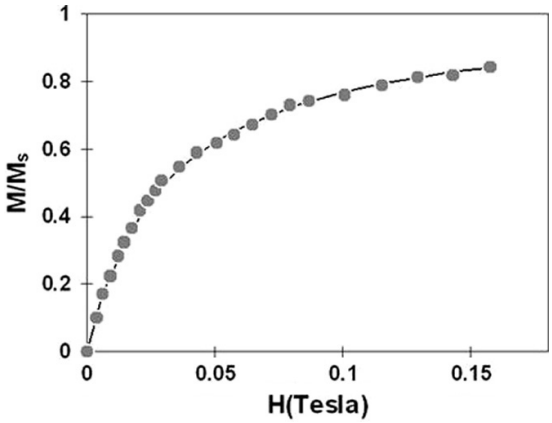

Figure 2. Reduced magnetization versus applied magnetic field for the water based double-surfacted ferrofluid. The theory used to fit the experiment is Langevin's function, mentioned in the text.

magnetization ($M = \chi H$) and Hookean elasticity of the magnetoelast. This estimation essentially implies that the shape of a deformed sphere is an ellipsoid of revolution. The schematic confinement of magnetic nanoparticles in micelles is shown in figure 1(A). In this type of magnetoelast, finely distributed magnetic particles are located in the hollow region of the soft, flexible network. These colloidal particles of ferrofluids are the elementary carriers of magnetic moments. As soon as an external field is applied, the magnetic moments tend to align with the field to produce a bulk magnetic moment and at relatively large values of the field the particle magnetization saturates. Upon removal of the field the magnetic dipole moments quickly randomize and the bulk magnetization again reduces to zero, thus exhibiting superparamagnetic behavior. Assuming the magnetization of individual particles in the magnetoelast to be equal to the saturation magnetization of the pure ferromagnetic material, M_s, the magnetization of magnetoelast, M, in the presence of an applied magnetic field can be described by the Langevin function, $M = M_s L(\alpha)$, where $L(\alpha) = (\coth\alpha - 1/\alpha)$, $\alpha = \mu_0\mu H/kT$. Here $L(\alpha)$ is the Langevin function, μ_0 is the permeability of free space, μ is the magnetic moment of the particle, H is the magnetic field, k is Boltzmann's constant and T is absolute temperature. In this framework, the non-conducting magnetically susceptible medium under the field H_0 introduces a magnetic potential as $H = H_0 - \Delta\psi$ and the magnetization M. This yields magnetostatics in the form of the Poisson equation, $\Delta\psi = 4\pi\nabla M$, where ψ is the magnetostatic potential. The detailed description of the theoretical background is given by Jarkova *et al* (2003), Stolbov and Raikher (2006), Raikher Yu and Stolbov (2005).

3. Experimental details

The visualization of micellar elongation is observed using a Magnus MLX microscope. The magnification used is 40×. The CCD camera used is Samsung (BW-360CD) attached to a personal computer (figure 1(B)). The ferrofluid used in this experiment is a double-surfacted aqueous ferrofluid. The magnetization of this fluid was measured using a search coil method. Magnetization measurements of water based double-surfacted magnetic fluid was carried out using an extraction method. Figure 2 shows the room temperature (303 K) magnetization curves of the double-surfacted water based magnetic fluid used in this experiment. The experimental magnetization is compared with the Langevin theory of magnetization (Lecommandoux *et al* 2005) given by

$$\frac{M}{M_s} = L(\alpha) \tag{1}$$

where $L(\alpha) = \coth\alpha - 1/\alpha$ and $\alpha = \mu_0\mu H/kT = M_d V H/kT$.

Here, μ, M_d, V, H, k, T are, respectively, the magnetic moment of the particle, domain magnetization of the particle, volume of the particle, applied magnetic field, Boltzmann constant and absolute temperature. In magnetic fluids, the dispersed particles are not monodispersed; therefore one has to consider the polydispersity in magnetic moment. Assuming that the particle moment is proportional to the volume of the particle (V), i.e. the domain magnetization does not change within the region of polydispersity, one can write the average magnetization as

$$M(H) = \phi_m M_d \int L(\alpha) P(V)\,\mathrm{d}V \tag{2}$$

where ϕ_m is the dispersed magnetic phase, $P(V)\,\mathrm{d}V$ is the log-normal distribution function:

$$P(V)\,\mathrm{d}V = \frac{1}{V\sigma(2\pi)^{\frac{1}{2}}} \exp\left[-\frac{(\ln V - \ln V_0)}{2\sigma^2}\right]\mathrm{d}V. \tag{3}$$

Here, σ is the standard deviation, $\ln V_0$ is the mean value of $\ln V$. The best fit parameters obtained from the fit are saturation magnetization $M_s = 22$ G, magnetic size of the nanomagnetic particles $D_m = 10.2$ nm, standard deviation $\sigma = 0.31$, domain magnetization $M_d = 320$ emu cm^{-3}, magnetic volume fraction ϕ_m is 0.52%, density of fluid 1.03 gm cm^{-3} and its capillary viscosity 2 cP at 35 °C. The micellar solution in distilled water is prepared using cetyltrimethyl ammonium bromide (CTABr—0.1 M) mixed with sodium salicylate salt (NaSal—0.03 M). The total volume of the mixture was kept at 5 ml. It is well studied that on

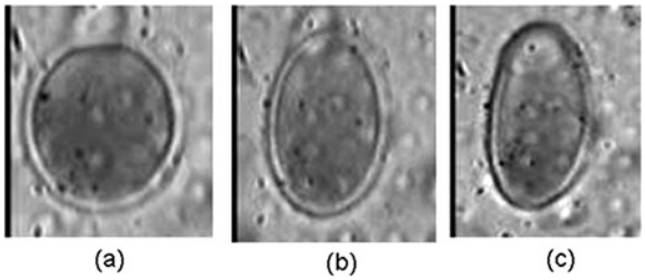

Figure 3. Magnetodeformational effect in CTABr–NaSal and ferrofluid nanocomposite micelles. (a) $H = 0$, (b) $H = 50$ G, (c) $H = 100$ G. The scale factor is 1 cm = 2 μm.

addition of small amounts of NaSal to CTABr the aqueous solution exhibits striking viscoelastic behavior (Aswal and Goyal 1998). Its zero-shear viscosity rises to about 10^6 cP. This is due to the aggregates formed, of various types, shapes and sizes, such as spherical or ellipsoidal micelle, cylindrical or thread-like micelle, disk-like micelle, membrane and vesicle. SANS and viscosity studies of CTABr–NaSal mixtures for different concentrations of NaSal show transitions of globular micelles to worm-like or thread-like micelles (Aswal and Goyal 1998). These micelles are swollen by ferrofluid (10% by volume). In this type of soft ferrogel, finely distributed magnetic particles are embedded in the swollen micelles. The stability of the sample was confirmed visually and by optical transmission.

4. Results and discussion

Figure 3 shows the magnetodeformational effect in hybrid colloids of CTABr–NaSal aqueous solution and double-surfacted water based ferrofluid. The microscopic pictures show that the hollow region of the spherical network formed is filled with magnetic nanoparticles of ferrofluid (some dark patches in the hollow region of the spherical micelle; it is the limitation of this microscope that we were not able to observe nanosize particles of ferrofluid). It is clear that when $H = 0$ the micelle is spherical. Upon application of the external magnetic fields $H = 50$ and 100 G, micelles elongate in the direction of the field. The micelle diameter is approximately $D_0 = 3$ μm at $H = 0$. It is observed that as the field increases the micelle diameter parallel to the direction of the field ($D_\parallel$) increases, whereas the micelle diameter perpendicular to the field ($D_\perp$) decreases. The field induced elongations of the micelles are calculated using $(D_\parallel - D_\perp)/D_0$. This elongation of a magnetic nanocomposite of micelles under application of a moderate magnetic field may be explained as due to the field induced chain formation in magnetic nanoparticles of ferrofluid and its further elongation in the direction of the applied field as the field strength increases (figures 1 and 3). As soon as the field is removed the elongation disappears. This also shows the superparamagnetic behavior of the magnetic nanocomposite micelles.

Figure 4 shows the field induced elongation of micelles. It is observed that in the direction of the field the micelle becomes

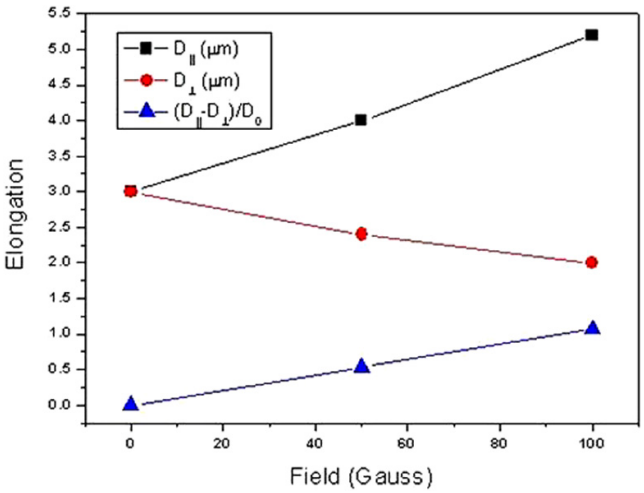

Figure 4. Field induced elongation of micelles. This shows that $D_\parallel$ (square) increases with the field while $D_\perp$ (circle) decreases. $(D_\parallel - D_\perp)/D_0$ (triangle) increases with the field.

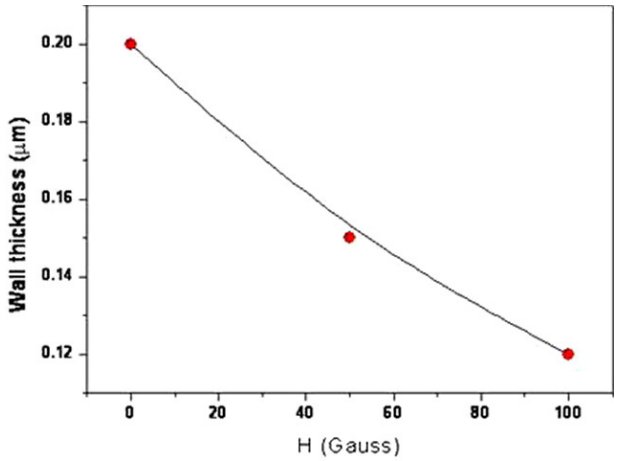

Figure 5. As the applied magnetic field increases, the elongation of the micelles increases in the direction of the field but the wall thickness decreases.

almost doubled in length; i.e. the change in diameter is 3–$\sim$6 μm, and hence 100% elongation is observed by applying a very moderate magnetic field of 100 G, while in the direction perpendicular to the applied field direction it contracts from 3 to 2 μm. The field induced elongation at $H = 100$ Oe is $\sim$107%.

After enlarging the microscopic photographs the change in wall thickness in the direction perpendicular to the field direction was measured. It is observed that the wall thickness decreases with the increase in the applied magnetic field (figure 5); this seems to be in agreement with the earlier work (Raikher Yu and Stolbov 2005). Further work on this system is in progress.

5. Conclusion

We studied field induced anisometry of a composite consisting of nanomagnets in hollow micelles. We show that as

the field increases elongation of the micelles increases but the wall thickness decreases. The soft magnetic shells are especially promising for drug delivery, their internal compartment being vacant for encapsulation of water-soluble species. Further, due to their small dimensions, these objects could be very useful for intravenous injection. In this regard, such superparamagnetic micelles will be useful in biomedicine and biotechnology.

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