# Ethylene Glycol Based Ferrofluid for the Fabrication of Magnetically Deformable Liquid Mirrors

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Stable ferrofluids composed of positively charged magnetic iron oxide nanoparticles coated with 2-[2-(2-methoxyethoxy)ethoxy]acetic acid (MOEEAA) are prepared in ethylene glycol. These new ferrofluids exhibit a magnetic response that is equivalent to that found for corresponding citrate stabilized particles. Unlike the uncoated positively charged particles, nanoparticles coated with MOEEAA and dispersed in ethylene glycol remained stable in the presence of a magnetic field. Infrared spectra indicate that surface grafting occurs through the terminal carboxylate group which is bound to the iron oxide nanoparticles both through bridging and unidentate structures. A surface grafting density of 1.2 molecules/nm$^2$ is determined from thermogravimetry measurements. Although MOEEAA functionalization increases the stability of nanoparticle suspensions in ethylene glycol, surface charge is also essential for the prevention of particle agglomeration. Importantly, the MOEEAA stabilized ferrofluid is compatible with the deposition of surface films of silver nanoparticles and thus allows for the preparation of magnetically deformable liquid mirrors.

## I. Introduction

Ferrofluids are colloidal dispersions of magnetic nanoparticles that combine fluidic and magnetic properties to yield magnetically deformable liquids. Ferrofluids are well-known and have many industrial applications including as seals, coolants for loudspeakers, and inks for printers.[1] More recently, we have employed ferrofluids for the fabrication of a new kind of deformable liquid mirror.[2−4] Since ferrofluids are not highly reflective, this application requires that they be coated with a reflective layer that can follow the surface contours as they are dynamically modified with an array of magnetic actuators in the base of the mirror. Over the past few years, we have been investigating surface films of silver nanoparticles for this purpose.[5,6] These films are based on reflective liquid-like films that were first reported by Yogev and Efrima[7] in 1988 and denoted as MELLFs (for metal liquid-like films) by their discoverers. Shortly after the initial literature report of the preparation of MELLFs, Gordon et al.[8] described an alternate synthetic route to similar reflective surface films. This method is employed in the present study and involves the vigorous shaking of an aqueous suspension of silver nanoparticles together with an organic solution of a suitable surface ligand. Upon coating with the organic ligand, the particles spontaneously assemble at both the liquid−liquid and the air−water interfaces to form a highly reflective, coherent surface film. We have demonstrated that these films can be isolated and transferred to other liquid substrates.[5,6] Furthermore, scanning electron microscopy images indicate that the reflective film is composed of a single monolayer of silver particles.[6] To fabricate a magnetically deformable mirror, this monolayer of silver particles must be successfully deposited on an appropriate ferrofluid.

Highly reflective surface films of silver nanoparticles can be spread on water,[5] ethylene glycol,[9] and several other hydrophilic liquids.[10] The majority of commercial ferrofluids, however, are oil based and therefore do not have sufficiently high surface energies to permit the facile spreading of surface films. Aqueous ferrofluids are known[11−14] but are not suitable for the preparation of stable magnetic mirrors because of the relatively rapid evaporation of water. To meet simultaneously the criteria of low vapor pressure and high surface tension, we have identified ethylene glycol as an appropriate carrier liquid. The use of ethylene glycol as a

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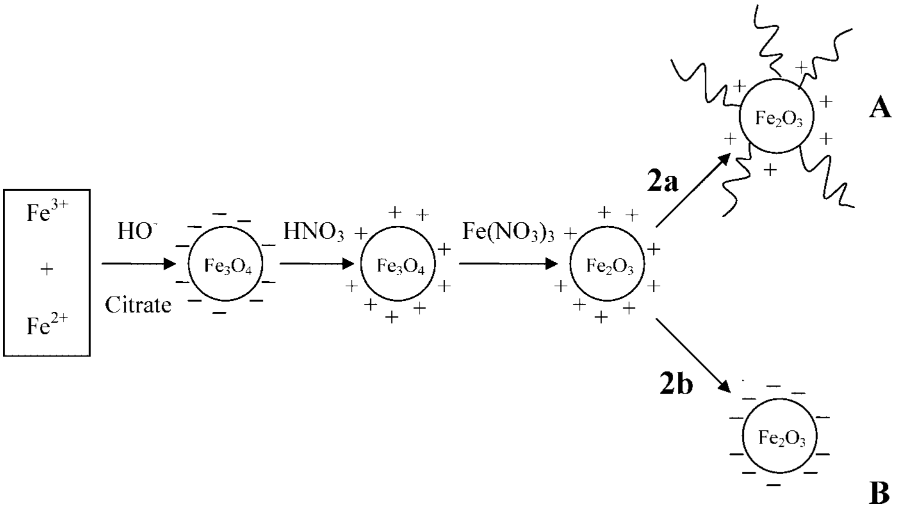

**Figure 1.** Schematic representation of the synthetic route leading to $\gamma$-$Fe_2O_3$ nanoparticles coated with either 2-[2-(2-methoxyethoxy)ethoxy]acetic acid (MOEEAA) (A) or citrate (B).

polar carrier liquid for ferrofluids has been previously proposed.[15−17]

A relatively large number of organic ligands, including, for example, fatty acids,[14] ionic surfactants,[16,18] amines, and alcohols,[19] have been investigated as stabilizing agents for magnetic nanoparticles. In all cases, however, these ligands were employed to enable particle dispersion in organic media. Particle stabilization in polar carrier liquids, such as water or ethylene glycol, has been achieved rather through the introduction of surface charges. In known preparations, particle aggregation is prevented by electrostatic stabilization employing the surface adsorption of citrate[20] or hydroxide[21] ions to produce negatively charged particles. Bilayers of ionic surfactants have also been reported to provide electrostatic stabilization through the outer layer of charged head groups surrounding the particles.[22] As described below, ferrofluids prepared from citrate stabilized magnetic particles are not compatible with the reflective surface films of silver nanoparticles. The present article reports the preparation and characterization of a new ethylene glycol based ferrofluid, specifically developed to be compatible with a surface MELLF and thus suitable for the fabrication of magnetically deformable liquid mirrors.

## II. Materials and Methods

Starting materials were commercially obtained from Aldrich and used as received. Water was purified using a Nanopure II (Barnstead) filtering system.

**II-1. Preparation of Magnetic Particles.** Iron oxide nanoparticles were prepared by coprecipitation as described in several articles.[20,21,23,24] The overall procedure employed for the preparation of the particles is summarized in Figure 1.

Separate solutions of $FeCl_3$ and $FeCl_2$ were first prepared in aqueous hydrochloric acid (0.09 M) with concentrations selected to maintain a molar ratio $[Fe(II)]/[Fe(III)] = 0.5$. The two solutions were heated to 70 °C and combined for a total volume of 200 mL ($[Fe]_{total} = 0.15$ M), just prior to the addition of the alkaline medium in the next step. Twenty milliliters of a solution containing both NaOH (10 M) and trisodium citrate dihydrate (0.085 M) (6% molar ratio of $[Fe]_{total}$) were added quickly to the iron solution with both solutions being previously heated to 70 °C. The solution was maintained at this temperature and under vigorous stirring for 30 min. The resulting magnetite ($Fe_3O_4$) particles were washed several times with nanopure water and dilute nitric acid (1 M). The particles were isolated between each washing using the magnetic field of a permanent magnet.

The particles were next treated with nitric acid (2 M) for 3 h to introduce a positive charge on the surface. They were then dispersed in 100 mL of water before being oxidized from magnetite ($Fe_3O_4$) to maghemite ($\gamma$-$Fe_2O_3$) by the addition of 100 mL of aqueous ferric nitrate (0.5 M) and heating at 100 °C for 30 min under vigorous stirring. The resulting particles were decanted with a strong magnetic field using a permanent magnet and washed twice with acetone (100 mL) before being dispersed in 100 mL of nanopure water.

**II-2. Surface Functionalization.** The particles obtained by the above procedure were treated with two different stabilizing agents according to the following procedures.

*II-2a. MOEEAA.* The aqueous suspension of particles was heated to 90 °C and 3.5 mL of 2-[2-(2-methoxyethoxy)ethoxy]acetic acid (MOEEAA) dissolved in 20 mL of nanopure water was added. The mixture was maintained at 90 °C and under vigorous stirring for 30 min. The MOEEAA coated particles were isolated by the

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addition of an equivalent volume of acetone, followed by centrifugation at 15 000 rpm for 90 min.

*II-2b. Trisodium Citrate.* This procedure is similar to that previously reported in literature.[20] The aqueous suspension of particles was heated to 90 °C, and 2 g of trisodium citrate was added to the mixture under vigorous stirring. The particles were washed twice with acetone before being collected by decantation with a magnetic field.

**II-3. Preparation of the Ferrofluid and Liquid Mirrors.** Ferrofluids were obtained by dispersion of the stabilized particles in ethylene glycol at a weight percentage of particles of 19%. Magnetically deformable mirrors were prepared by coating the ferrofluid with a surface film of silver nanoparticles. The metallic silver particles were prepared and concentrated as described elsewhere.[5] The formation of interfacial films of silver nanoparticles involves three basic steps. Particles, about 50 nm in diameter, are first prepared by the chemical reduction of silver nitrate in aqueous solution.[25] The aqueous suspension of the particles is then vigorously shaken together with a solution of a copper complex of 2,9-dimethyl-1,10-phenanthroline in 1,2-dichloroethane. This step results in the coating of the particles with a stabilizing organic layer and their spontaneous flocculation to the interface between two liquid phases.[8] The final step in the preparation of the reflective surface film involves the isolation of the concentrated interfacial suspension of particles and its subsequent spreading on a liquid surface. To isolate the interfacial suspension, a portion of the two phase system is poured into a polypropylene separatory funnel. At this point, the flocculated particles form a coherent film that completely envelopes the aqueous phase. The denser organic phase is then removed through the funnel stopcock, and the upper aqueous phase is reduced by aspiration. The silver particles, along with the remaining water and residual organic phase, can then be stored in a polypropylene container.

Typical mirrors were prepared with 6 mL of ferrofluid and placed in an aluminum dish having a diameter of 7 cm. The metallic silver particles, prepared and concentrated as described above, were sprayed onto the ferrofluid surface with a commercial paint spray gun connected to a nitrogen cylinder at a pressure of 275 kPa.

**II-4. Characterization methods.** X-ray diffraction patterns of dry magnetic particles were obtained with a Siemens XRD system with Cu K radiation.

Transmission electron microscopy images of iron oxide nanoparticles were obtained with a JEOL JEM-1230 microscope operated at an acceleration voltage of 80 kV. Samples were prepared by evaporation of a drop of the particle suspension on a Formvar coated nickel grid.

Infrared spectra of the dried particles were recorded using a Nicolet Magna IR 850 spectrometer equipped with a Golden Gate single reflection diamond ATR series MkII.

Thermogravimetric analyses were performed with a Mettler Toledo instrument (model TGA/SDTA851$^{e}$) using an aluminum oxide crucible. Samples were heated under a simultaneous flow of air and nitrogen at a rate of 50 mL/min for each gas. Samples were heated from 25 to 900 °C at the heating rate of 10 °C/min.

Zeta potential and particle size were determined from dynamic light scattering measurements carried out with a Malvern Zetasizer nano series Nano-ZS. Particles were dispersed in ethylene glycol at a weight percentage of 0.6%. The viscosity of the pure solvent was employed in the particle size calculations.

The surface roughness of the silver coated ferrofluids was evaluated with a general purpose Zygo Mach−Zehnder interferometer. Magnetic deformations were induced by placing an electromagnetic coil, capable of generating magnetic fields of the order of a few Gauss, directly below the mirrors as described elsewhere.[26] An Imagine Optics Shack-Hartmann wavefront analyzer was employed to measure the resulting surface deformation.

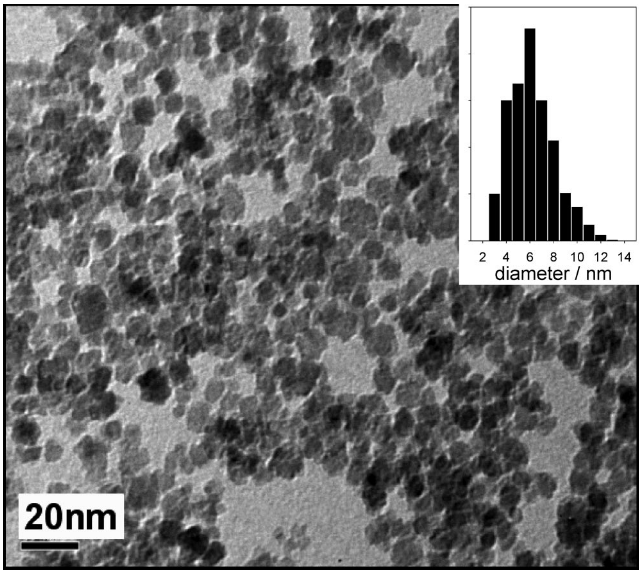

**Figure 2.** TEM micrograph of uncoated iron oxide nanoparticles dried from aqueous suspension on a Formvar coated nickel grid. The particle size distribution is shown in the inset.

## III. Results and Discussion

**III-1. Iron Oxide Nanoparticles.** Although the coprecipitation method employed to prepare the particles has been previously reported to yield maghemite ($\gamma$-$Fe_2O_3$),[23] the possibility of obtaining mixtures containing residual magnetite ($Fe_3O_4$) has also been noted.[22] Comparison of the X-ray diffraction pattern recorded for the iron oxide nanoparticles isolated before functionalization with MOEEAA or citrate (see Supporting Information) with known X-ray diffraction patterns[27] for $\gamma$-$Fe_2O_3$ and $Fe_3O_4$ indeed indicates that it is very difficult to distinguish between the two forms by this method. Given the oxidizing conditions used in particle preparation, it can be assumed that maghemite ($\gamma$-$Fe_2O_3$) is primarily obtained, but the possibility of residual magnetite remaining in the core of the particles cannot be excluded.

A typical transmission electron micrograph of the iron oxide nanoparticles particles is shown in Figure 2. The particles are found to be roughly spherical with a mean diameter of about 6 nm. The particle size distribution, as evaluated from manual measurements of about 1000 particles, is also shown in Figure 2 and agrees well with that typically obtained by the coprecipitation method of particle preparation.[21] Similar images are obtained for the particles functionalized with either citrate or MOEEAA.

**III-2. Surface Functionalized Particles.** Particles functionalized with either MOEEAA or citrate were characterized by infrared spectroscopy and thermogravimetry. Infrared

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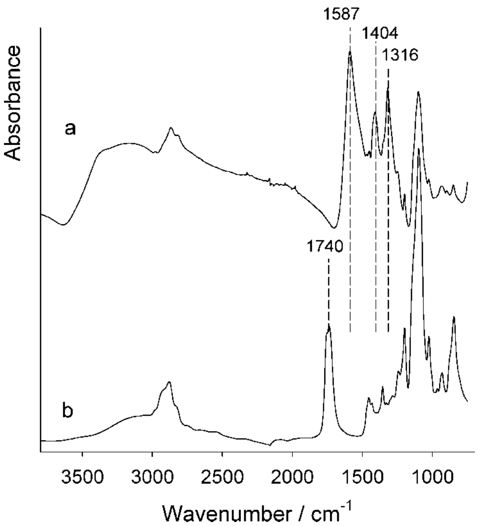

**Figure 3.** IR spectra of (a) dried iron oxide nanoparticles coated with MOEEAA and (b) pure MOEEAA.

**Table 1. Infrared Band Position and Vibrational Assignments for 2-[2-(2- Methoxyethoxy)ethoxy]acetic Acid (MOEEAA) and Dried Iron Oxide Nanoparticles Coated with MOEEAA**

| band frequency, $cm^{-1}$ | | |
|---|---|---|
| MOEEAA | MOEEAA coated $\gamma$-$Fe_2O_3$ particles | band assignment |
| 2881 | 2866 | $\nu$(C—H) for $-CH_2$ |
| 1740 | | $\nu$(C=O) for free —COOH |
| | 1587 | $\nu(COO^-)$ asym for adsorbed $COO^-$ |
| | 1404 | $\nu(COO^-)$ sym (bridging coordination)[26] |
| | 1316 | $\nu(COO^-)$ sym (unidentate coordination)[26] |
| 1200 | 1190 | $\nu$(C—O—C) asym |
| 1098 | 1093 | $\nu$(C—O—C) sym |

measurements provide information about the chemical nature of the coating layer, whereas thermogravimetry allows for the quantitative evaluation of the grafting density.

*III-2a. Infrared Spectroscopy.* The infrared spectra of pure MOEEAA and of dried MOEEAA coated particles are shown in Figure 3. The absorption frequencies corresponding to the principal bands are reported in Table 1 along with peak assignments. In the case of pure MOEEAA, the most intense absorption bands are found at 1098 $cm^{-1}$, 1740 $cm^{-1}$, and 2881 $cm^{-1}$, arising from vibrations characteristic of the constituent ether, carboxylic acid carbonyl, and methylene groups, respectively. The spectrum of the coated particles exhibits bands corresponding to the ether and methylene stretching frequencies at 1093 $cm^{-1}$ and 2866 $cm^{-1}$, thus confirming the presence of MOEEAA. Bands arising from the carboxylate group are also evident, appearing at positions that differ significantly from that observed for the carbonyl of the free molecule. In fact, three relatively intense bands are observed at 1587 $cm^{-1}$, 1404 $cm^{-1}$, and 1316 $cm^{-1}$. The strong band at 1587 $cm^{-1}$ can be attributed to the carboxylate asymmetric stretch indicating that the free acid is deprotonated upon binding to the surface of the particle. The two bands at 1404 $cm^{-1}$ and 1316 $cm^{-1}$ can both be assigned to the symmetric stretching vibration of the carboxylate group, suggesting the presence of two different modes of surface coordination. In a detailed infrared study of the binding of a number of carboxylic acids to oxidized aluminum, Allara et al.[28] also reported two distinct symmetric carboxylate stretching frequencies (1475 $cm^{-1}$ and 1417 $cm^{-1}$). Although these authors attributed the observation of two bands to the presence of two types of adsorbate—substrate bonding, they were unable to provide specific structural assignments. Extensive studies of metal complexes of carboxylic acids indicate that the frequency difference between the asymmetric and the symmetric stretching vibrations can be correlated with the bonding mode.[29] Bidentate complexes, in which both carboxylate oxygen atoms are bound to a single metal ion, exhibit frequency differences between the two vibrations of 40−70 $cm^{-1}$. Bridging complexes in which the two oxygen atoms are bound to neighboring metal ions show larger frequency differences, of the order of 140−170 $cm^{-1}$. The largest frequency differences, in some cases exceeding 300 $cm^{-1}$, are observed for unidentate complexes in which only one oxygen atom is bound to the metal. The IR spectrum of the MOEEAA functionalized magnetic particles exhibit two bands assigned to the symmetric carboxylate stretch, at frequencies corresponding to $[\upsilon_a(COO^-)-\upsilon_s(COO^-)]$ equal to 183 $cm^{-1}$ and 271 $cm^{-1}$, respectively. These frequency differences indicate that the ligand is bound to the surface both through bridging and unidentate structures.

Willis et al.[30] recently reported that the infrared spectrum of oleic acid bound to $\gamma$-$Fe_2O_3$ exhibits asymmetric and symmetric carboxylate stretching bands at 1527 $cm^{-1}$ and 1430 $cm^{-1}$, respectively. While the identification of a single symmetric stretching frequency implies a single bonding mode in this case, the authors note that the bands are relatively large and attribute this to the presence of a mixture of compounds on the surface.

It is relevant to note that the symmetric carboxylate stretching frequencies observed for MOEEAA bound to iron oxide nanoparticles appear at significantly lower frequencies than those found for carboxylic acids on $Al_2O_3$.[28] The stretching frequencies of coordinated carboxylates are known to vary significantly from one metal ion to another.[31] IR spectra of a series of *n*-alkanoic acids self-assembled on metal oxide surfaces indicate that both the carboxylate symmetric and asymmetric stretching frequencies shift to lower frequencies as stability of the ligand to surface bond increases.[32] The relatively low frequencies observed for the MOEEAA functionalized particles thus imply relatively strong bonding.

Figure 4 shows the infrared spectrum of dried iron oxide nanoparticles coated with citrate. The spectrum of trisodium citrate is also shown for comparison. Both spectra exhibit bands characteristic of the asymmetric and symmetric stretching vibrations of the carboxylate moiety. In this case, the spectral changes that accompany surface bonding are less significant than those observed for MOEEAA coated particles. This is because the precursor ligand is introduced as

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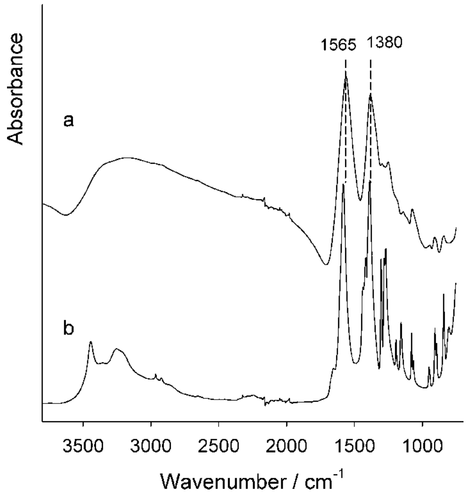

**Figure 4.** IR spectra of (a) dried iron oxide nanoparticles coated with trisodium citrate and (b) pure trisodium citrate.

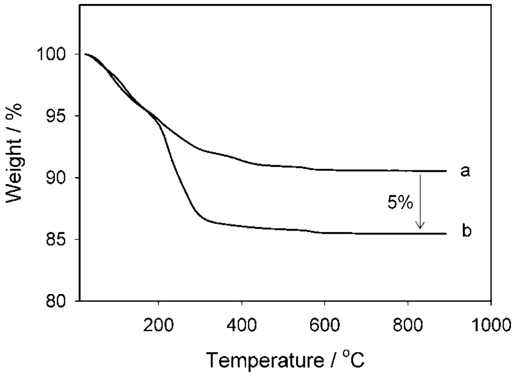

**Figure 5.** Thermograms of (a) dried uncoated iron oxide nanoparticles and (b) dried iron oxide nanoparticles coated with MOEEAA.

a carboxylate salt rather than in the acid form. Furthermore, each ligand molecule contains three carboxylate groups, and not all are involved in direct interactions with the surface. Nevertheless, small shifts to lower frequencies are observed for both asymmetric (1574 $cm^{-1}$ to 1565 $cm^{-1}$) and symmetric (1385 $cm^{-1}$ to 1380 $cm^{-1}$) stretching bands upon the adsorption of citrate to the particle surface.

*III-2b. Thermogravimetric Analyses.* The weight loss observed upon iron oxide nanoparticles coated with MOEEAA is plotted in Figure 5. The thermogram obtained for the uncoated particles is also provided for comparison. Upon heating between room temperature and 900 °C, the uncoated particles show a weight loss of 9.4% that can be attributed to water desorption from the surface. Over the same temperature range, the coated particles exhibit a greater weight loss due to the decomposition of the organic ligand. If it is assumed that the coated and uncoated particles have the same water content, the weight percent of MOEEAA bound to the functionalized particles can be evaluated from the difference in weight loss between the two samples. In the present case, this difference is 5%. This result can be combined with the average particle size determined by TEM to estimate the grafting density of the MOEEAA chains on the particle surface as 1.2 molecule/$nm^2$. This relatively low grafting density provides a reasonable justification for the assumption that the water content of the particles is not significantly altered by the presence of the MOEEAA chains.

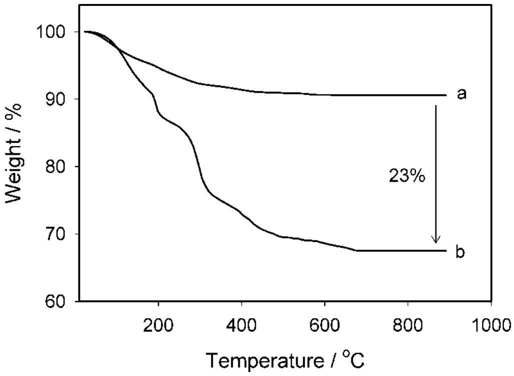

**Figure 6.** Thermograms of (a) dried uncoated iron oxide nanoparticles and (b) dried iron oxide nanoparticles coated with trisodium citrate.

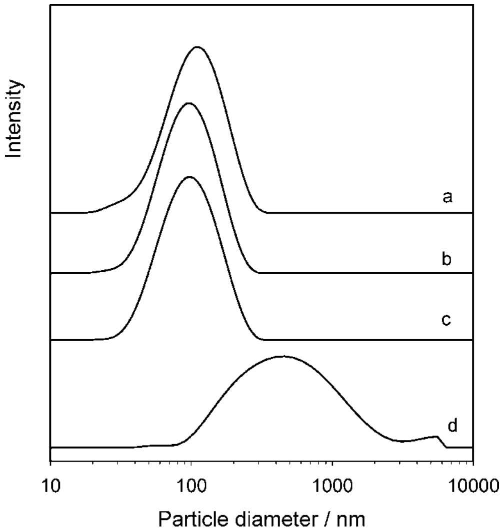

**Figure 7.** Intensity weighted *z*-average particle size distributions obtained from dynamic light scattering measurements on ethylene glycol suspension of (a) uncoated iron oxide nanoparticles, (b) iron oxide nanoparticles coated with citrate, (c) iron oxide nanoparticles coated with MOEEAA, and (d) iron oxide nanoparticles coated with MOEEAA and subsequently treated with sodium hydroxide.

Figure 6 shows the thermograms obtained for the citrate coated particles. The functionalized particles exhibit a weight loss that exceeds that observed for the uncoated particles by 23%. If this difference is entirely attributed to the mass of citrate present, a grafting density of 6.4 molecules/$nm^2$ is obtained. It is, however, important to note that in the case of citrate adsorption, the assumption that the water content is unaltered by the presence of the ligand is probably not justified, and the grafting density obtained in this way can only be considered as an estimate.

**III-3. Dispersed Particles.** Dynamic light scattering measurements were performed on ethylene glycol suspensions of uncoated iron oxide nanoparticles and of iron oxide nanoparticles coated with either citrate or MOEEAA. The resulting particle size distributions are plotted in Figure 7 (curves a, b, and c). The three samples exhibit near identical particle size distributions centered near diameters of 100 nm. This average particle size is much greater than that evaluated from TEM images. Dynamic light scattering typically yields particle sizes that exceed those obtained by microscopy. This

**Table 2. Zeta Potential of Iron Oxide Nanoparticles with Differing Surface Coatings, Dispersed in Ethylene Glycol**

| nature of the particles | zeta potential, mV |
|---|---|
| uncoated | +45 |
| coated with citrate | −50 |
| coated with MOEEAA | +44 |
| coated with MOEEAA, hydroxide treated | 0 |

is in part because dynamic light scattering measures the hydrodynamic radius which is larger than the radius of a dry particle. In addition, the dynamic light scattering results are expressed as the intensity weighted *z*-average which is biased toward larger particles since the scattering intensity is proportional to the square of particle molecular weight. However, neither of these factors is sufficient to explain the large difference in particle size obtained here. Similar differences have been reported for maghemite particles dispersed in both water and dodecane and attributed to particle aggregation.[22] The aggregation of magnetic particles in the absence of a magnetic field has been theoretically investigated by the Monte Carlo technique.[33] In the case of particles having a diameter of 10 nm, the attractive magnetostatic interaction energy between particles can be evaluated as being on the order of 10 kT. This attraction is sufficient to cause the formation of dynamic particle clusters containing on the order of 5−15 particles.[33] The presence of such clusters in the particle suspensions would clearly explain why the hydrodynamic diameters obtained by dynamic light scattering are an order of magnitude larger than the diameters observed by TEM. This interpretation is supported by the observation that similar size distributions are observed for the three populations of particles (uncoated and coated with either citrate or MOEEAA) despite the large difference in their surface properties. Furthermore, the particle size distributions do not evolve as a function of time and therefore cannot be attributed to irreversible aggregation due to insufficient surface passivation.

Dynamic light scattering was also employed to evaluate the zeta potential of the various particles. The results for particles dispersed in ethylene glycol are summarized in Table 2. The uncoated particles are found to be positively charged, as expected from surface protonation through their prior treatment with nitric acid. Water dispersions of the same particles are found to be acidic, with a pH near 4. As described elsewhere for similar iron oxide nanoparticles,[34] aqueous dispersions become unstable as the pH is raised to between 5 and 10, and the positive surface charge is lost due to deprotonation. The introduction of MOEEAA does not significantly alter the particle surface charge. This observation is consistent with the relatively low grafting density determined by thermogravimetry measurements.

As discussed in further detail below, the presence of surface grafted MOEEAA has an important effect on the stability of the ferrofluid prepared in ethylene glycol. To determine whether the steric repulsion between particles generated by the MOEEAA chains is sufficient to prevent particle agglomeration, the positive particles were neutralized by the addition of sodium hydroxide ([NaOH] = 0.06 M). As illustrated in Figure 7 (curve d), this treatment has an important effect on the particle size distribution, which is shifted to larger hydrodynamic diameters and significantly broadened, suggesting increased aggregation. This observation indicates that the particle suspension is primarily stabilized by electrostatic repulsions and the grafted MOEEAA chains alone do not provide sufficient steric stabilization.

**Table 3. Peak-to-Valley Amplitude of Deformation as a Function of Applied Voltage for Ethylene Glycol Based Ferrofluids Prepared from Iron Oxide Nanoparticles Coated with either MOEEAA or Citrate**

| | amplitude of deformation, μm | |
|---|---|---|
| actuator potential, V | MOEEAA | citrate |
| 5 | 3.5 | 2.6 |
| 10 | 14 | 9.7 |

**III-4. Ferrofluids and Magnetically Deformable Mirrors.** Ferrofluids were prepared by the dispersion of the various particles in ethylene glycol at a particle weight percent of 19%. The relative performance of the ferrofluids was evaluated from the amplitude of the surface deformation resulting from the application of a static magnetic field. The deformation $h$ can be approximated[35] as

$$h = \frac{\mu_0(\mu_r - 1)}{2pg}(\mu_r {H_n}^2 + {H_t}^2) \qquad (1)$$

where $\rho$ is the density of the ferrofluid, $H_n$ and $H_t$ are the normal and tangential components of the magnetic field inside the ferrofluid, $\mu_r$ is the relative magnetic permeability, and $\mu_0$ is the permeability of free space. This equation indicates that for a fixed magnetic field strength, the observed deformation is a measure of $\mu_r$, which is, in turn, related to the magnetic susceptibility $\chi$ by

$$\mu_r = \chi + 1 \qquad (2)$$

Ferrofluids prepared from the uncoated particles show unstable surface deformations when a magnetic field is applied. Ferrofluids prepared from particles coated with either MOEEAA or citrate, on the other hand, are stable and exhibit surface deformations that depend on the magnetic field strength, as illustrated by the values reported in Table 3. For a given magnetic field strength, larger deformations are found for the MOEEAA coated particles than for those stabilized with citrate. This may in part be a result of the lower grafting density of MOEEAA which results in a greater concentration of magnetic material in the ferrofluid suspension at a given weight fraction of particles. Further measurements would, however, be required to conclude definitively that the ferrofluid performance is enhanced by the grafting of MOEEAA to the particles.

The clear advantage of the MOEEAA stabilized ferrofluid is demonstrated during coating with a thin reflective film of silver nanoparticles to fabricate magnetically deformable mirrors.[5] The photographs of mirrors prepared in this way are provided in Figure 8 for ferrofluids containing MOEEAA and citrate stabilized magnetic particles. The surface film of silver nanoparticles is clearly disrupted by the citrate

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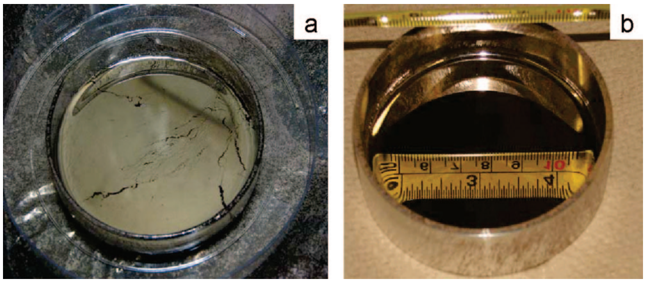

**Figure 8.** Magnetically deformable liquid mirrors prepared from silver nanoparticles spread on the surface of ethylene glycol based ferrofluids containing (a) iron oxide nanoparticles coated with citrate and (b) iron oxide nanoparticles coated with MOEEAA.

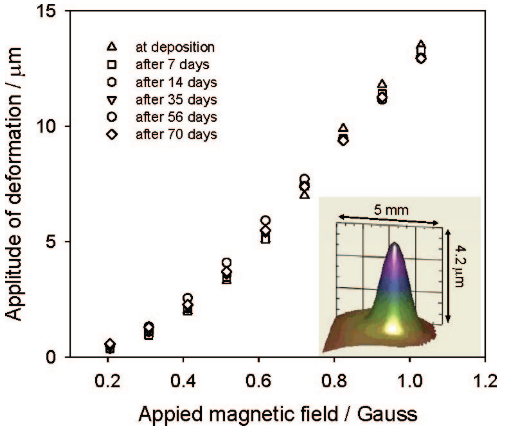

**Figure 9.** Peak-to-valley amplitude of deformation as a function of applied magnetic field for a liquid mirror prepared from an ethylene glycol based ferrofluid containing MOAAEE coated iron oxide nanoparticles and a thin film of silver nanoparticles deposited at the surface. A typical profile of the surface deformation obtained at a magnetic field strength of about 0.5 Gauss and recorded with a Shack-Hartmann wavefront analyzer is provided in the inset.

stabilized suspension. The liquid mirror spread on the MOEEAA stabilized ferrofluid, on the other hand, exhibits excellent reflectivity properties, comparable to those previously reported for silver nanoparticles spread on water.[5] Furthermore, interferometry measurements indicate that the reflective film forms a smooth surface with a root-mean-square roughness of approximately $\lambda/20$ at 624 nm.

The stability of the liquid mirror was also investigated through repeated magnetic deformation over a period of three months. Figure 9 shows that the magnetic response remains constant over this time period, further illustrating the compatibility between the surface film of silver particles and the ferrofluid. Results are plotted as peak-to-valley amplitudes, and a typical deformation profile is illustrated in the inset. It is important to note that comparative results for the citrate coated particles cannot be provided since the resulting mirrors are not of sufficient optical quality (as illustrated in Figure 8) to allow for the characterization of surface deformation by wavefront analysis.

While it is clear that the MOEEAA coated particles allow for the preparation of a ferrofluid that is compatible with the reflective silver surface layer, the reason for this cannot be unambiguously identified. The MOEEAA and citrate stabilized particles differ not only in the chemical nature of the ligand but also in the sign of the electrostatic charge. The MOEEAA coated particles are positive, whereas those stabilized with citrate are negatively charged. Unfortunately, it is difficult to evaluate the electrostatic charge of the silver nanoparticles. Although negatively charged when initially prepared in aqueous solution, the particles spontaneously flocculate to form a surface film upon coating with an organic ligand.[5] The expulsion of the particles from the aqueous phase during this step implies that their surface charge is significantly reduced. The sign of any residual charge, however, is unknown. If the silver particles carry a net positive charge, their compatibility with the MOEEAA stabilized ferrofluid could originate in electrostatic repulsions.

As noted above, the uncoated positively charged particles do not form a stable suspension in ethylene glycol. The presence of MOEEAA, even at a relatively low grafting density, allows for the preparation of a stable suspension. This ligand therefore clearly creates a repulsive barrier to particle aggregation and an increased affinity of the particles for the suspending medium. It is possible that the MOEEAA chains are also responsible for the screening of disruptive interactions between the magnetic nanoparticles of the ferrofluid and the silver particles spread at its surface.

## IV. Conclusions

Stable ferrofluids composed of positively charged iron oxide nanoparticles coated with MOEEAA have been prepared in ethylene glycol. These new ferrofluids exhibit a magnetic response that is equivalent, or perhaps even superior to, that found for corresponding citrate stabilized particles. Unlike the uncoated particles, maghemite nanoparticles coated with MOEEAA and dispersed in ethylene glycol remained stable in the presence of a magnetic field. MOEEAA should exhibit a strong affinity for the carrier liquid (ethylene glycol) due to the ethoxy group ($-O-CH_2-CH_2-$) within the chain. Furthermore, the presence of the terminal carboxylate group ensures stable grafting to the magnetic iron oxide nanoparticles. Although MOEEAA functionalization increases the stability of iron oxide nanoparticles suspensions in ethylene glycol, surface charge is also essential for the prevention of particle agglomeration.

Importantly, the MOEEAA based system is compatible with the deposition of surface films of silver nanoparticles, allowing the preparation of magnetically deformable liquid mirrors. Such mirrors exhibit optical quality surfaces and magnetic performance that remains stable over 70 days. Corresponding mirrors supported by ferrofluids composed of citrate coated nanoparticles exhibit dull nonreflecting surfaces with numerous cracks that appear shortly after the spreading of the reflective silver layer. The identification of a ferrofluid compatible with the silver particles constitutes a key step in the development of commercial mirrors based on this technology.

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**Supporting Information Available:** X-ray diffraction details and data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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