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Short Communication—Magnetically-responsive electrophoretic silica organosols

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Abstract

Hypothesis Silica nanoparticles can be dispersed in organic solvents (organosols) using surfactants, such as didodecyldimethylammonium bromide (DDAB). DDAB analogues prepared with lanthanide tetrahalide counterions, either a high-magnetic moment ion (HoCl$_3$Br, DDAH) or low-magnetic moment one (NdCl$_3$Br, DDAN), are expected to produce charged particles but only DDAH-stabilized dispersions are expected to be magnetically responsive.

Experiments Phase-analysis light scattering (PALS) measurements have been performed to determine the charge on DDAH- and DDAN-stabilized organosols. Magnetic sedimentation experiments have been performed to determine whether or not the silica dispersions are magnetically responsive. Sedimentation was monitored both by visual observations and UV-vis spectroscopy.

Findings Both DDAH and DDAN organosols are negatively charged, the same as DDAB-stabilized nanoparticles. The DDAH-stabilized nanoparticles are found to respond to a magnetic field, whereas the DDAN-stabilized nanoparticles do not. This opens up possibilities for creating nanoparticle dispersions in nonpolar solvents which can be tailored to respond to desired external stimuli.

Keywords: Electrophoresis, magnetophoresis, nanoparticle dispersions, organosols, nonpolar solvents

Highlights

- Silica nanoparticles were dispersed in organic solvent with cationic surfactants.
- Both Ho and Nd surfactants produce charged, electrophoretic particles.
- Only the surfactant with Ho (high magnetic moment) produces magnetically-responsive particles.

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The term “organosol” is used to describe a classic system in colloid science, consisting of inorganic nanoparticles stabilized in a nonaqueous, organic solvent [1]. Organosols are of general interest, for example, as inorganic nanoparticles as acid-neutralizers in petrochemical fluids [2]. Furthermore, mineral oxides can be charged by surfactants in nonpolar solvents [3]. Of the many possible inorganic nanoparticles, silica has by far been the most studied [7, 9–15]. Despite the extensive studies of charged nanoparticles in organic solvents, the detailed origin of the production of charge on the particle surfaces is still not fully understood [16, 17].

The use of charged nanoparticles has been motivated in recent years by their applications in electrophoretic displays, which are used to form the electronic paper screens used in e-Reader devices [18]. This initial report has been cited over 500 times and receives approximately 50 citations per year. Additionally, there have been approximately 2000 US and EU patents registered for electrophoretic display particles. Many of the proposed technologies for next-generation electronic paper, with lower power consumption and a full color gamut, require control of the charge of either the particles or the fluid [19]. While previous electronic paper technologies have relied on electrophoresis, a recent idea is to develop dual-functionality, magnetic-electric electronic paper [20].

Recently, a simple method to prepare surfactant-stabilized silica organosols through phase transfer from aqueous to organic solvents has been demonstrated [21]. Of the particle-surfactant combinations presented, didodecyldimethylammonium bromide (DDAB) stabilized silica particles in toluene-heptane solvent mixtures are most promising for generating electrophoretic and magnetophoretic dual-functionality. Quaternary ammonium surfactants with lanthanide tetrahalide anions have previously been prepared and shown to exhibit magnetic responsivity [22–24]. In this study, the HoCl₃Br analogue of DDAB (DDAH) was chosen due to the high magnetic moment of Ho³⁺ (10.6 µB), and the NdCl₃Br analogue (DDAN) was prepared as non-magnetic lanthanide control due to the much lower magnetic moment of Nd³⁺ (3.58 µB) [25]. Both surfactants result in charged particles with larger magnitude electrophoretic mobilities than DDAB-stabilized particles; only DDAH, however, shows a response to magnetic fields. This demonstrates that it is possible to design small-molecule dispersants which can impart both magnetic and electrophoretic mobility to mineral oxide nanoparticles.

DDAH and DDAN were synthesized according to literature procedures for preparing magnetic cationic surfactants [23]. (The details and analysis of the surfactants are shown in the Supporting Information,†) The silica organosols were prepared in toluene-heptane (70:30 w/w) using a drying method previously described [21]. The transfer efficiency (mass of dispersed surfactant and silica over the whole solid mass) was determined after gentle centrifugation for 300 s at 3000 rpm (DDAB 97%, DDAH 59%, and DDAN...
Table 1: Electrophoretic mobility ($\mu$) for silica organosols

<table>
<thead>
<tr>
<th>Dispersant</th>
<th>$\mu / (10^{-10} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1})$</th>
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</thead>
<tbody>
<tr>
<td>DDAB</td>
<td>$-5.9 \pm 0.3$</td>
</tr>
<tr>
<td>DDAH</td>
<td>$-17.8 \pm 0.7$</td>
</tr>
<tr>
<td>DDAN</td>
<td>$-12.1 \pm 0.6$</td>
</tr>
</tbody>
</table>

75%). The DDAH and DDAN organosols were not as stable as those with DDAB, but sufficient mass was transferred to enable studies of the response of the particles to electric and magnetic fields. (Further details of the preparation procedures are provided in the Supporting Information.†)

The electrophoretic mobilities ($\mu$) of DDAH- and DDAN-stabilized dispersions were measured using phase-analysis light scattering, and the results of these measurements are shown in Table 1 (Experimental details are provided in the Supporting Information.†) As has previously been determined for DDAB-stabilized silica organosols [21], both of the lanthanide surfactants also induce a negative charge on the silica particles. Additionally, the magnitude of $\mu$ is greater for both lanthanide surfactants, indicating that the two are more effective charge control agents than DDAB. The DDAH-stabilized dispersions are more highly charged than the DDAN-stabilized ones, but the value of $\mu$ when using DDAN is more similar to DDAH than DDAB. In terms of the electrophoretic response, there is little difference between the two lanthanide tetrahalide surfactants.

This demonstrates that the particles respond to the application of electric fields. In addition to this, the response of the dispersions to magnetic fields has been studied to determine the effect of the Nd and Ho counterions. NdFeB rod magnets were used to apply to a magnetic field to the sample. (Details of the magnets are provided in the Supporting Information.†) In the absence of a magnetic field, the particles do not sediment significantly over one hour. More occurs in the DDAH-stabilized organosol, which can be expected due to the decreased stability reflected by the lower transfer efficiency. The organosols were redispersed after all sedimentation experiments (magnetic or non-magnetic) using vortex mixing. The stability and performance of the dispersions were similar regardless of the number of time the particles had been sedimented and redispersed. (Through the course of this study, particles were cycled through sedimentation and redispersion approximately ten times.)

In the first set of magnetic sedimentation experiments, the magnets were placed at the bottom of the vials, either under the bottom of the vial or set to the side. As can be seen in Figure 1 there is a large difference between the two surfactants. The amount of magnetically-induced sedimentation in the DDAN-stabilized dispersion is minimal; however, there is significant magnetic sedimentation in the DDAH-stabilized dispersion. The presence of a magnet has caused nearly complete sedimentation of the dispersion over one hour, and as can be seen in Figure 1C, the sediment forms a disk around the edge of the vial where the magnet was placed. Clearly, the DDAH-stabilized organosol is magnetically responsive.

Solutions of DDAN and DDAH surfactant alone were tested without dispersed silica nanoparticles. The results were similar to those from the organosols: DDAN shows no magnetic response whereas DDAH does. However, as can be seen in Figure 1A, the nanoparticle dispersion completely sedimented after one hour. Much less sediment was produced in the DDAH-only solution, which demonstrates that the sediment shown in Figure 1A consists of surfactant stabilized nanoparticles rather than free surfactant.

These results, however, only qualitatively demonstrate that sedimentation of the DDAH-stabilized dispersion is magnetically enhanced. In order to quantify this, UV-vis spectroscopy has been used to monitor the sedimentation. (Experimental details are provided in the Supporting Information.†) For magnetic sedimentation experiments, the magnet was centered below the cuvette between measuring spectra. Magnetic sedimentation experiments were performed initially, and the particles were redispersed using vortex mixing before performing the non-magnetic sedimentation experiments.

The absorbance ($A$) at 700 nm, normalized by the initial absorbance ($A_{t=0}$), is shown in Figure 2 for both magnetic and non-magnetic sedimentation experiments. The value of $A$ is normalized because small variations in the particle concentration in the initial state were reflected in differences in $A_{t=0}$. At 700 nm, the apparent absorbance is primarily due to Tyndall scattering by particles [26, 27]. There are no
Figure 1: Photographs of silica organosols after one hour sedimentation in the presence of a magnetic field (either below the vial or set to the side). The photographs were taken immediately after the magnets were removed. The magnetic field causes no visible difference to the DDAN-stabilized dispersion. For the DDAH-stabilized dispersion, however, an enhanced sedimentation is observed, causing either near-total sedimentation or a ring of sediment to form on the wall of the vial.
Figure 2: Normalized absorbance ($A/A_{t=0}$) at 700 nm measured as a function of time for both DDAH-stabilized dispersions, both with and without a magnet present. The DDAH-stabilized nanoparticles show enhanced sedimentation (decrease in $A$) when a magnet is present. This supports the visual observations in Figure 1 which show that the DDAH-stabilized system sediments significantly when a magnet is present.

Table 2: Fit parameters for magnetic and non-magnetic DDAH organosol sedimentation

<table>
<thead>
<tr>
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<th>$A_{t=\infty}/A_{t=0}$</th>
<th>$\kappa$ / min$^{-1}$</th>
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</thead>
<tbody>
<tr>
<td>Magnetic sedimentation</td>
<td>0.138 ± 0.009</td>
<td>0.048 ± 0.002</td>
</tr>
<tr>
<td>Non-magnetic sedimentation</td>
<td>0.10 ± 0.03</td>
<td>0.019 ± 0.001</td>
</tr>
</tbody>
</table>

spectroscopic absorbance peaks above 660 nm for the DDAH-stabilized nanoparticles so that the value of $A/A_{t=0}$ can be reliably related to the turbidity.

The results show that for DDAH-stabilized dispersions, there is a large discrepancy between magnetic and non-magnetic sedimentation. Both begin to approach a plateau over the course of one hour, but the decrease in light scattering (proportional to $A$) is more rapid when a magnet is present. This decrease in $A$ can be fit to an exponential decay, as shown in Equation 1, to allow a quantification of the difference between the two.

$$\frac{A}{A_{t=0}} = \frac{A_{t=\infty}}{A_{t=0}} + \left( 1 - \frac{A_{t=\infty}}{A_{t=0}} \right) e^{-\kappa t}$$  \hspace{1cm} (1)

The fit values can be related to physical parameters describing the sedimentation. In the limits of $t = 0$ and $t = \infty$, the magnetic and non-magnetic sedimentation should appear identical; only the rate of sedimentation should be different. As can be seen in Table 2, this is indeed the case. Within the standard error from fitting, the asymptotic values of the normalized absorbance ($A_{t=\infty}/A_{t=0}$) are identical for the magnetic and non-magnetic cases. Additionally, at $t = 0$ and therefore $e^{-\kappa t} = 1$, the fit values of $A/A_{t=0}$ are equal to 1 for both cases.

The difference between the two experiments, which is apparent from Figure 2, is the rate of sedimentation. The term $\kappa$ in Equation 1 can be considered as a “rate constant” for the sedimentation process. The values of $\kappa$ are in line with the visual observations in Figure 1.

In addition to studying the effects of magnetic fields on sedimentation, it is worth determining if the magnet can overcome the gravitational sedimentation force. This has been studied by placing the magnet at
the top of the dispersion while performing a sedimentation experiment, and the results are shown in Figure 3. Again, the DDAN-stabilized dispersion does not respond to a magnetic field. However, by placing the magnet on the side of the sample rather than at the bottom, a portion of the DDAH-stabilized dispersion can be held in the bulk against gravity. If such a particles were to be used in an electronic paper application, the ability to overcome gravitational sedimentation and Brownian forces is imperative.

Surfactant-stabilized organosols have been established as a simple way to prepare stable dispersions of inorganic nanoparticles in organic solvent [21]. Other popular methods of stabilizing silica dispersions in organic solvents involve grafting hydrophobic layers to the particle surface, a chemically wasteful and irreversible process [28, 29]. The advantages of using surfactant molecules for the stabilizing layers are simplicity and flexibility. By modifying the dispersant used in the preparation of the nanoparticles, it has been shown that novel particle functionality can be obtained.

The two lanthanide surfactants used in this study (DDAN and DDAH) are chemically very similar; both are Ln(III) metals that form tetrahalide complexes when combined with DDAB surfactant. However, the magnetic-field response of silica organosols prepared with the two is very different. Nd$^{3+}$ does not have a significant magnetic moment, and so silica dispersions prepared with DDAN are charged but not magnetically responsive. On the other hand, Ho$^{3+}$ has a much higher magnetic moment, and so dispersions prepared with DDAH are both charged and show significant magnetic responses. This offers possibilities for using such dispersions in applications which demand response to multiple external stimuli, such as dual-driven electronic paper.

Acknowledgements

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References


Supporting Information

Materials

**DDAH and DDAN**

Didodecyldimethylammonium bromide (DDAB) was obtained from Sigma-Aldrich (Gillingham, Dorset, U.K.) and was purified by centrifugation in distilled acetone before use. Holmium(III) chloride hexahydrate, Didodecyldimethylammonium bromide (DDAB) was obtained from Sigma-Aldrich (Gillingham, Dorset, U.K.) and was purified by centrifugation in distilled acetone before use. Holmium(III) chloride hexahydrate, Didodecyldimethylammonium bromide (DDAB) was obtained from Sigma-Aldrich (Gillingham, Dorset, U.K.) and was purified by centrifugation in distilled acetone before use. Holmium(III) chloride hexahydrate, Didodecyldimethylammonium bromide (DDAB) was obtained from Sigma-Aldrich (Gillingham, Dorset, U.K.) and was purified by centrifugation in distilled acetone before use. Holmium(III) chloride hexahydrate, Didodecyldimethylammonium bromide (DDAB) was obtained from Sigma-Aldrich (Gillingham, Dorset, U.K.) and was purified by centrifugation in distilled acetone before use. Holmium(III) chloride hexahydrate, Didodecyldimethylammonium bromide (DDAB) was obtained from Sigma-Aldrich (Gillingham, Dorset, U.K.) and was purified by centrifugation in distilled acetone before use. Holmium(III) chloride hexahydrate.
and neodymium(III) chloride hexahydrate (99.9%) were obtained from Sigma-Aldrich (Gillingham, Dorset, U.K.) and used as provided.

DDAB was mixed with a stoichiometric amount of lanthanide salt (Ho(III)Cl₃ for DDAH and Nd(III)Cl₃ for DDAN) in methanol. The samples were mixed at room temperature overnight, and the solvent was removed under vacuum at 70°C for 24 hours.

The products were identified using ¹H-NMR (for DDAB only) and elemental analysis (for DDAN and DDAH). NMR spectra were recorded on a Jeol ECS 400 instrument. NMR was not performed for DDAN and DDAH due to the paramagnetic ordering of the metal ions hampering spectral acquisition.

**DDAB.** ¹H-NMR—δH (400 MHz, CDCl₃) 0.88 (6 H), 1.27 (36 H), 1.69 (4 H), 3.41 (6), 3.51 (4 H).

**DDAN.** Elemental analysis—Calc. for NC₂₆H₅₆NdCl₃Br: C, 43.8%; H, 7.9%; N, 2.0%; Br, 11.2%, Cl, 14.9%. Found: C, 44.9%; H, 9.0%; N, 1.9%; Br, 11.9%, Cl, 14.8%.

**DDAH.** Elemental analysis—Calc. for NC₂₆H₅₆HoCl₃Br: C, 42.5%; H, 7.7%; N, 1.9%; Br, 10.9%, Cl, 14.5%. Found: C, 41.7%; H, 8.7%; N, 1.8%; Br, 8.8%, Cl, 13.6%.

**Silica organosols**

The silica suspension (Klebosol 30R50, provided as a gift from AZ Electronic Materials, France) was a 30 weight % dispersion in water. The silica concentration in the organosols was fixed at 4 weight %, and the surfactant cation concentrations were fixed to 3 weight %. This gave a total surfactant mass concentration of 6 weight % for DDAH and DDAN, due to the increased mass of the anion. A solvent mixture of 70:30 (w/w) toluene-heptane was used.

**Techniques**

**Electrophoretic mobility**

Measurements were performed on a Malvern Zetasizer NanoZ (Malvern, Worcestershire, UK) using a dip cell electrode for nonaqueous solvents in a quartz or optical glass capillary. Five measurements of 75 runs were performed for each sample at a drive voltage of 30 V.

**Magnetic sedimentation**

The NdFeB magnets used were EP375 rod magnets (e-Magnets UK; Berkhamsted, Hertfordshire, UK), which were 8 mm in diameter and 30 mm in length. The magnetic pull is given as 2.70 kg, and the surface field on the axis was calculated to be 0.65 T²

**UV-vis spectroscopy**

UV-vis spectra were measured using a Nicolet Evolution 300 Spectrophotometer (Thermo Electron Corp.) from 300–700 nm. For magnetic sedimentation experiments, the cuvette was moved from on top of the magnet into the spectrometer, and the measurement with auto-resolution selected (approximately 60 s runs). For non-magnetic sedimentation experiments, the cuvette was placed in the spectrometer, and spectra set to measure over 60 s.

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