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Synthesis of Goethite as a Model Colloid for Mineral Liquid Crystals

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We describe the synthesis and modification of lathlike goethite (α-FeOOH) model colloids, where we focused on the reduction of the size polydispersity (determined from transmission electron microscopy pictures.) The length polydispersity could be strongly reduced from 55% down to 17% using a combination of a forced hydrolysis method and an improved centrifugation procedure. Preliminary small-angle X-ray scattering experiments demonstrated the potential of these model particles to study the influence of the length polydispersity on the occurrence of different liquid crystalline phases. A coating of polyisobutene was applied on the goethite surface to obtain a stable dispersion of hard-core laths in toluene, which retained the peculiar magnetic alignment behavior of aqueous goethite particles (changing from parallel to perpendicular orientation at increasing field strength.) The goethite laths could further be coated with a silica layer of tunable thickness which also allowed the incorporation of a fluorescent dye. Finally, the goethite core of silica-coated goethite was dissolved with acid to obtain hollow silica laths. These modifications give additional possibilities for the use of goethite as model colloids.

1. Introduction

The mineral goethite (α-FeOOH) already has a very long history of application since it was used as a dark-yellow ochre pigment in paleolithic cave paintings over 30 000 years ago. Also as a colloidal system it has quite a long history since it readily forms crystallites of colloidal dimensions, which can be stabilized in water at pH below about 4. It has a particularly rich literature for its applications as a model adsorbent in soil science and in environmental science and technology (see ref 1 for a recent review). In addition, goethite finds application as a precursor in magnetic carrier systems, where it can be transformed by thermal treatment into maghemite (γ-Fe_2O_3)[2] or into metallic particles.[3]

In the present paper we instead focus on the use of goethite as colloidal model particles of rodlike and lathlike shape. The special magneto-optical properties of iron oxide dispersions (containing goethite) were already recognized in 1902 by Majorana[4] and slightly later by Cotton and Mouton,[5] who noted that in these dispersions the positive birefringence at low fields changes to a negative birefringence at higher field strengths. However, these observations remained largely unexplained until Lemaire, Davidson and co-workers[6−9] recently showed that lathlike goethite particles combine a permanent magnetic moment along their long axis (presumably due to partially uncompensated surface spins within their antiferromagnetic crystal structure) with a negative magnetic susceptibility leading to a mainly perpendicular induced moment which turns the particles when the magnetic field passes a threshold. In addition, they found that these lathlike goethite dispersions form liquid crystals at increasing concentrations, not only the directionally ordered nematic structure[6,7] but also a more highly ordered 2-D columnar liquid crystal.[8] Theoretical calculations also show interesting possibilities for the phase diagrams in an external magnetic field.[10]

Very recently, we observed[11] that a highly polydisperse (>50%) goethite dispersion developed an additional new phase with red Bragg reflections, which indicates either smectic or crystalline layering. Small-angle X-ray scattering (SAXS) unambiguously showed that the phase responsible for the Bragg reflections has a smectic-A structure. In one sample even a four-phase coexistence of an isotropic, a nematic, a smectic-A, and a columnar phase was identified. Although at first sight this seems to defy the notion that smectic-A systems can only support a maximum length polydispersity of 18% as found in computer simulations of hard spherocylinders,[12] this can be rationalized by a subtle

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interplay of sedimentation and fractionation effects.[11] This formed the motivation for the present study that aims at systematically reducing the polydispersity and varying the dimensions of goethite laths and also looks at various possibilities to extend the use of goethite as colloidal model particles. In the literature some work on the synthesis of monodisperse goethite has appeared, but a length polydispersity of 25% at best was found with rather complicated synthesis routes,[13,14] or an extremely low polydispersity was claimed which did not seem to agree with the pictures presented.[15]

Goethite can easily be obtained as stable aqueous dispersions of lathlike, (quasi) monocrystalline particles. Typical dimensions are 240 × 40 × 20 nm^3, but these can be varied considerably depending on the reaction conditions. Several methods to produce colloidal goethite were already described,[1,13−26] where variation of the pH, the temperature, and added ions led to a better insight in the crystalline structure of goethite. However, mostly dried goethite particles were studied, and stable dispersions of monodisperse goethite laths have not been given much attention so far. Here, we start with the hydrolysis of iron nitrate at high pH according to the procedure Lemaire et al. used for the synthesis of their model particles[6] (section 2.3.). We extend our synthesis work in section 2.4. with reactions at higher temperatures, a so-called forced hydrolysis, based on the work of Krehula et al.[23] Transmission electron microscopy was used to obtain digital pictures of the particles, which allows us to accurately determine the particle size and its polydispersity.

Most available theoretical results in colloidal liquid crystals were obtained for purely entropic systems of particles interacting solely via the hard-core interaction potential. In order to eliminate the Coulomb repulsion in the charge-stabilized goethite dispersions described above, we apply a synthesis route according to Pathmamanoharan[27] to coat the goethite particles with a thin polymer layer of polyisobutene in order to disperse them in an apolar solvent (section 2.5.). In future, this will allow us to study the phase behavior of uncharged hard-core rectangular particles.

Finally, we use goethite particles as templates for composite particles. Silica coatings on inorganic particles are widely used, because particle interactions can be manipulated due to such a coating and the particles can be dispersed in a variety of solvents, ranging from very polar to apolar.[28] In section 2.6. the coating of goethite laths with a silica layer is described. It is demonstrated that fluorescent dye can also be incorporated into silica to obtain fluorescent laths useful for optical microscopy (section 2.7). Finally, dissolving the goethite core of the silica−goethite laths yields hollow silica laths (section 2.8.), which might be used as a low-mass-density model system in light scattering or phase separation experiments.

In section 4 we show some typical SAXS experiments performed on the suspensions obtained as an illustration of the interest of such model particles for studies of phase separation and structural properties of colloidal dispersions. We also checked whether the peculiar magnetic properties of goethite particles are preserved after the coating of the particles with polyisobutene.

2. Materials and Methods

2.1. Chemicals. For the synthesis of goethite were used $Fe(NO_3)_3 \cdot 9H_2O$ (Fisher Scientific, p.a.), NaOH (Acros, reagent ACS, pellets, 97+%), HNO_3 (Merck, p.a., 65%), TMAH (tetramethyl ammonium hydroxide, Aldrich, 25% w/w in water), and $FeCl_3$ (Acros, anhydrous, 98%). All were used as received.

The coating with polyisobutene was performed using 1-propanol (Acros, 99+%), tetrahydrofuran (Acros, stabilized p.a.), and toluene (Baker, “baker analyzed”). The modified polyisobutene consists of a polyalkyl amine anchor group, which is chemically connected to two polyisobutylene tails with a molecular weight of 1000 g/mol each. The code is SAP230TP (C9237, obtained from Infineum). The silica coating was applied with tetraethoxysilane (TES, Fluka, puriss, ≥ 99.0%), ethanol (Merck, absolute GR p.a.), polyvinylpyrrolidone (PVP, Sigma, 40K), and ammonia (Acros, 28−30 wt % solution of NH_3 in water, p.a.). Further, hydrochloric acid (Merck, fuming 37%, p.a.), 3-(aminopropyl)triethoxysilane (APS, Fluka), and fluorescein isothiocyanate (FITC, Fluka) were used. The water used in all reactions was doubly distilled.

2.2. Characterization. Particle size distributions were determined by transmission electron microscopy (TEM) using a Technai 12 (FEI Company) electron microscope. A carrier grid, coated with polymer, was dipped in a dilute dispersion and dried. With AnalySIS Pro imaging software the dimensions of 500 particles were determined to obtain the number-averaged length $\langle L \rangle$ and width $\langle W \rangle$ and their standard deviations δ_L and δ_W. The polydispersity σ is defined as $\sigma_L = \delta_L/\langle L \rangle$ (and $\sigma_W = \delta_W/\langle W \rangle$). Mostly the particles lay flat on the grid, which makes it hard to determine the thickness T of a particle. For each sample we could only find 10−20 values for the thickness, not enough to obtain good statistics.

A weighed amount of goethite dispersion (of known mass density) was dried at 80 °C under a slow nitrogen flow to constant weight to obtain the goethite mass concentration c_m. With the density of goethite[2] of 4.26 g/mL the volume fraction $\varphi = c_m/4.26$ was calculated.

2.3. Synthesis at Room Temperature. To a 0.1 M iron nitrate solution in water, 1 M NaOH was added under vigorous stirring until the pH reached a value of about 11−12. Immediately upon addition of the base a dark red-brown precipitate formed, which settled fast when the stirring stopped. During the aging period of

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9 days at room temperature, the color of the sediment turned from dark red-brown into the ochre color of goethite.

After 9 days, the supernatant was removed and fresh water was added. The dispersion was homogenized and centrifuged (Beckman Coulter Avanti J-20XP, rotor JLA-8.1000, 5500 rpm for 35 min). The supernatant was replaced by water, and the dispersion was homogenized again. This centrifugation step was repeated. The sediment was then dispersed in 3 M HNO_3 (in two 50 mL tubes) to positively charge the particles. The dispersion was centrifuged (rotor JA25.50, 10 000 rpm for 25 min), the acid supernatant was replaced by water, and the sediment was redispersed by stirring and ultrasonication. These last steps were repeated three times to obtain a stable dispersion of goethite in water at pH = 3, showing streaming birefringence. The obtained dispersion was coded g55.

The synthesis was repeated with different concentrations of iron nitrate, and also the aging time was varied. In later experiments more centrifugation steps were used (g35), and additionally, also after the charging, large centrifuge tubes (of 1 L) were used (g25-1) in order to reduce the size polydispersity.

2.4. Synthesis at Higher Temperatures. For this section we slightly adjusted the forced hydrolysis method described by Krehula et al.,[23] by using iron nitrate instead of the very hygroscopic iron chloride. The results obtained were similar, although unfortunately, the synthesis with the highest $FeCl_3$ concentration (yielding particles with an aspect ratio of 9) could not be reproduced. The use of glass bottles instead of plastic ones also did not lead to significant differences in size and polydispersity. The solution of silicate from the glass does not seem to play a role, otherwise larger particles would have been expected.[29]

To a solution of (0.106−0.190 M) $Fe(NO_3)_3 \cdot 9H_2O$ in 70 mL of water, 25 mL of 25% TMAH was added under vigorous stirring. After the addition of TMAH a dark-brown precipitate was visible for a few seconds, which dissolved resulting in a transparent (but very dark) mixture. After 30 min of stirring the solution was poured into a glass bottle and closed carefully with a screw cap. The bottle was placed in a preheated oven ($T = 60$, 80, 100, or 120 °C), letting the solution age for 12 days. After a few hours an ochre sediment started to form at the bottom with a dark supernatant, which turned colorless and transparent over the aging period. At 120 °C the goethite formation was very fast so that the aging period could be limited to 2 days preventing complete evaporation of the solvent. After aging, the dispersion obtained was centrifuged and the particles were stabilized with nitric acid, as described for the particles synthesized at room temperature.

2.5. Coating with PIB. Before coating goethite with PIB, the particles were stabilized at pH = 3, as described above, to prevent the formation of aggregates during the coating process. Then, 1200 mL of 1-propanol was slowly added to 600 mL of goethite dispersion (0.006 g/mL) under stirring and ultrasonication. Water was removed by distillation, while keeping the dispersion volume constant by addition of 1-propanol. An amount of 15 g of SAP230TP was dissolved in 1.2 L of tetrahydrofuran, and this polyisobutene solution was slowly added under stirring and sonication. Tetrahydrofuran and propanol were distilled off, while toluene was added, until the boiling point of toluene of 110 °C was reached. The stable dark-ochre dispersion was transferred to glass centrifugation tubes, and the excess polyisobutene was removed by centrifugation (Beckman Spinchron DLX centrifuge; 2000 rpm for 3 h). The sediment was redispersed in toluene, after which three more centrifugation/redispersion steps followed. The goethite dispersion thus obtained was named g28P.

2.6. Coating with Silica. Coating of particles with silica according to the well-known Stöber method needs a nonaqueous medium like ethanol or propanol, in which the charge-stabilized goethite particles proved not to be stable. To overcome these stability problems we performed the silica coating described by Graf et al.[28] For these experiments goethite particles, coded g25-2, were synthesized similarly to g25-1 (section 2.3.). The charge-stabilized particles were mixed with a solution of PVP (200 g/L) in water and slowly stirred overnight to complete the adsorption of PVP on the goethite surface. The mixture was centrifuged slowly at 1100*g* for 16 h, and the sediment redispersed in ethanol by stirring and sonication.

In a reaction vessel 12.5 mL of g25-2 (goethite concentration 0.018 g/mL) was diluted with 219 mL of ethanol and 20 mL of ammonia. Under vigorous stirring and ultrasonication 0.75 mL of TES was added under the surface of the reaction mixture. The color of the dispersion became less pronounced ochre-like and turned whitish within 5 min. Ultrasonication was pursued for 2 h (keeping the bath at room temperature) while the stirring was continued for 24 h at normal speed. The dispersion was centrifuged, and the sediment was redispersed in pure ethanol. The suspension was coded g25-2sil1. The coating was repeated using 1.5 mL of TES (g25-2sil2).

2.7. Fluorescent Particles. Fluorescein isothiocyanate was coupled to APS by mixing 0.0968 g of FITC with 0.62 g of APS and 2.9138 g of ethanol in a dried vial. The reaction vessel was covered with aluminum foil and left under N_2 atmosphere for 24 h. A Stöber mixture was made of 120 mL of 0.82 g/L goethite dispersion in ethanol with an ammonia concentration of 6% (v/v). Under vigorous stirring and ultrasonication, 0.009 mL of APS−FITC was added under the surface of the Stöber mixture, followed by the addition of 0.3 mL of TES. After 4 h again 0.3 mL of TES was added. Sonication was stopped after 2 h, but stirring was continued for 24 h. In order to remove unreacted APS and FITC, the suspension was centrifuged and the sediment was redispersed in ethanol. The suspension was left undisturbed for 2 h to let aggregates settle. The upper part of the suspension was poured carefully into a clean bottle.

2.8. Hollow Particles. In a reaction vessel 15 mL of silica−goethite dispersion g25-2sil1 (of concentration 1.5×10^{-3} g/mL) was mixed with 50 mL of fuming HCl. The mixture was stirred for 24 h. during which the color of the dispersion turned from ochre to transparent light yellow. About 50 mL of water was added, and after mixing, stirring was stopped. The clear suspension was centrifuged, and the sediment was redispersed in water. The result is a stable dispersion of hollow silica laths in water, coded g25-2sil1hol.

2.9. SAXS Experiments. Samples of the dispersions were prepared by putting an amount of dispersion (of known φ) into flat capillaries (Vitrocom RT3524) of internal dimensions of 0.2 × 4.0 × 10 mm^3. The capillaries were sealed using two-component epoxy glue (Bison Kombi rapide), and for samples in toluene additional glue (Araldite2014) was used. After the glue dried the capillaries were placed in a vertical position and left undisturbed. The samples were checked for phase separation by investigating them between crossed polarizers. Some samples were selected for a SAXS study. The SAXS measurements were performed at the Dutch−Belgian beamline BM-26 DUBBLE at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). A recently developed microradian-resolution setup was used.[30] The synchrotron beam was focused by a compound refractive lens (CRL)

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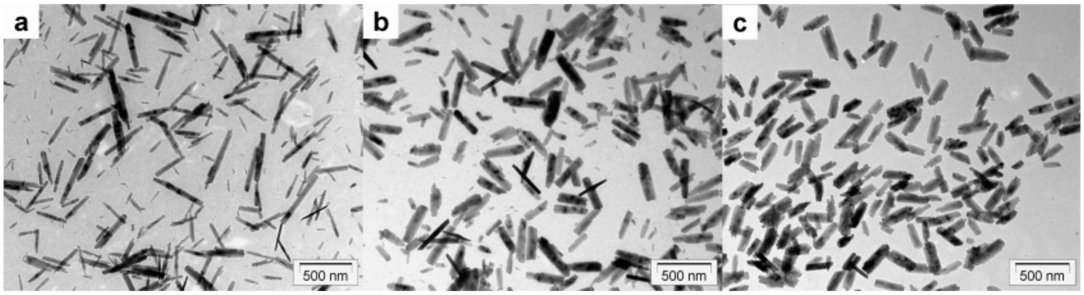

Figure 1. TEM pictures of goethite dispersion synthesized at room temperature: (a) g55, (b) g35 using more centrifugation steps, and (c) g25-1 using more centrifugation steps with larger volumes. The particles are lathlike and polydisperse. The polydispersity is clearly the highest for g55 (a) and the lowest for g25-1 (c).

at the phosphor screen of a Photonic Science CCD (charge-coupled device) detector (4008 × 2670 pixels of about 22 μm). The CRL was installed in the experimental hutch just before the sample. The sample−detector distance was about 8 m. The samples were placed in between the poles of an electromagnet, which allowed us to generate magnetic fields up to 0.6 T in the sample (homogeneous over 0.5 cm length of a capillary). The scattering data are presented as a function of the scattering wave vector $q = 4\pi/\lambda \sin \theta$, where λ is the wavelength of the X-rays and 2θ the scattering angle.

3. Results and Discussion

3.1. Analysis. The obtained goethite dispersions are colloidally stable and show streaming birefringence. The color of the dispersions is ochre. During the synthesis of goethite first an intermediate, the reddish-brown ferrihydrite, is formed,[2] which depending on the pH transforms into hematite (pH < 4, 7 < pH < 10, and pH ≥ 14) or goethite (4 < pH < 7 and 10 < pH < 14).[2,19,24] Although its dark-red color seems to distinguish hematite easily from goethite we did X-ray diffraction (XRD) to check the crystalline structure. Of several particle dispersions, samples were taken and dried at 80 °C under a nitrogen flow. These samples were analyzed by powder XRD at $\lambda = 1.78897$ Å. The peaks in the diffractogram could be assigned to pure goethite (see also Figure 4), without clear peaks of hematite (α-Fe_2O_3) or other iron compounds.[2]

The pH of the dispersions is set to 3, to prevent dissolution at lower pH and to charge them maximally. Since the isoelectric point of goethite is at pH = 9,[6,31] the goethite laths are positively charged by adsorbed H^+ at the OH groups at the surface.

Assuming that after many centrifugation steps the salt concentration is determined by H^+ and OH^- ions, the Debye length is 10 nm at most.

3.2. Synthesis at Room Temperature. With the use of the hydrolysis of iron nitrate at room temperature three goethite dispersions were prepared, which were purified from salt ions by centrifugation. The centrifugation procedure differed for the dispersions; g55 was centrifuged in small volumes, for g35 the number of centrifugation steps was increased, and for g25-1 also larger volumes were used during centrifugation.

Table 1. Goethite Dimensions, Room-Temperature Synthesis

system	$\langle L \rangle$ (nm)	σ_L (%)	$\langle W \rangle$ (nm)	σ_W (%)	thickness T (nm)	ratio $\langle L \rangle / \langle W \rangle$
g55	216	55	35	48	∼16	6.2
g35	282	35	68	32	∼25	4.1
g25-1	260	25	86	26	∼33	3.0

TEM pictures of the dispersions are presented in Figure 1, and the dimensions of the particles are summarized in Table 1. In Figure 1a a continuous distribution of long and small lathlike particles is present, whereas in Figure 1b the number of small particles is strongly reduced, and in Figure 1c small particles are hardly present. Increasing the number of centrifugation steps strongly decreases the fraction of small particles and lowers the length polydispersity from 55% to 35%. The use of large volumes (1 L instead of 50 mL flasks) during centrifugation lowers the length polydispersity even further to 25% for g25-1. Obviously, the particle width increases from g55 to g25-1, resulting in a lower length-to-width ratio. Some particles are very straight, thin, and dark-colored, which indicates that these particles are lying on their sides. From these particles an estimate of the thickness is obtained.

Both the concentration of iron nitrate and the aging time were varied, but we did not find any relation with the obtained particle size and polydispersity.

Goethite is formed via a dissolution/reprecipitation process with ferrihydrite as intermediate. NaOH is added to induce the hydrolysis into ferrihydrite, although the use of NaOH has some disadvantages. According to Cornell and Schwertmann[2] the addition of NaOH yields local pH gradients and thus variations in the formed hydrolyzed species, which makes it difficult to reproduce results. The obtained goethite crystals consist of parallel subunits, the so-called domains or intergrowths. Cornell and Schwertmann[2] suggest that the domains nucleate during the initial stages of the goethite formation, extend along the long axis, and that they differ in length due to different growth rates. The domains are often slightly misoriented with respect to their neighbors due to some atomic dislocations. At these dislocations a possible proton attack might take place; the influence of acid on goethite is given some attention in the Supporting Information. Due to the unequal lengths of the subunits the particles often show irregular ends, as is presented in Figure 2. For the determination of L the maximal value is taken.

Cornell and Giovanoli[16] mentioned that a high pH (≥13) or a low reaction temperature (20 °C) enhance domain formation. Although the reaction pH was about 11−12, the

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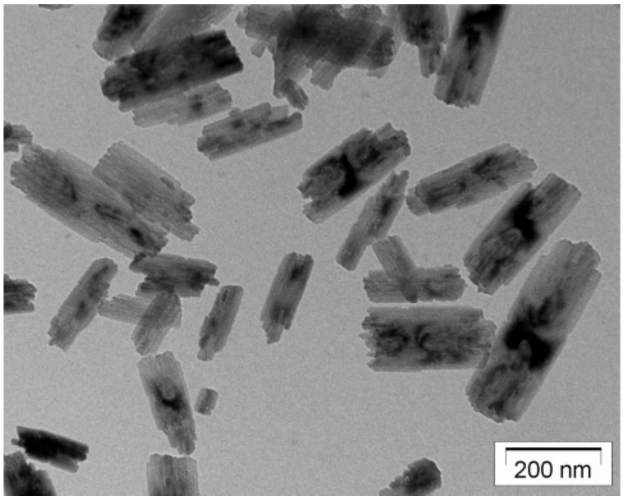

Figure 2. TEM picture of g25-1 at a higher magnification. The multidomain structure of the goethite crystals is clearly visible by the irregular ends of the particles and by the dark spots on the particles that are caused by scattering of electrons on the imperfect crystal surface.

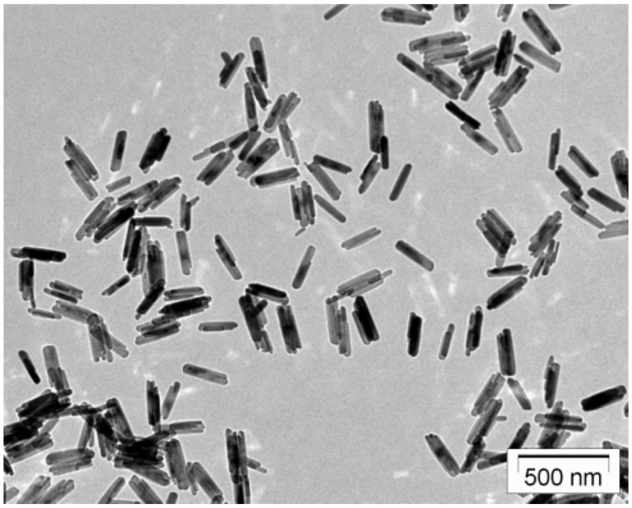

Figure 3. TEM picture of goethite prepared with the forced hydrolysis method. These particles were synthesized at 100 °C with 0.186 M iron nitrate. The polydispersity is significantly lower than for the dispersions shown in Figure 1. Due to intergrowth it is sometimes hard to distinguish between different particles.

reaction took place at room temperature, and so the formation of domains could be expected.

For the study of liquid crystalline behavior low size polydispersities (<20%) and a high length-to-width ratio (>3) are preferable. Although we are able to significantly reduce the size polydispersity of the goethite particles, the length-to-width ratio also reduces from 6.3 to 3.0.

It is difficult to tune the particle dimensions precisely with the use of NaOH to induce the hydrolysis of iron nitrate and with our method of using many centrifugation steps. Therefore, all batches show some differences, although the observed trends are predictable.

3.3. Synthesis at Higher Temperatures. Goethite synthesized at different temperatures and with varying iron nitrate concentrations forms stable ochre-like dispersions in water. A TEM picture of goethite synthesized at $T = 100$ °C at an iron nitrate concentration of 0.186 M is given in Figure 3. Tetramethyl ammonium hydroxide causes a very high pH of the dispersion (pH > 13), and so any initially formed precipitate completely dissolves, resulting in homogeneous precipitation conditions.[23]

Table 2. Particle Dimensions of Dispersions Prepared at Higher Temperatures

	$[Fe(NO_3)_3{\cdot}9H_2O]$ (M)	$\langle L\rangle$ (nm)	σ_L (%)	$\langle W\rangle$ (nm)	σ_W (%)	T (nm)	ratio $\langle L\rangle/\langle W\rangle$
$T = 60$ °C	0.106	202	22	59	29	11	3.4
	0.186	243	21	64	30	16	3.8
$T = 80$ °C	0.106	233	17	65	26	16	3.6
	0.186	257	20	63	33	18	4.1
$T = 100$ °C	0.106	203	18	60	22	16	3.4
	0.186	238	19	62	29	17	3.8
$T = 120$ °C	0.106	202	17	54	28	16	3.7
	0.186	246	16	62	28	18	4.0

TMAH dissociates into tetramethyl ammonium, which is a relatively large cation. From the early work of Massart[32] and recent studies by Sacanna et al.[33] this large cation seems to adsorb on iron oxides stabilizing them. Probably this cation also plays a role in the transformation of ferrihydrite to goethite at very high pH. Normally at pH = 14 hematite is formed instead of goethite[24] and—as opposed to the dissolution/reprecipitation mechanism of goethite—hematite is formed by a kind of aggregation of ferrihydrite species. A working hypothesis can be that the TMA ion stabilizes the negatively charged ferrihydrite and, thus, prevents aggregation to form hematite. In that case, dissolution of ferrihydrite might remain possible, and thus goethite is formed.

The particles are obviously more regularly shaped and have a smoother surface than the ones obtained at room temperature. It is also clear from the TEM pictures that the size polydispersity is remarkably lower. The synthesis of goethite at high pH favors the formation of multidomain particles. However, the domains seem to be more or less of the same length (and so are grown at the same rate). It is obvious from the TEM picture that sometimes it is difficult to determine the exact width of the particles due to particle intergrowth. The results for the lowest and the highest iron nitrate concentration are presented in Table 2 (while the table with results for all concentrations can be found in the Supporting Information).

A higher concentration of $Fe(NO_3)_3{\cdot}9H_2O$ yields longer particles, as can be seen from Table 2, although the length polydispersity hardly changes. The particles synthesized with an iron nitrate concentration of 0.186 M are 10−20% longer than the goethite laths prepared with 0.106 M iron nitrate. The width and thickness of the laths do not show a significant change due to this variation in concentration. So, also the length-to-width ratio shows a slight increase due to an increase of the iron nitrate concentration.

The obtained length polydispersity for the particles of 16−22%, synthesized with the forced hydrolysis is significantly lower than the ones obtained with the normal hydrolysis (see Table 1). However, in this experiment we do not find a clear relation between the reaction temperature and the obtained particle dimensions, except that we observed a higher transformation rate of ferrihydrite into goethite with temperature. Especially at 80, 100, and 120 °C the length polydispersity is below 20%. The polydispersity does not

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(32) Massart, R. *IEEE Trans. Magn.* **1981**, *MAG-17*, 1247.

(33) Sacanna, S.; Rossi, L.; Philipse, A. P. **2007**, *23*, 9974.

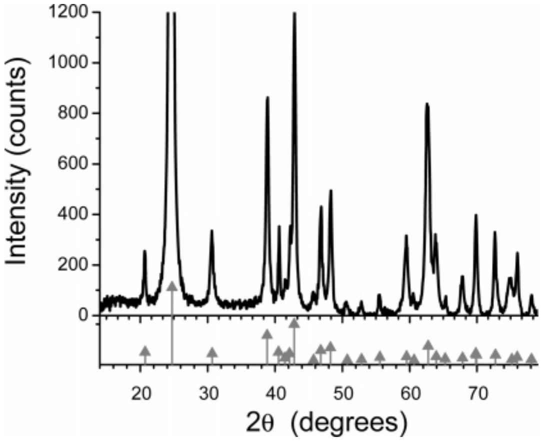

Figure 4. X-ray diffractogram of the goethite dispersion g28P, a polymer-coated goethite in toluene. The peaks coincide with the diffraction data for goethite crystals (ref 2) as presented in the lower part of the figure.

seem to change as a function of the iron nitrate concentration. The results of the two intermediate iron nitrate concentrations presented in the Supporting Information give particle dimensions and aspect ratios in accordance with the trends described above.

3.4. Coating with PIB. The coating of goethite with PIB yields a stable dispersion of particles in toluene (particle dimensions $\langle L\rangle = 273$ nm, $\sigma_L = 28\%$, $\langle W\rangle = 61$ nm and $T \sim 20$ nm). The color of this dispersion is darker than the light-ochre color of goethite in water. X-ray diffraction of these uncharged goethite particles completely matches the result of charged goethite (Figure 4). So, no significant crystalline phase transformation occurred due to the coating process.

With the use of Scherrers' formula[26,34,35] the crystallite width of g28P was calculated from the full width at half-maximum of the (002) reflection (at $2\theta = 20.6°$). The obtained width of 29 nm is much smaller than the width obtained from TEM, which confirms the goethite laths to consist of parallel subdomains.

Similarly the particle thickness was estimated from the width of the (110) reflection (at $2\theta = 24.6°$) as described in more detail in ref 6. Again, the obtained value of 15 nm is smaller than the TEM result suggesting that multiple domains might also occur along the thickness direction.

3.5. Coating with Silica. It is known that in a Stöber reaction the ammonia concentration is important, a too low concentration yielding secondary nucleation of silica and a too high concentration resulting in the formation of aggregates.[36,37] In some preliminary experiments we found that an ammonia concentration of 8% was optimal.

In Figure 5a–c TEM pictures are given for the bare g25-2 goethite particles and of g25-2sil1 and g25-2sil2 particles. The silica coating is clearly visible, and the thickness of the coating is 19 nm for g25-2sil1 and about 30 nm for g25-2sil2. The silica is evenly distributed around the whole particle, and the coating is very smooth. Surface irregularities of the bare goethite particles are less pronounced after the coating with silica.

The color of the silica goethite dispersions clearly is somewhat lighter (whitish) than the pure goethite dispersions.

3.6. Fluorescent Laths. Addition of fluorescent dye to a Stöber mixture with a goethite dispersion yields stable fluorescent silica goethite. Adding APS–FITC to a Stöber mixture often leads to some aggregation of particles. For this reason the addition of APS–FITC took place under stirring and ultrasonication. The small amount of aggregates, still formed, could simply be removed by sedimentation.

A sample was prepared for the confocal microscope to check if the fluorescent dye was really built into the silica layer. Although the particles are rather small for this technique, clearly some fluorescent particles were observed. This means that the concentration of fluorescent dye was high enough. The use of a refractive-index-matching solvent would increase the resolution of the images.

3.7. Hollow Particles. The hollow silica particles obtained by adding fuming HCl form a stable dispersion in water. On the TEM picture of Figure 5d it is clear that the goethite core has disappeared. The silica coating looks dark in comparison with the hollow core. When the goethite was still there (Figure 5b), the goethite core is very dark with respect to the silica coating around. The use of lower acid concentrations or shorter dissolution times resulted in a partly dissolved goethite core, which was observed with TEM by some dark residuals in the silica shell.

The whitish, almost colorless appearance of the suspension is typical for silica dispersions.

4. SAXS Experiments on Goethite Model Particles

To illustrate the potential of the use of goethite as model particles in studies of phase separation and structural properties of colloidal dispersions we address two issues, on which the use of well-defined particles may shed light.

4.1. Influence of the Polydispersity on the Phase Behavior. Our recent observation[11] that the highly polydisperse (>50%) goethite dispersion g55 prepared at room temperature developed a new additional smectic-A phase with red Bragg reflections seemed in flat contradiction with the notion that smectic-A systems can only support a maximum length polydispersity of 18% (as found in computer simulations of hard spherocylinders[12]). Although this finding was rationalized by assuming a subtle but complicated interplay of sedimentation and fractionation effects,[11] this remains speculative to a certain extent. The different ways of reducing the polydispersity described in this paper now open the way to unravel these questions.

It turned out that also dispersion g35, with a significantly lower length polydispersity of 35%, phase separates into an isotropic, a nematic, a smectic, and a columnar phase just like the four-phase equilibrium found for g55 (of which we present pictures in the Supporting Information). In Figure 6a a typical scattering pattern of g35 is given from the lower part of the capillary (corresponding to section II of the above-mentioned pictures in the Supporting Information). It shows a sharp ring at small angles and a combination of a broader powder-like ring and sharp reflections at larger angles. Figure

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[34] Schwertmann, U.; Cambier, P.; Murad, E. *Clays Clay Miner.* **1985**, *33*, 369.
[35] Kurokawa, H. *Mater. Sci. Eng., A* **1995**, *202*, 201.
[36] Wijnhoven, J. E. G. J. *Chem. Mater.* **2004**, *16*, 3821.
[37] Vonk, C.; Oversteegen, S. M.; Wijnhoven, J. E. G. J. *J. Colloid Interface Sci.* **2005**, *287*, 521.

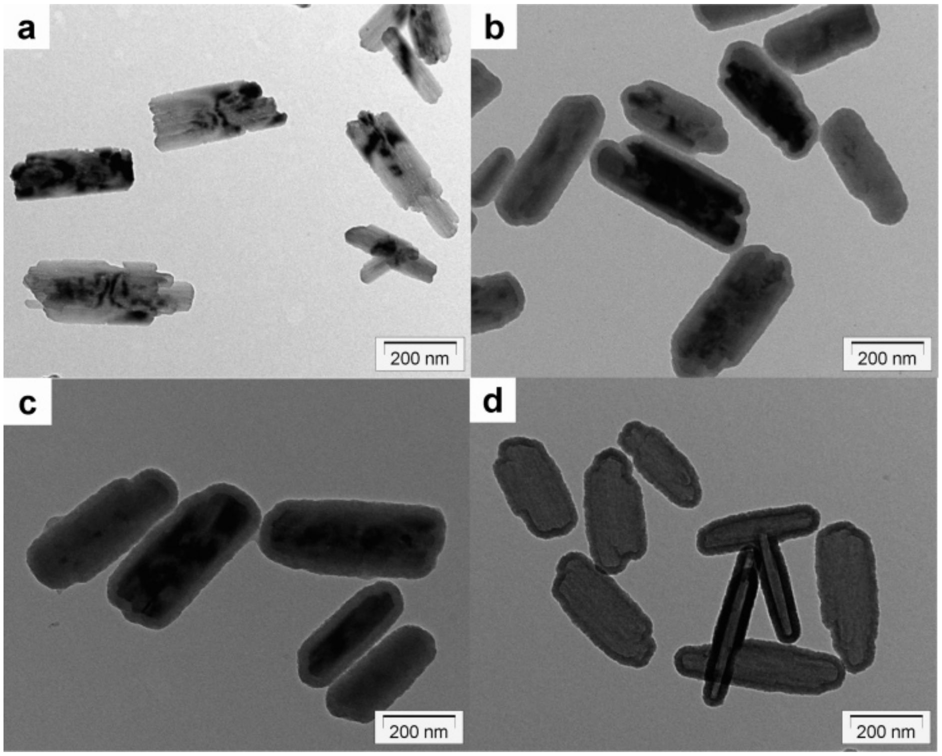

Figure 5. TEM pictures of (a) bare goethite g25-2, (b) g25-2sil1 with a silica coating of 19 nm, (c) g25-2sil2 with a 30 nm silica coating, and (d) g25-2sil1hol hollow silica particles with a dissolved goethite core.

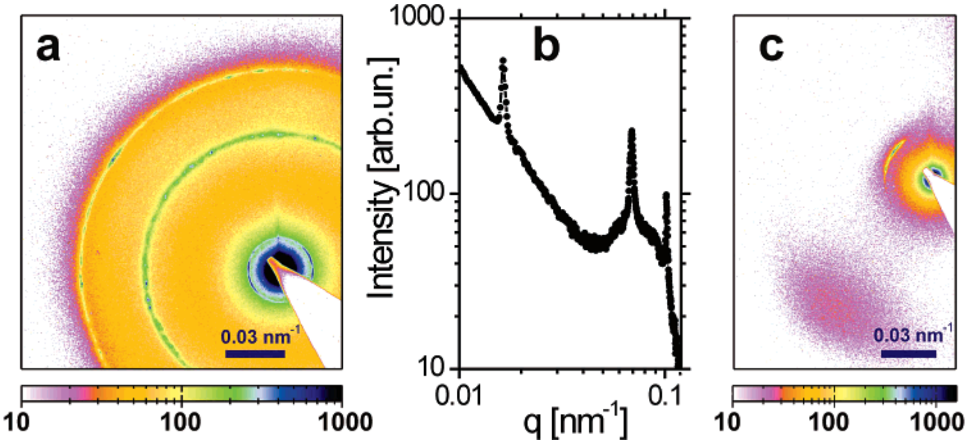

Figure 6. SAXS patterns (photon energy 12 keV, wavelength 1.0 Å) of (a) g35 showing at small scattering angles a ring, corresponding to a smectic ordering, and at large angles two powder-like rings of columnar ordering, (b) horizontal cross section through the diffraction pattern of (a), and (c) a SAXS pattern of goethite particles g17 with a length polydispersity of 17% showing sharp small-angle reflections and perpendicular diffuse liquid-like scattering corresponding to a smectic-A phase.

6b displays a horizontal cross section through the diffraction pattern shown in panel a. The width of the sharp peak at $q = 0.016$ nm^{-1} is practically instrument-limited, and it can be assigned to a smectic phase with a layer periodicity of 384 nm. The averaged particle length is 284 nm, but the length distribution is quite broad, and the found periodicity of 384 nm is consistent with fractionation of the larger particles in the sample to the smectic phase (see the histogram of the length of g35 particles presented in the Supporting Information.) A stronger fractionation has been observed in the g55 system, where the found periodicity was twice the averaged particle length. Presumably, the broad scattering peak at 0.05 nm^{-1} $< q <$ 0.11 nm^{-1} is related to the fluid-like structure of the smectic structure. The sharp peaks at $q = 0.07$ nm^{-1} and $q = 0.1$ nm^{-1} originate from the columnar phase, with a distorted-hexagonal intercolumnar structure.[8] These peaks correspond to distances of about 92 and 62 nm, characteristic of the lateral spacing in a columnar phase.[8] Since simulations[10] indicate that the particles should have more or less the same length to fit into a smectic phase, one can speculate that the columnar phase, where different particle lengths are allowed, functions as a waste disposal for the particles that are expelled from the smectic phase.

The goethite synthesis at higher temperatures yields particles with significantly lower size polydispersities. We used SAXS to study the phase behavior of dispersion g17 ($\sigma_L = 17\%$; made with 0.16 M iron nitrate at 100 °C.) For low volume fractions (5.3%, 5.8%, and 6.6% v/v) isotropic and nematic phases were observed, whereas for higher volume fractions (6.8%, 7.4%, 8.0%, and 9.1% v/v) an

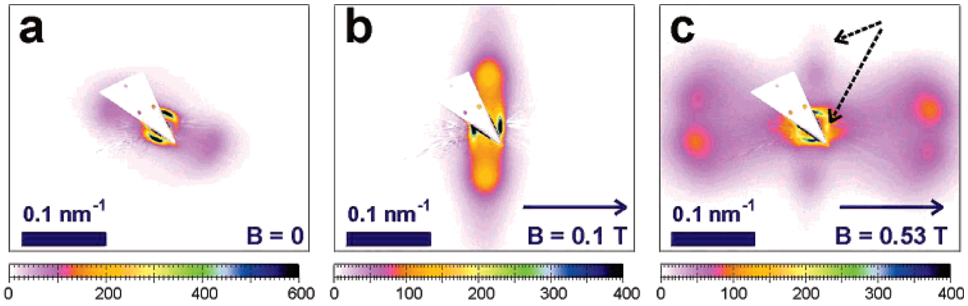

Figure 7. SAXS patterns (photon energy 16 keV, wavelength 0.77 Å) of g28P ($\varphi \sim 18$ %v/v): (a) the sample at $B = 0$, showing a nematic ordered structure; (b) at $B = 0.10$ T the nematic structure orients in the direction of the magnetic field; (c) at $B = 0.53$ T a part of the particles remains fixed in the nematic position (see dashed arrow) and a part orients perpendicular to the magnetic field but at clearly larger angles than the nematic phase at $B = 0$ and $B = 0.10$ T.

additional smectic phase was found. In contrast with the SAXS results of the dispersions with length polydispersities of 35% (g35) and of 55% (g55), this sample never shows the sharp scattering peaks at large angles corresponding to a columnar phase. In Figure 6c a purely smectic scattering pattern is presented with a smectic periodicity of 224 ± 10 nm which is closely related to the average particle length of 220 nm. The results are consistent with the notion that the particles with roughly the same length all fit into smectic layers and that no columnar domains are needed for ill-fitting particles.

4.2. Magnetic Behavior of Uncharged Goethite Dispersions. Another issue is the (qualitative) effect of the charge of goethite. To this end we use our sterically stabilized version of goethite in toluene. An important issue is whether this also forms liquid crystals and if the special magnetic properties of goethite particles are retained (since the grafted polymers might influence the surface spins).

Samples of different concentrations of uncharged goethite, g28P, were investigated with SAXS. These laths showed isotropic and nematic phases; an example of the scattering pattern of the nematic ordering is shown in Figure 7a. At a low magnetic field strength of $B = 0.10$ T the direction of the nematic ordering rotates parallel to the field, but the nematic structure remains preserved (Figure 7b).

At a strong magnetic field of $B = 0.53$ T goethite particles were found to align perpendicular to the magnetic field in aqueous dispersions. However, for our uncharged goethite particles a part of the sample seems to be fixed in a parallel alignment. In samples of high concentrations of uncharged goethite we hardly see any alignment, and the particles seem to be fixed in their position and orientation. Both observations can probably be due to the formation of a gel structure (see the dashed arrows in Figure 7c), although the possibility of strong anchoring on the capillary walls cannot be completely excluded. The other particles align almost perpendicular to the magnetic field although there seem to be two slightly different orientations that were observed before (see ref 7). The liquid-like scattering is found at larger angles than in the nematic phase of Figure 7, parts a and b. This means that the particles are now at closer distances of each other (of about 42 nm), with a preferential positioning of the order of magnitude of the thickness of the particles. In the original nematic phase (Figure 7a) and at a low field (Figure 7b) the lobes correspond to a distance of about 96 nm meaning that the particles can freely rotate along their long axis, while the rotational degree of freedom is frozen at higher field (Figure 7c). When we looked at samples of high concentrations or at lower parts of a capillary, we hardly saw any influence of the magnetic field on the direction of the scattering. This strengthens our idea that at high concentrations the particles form a gel structure.

These qualitative results show that the sterically stabilized goethite systems offer interesting perspectives. For future phase separation experiments on hard-core goethite laths lower concentrations should be used and furthermore stronger magnetic fields to align the laths more easily. More time is needed to reach a complete phase separation and more time to obtain complete alignment under the influence of a magnetic field. However, these measurements show that goethite preserves its special magnetic properties after coating with polyisobutene.

5. Conclusions and Outlook

The synthesis of goethite laths has been studied before but not by focusing on the accurate measurement and reduction of the size polydispersity in view of their use as model particles. We have shown that some simple measures such as increasing the number of centrifugation steps and using larger centrifugation volumes leads to a spectacular reduction in length polydispersity from 55% to 25%. With a forced hydrolysis synthesis method we are able to reduce the length polydispersity below 18%, which is low enough to expect a purely smectic phase at high concentrations.[12] A disadvantage of these suspensions is that also the length-to-width ratio lowers from 6.2 to about 3 although in combination with their even smaller thickness this is still sufficient to cause liquid crystal formation. The synthesis of particles with a high length-to-width ratio and a low size polydispersity needs further examination.

SAXS experiments demonstrate the potential of such model particles in obtaining different liquid crystalline phases. Dispersions with large length polydispersities show that the particles form four phases: an isotropic, a nematic, a smectic, and a columnar phase. In contrast, for particles with a length polydispersity of only 17% the high-concentration phase is a pure smectic-A phase (without a columnar phase). It looks as though the columnar phase might function as a “waste disposal” for particles that do not fit into a smectic phase, which would explain why a columnar phase does not occur for low polydisperse particles. The influence of the size polydispersity and the aspect ratio on phase separation needs further investigation.

In addition goethite particles have been coated with a thin polymer layer to obtain a stable dispersion of uncharged hard-core laths in toluene, which show the same peculiar alignment phenomena in a magnetic field as charged goethite in water. At high concentrations some gelation seems to occur. For future SAXS measurements it is necessary to use a stronger magnet and to give the laths more time to align in a magnetic field.

Finally, we demonstrated that goethite can be easily covered with a silica layer of tunable thickness and also fluorescent dye can be incorporated without loss of particle stability. Afterward, the goethite cores can be easily dissolved yielding hollow silica laths, which are almost transparent in organic solvents. These modifications give additional possibilities for the use of goethite-based model particles.

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Supporting Information Available: Table of particle dimensions of dispersions prepared at higher temperatures, study of the influence of possible proton attack on goethite, picture of a phase-separated, highly polydisperse, goethite dispersion, histogram of the length of g35 goethite (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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