Anomalous Attraction between Colloidal Magnetite and Silica Spheres in Apolar Solvents

2 **AUTHORS**, INCLUDING:

Albert P Philipse

Utrecht University

189 PUBLICATIONS   **6,457** CITATIONS

Anomalous Attraction between Colloidal Magnetite and Silica Spheres in Apolar Solvents

Gerard A. van Ewijk and Albert P. Philipse*

Van't Hoff Laboratory for Physical and Colloid Chemistry, Debye Institute, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

We demonstrate the existence of an anomalous, strong attraction between small (9 nm) oleic acid-grafted magnetite particles and octadecanol-grafted silica spheres (420 nm) in apolar solvents. This attraction manifests itself by irreversible adsorption of magnetite particles onto silica spheres, with surface coverages up to 30%. This "heteroflocculation" is, quite surprisingly, orders of magnitude slower than a diffusion-limited process. The adsorption can be reversed by transferring covered silica particles to solvents with a higher dielectric constant. The findings practically rule out van der Waals forces or Coulomb forces between any pre-existing surface charges as the source of attraction.

1. Introduction

The interaction between colloidal particles is of paramount importance for the stability of colloidal dispersions and is therefore one of the main topics in colloid science. In polar media, such as water, the interaction between colloids is often well-described by the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, combining van der Waals attraction between particles and repulsion due to overlap of the ion clouds surrounding the particles. Although this theory successfully explains the stability of many colloidal systems, the existence of so-called non-DLVO forces, such as hydrophobic interactions, has been frequently demonstrated.[1]

Colloids can also be sterically stabilized by chemically or physically attaching polymers to the particle surface.[2] In good solvents or θ solvents for the polymer, colloids repel each other when overlap of their polymer layers forces the polymers into entropically unfavorable conformations. In contrast to the many papers on non-DLVO forces, reports on anomalous interactions between sterically stabilized colloids are scarce, even though such colloids are widely applied and studied. One example of a yet unexplained attraction concerns stearyl alcohol-grafted silica spheres in a good solvent. Although dispersions of monodisperse stearyl-silica spheres in cyclohexane behave as hard-sphere fluids,[3] deviations from the hard-sphere character emerged in studies on bidisperse mixtures. Several techniques, such as rheology,[4] phase separation experiments,[5] small-angle neutron scattering,[6] and sedimentation experiments,[7] indicate a significant attraction between spheres with widely different sizes, even though interactions between particles with similar sizes were demonstrated to be purely repulsive. This phenomenon does not seem to be limited to silica mixtures. Recently, a first indication for attraction between small

sterically stabilized magnetite (Fe_3O_4) particles and large silica spheres was found;[8] it was speculated[8] that the attraction could be large enough for magnetite to irreversibly adsorb onto the silica surface.

Because only indications for this anomalous attraction in bidisperse mixtures of sterically stabilized colloids have been obtained so far, we decided to investigate this phenomenon in detail. Our aim is to demonstrate the existence of the attraction and to quantify any adsorption of the small particles on the larger colloids. The mixture studied here consists of small oleic acid-grafted magnetite particles and large octadecanol-grafted silica spheres in cyclohexane. Its ferromagnetic properties make magnetite easy to quantify with magnetization measurements without interference by silica. Moreover, visual observations are facilitated by the deep black color of magnetite.

The results of this investigation indeed show that there is an unexpectedly strong attraction between magnetite and silica colloids, despite the fact that the separate silica and magnetite dispersions are colloidally stable. The attraction manifests itself in irreversible adsorption of magnetite onto silica, resulting in colloidally stable, decorated silica spheres with surface coverages up to 30%. The adsorption process proceeds over a period of weeks, which is orders of magnitude slower than a simple diffusion-limited adsorption. The slow kinetics is inconsistent with adsorption due to van der Waals attraction or due to Coulomb attraction between pre-existing charges. A charge transfer may be responsible for the adsorption. Such a transfer is consistent with the strong attraction and slow adsorption kinetics and also with the observed desorption in solvents with a higher dielectric constant.

2. Experimental Section

2.a. Description of Dispersions. The silica (SiO_2) dispersion consisted of silica spheres (diameter 420 nm) grafted with octadecanol and dispersed in cyclohexane. A detailed description of the preparation and characteristics of these particles can be found elsewhere.[9] The stock dispersion, coded SS, contained 164.3 g L^{-1} of solid material.

The Fe_3O_4 dispersion, coded FFS, contained particles (diameter 9.1 nm) grafted with purified oleic acid and dispersed in cyclohexane.[10] The solid content of FFS was 126.3 g L^{-1}. A second

* Corresponding author e-mail, a.p.philipse@chem.uu.nl; fax, +31-30-2533870.

(1) Ninham, B. W. *Adv. Colloid Interface Sci.* **1999**, *83*, 1.
(2) Israelachvili, J. *Intermolecular and Surface Forces*; Academic Press Ltd.: London, 1992.
(3) van Helden, A. K.; Vrij, A. *J. Colloid Interface Sci.* **1980**, *78*, 312.
(4) Woutersen, A. T. J. M.; de Kruif, C. G. *J. Rheol.* **1993**, *37*, 681.
(5) van Duijneveldt, J. S.; Heinen, A. W.; Lekkerkerker, H. N. W. *Europhys. Lett.* **1993**, *21*, 369.
(6) Duits, M. H. G.; May, R. P.; Vrij, A.; de Kruif, C. G. *J. Chem. Phys.* **1991**, *94*, 4521.
(7) Thies-Weesie, D. M. E.; Philipse, A. P.; Lekkerkerker, H. N. W. *J. Colloid Interface Sci.* **1996**, *177*, 427.

(8) de Gans, B. J.; Blom, C.; Philipse, A. P.; Mellema, J. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **1999**, *60*, 4518.
(9) Philipse, A. P; Pathmamanoharan, C. *J. Colloid Interface Sci.* **1993**, *159*, 96.

Table 1. Characteristics of Dispersions

sample	d_{TEM} (nm)[a]	σ_{TEM} (nm)[a]	d_M (nm)[b]	ρ (kg m^{-3})
SS	420	46		1781
FFS	9.1	2.3	11.3	2900
FF2S	14	4.2	13.6	

[a] Diameter and standard deviation determined from electron micrographs. [b] Diameter obtained from magnetization measurements (section 2.b).

Fe_3O_4 dispersion (FF2S) consisted of particles grafted with octadecanoic acid.[11]

Table 1 contains particle characteristics of SS, FFS, and FF2S. All dispersions contained solvents of analytical quality and were freed of unreacted grafting material by centrifugation/redispersion (SS), precipitation/redispersion (FFS), or washing with absolute ethanol (FF2S). The separate silica and magnetite dispersions were stable: no sign of aggregation was observed in any dispersion over a period of more than a year. Moreover, sedimentation experiments (section 3.b) confirm the hard-sphere behavior of SS, described elsewhere.[9]

2.b. Magnetization Measurements. The amount and size of magnetite particles in a sample were measured with a MicroMag 2900 alternating gradient magnetometer (AGM, Princeton Measurements Corp.). Samples were contained in glass cups with internal dimensions of $4 \times 3 \times 0.4$ mm^3 and sealed with a cover glass glued over the open end. All measurements were performed at room temperature.

The saturation magnetization (M_s) and diamagnetic susceptibility (χ_{dia}) were determined by fitting the magnetization curve at high fields (up to 1.2×10^6 A m^{-1}) with the Langevin function[12] with an added diamagnetic contribution:

$$M = M_s\{\coth(\alpha) - (1/\alpha)\} + \chi_{dia}H \quad \alpha = \mu_o mH/kT \quad (1)$$

where H is the applied field strength, m is the magnetic moment of particles, μ_o is the permeability of vacuum, and kT is the thermal energy. The magnetic particle concentration can be obtained from M_s using the linear dependence of M_s on that concentration.

Combined with the initial susceptibility (χ_i), i.e., the slope of the magnetization curve at low field strength ($H < 10^3$ A m^{-1}), M_s and χ_{dia} yield the magnetic core diameter (d_M) of particles when substituted in the low-field approximation of eq 1:[12]

$$\chi_i = M_s(\mu_o m/3kT) + \chi_{dia} =$$
$$M_s(\mu_o M_{s,Fe_3O_4}\pi d_M^3/18kT) + \chi_{dia} \quad (2)$$

where M_{s,Fe_3O_4} is the saturation magnetization of bulk Fe_3O_4 (4.8×10^5 A m^{-1}) and $d_M = (\langle d_m^6\rangle/\langle d_m^3\rangle)^{1/3}$ is an average diameter of the magnetic cores. It should be noted that due to the strong influence of polydispersity, d_M can be larger than the average physical diameter of the core. Equation 2 was only applied on dilute samples with a solid content below 10 g L^{-1}, so that magnetic interaction between particles is negligible.

Because the AGM actually measures the magnetic moment ($M_s V$) of a sample, the inaccuracy in the small sample volume (2.5 μL) inhibits the precise determination of M_s. Therefore, AGM results were combined with susceptibility measurements performed on a Kappabridge KLY-3 susceptibility meter (Agico). The AGM data were used to calculate the reduced initial susceptibility ($\chi_{i,AGM} - \chi_{dia,AGM}$)/$M_{s,AGM}$, which is independent of the sample volume. Using this value, the saturation magnetization was obtained from

$$M_s = \frac{\chi_{i,\kappa b} - \chi_{dia,\kappa b}}{(\chi_{i,AGM} - \chi_{dia,AGM})/M_{s,AGM}} \quad (3)$$

The subscripts AGM and κb in eq 3 refer to measurements done with the AGM and Kappabridge, respectively.

2.c. Initial Adsorption Experiments. The anomalous behavior of mixtures of sterically stabilized silica and magnetite in a good solvent (cyclohexane) was illustrated by mixing 5 mL of SS with 1.2 mL of FFS. After a few minutes, free magnetite was removed by centrifuging the sample at 1000 rpm in a Beckmann table centrifuge and replacing the supernatant with fresh solvent. This procedure was repeated until the supernatant remained colorless.

The purified dispersions were examined visually and on a Philips CM10 transmission electron microscope (TEM). TEM samples were prepared by dipping Formvar-coated copper grids in a dilute dispersion and drying them in air.

The influence of the chemical nature of the grafting layer on the stability of magnetite–silica and magnetite–magnetite mixtures was qualitatively investigated as follows. An excess of FF2S, magnetite grafted with stearic acid, was added to SS. After 1 h, free magnetite was removed. FF2S was also mixed with FFS in a 1:1 mass ratio of the two colloids. The stability of both mixtures was examined visually.

2.d. Sedimentation Experiments. The stability of silica spheres in the presence of magnetite particles was studied with sedimentation experiments in the earth's gravity field. Samples were kept in 20 cm long glass tubes with a 5 mm internal diameter. Temperature fluctuations were minimized by performing the experiments in a thermostated room (294.7 K) and immersing the sample tubes in a large water bath. To minimize any influence of vibrations, the water bath was put on a heavy marble table.[7]

Sedimentation rates were obtained by measuring the height of the sedimentation boundary with respect to the bottom of the tube at varying time intervals after the sample was homogenized. Using a Zeiss Ni-40 leveling instrument connected to a Mutiyoto AT-11-N linear scale system, the height could be measured with an accuracy of approximately 0.01 mm. During measurements, samples were illuminated at 90° with a slide projector to obtain enough contrast to see the boundary between dispersion and supernatant. The time of illumination was reduced to a minimum to avoid any convection that can be caused by absorption of light by iron oxide.[13]

Samples were prepared by diluting 1.00 mL of SS with 1.00 mL of cyclohexane, followed by adding a small amount (between 0 and 80 μL) of FFS. In addition, two dilute samples were prepared in tubes with a 10 mm internal diameter by mixing 0.50 mL of SS with 9.50 mL of cyclohexane. Forty microliters of FFS was added to one of the dilute samples. All sample tubes were shaken thoroughly before each sedimentation experiment.

2.e. Quantification of Adsorption. The samples used in sedimentation experiments were characterized using magnetization measurements (section 2.b). Prior to characterization, free magnetite particles were removed by repeated centrifugation steps (see section 2.c).
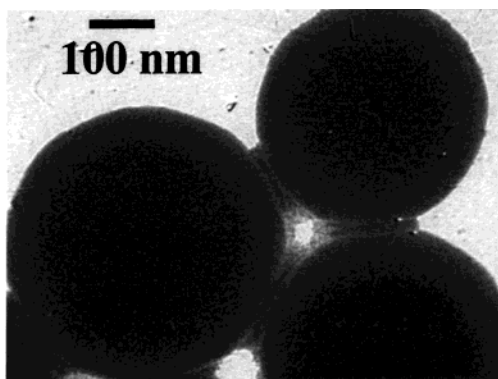
The amount of adsorbed magnetite was calculated by combining the saturation magnetization of a sample and that of a calibration sample with known magnetite concentration. Magnetization curves of the removed supernatant were also recorded to examine if adsorption is size-selective. Particle sizes were calculated using eq 2.

2.f. Adsorption Kinetics. The time dependence of adsorption was investigated by preparing three tubes, each containing a mixture of 1.00 mL of SS, 1.00 mL of cyclohexane, and 50 μL of FFS, and one tube with the same silica concentration but twice as high a magnetite concentration. After different periods of time, samples were purified from free magnetite and analyzed following the procedure described in section 2.e. Samples were gently shaken every day to keep the silica concentration homogeneous.

For reference, the maximum amount of adsorption was determined by sedimenting 5.00 mL of SS and replacing the supernatant with 5 mL of FF. The sample was analyzed after 1 month. During the adsorption process, the sample was regularly shaken.

2.g. Solvent Variation. To study desorption, if any, in other solvents, silica with adsorbed magnetite was transferred to other

(10) Bica, D. *Rom. Rep. Phys.* **1995**, *47*, 265.
(11) van Ewijk, G. A.; Vroege, G. J.; Philipse, A. P. *J. Magn. Magn. Mater.* **1999**, *201*, 31.
(12) Rosensweig, R. E. *Ferrohydrodynamics*; Cambridge University Press: Cambridge, 1985.

(13) Thies-Weesie, D. M. E.; Philipse, A. P. *Langmuir* **1995**, *11*, 4180.

Figure 1. TEM picture of silica spheres coated with magnetite particles. The coating is accumulated in the most narrow spaces, whereas the rest of the silica surface contains almost no magnetite.

solvents by centrifugation and redispersion. The following solvents were used, *n*-hexane, *n*-dodecane, *n*-hexadecane, *p*-xylene, toluene, and chloroform. All solvents were of analytical grade.

Adsorption in toluene and chloroform was also examined. Particles were transferred to the other solvent before they were mixed; SS was transferred by centrifugation/redispersion, and FFS was transferred by drying/redispersion. Samples were prepared according to the procedure used in section 2.f: 1.00 mL of silica dispersion was mixed with 1.00 mL of solvent and 50 μL of magnetite dispersion. After 50 h, the mixtures were purified and analyzed as described in section 2.e.
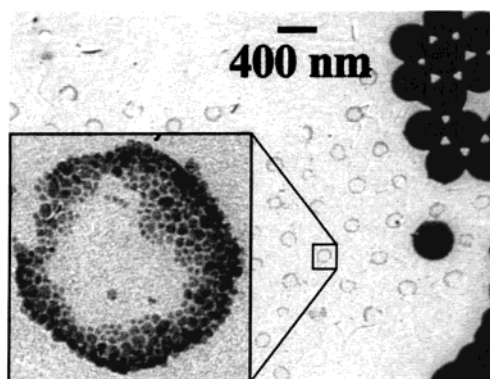
3. Results and Discussion

3.a. Initial Adsorption Experiments. Because of the large extinction coefficient of magnetite in the entire visible light spectrum, traces of this material can be easily detected visually. The brownish color that was observed in silica spheres freed from nonadsorbed magnetite was therefore the first evidence that magnetite adsorbs on silica. The supernatant remained almost colorless for weeks, indicating that desorption hardly took place. On the time scale of months, the supernatant became yellow, indicating that some desorption occurred, albeit at a very low rate. The fact that a significant amount of magnetite adsorbs on silica was also evident from the migration of concentrated dispersions of magnetite–silica particles in the field gradient of a permanent magnet.

A representative TEM picture of dried silica spheres with adsorbed magnetite is shown in Figure 1. Free magnetite had been removed prior to preparing the TEM samples. The surfaces of the spheres look smooth except at sites where they touch other spheres. At contact points between silica spheres, there is an accumulation of magnetite particles. Local accumulation of small particles is also visible in previous work[7] and may be due to capillary forces of the solvent–air interface and to convective flux toward narrow spaces[14] (if solvent evaporates from a narrow space, capillary suction draws other solvent from the surroundings, causing a net solvent flux).

Accumulation of magnetite also occurred between the silica spheres and the polymer coating of the TEM grid. Figure 2 shows a TEM picture of a sample from which some silica spheres were removed by gently wiping the grid with a piece of tissue paper, thereby exposing rings of magnetite particles that lay below the spheres.

The experiments described here clearly demonstrate that there is an attraction between sterically stabilized

(14) Denkov, N. D.; Velev, O. D.; Kralchevsky, P. A.; Ivanov, I. B.; Yoshimura, H.; Nagayama, K. *Langmuir* **1992**, *8*, 3183.

Figure 2. TEM picture of a grid with coated silica spheres. Some silica spheres have been removed by gentle wiping with tissue paper, making rings of magnetite particles visible (enlargement) that had accumulated between the silica sphere and the grid.
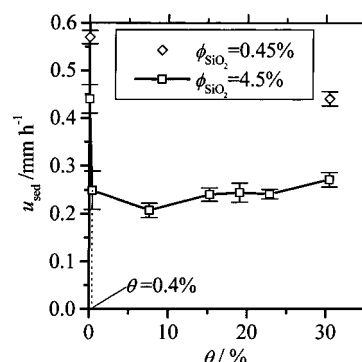
Figure 3. Sedimentation rate of silica spheres as a function of the amount of magnetite added (θ denotes the surface coverage of silica with magnetite if all of the magnetite would adsorb). Despite the strong attraction between magnetite and silica, bridging does not occur; even the smallest amount of magnetite reduces the sedimentation rate.

magnetite and silica, which is strong enough to lead to irreversible adsorption of magnetite on silica. This anomalous attraction is not limited to this particular mixture; magnetite grafted with octadecanoic acid (FF2S) instead of oleic acid also adsorbs on silica. No instability was observed in the mixture of octadecanoic acid-grafted magnetite and oleic acid-grafted magnetite, demonstrating that the attraction is not due to a difference in the nature of the grafting layer but rather to a difference in particle size or core material.

3.b. Sedimentation Experiments. The colloidal stability of the silica spheres was expected to be influenced by the presence of magnetite. In particular, because magnetite is bound irreversibly to silica, bridging flocculation was expected to occur at small amounts of magnetite. Surprisingly, bridging flocculation was not observed, as can be seen in Figure 3. This graph shows the sedimentation rate of silica as a function of the maximum surface coverage (θ) that could be reached, given the amount of magnetite added. The surface coverage is calculated considering magnetite particles as disks adsorbed on the surface of a sphere:

$$\theta = \frac{N_{Fe_3O_4}(1/4)\pi d_{Fe_3O_4}^\ell}{N_{SiO_2}\pi d_{SiO_2}^\ell} = \frac{m_{Fe_3O_4}\rho_{SiO_2}d_{SiO_2}}{4m_{SiO_2}\rho_{Fe_3O_4}d_{Fe_3O_4}} \quad (4)$$

where N is the total number of particles, d is the particle diameter including the grafting layer ($d_{Fe_3O_4} = 13$ nm,
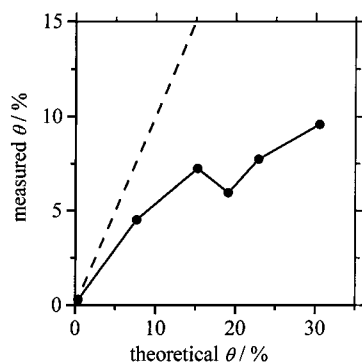
Figure 4. Measured surface coverage of magnetite on silica vs theoretical coverage, i.e., the coverage in case all of the magnetite adsorbs. Complete adsorption (dashed line) is only seen in the sample with $\theta = 0.4\%$.

$d_{SiO_2} = 420$ nm), m is the total mass, and ρ is the particle density (see Table 1).
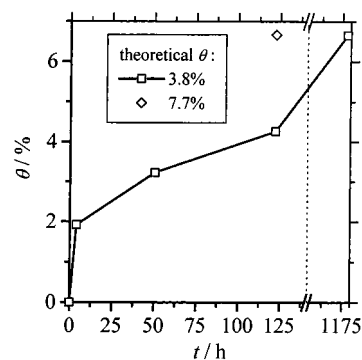
According to Figure 3, even the smallest addition of magnetite results in a significant decrease in sedimentation rate, whereas bridging would have led to an increase. The decrease is most likely due to an increase of the friction factor of silica spheres[7] upon adsorption of magnetite particles. Further evidence for the repulsive character of magnetite covered silica spheres follows from the decrease of sedimentation rate with increasing silica concentration[15] (see Figure 3).

The sediment volume in the sample with bare silica spheres corresponds to a silica volume fraction of 54.3%. In the samples containing magnetite, the silica volume fraction was $46.6 \pm 1.5\%$ with no particular dependence on the amount of magnetite. Assuming that the lower packing density of coated silica spheres can be ascribed to a larger effective radius, the increase in radius is 11 nm, which is close to the diameter of adsorbed particles (13 nm).

The high sediment densities are a strong indication that the colloids are (nearly) uncharged. In apolar solvents, such as cyclohexane ($\epsilon_r = 2.0$), electrostatic screening is not operative[16] and the interaction between charged spheres can be described by Coulomb's law.[17] The high sediment density requires the Coulomb repulsion at closest contact to be smaller than kT, corresponding to a number of charges per sphere of at most four.

3.c. Quantification of Adsorption. Magnetization measurements on the samples used in sedimentation experiments reveal that a significant amount of magnetite is adsorbed (Figure 4). Because the adsorption is irreversible, it was expected that initially all magnetite would adsorb and that the coverage (θ) would remain constant after the surface has been saturated. Indeed, all magnetite was adsorbed at low magnetite concentration ($\theta = 0.4\%$), but neither complete adsorption nor saturation was found at higher concentrations.

Of course, incomplete adsorption could be explained if only a fraction of the polydisperse magnetite particles are able to adsorb, and according to Table 2, there is indeed such a size selectivity toward the larger particles (size differences are small but significant; note that d^8 is measured in magnetization measurements, which are very sensitive to variations in d). However, this explanation

(15) Philipse, A. P. *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 200.
(16) van der Hoeven, P. C.; Lyklema, J. *Adv. Colloid Interface Sci.* **1992**, *42*, 205.
(17) Kitahara, A. In *Electrical Phenomena at Interfaces: Fundamentals, Measurements and Applications*; Kitahara, A., Watanabe, A., Eds.; Marcel Dekker: New York, 1984.

Figure 5. Amount of magnetite adsorbed on silica as a function of time (note the axis break). The adsorption process proceeds over a time span of weeks, which is about 6 orders of magnitude slower than a diffusion limited process would be.

Table 2. Size of Nonadsorbed Particles in Sedimentation Samples

$\theta^{(a)}$ (%)	d_M (free Fe$_3$O$_4$) (nm)
7.6	9.8
30.5	10.3
FFS	11.3

[a] Maximum surface coverage at given magnetite/silica ratio.

disagrees with complete adsorption at low magnetite content and the nonlinear relation between adsorbed and added magnetite.

Another possibility is that the adsorption process is so slow that it is still in progress at the time of quantification, i.e., 7 weeks after mixing. This would also explain the absence of bridging flocculation (previous section) in mixtures where the surface is far from saturated, because bridging is simply too slow to be observed within the duration of the sedimentation experiments.

3.d. Adsorption Kinetics. The suggestion made in the previous section that the adsorption process is very slow is confirmed by the kinetics measurements in Figure 5. The plot clearly shows that at constant amounts of magnetite and silica, the amount of adsorbed magnetite increases over a time span of at least 5 days. The point at $t = 1175$ h (=7 weeks) was a sample used in sedimentation experiments, added to demonstrate that the adsorption process is certainly not complete after 5 days. The adsorption kinetics also depends on magnetite concentration: doubling it almost doubles the surface coverage at $t = 120$ h.

It is interesting to note that van Duijneveldt et al.[5] reported a similar time dependence; they observed that a mixture of small and large stearyl-silica spheres in cyclohexane, which initially exhibited aggregation or phase separation, sometimes became homogeneous again after a few days.

Such slow kinetics as seen in Figure 5 cannot be explained by diffusion limitation only. This can be shown by calculating the steady state collision frequency (Z) of magnetite particles on a silica sphere with radius a_{SiO_2}:[18]
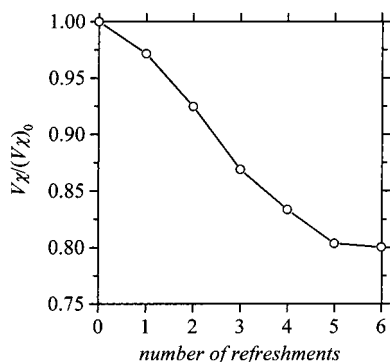
$$Z = 4\pi a_{SiO_2} D_{Fe_3O_4} n_{Fe_3O_4} \qquad (5)$$

where $D_{Fe_3O_4}$ and $n_{Fe_3O_4}$ are the diffusion coefficient and number density of magnetite particles. Using the Stokes–Einstein equation, $D = kT/(6\pi\eta_o a)$, with a solvent viscosity of 1 mPa, we find a collision frequency of 3×10^6 s^{-1} for our samples. If the rate of adsorption would be limited

(18) Adamczyk, Z.; Siwek, B.; Zembala, M.; Belouschek, P. *Adv. Colloid Interface Sci.* **1994**, *48*, 151.

Figure 6. Amount of magnetite adsorbed on silica (measured as $V\chi$) is decreased by successive replacement of the supernatant by fresh toluene.

purely by diffusion, each sphere would be completely occupied within a millisecond. This is clearly not the case: the experimental adsorption rate is roughly 8 orders of magnitude smaller than the rate calculated with eq 5. Blocking of available surface can slow down adsorption[18] but certainly not enough to explain such slow kinetics as seen here. Besides, the maximum coverage that we found was $\theta = 0.30$, which means that, in Figure 5, a large part of the surface is still available for adsorption.

Hindrance of adsorption by an (electrostatic) energy barrier can have a strong effect on the kinetics.[18] If particles have to cross an energy barrier (ψ) in order to reach the surface, the particle flux toward the surface is reduced by roughly a factor $\exp(\psi/kT)$. A barrier of 20 kT is already sufficient to slow kinetics down by a factor of 10^8 and could in principle explain our measurements. Such a barrier would, however, require a charged silica surface, which was already excluded by sedimentation experiments. Moreover, only charged magnetite particles would be hindered by the electrostatic barrier; hence, all magnetite particles must be charged in order to explain the slow kinetics with an energy barrier. Given the magnetite concentration in these experiments, 1.5×10^{-6} mol L^{-1}, the counterion concentration must be at least this large. Such a high ionic concentration in cyclohexane cannot be reached without the addition of a surfactant, such as AOT.[17] We therefore conclude that the slow kinetics is not caused by an energy barrier between the magnetite particles and the silica surface. More likely, adsorption is pre-empted by some chemical or physical process, and this process limits the rate of adsorption.

3.e. Solvent Variation. Magnetite remained adsorbed on silica in most solvents, which followed from the colorless appearance of the supernatant after sedimentation. However, desorption was observed in chloroform and toluene. An attempt was made to completely remove magnetite by replacing the supernatant repeatedly by solvent. In chloroform, almost complete desorption was found after 10 solvent refreshments. In toluene, only a fraction of the adsorbed material was released. Figure 6 shows that in toluene $\chi_i V$, a measure for the absolute amount of magnetite, decreases after each of the first five refreshments of the supernatant. Subsequently, desorption ceases.

The amount of magnetite removed with each toluene refreshment did not depend noticeably on the desorption time, indicating that the system is in adsorption–desorption equilibrium. This is confirmed by an adsorption experiment in toluene. In toluene, and also in chloroform, magnetite readily adsorbs on silica. After 50 h, the surface coverages in toluene and chloroform are 10 and 22%, respectively, which are significantly more than the cover-

age of 3.2% found in cyclohexane under the same conditions. The difference is likely due to a difference in adsorption kinetics. In connection to this, it is interesting to note that the magnetite–silica mixture in chloroform immediately flocculated when it was mixed, whereas the separate dispersions in chloroform were stable. The postulation of slow kinetics as a reason for the absence of bridging flocculation of magnetite and silica in cyclohexane (section 3.b) agrees with this observation.

3.f. General Discussion. All experiments presented in this paper clearly demonstrate that small sterically stabilized magnetite particles adsorb onto large silica spheres in various organic solvents. Any mechanism to account for this attraction must at least explain (i) strong attraction, in the order of 10 kT or more, which only acts between silica and magnetite particles and not between similar particles; (ii) slow adsorption kinetics, roughly 8 orders of magnitude slower than diffusion limited adsorption; and (iii) absence of a significant amount of charges on bare as well as magnetite covered silica spheres. In this section, some mechanisms will be discussed and compared with our experimental data.

As van der Waals attraction plays an important role in the stability of colloids, this is the first option that we consider. The energy between two smooth spheres with radii a_1 and a_2 at a center-to-center distance r is[19]

$$U_{vdW}(a_1,a_2) = -\frac{A}{6}\left[\frac{2a_1a_2}{r^2 - (a_1 + a_2)^2} + \frac{2a_1a_2}{r^2 - (a_1 - a_2)^2} + \ln\frac{r^2 - (a_1 + a_2)^2}{r^2 - (a_1 - a_2)^2}\right] \quad (6)$$

The Hamaker constant (A) for the interaction between magnetite (subscript "F") and silica ("S") in cyclohexane ("c") can be estimated with[2]

$$A_{FcS} \approx (A_{FcF} A_{ScS})^{1/2} \quad (7)$$

Substitution of the Hamaker constants $A_{FcF} \approx 10\ kT$ and $A_{ScS} = 0.15\ kT$ gives $A_{FcS} \approx 1.2\ kT$. The van der Waals interaction at the closest approach ($H = r - a_1 - a_2 = 3$ nm) is then $U_{vdW} = -0.1\ kT$, which is much too small to explain the almost irreversible adsorption observed in cyclohexane. As put forward in ref 7, the surface-to-surface distance can be smaller at spots with low grafting density, but the large number of such spots needed to cover 30% of the silica surface with magnetite is incompatible with the well-documented high grafting density of alkyl chains on silica.[3] Moreover, van der Waals attraction would lead to instantaneous adsorption upon collision and hence a diffusion limited adsorption rate. This is also contradicted by our experimental results.

As argued in ref 7, the surface roughness of the large spheres can enhance van der Waals attraction by increasing the contact area between small and large particles. For their system, Ludox (silica) particles of 14.6 nm and silica spheres of 250 nm, the authors of ref 7 considered a small particle residing in a half-spherical "pit" and estimated an attraction of $-2.8\ kT$, indeed significant. Using eq 6, a better estimation can be made. When van der Waals forces are taken as additive, the energy of a small sphere in a pit with radius a_c, located on an infinite surface, is equivalent to half the energy of a small particle

(19) Russel, W. B.; Saville, D. A.; Schowalter, W. R. In *Colloidal Dispersions*; Batchelor, G. K., Ed.; Cambridge University Press: Cambridge, 1989.

placed inside the cavity of a large hollow sphere:

$$U = (1/2)[U_{vdW}(a_1, a_2) - U_{vdW}(a_1, a_c)]_{r \to 0, a_2 \to \infty} \quad (8)$$

Equation 8 gives an attraction of only -0.7 kT for the situation considered in ref 7 (a mistake appeared to be made in ref 7: use of a diameter instead of a radius makes their estimate too high by a factor of four). For our system, using again a surface-to-surface distance of 3 nm, an attraction of -0.5 kT is found, which cannot explain irreversible adsorption.

In toluene, van der Waals forces may even counteract adsorption; because the refractive index of the solvent (1.496) is between the refractive indices of silica and magnetite (1.44 and 2.4, respectively), the Hamaker constant in toluene is expected to be negative, giving rise to van der Waals repulsion. Repulsion between magnetite and silica could explain why some magnetite desorbs in toluene and not in other apolar solvents.

van der Waals forces between the grafting layers can under some conditions, such as low solvent quality, also give rise to attraction. However, because cyclohexane is a good solvent for both stearyl and oleyl chains, attraction between the grafting layers is not expected in the experiments described here. This argument is supported experimentally by the absence of any sign of aggregation in mixtures of stearyl- and oleyl-grafted magnetite (section 3.a).

Another possible source of attraction is due to the presence of surface charges. These may be formed by, for example, ionization of surface hydroxyl groups or by adsorption of ions from dissociated water molecules (apolar solvents always contain traces of water).[17] Especially in apolar solvents, like cyclohexane, Coulomb attraction can be considerable. For instance, the interaction between two elementary charges at 3 nm distance is about 10 kT, which would be high enough to explain irreversible adsorption. Also, magnetite desorption in toluene is consistent with Coulomb attraction: because of the higher dielectric constant of toluene (2.4) as compared to cyclohexane (2.0), the most weakly adsorbed particles can desorb. In chloroform, which has an even higher dielectric constant (4.8), almost complete desorption of magnetite was observed.

It is quite inconceivable that each silica sphere carries enough charges beforehand to adsorb up to 1000 oppositely charged magnetite particles (this is the number of magnetite particles that corresponds to a surface coverage of 30%). That many charges would correspond to the energetically unfavorable and unrealistic surface potential of 3.4 V and is, moreover, contradicted by the high sediment density found in sedimentation experiments. Nevertheless, Coulomb attraction should not be ruled out. The presence of many surface charges on a silica sphere is imaginable if a nearly equal number of oppositely charged magnetite particles are adsorbed. Thus, a mechanism in which particle charging occurs together with adsorption might explain our findings. In particular, it is consistent with the notion made in section 3.d that the slow adsorption kinetics points to a chemical or physical process preceding adsorption.

Such a charging of particles when they are mixed may for instance be due to a difference in Brönsted acidity of the two kinds of particles. If the difference is large enough, one surface could donate a proton to the other, making the two surfaces oppositely charged. By "donation" or "transfer", we mean any process that leads to a change in the surface charge due to mixing of the two types of colloids, not necessarily a direct transfer.

Although this cannot be directly translated to apolar solvents, we mention that the isoelectrical points of silica (≈ 2.5) and magnetite (≈ 7) in water correspond to a significant difference in Brönsted acidities of the two materials. In apolar media, the situation is complicated by the fact that the charging behavior of hydrophilic surfaces is very sensitive to the presence of traces of water.[20]

Acid–base reactions between colloids in apolar media have to our knowledge not been reported yet, but proton transfer between inorganic pigment particles and dispersants in apolar solvents is known[21] and has been held responsible for the charging of pigment particles. Also, the attachment of amine-terminated poly(isobutene) and dodecanoic acid to alumina is known to involve a proton exchange.[22]

4. Conclusions

In contrast to the colloidal stability of separate dispersions of small oleyl-grafted magnetite colloids and large stearyl-coated silica colloids in cyclohexane, an unexpectedly strong attraction appeared to be present between these magnetite and silica colloids. Several independent techniques clearly demonstrated that magnetite particles adsorb irreversibly on silica spheres. The amount of magnetite adsorbed is significant: up to 30% coverage of the silica surface was found.

Surprisingly, despite the strong attraction between magnetite and silica, no bridging flocculation was observed, not even under conditions where the silica surface was far from saturated with magnetite. This suggested that the "decorated" silica spheres are kinetically stable due to a low adsorption rate of magnetite on silica. Indeed, adsorption kinetics measurements confirmed the low rate: the absorption process was found to proceed over a period of weeks, whereas a diffusion limited adsorption process would have been completed in milliseconds. The slow kinetics is likely due to a chemical or physical process other than diffusion, which precedes adsorption.

van der Waals attraction is too weak to account for the adsorption and is, moreover, instantaneous, which is inconsistent with the slow adsorption kinetics. Coulomb attraction between surface charges may explain both adsorption in cyclohexane and desorption in solvents with a higher dielectric constant (toluene and chloroform). However, to be consistent with the slow kinetics and the absence of electrostatic repulsion in the separate dispersions, the charges must be generated as the adsorption progresses.

(20) Morrison, I. D. *Colloids Surf., A* **1993**, *71*, 1.
(21) Fowkes, F. M.; Jinnai, H.; Mostafa, M. A.; Anderson, F. W.; Moore, R. J. In *Colloids and Surfaces in Reprographic Technology*; Hair, M., Croucher, M. D., Eds.; American Chemical Society: Washington DC, 1982; p 307.
(22) Lee, B. I.; Rives, J. P. *Colloids Surf.* **1991**, *56*, 25.