

Stability of mixtures of charged silica, silica–alumina, and magnetite colloids

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Received 20 October 2004; accepted 20 April 2005

Available online 9 June 2005

Abstract

We report experiments on the stability of aqueous mixtures of charged colloidal magnetite and charged silica and silica covered with alumina particles of similar size. First, positively charged magnetite dispersions were mixed with negatively charged silica dispersions at pH 4, at different volume ratios and low colloid volume fractions, producing mixtures which were stable over a period of weeks despite the expected electrostatic attraction between the oppositely charged particles. When magnetite particles were mixed with positively charged silica covered with alumina at pH 4 under exactly the same conditions, some of the systems separated to form a magnetite sediment. When the volume fraction of the initial dispersions was increased, the behavior of the mixtures was the opposite: positive magnetite/negative silica mixtures were unstable at intermediate volume ratios. The unexpected behavior of the mixtures was investigated by means of electrophoretic mobility, initial susceptibility, and dynamic light scattering measurements as well as sedimentation experiments.

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Keywords: Colloidal silica particles; Colloidal alumina particles; Magnetic colloids; Magnetic fluids; Heteroaggregation; Stability; Binary mixtures

1. Introduction

Heteroaggregation is the aggregation of colloidal particles which may differ in charge, size, or shape. This phenomenon is of importance in many areas, including core–shell composites, advanced ceramics, cellulose-based materials, and pharmaceuticals [1]. If the system consists of particles significantly different in size and charge, adhesion of small particles on the larger ones may take place. This adhesion process can greatly affect the properties of the resulting dispersed system [2]. It is expected that particles with opposite charge will attract one another, leading to heteroaggregate formation, whereas particles with like charge should repel one another, keeping the system stable.

In addition to its fundamental importance, heteroaggregation plays a fundamental role in the process of particle deposition or adhesion, important in a number of technological processes. For example, the transport of pollutants and microbes in groundwaters, selective flocculation, dewatering of suspensions, wafer cleaning in semiconductor manufacturing, and so on, are processes involving aggregation between particles of different natures [3]. In particular, if one of the types of particles involved is magnetic, as is the case in the present work, new applications can be thought of, not only in the field of water treatment technology [4], but also in the preparation of ferrite films for magnetic tapes or hard drives [5–7].

Several authors have reported results on mixtures containing colloidal silica. Kim and Berg [1] investigated suspensions of negatively charged silica and positively charged alumina-coated silica particles, and they reported the formation of fractal structures controlled by the mixture composition and shear conditions at fixed pH. DiFeo et al. [8] studied the interaction between sphalerite (ZnS) and silica, including

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the effects of pH and calcium ion effects, and they reported sphalerite homoaggregation at pH 2 and 8.5, while heteroaggregation occurred at pH 3–7. Uricanu et al. [9] studied the stability in colloidal mixtures containing latex and Ludox AS-40 silica particles with a large disparity in size. Their experimental results support the adsorption of the small silica particles onto the larger latex ones, even though both colloids were negatively charged. In Ref. [10], Raşa et al. studied heteroaggregation of oppositely charged silica particles of similar size and reported, among other things, reptization of aggregates due to charge inversion of the negative silica particles.

Because flocculated particles show a larger tendency to settle under gravity compared to single particles, the growth of heteroaggregates will make the suspension more prone to sedimentation, which in practice may be convenient for solid–liquid separation. If one of the colloid species were magnetic, the aggregates could also be manipulated with a magnetic field gradient. For example, one could transport in this way nonmagnetic colloids or prepare gels which respond to a magnet. As a first step in this direction we present here results on aqueous mixtures of positively charged magnetite with either positively charged alumina or negatively charged silica particles, at different volume ratios and at pH 4. In our first exploration of the silica–magnetite and alumina–magnetite mixtures we investigate their stability using electrophoresis, magnetic susceptibility, and dynamic light scattering measurements as well as sedimentation experiments.

2. Experimental

2.1. Materials

Magnetite particles were prepared by chemical coprecipitation following the method of Massart [11], which comprises mixing ferric chloride and ferrous chloride in an ammonia solution. To obtain an acidic sol, the precipitate was stirred with aqueous 2 M perchloric acid and the particles were separated by magnetic decantation. Their peptization was accomplished by the mere addition of water. Negatively charged silica sol Ludox HS-40 (DuPont) consists of silica particles, with an average diameter of 12 nm according to the manufacturer. Positively charged silica sol Ludox CL (DuPont) consists of similar 12-nm silica particles coated with a thin layer of alumina, which is responsible for the positive surface charge. In what follows, the dispersions of negatively charged silica particles will be referred to as silica, and the suspensions of alumina-coated silica will be named alumina.

2.2. Electrophoretic mobility

Electrophoretic mobility measurements of diluted dispersions were performed with a Delsa 440 SX (Coulter Elec-

tronics, Inc., USA). The mobility was determined from a Lorentzian fit to the measured distributions of scattered intensity vs electrophoretic mobility at four scattering angles; the corresponding four values of the mobility were averaged. The pH of all the samples was adjusted to 4 at least 12 h before the mobility measurements with 10^{-2} M HCl. The signs of the surface charge of Ludox CL and Ludox HS40 were confirmed, while magnetite, as expected, is positively charged at this pH.

2.3. Volume fraction of solids

The volume fraction Φ of particles in the initial dispersions was determined from mass density measurements according to the equation

$$\Phi = \frac{\rho_D - \rho_S}{\rho_p - \rho_S}, \quad (1)$$

where ρ_D is the density of the dispersion, ρ_S the density of the carrier liquid, and ρ_p that of the solid particles. Densities were measured with a DMA5000 density meter (Anton Paar) at $T = 293$ K.

2.4. Initial susceptibility measurements

The initial magnetic susceptibility of the suspensions was measured with a KLY-3S Kappabridge susceptometer (AGICO, Czech Republic), which uses a small applied field of 300 A/m at a frequency of 875 Hz. The volume fraction dependence of the initial susceptibility χ of the mixtures was determined immediately after their preparation. The measurements were performed at constant temperature (22.0 ± 0.1 °C) using in all cases the same thin cylindrical sample holder containing 3 ml of samples, oriented parallel to the field. Due to the small magnetite content in the samples, and the high aspect ratio of the cylinder, the demagnetizing field is negligible.

2.5. Magnetic diameter

Initial magnetic susceptibility (χ) measurements were performed in order to determine the magnetic diameter and to get information about the possible formation of heteroaggregates. In order to estimate the magnetic diameter the data were fitted to Eq. (2) based on Langevin model. The Langevin model assumes that the magnetic fluid consists of Brownian, monodisperse, noninteracting spheres, each having a permanent magnetic moment m , which rotates together with the particle to align to an external magnetic field. This model is also known as the ideal magnetization model [12], and yields the ideal (Langevin) initial susceptibility, given by

$$\chi_{iL} = \frac{\mu_0 \pi M_d^2 D_m^3 \Phi_m}{18k_B T}, \quad (2)$$

where D_m is the magnetic diameter of the particles, μ_0 is the magnetic permeability of vacuum, k_B is Boltzmann's constant, T is the absolute temperature, M_d is the spontaneous magnetization of particles, and Φ_m is the magnetic volume fraction (i.e., the volume of the magnetic cores).

2.6. Transmission electron microscopy (TEM)

The magnetite particle size distribution was determined from TEM (Philips Tecnai 12, The Netherlands). Image analysis on 114 particles yielded an average diameter of 9 ± 2 nm.

2.7. Dynamic light scattering (DLS)

Particle sizes were also estimated from dynamic light scattering measurements performed using an argon laser (Spectra Physics Model 2000) at a wavelength of $\lambda = 514.5$ nm. Highly diluted dispersions, prepared at pH 4, were filtered using 0.3- μm PHWP Millipore membranes (Millipore, France) to remove dust. Intensity autocorrelation functions (IACFs) were obtained at six scattering angles between 35 and 120° with a Malvern 7032 CE, 128-channel correlator (Malvern Instruments, UK).

Data were fitted with the IACF for monodisperse spheres,

$$g_1(k, t) = A + B \exp(Ct), \quad (3)$$

where A , B , and C are fitted parameters and k is the scattering vector. Parameter C should equal $-D_0k^2$, where D_0 is the diffusion coefficient at infinite dilution from which the particle size can be obtained via the Stokes–Einstein equation.

2.8. Sedimentation experiments

All sedimentation experiments were performed in cylindrical glass tubes (height 10 cm, diameter 9 mm) stored undisturbed on a marble table. Three series were prepared for this study, at different initial concentrations of magnetite particles and at different volume ratios of magnetite–Ludox HS40 mixture, magnetite–Ludox CL mixture, and magnetite–water dilution. Pictures were taken regularly in order to observe the stability of the mixtures as a function of time.

3. Results

3.1. Visual observations of concentration profiles

We observed the sedimentation process in three series (see Figs. 1–3) of mixed dispersions—referred to as series I, II, and III, described in Table 1—which differ from each other in concentration of mixed particles. In each series, the mixtures of magnetite and silica/alumina (a, b) are compared with dilutions of magnetite dispersion (c), in which the content of magnetite was the same as in the corresponding mixtures (a) and (b).

Fig. 1 shows that the stability of the mixed suspensions (a) and (b) is similar to that of the corresponding magnetite system (c) except for case I.4, particularly in the case of the positive magnetite and positive alumina mixture (b), in which electrostatic repulsion should have kept the system stable. We point out that for the suspension I.4 (b) most of the magnetite was sedimented and the sediment presents yield stress.

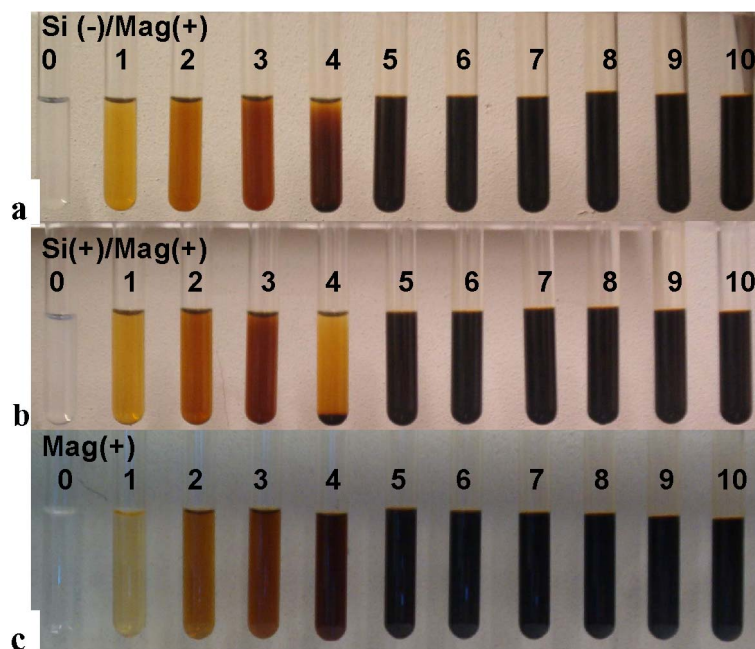


Fig. 1. Images of the mixed suspensions of series I (see also Table 1) taken 2 weeks after the preparation. (a) Negative (HS40) silica-positive magnetite, (b) positive (CL) silica-positive magnetite, (c) magnetite diluted with distilled water (no added silica).

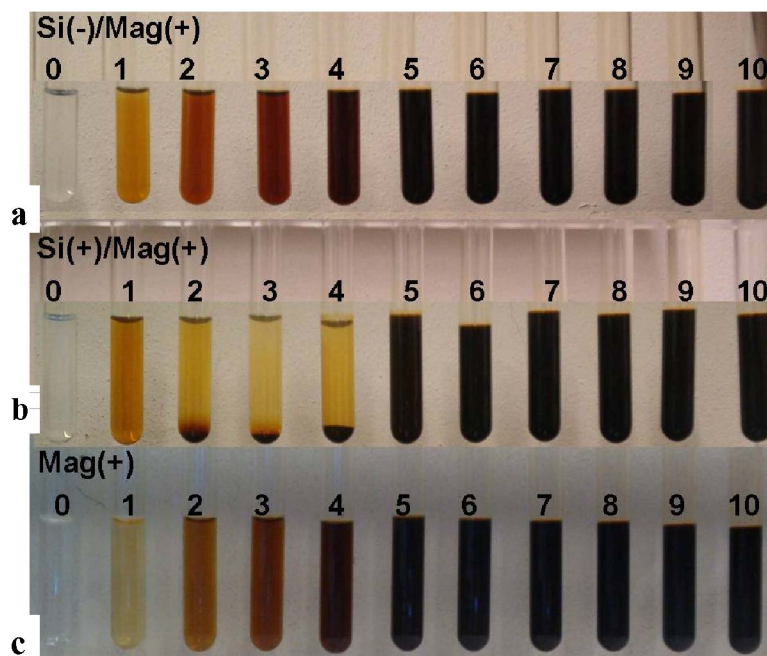


Fig. 2. The same as in Fig. 1, but for series II (see also Table 1).

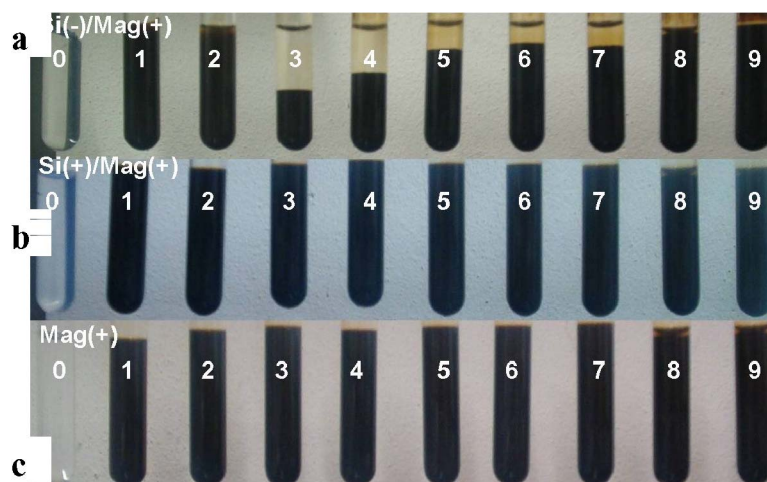


Fig. 3. The same as in Fig. 1, but for series III (see also Table 1).

In the case of series II (see Fig. 2), the suspensions prepared with positive magnetite and alumina (b) were unstable up to a volume fraction of magnetite dispersion of 20% (II.1–II.4). No aggregation was observed in positive magnetite–negative silica (a) mixtures.

The situation changes drastically for series III (Fig. 3). Positive magnetite–positive alumina suspensions (b) appear now stable, while sedimentation of positive magnetite and negative silica (a) can be observed at several intermediate concentrations of magnetite. For this last series, all sedimented samples were shaken up 4 weeks after their preparation and the pH was checked. In all cases the pH was close to 4 and, after they were allowed to sediment again, they all behaved similarly.

3.2. Initial susceptibility measurements

Initial magnetic susceptibility (χ) measurements were performed in order to determine the magnetic diameter and to get information about the possible formation of heteroaggregates. All measurements were done just after the preparation of each series. Fig. 4 shows that χ depends linearly on volume fraction, no appreciable differences being found between the mixtures of negative silica with positive magnetite and positive alumina with positive magnetite. Similar results were found for series II. In all cases the data were fitted to Eq. (2). The obtained results are shown in Table 2.

In all cases, the obtained magnetic diameter is higher than the average TEM diameter (9 nm), but we must take into ac-

Table 1
Composition (in wt%) of the studied mixtures

Series I											
Code	I.0	I.1	I.2	I.3	I.4	I.5	I.6	I.7	I.8	I.9	I.10
Silica (%)	100	99	95	90	80	70	50	30	20	10	0
Fe ₃ O ₄ (%)	0	1	5	10	20	30	50	70	80	90	100
Series II											
Code	II.0	II.1	II.2	II.3	II.4	II.5	II.6	II.7	II.8	II.9	II.10
Silica (%)	100	99	95	90	80	70	50	30	20	10	0
Fe ₃ O ₄ (%)	0	1	5	10	20	30	50	70	80	90	100
Series III											
Code	III.0	III.1	III.2	III.3	III.4	III.5	III.6	III.7	III.8	III.9	III.10
Silica (%)	100	83	71	53	45	34	24	18	1	0.5	0
Fe ₃ O ₄ (%)	0	17	29	47	55	66	76	82	99	99.5	100

The particle concentrations in the magnetite and silica dispersions, respectively (i.e., before the mixtures were done) were 1 wt% for series I, 2 wt% for series II, and 1.5 wt% for series III.

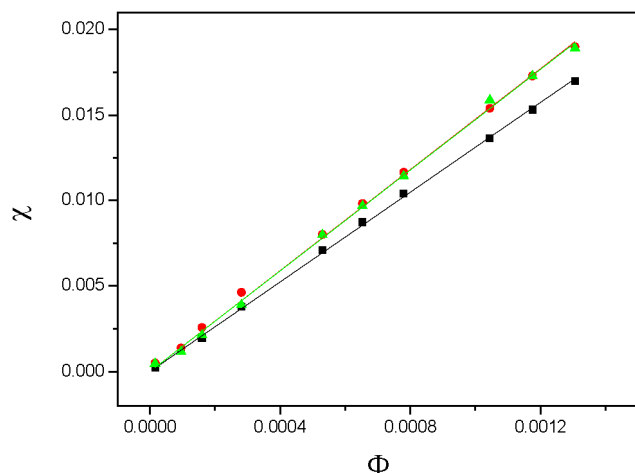


Fig. 4. Initial magnetic susceptibility for series I of the samples (see Table 1) as a function of magnetite volume fraction. (■) Magnetite diluted in water, (●) negative silica–positive magnetite mixtures, (▲) positive silica–positive magnetite mixtures.

count the fact that mainly the largest particles of the size distribution contribute to the magnetization of the magnetic fluids at very low fields. Practically, no differences can be observed between the magnetic diameters determined from mixtures of types (a) and (b) in the three series. The fact that we obtained a slightly higher diameter (and susceptibility) for the mixtures of types (a) and (b) in comparison with that found from measurements on magnetite dispersions (c) may indicate the formation of some (hetero)aggregates in the mixtures. However, the linear dependence of susceptibility on the volume fraction suggests that the interaction between aggregates is negligible.

3.3. Dynamic light scattering

Dynamic light scattering measurements were performed to obtain information about the hydrodynamic diameter of the particles. The results might be affected by the small size of the particles, due to which the scattered intensities at very

Table 2
Magnetic diameter of magnetite particles obtained from initial susceptibility measurements on series I–III and mixture types (a), (b), and (c)

Series	D_m^a (nm)	D_m^b (nm)	D_m (nm)
I	11.1	11.1	10.7
II	11.7	11.7	11.0
III	12.6	12.5	12.9

D_m^a and D_m^b were obtained from measurements on mixtures containing negative (a) and positive silica (b). D_m is the diameter obtained from measurements performed on the magnetic fluids diluted with water (c).

low volume fractions are low and even small impurities may introduce errors. In the case of magnetite particles, the absorbance may affect the results, but this aspect is beyond the goal of this paper and will be investigated in a future work. For magnetite particles, the hydrodynamic diameter was on the order of 24 nm, a value higher than the TEM diameter, but we must take into account that this is an approximate result, since the presence of even a small fraction of aggregates can significantly affect the average diameter deduced from light scattering.

In the case of positive alumina and negative silica, the measured hydrodynamic diameters were significantly higher than the values reported by the manufacturer: the estimated average values were 90 and 32 nm for the positive alumina and negative silica particles, respectively. The value for the negative silica particles (Ludox HS40) is in agreement with that reported previously by several authors, such as Honing et al. [13] and Finsy et al. [14]. It is very likely that Ludox dispersions contain aggregates, which lead to higher values of the diameter in DLS experiments.

4. Discussion

The main features of Figs. 1–3 can be summarized as follows:

- (i) At low volume fraction of solid (Figs. 1 and 2), negative silica–positive magnetite mixtures are rather stable, despite the expected electrostatic attraction between oppositely charged particles.
- (ii) At low volume fraction of solid (Figs. 1 and 2), positive alumina–positive magnetite mixtures with low concentration of magnetite are unstable.
- (iii) At higher volume fraction of particles (Fig. 3), the situation is reversed, i.e., the negative silica–positive magnetite mixtures appear to be unstable at intermediate magnetite content.

The behavior shown by the negative silica–positive magnetite mixtures, in our case the potentials are -20.4 mV for silica vs 32 mV for magnetite, can be explained in terms of charge inversion, using arguments similar to those proposed in [10]: since silica particles have a significant solubility, the

dissolved silicate species may adsorb on a positively charged surface to reverse its charge sign.

In the case of series III, mixture type (a) (see Fig. 3), suspensions 1 and 2 are stable also because of the charge inversion. If the magnetite concentration is increased (samples 3–7), the “charge inversion” is probably insufficient to maintain the stability of the mixtures, and heteroaggregation occurs. Finally, at the highest concentration of magnetite and low concentration of silica (samples 8 and 9), the suspensions appear stable again, as they are in the absence of silica (c); some heteroaggregates are probably present but they are not seen in Fig. 3.

The hypothesis of charge inversion was checked by means of electrophoretic mobility measurements: a sample containing only negative silica particles (system 0, series III in Table 1) was centrifuged at 20,000 rpm for 24 h. The upper part of the supernatant was subjected to an electrophoretic mobility measurement, and a null mobility was measured. This result, together with visual evidence of absence of any Tyndall effect, suggested that the supernatant was almost free of particles. A small amount of initially positive magnetite dispersion was introduced in this supernatant and the electrophoretic mobility was measured after 2 h: it changed from the initially positive value ($u_e = 2.1 \pm 0.3 \mu\text{m cm/V s}$) to $u_e = -2.1 \pm 0.6 \mu\text{m cm/V s}$, thus demonstrating the charge inversion of magnetite in the silica dispersion solvent.

In the case of positive alumina–positive magnetite particles (middle rows in Figs. 1–3), the most significant observation is the instability observed at high relative volume fractions of alumina. A possible explanation might lie in the effect of particles of one type on the surface charge or potential of the other particles. This phenomenon, if it occurred, might change a repulsive interaction into an attractive one or vice versa. A rigorous numerical analysis of the double-layer force and free energy between charged interfaces at different distances was performed by McCormack et al. [15] using the nonlinear Poisson–Boltzmann theory. It is strictly applicable to planar interfaces or, at most, particles with thin double layers (compared to either particle radii). Since our smallest particles are 10 nm in diameter, κa values as low as 4.8 are typical, i.e., we are far from the necessary condition $\kappa a \gg 1$. However, some qualitative conclusions might still be used in connection with our results; we must ask ourselves whether changing the average distance of approach between two dissimilar, positive particles can change the charge or the potential of either of them to the extent that their repulsive interaction becomes attractive. Checking the results of McCormack et al. results, one finds that if the potentials are of equal magnitude, the double-layer interaction is always repulsive. If, as in our case, one of the potentials is slightly larger than the other (43 mV for alumina vs 32 mV for magnetite) the repulsion sensed at large separations can shift to attraction only at very short distances (the shorter the distance the closer the similarity between the potentials), typically below a double-layer thickness (1.5 Å in our case).

Since the volume fractions of solids are on the order of a few percent, we cannot expect such a close average proximity between our particles. However, for the ζ potentials and particle sizes involved, the height of the repulsive potential energy barrier is only a few kT , so that there is a finite probability for the particles to surpass that barrier, because of their thermal energy, giving rise to heterocoagulation. The long time of the experiments favors this process.

We also suggest a different explanation, based on the osmotic depletion effect [16,17], to explain the instability. In Ref. [17] it is demonstrated that depletion by nanoparticles is possible and in fact affects considerably the adhesion and deposition of the bigger particles. An approach based on nanoparticles as depletants is valid as long as the value of κa is larger than 1 for the small particles (it is 4.7 for magnetite in our case), and also their concentration is much smaller than that of the bigger particles (this is also our case). Hence, depletion is possible in the systems we are referring to.

Several authors have reported on hard-sphere fluid phase separation based on this effect: Sanyal et al. [18] performed experiments on mixtures of latex particles with a diameter ratio of 0.2 and observed formation of aggregates in the sediments of their samples. Kaplan et al. [19] reported experiments on mixtures of latex particles with size ratios between 0.069 and 0.294 and demonstrated that phase separations were entropically driven by an attractive interaction between large spheres mediated by the smaller ones. Rosenfeld [20] applied a density functional theory to binary hard-sphere systems and predicted that these systems are unstable against phase separation if the ratio of their sizes is ≤ 0.25 , due to the osmotic depletion effect. In our case, according to the DLS measurements, the size ratio is on the order of 0.27, so that the depletion interaction may contribute to explaining the experimental facts.

However, as shown in Fig. 5, the larger sediment volume of the mixture compared to that of the pure ferrofluid with the same magnetite concentration as in the mixture suggests the formation of heteroaggregates rather than magnetite aggregates. The sedimentation of magnetite in Fig. 5, right, was induced by changing the pH of the magnetic fluid. A TEM picture of the sediment of the mixture (Fig. 5, left) is presented in Fig. 6 and shows alumina structures as well as

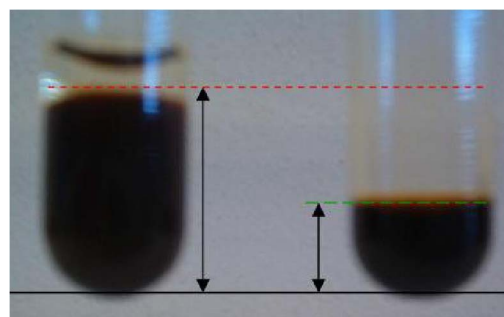


Fig. 5. Sediment heights, 2 weeks after the preparation of (left) the mixed system 4 of series II (Fig. 2b) and (right) the magnetite diluted with water with the same volume fraction of magnetite (system 4, Fig. 2c).

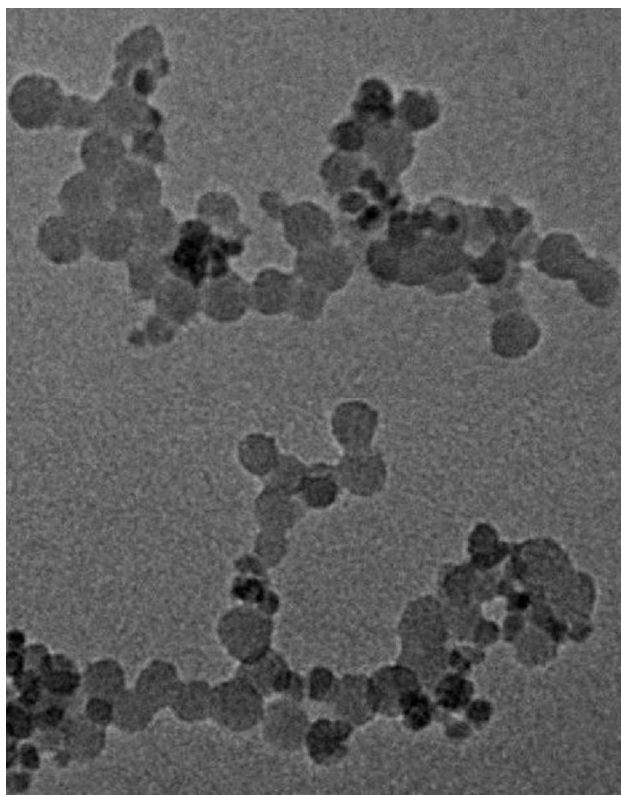


Fig. 6. TEM image of the sediment of mixture II.4 (see Table 1 and Fig. 2b).

magnetite particles (smaller in size and darker), so the sediment indeed contains both species of particles. It is possible that the van der Waals attraction is responsible for heteroaggregation and gel formation in the sediment, subsequent to the initial separation due to depletion attraction.

5. Conclusions

We studied experimentally the structure formation and stability of aqueous mixtures of charged magnetite and silica particles. On a very short time scale, initial susceptibility measurements showed weak aggregation. Stability in the negative silica–positive magnetite mixtures is ascribed to a charge inversion due to the absorption of soluble silicates species onto the magnetite particles. At higher concentration of particles in the initial dispersions to be mixed, most of these mixtures become unstable, except for those with extreme magnetite/silica ratios.

In the case of positive alumina–positive magnetite mixtures at low concentration of particles in the initial dispersions, the observed separation at higher silica-to-magnetite ratios might be due to depletion attraction. The in situ size

ratio of alumina and magnetite particles, determined from DLS measurements (different from the size ratio from TEM statistics on single particles, which is close to 1), supports the hypothesis of depletion attraction. The sediment observed presents yield stress and contains both alumina and magnetite particles, the gel formation being possible due to van der Waals attraction.

Acknowledgments

Dr. A.V. Delgado, Dr. J.D.G. Durán (Departamento Física Aplicada, Universidad de Granada), and Dr. M. Oversteegen (Van 't Hoff Laboratory, Utrecht University) are thanked for helpful discussions. This work was financially supported by MCYT, Spain, Project MAT 2004-00866.

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