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Preparation and properties of monodisperse magnetic fluids

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Abstract

A 'size sorting' method performed on ionic magnetic fluids, constituted by polydisperse anionic particles dispersed in water at pH 7 allows 'monodisperse' samples to be obtained. Here results on phase transitions observed in these samples with decreasing temperature, application of a magnetic field or increasing ionic strength are presented.

1. Introduction

Whatever the procedure used to synthesize magnetic fluids (grinding or chemical procedures), the system of nanoparticles dispersed in the liquid carrier is always polydisperse [1,2]. It is a serious problem when relations between theories and experiments are needed and, moreover, it may be at the origin of specific behaviours, as for example when the stability of the colloidal solution is discussed [3]. Many studies have been performed in order to calibrate the particles during the synthesis process [2]. Synthesis of ferric oxide particles in microemulsion for example may be considered [4]. A permanent problem is that of quantities because this kind of synthesis needs very low concentrations of reactants. That is why 'size sorting' methods still have great interest. This size sorting may be performed using a physical method [5] (centrifugation or magnetic separation) or physicochemical methods. These latter were first used in the case of anionic particles dispersed in alkaline magnetic fluids [6] and they were also used successfully in the case of emulsions [7]. They are based on the thermodynamical properties of the colloidal system.

We propose here a 'size sorting' method performed on aqueous ionic magnetic fluids, constituted by anionic particles dispersed in water at pH 7 [8]. It is cheap, may be performed on significant amounts of fluid and is efficient as it allows 'almost monodisperse' magnetic fluids, to be obtained. Preliminary results on phase transitions observed in these samples when the temperature is decreased, a magnetic field is applied or ionic strength is increased are presented here.

2. Theoretical and experimental background [3]

When it is stable, a magnetic fluid may be compared to a 'gas of particles' using the now usual description of colloidal solutions [9]. In the case of aqueous magnetic fluids constituted by nanoparticles bearing a permanent magnetic dipole and surface charges, the particle interactions are the Van der Waals interactions, the screened electrostatic repulsions, and the magnetic dipolar interactions. By modifying one of these interactions, it is possible to induce phase transitions, which may be 'gas-liquid' like or precipitations.

'Gas-liquid' like transitions were first observed for magnetic fluids in the case of anionic particles dispersed in alkaline aqueous solutions, in which the ionic strength was increased, through the addition of an electrolyte in order to decrease electrostatic repulsions. Phase diagrams have been constructed for different size distributions of the particles.

These magnetic fluids were indeed polydisperse and the size distribution is usually assumed to be well described by a log-normal law:

$$p(D) = \frac{1}{\sqrt{2\pi}\sigma D} \exp\left(-\frac{1}{2\sigma^2}\left(\ln\frac{D}{D_0}\right)^2\right)$$

In D_0 being the mean value of $\ln D$ and σ the standard deviation. In usual magnetic fluids (synthesized by Massart's method [10]), D_0 ranges between 5 and 10 nm, and σ between 0.3 and 0.45. It is also possible to define an average diameter d_{bir} , determined from the analysis of birefringence measurements. This diameter is of hydrodynamical nature and is more like an 'average in weight'. d_{bir} takes into account the biggest particles and is very sensitive to σ ($d_{\text{bir}} = 30$ nm for $\sigma = 0.4$ and $D_0 = 7$ nm; $d_{\text{bir}} = 15$ nm for $\sigma = 0.1$ and $D_0 = 7.8$ nm).

It has been established [3], in the case of anionic particles, that there is a strong correlation between the size

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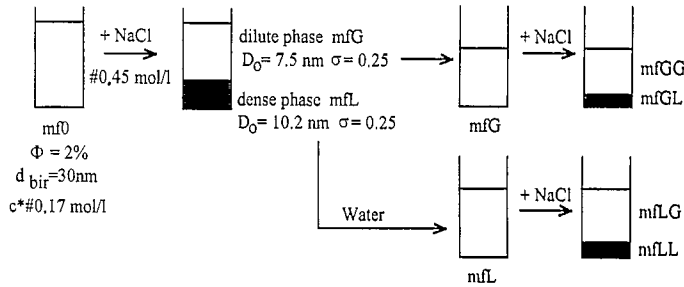


Fig. 1. Schematic diagram of the size sorting procedure.

distribution characteristics and the concentration of electrolyte at the onset of the transition, the appropriate fitting parameter being the diameter d_{bir} .

3. Materials and experimental methods for characterization

Materials: The present results have been obtained with magnetic fluids constituted by maghemite particles ($\gamma\text{-Fe}_2\text{O}_3$), anionic over a wide range of pH because of the specific adsorption of citrate anions ($\text{NaOOC-C(OH)-(CH}_2\text{-COONa)}_2$) on the ferric oxide surface [8,10].

Methods for characterization: The magnetic fluids are characterized by the particle size distribution and the volume fraction in magnetic material. Stability of the sample is checked by observation with an optical microscope. The particle size distribution is determined by transmission electron microscopy (microscope JEOL 100 CX2) on ferrofluids spread on a grid and dried, or from an analysis of the shape of the magnetization curve of magnetic fluids in which the volume fraction in magnetic particles is around 1% using a vibrating magnetometer (Foner) [11]. The diameter d_{bir} is determined by relaxation of birefringence. This method is described in Ref. [12]. The volume fraction of particles is determined from chemical titration of iron [13] and optical microscopy is performed on the magnetic fluid sampled in a cell, which can be thermostated and placed between coils in order to determine the phase transition onset when the temperature is decreased or when a magnetic field is applied.

4. Synthesis and characterization of monodisperse magnetic fluids

Standard magnetic fluids are rather polydisperse. Analysis of the magnetization curve leads to the parameters of the size distribution: $D_0 = 7$ nm, $\sigma = 0.4$. Relaxation of birefringence performed on the same sample leads to an average hydrodynamical diameter $d_{\text{bir}} = 30$ nm.

Size sorting method: The synthesis of monodisperse magnetic fluids from polydisperse ones is a size sorting method based on the dependence of the phase transition onset with the particle size. In magnetic fluids at pH7,

phase separation may be induced by addition of NaCl which has been chosen because of its low price and the concentration of salt necessary to induce the transition (onset concentration c^*) in magnetic fluids which the volume fraction in particles is around 2%, is related to the average diameter d_{bir} , and thus to D_0 and σ through the experimental relation: $\ln c^* = 9.77/d_{\text{bir}}^{2.06}$ [14]. The size sorting procedure is schematized in Fig. 1 and may be compared to a fractional distillation. After two steps the samples mfGG and mflL are almost monodisperse ($\sigma = 0.15$ or 0.1 in some cases). These samples have however to be washed to eliminate the excess of NaCl.

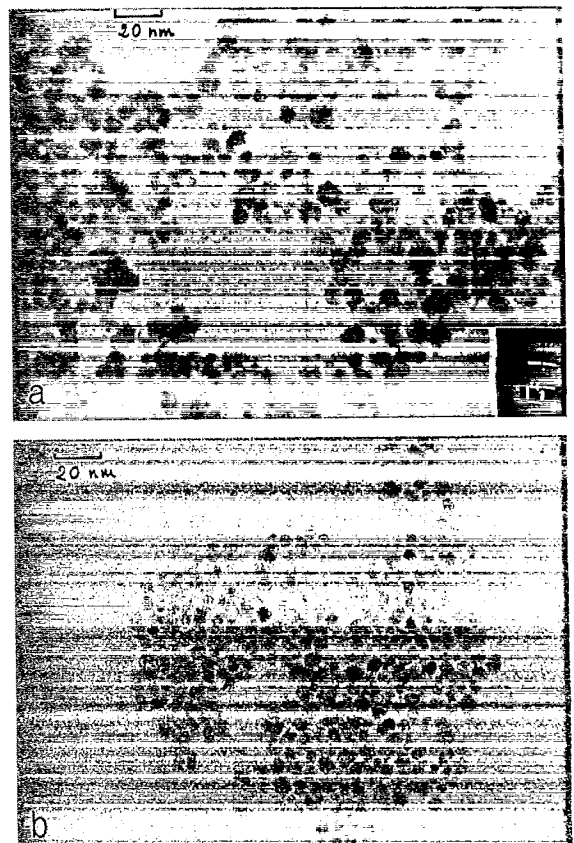


Fig. 2. Electron microscopy photographs: (a) mf0 (b) mfGG.

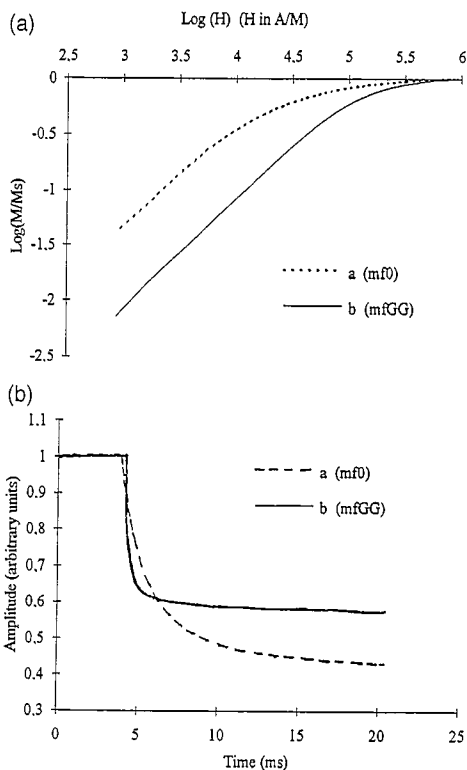


Fig. 3. Magnetization curves (a) and relaxation of the birefringence signal (b).

Characterization of monodisperse magnetic fluids: Fig. 2 shows the difference observed by electron microscopy between the sample mf0 (Fig. 2(a)) and the sample mfGG (Fig. 2(b)) obtained as described above. In Fig. 3 are plotted the magnetization curves (Fig. 3(a)) and the relaxation of birefringence signal (Fig. 3(b)) for the two samples. The curves lead to the following characteristics:

mf0: $D_0 = 7$ nm, $\sigma = 0.4$ and $d_{\text{bir}} = 30$ nm;

mfGG: $D_0 = 6.9$ nm, $\sigma = 0.1$ and $d_{\text{bir}} = 14.5$ nm.

These measurements are in good accordance altogether and show that it is possible to reduce significantly the polydispersity of a magnetic fluid using such a size sorting procedure.

5. Phase transitions in monodisperse magnetic fluids

It has sometimes been said that obtaining a dense magnetic liquid phase instead of a precipitate was perhaps only due to polydispersity. Moreover, even when a real thermodynamic phenomenon was assumed, polydispersity complicates the calculations so much that it is quite impossible to compare experimental results with theory [15]. Obtaining monodisperse magnetic fluids (σ value of 0.1 corresponds to a ratio of the average mass in weight to the average mass in number (M_w/M_n) equal to 1.1) allows these problems to be solved. That is why the phase behav-

ior of magnetic fluids has been studied in these monodisperse systems as a function of the ionic strength, the temperature and the applied magnetic field.

5.1. Phase separation induced by an increase of ionic strength

The first result is that a liquid phase dense in magnetic particles is obtained even in monodisperse samples, when, for example, NaCl is added to the fluid. This result is important because it confirms the thermodynamical aspect of the observed transition.

The phase diagrams plotted in Fig. 4 show the influence of the mean size on the concentration of the dilute phase. It has to be noted that the behaviour of a polydisperse sample ($D_0 = 7$ nm, $\sigma = 0.4$) seems to be close to that of a monodisperse sample with $D_0 = 9.4$ nm, $\sigma = 0.15$. This result indicates the monitoring role played by the biggest particles of the distribution in the phenomenon.

Although the volume fraction in the dilute phase is very sensitive to a small variation of NaCl concentration, the concentration in the dense phase is always around 30%. This result was observed also in the case of alkaline systems but the volume fraction was around 24%.

When NaCl is added, the ‘gas–liquid’ like transition (Fig. 5(a)) is observed first, then a precipitation phenomenon appears. A three-phase area seems to exist for intermediate concentrations of salt: Fig. 5(b) shows the coexistence of dense liquid phase droplets and precipitate. This three-phase area has also been observed by other authors in the case of a phase transition induced by adding non-adsorbing polymer to a colloidal solution of monodisperse latex [16].

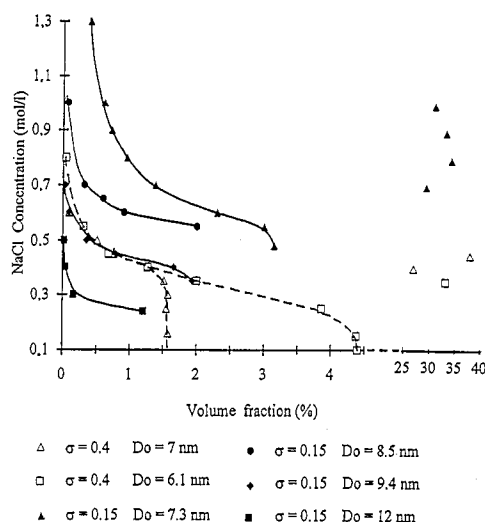


Fig. 4. Volume fraction versus salt concentration for different size characteristics.

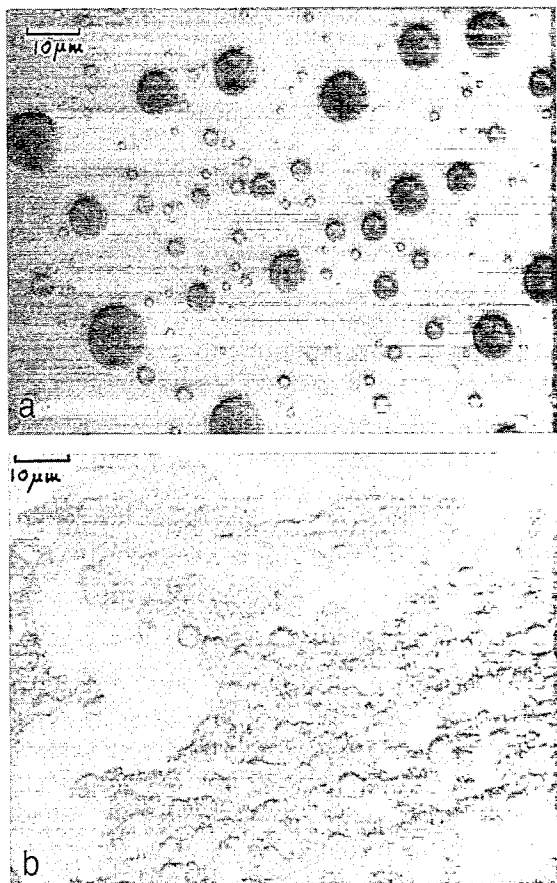


Fig. 5. (a) Two-phase system (dense phase droplets and dilute phase); (b) three-phase sample.

5.2. Phase separation induced by a decrease of temperature

A temperature decrease is equivalent to an increase of the ionic strength and can thus induce a phase transition in a sample that is a single-phase system at room temperature. Conversely, a two-phase sample at room temperature can become a one phase system if the temperature is increased. The temperatures at the onset of the transition is determined as a function of the ionic strength in the samples using this second experiment for technical reasons. Both magnetic fluids are almost monodisperse ($\sigma = 0.1$) but with different sizes: $D_{02} = 7.8$ nm (C2) et $D_{03} = 9.4$ nm (C3). The transition is observed with an optical microscope when decreasing T .

The results are shown in Fig. 6, which shows that the temperature at the onset of the transition increases with the concentration of salt and that the size and the volume fraction in magnetic particles do not modify the shape of the curve.

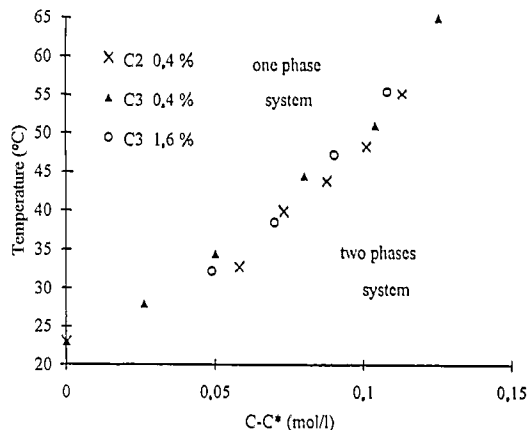


Fig. 6. Temperature transition onset versus $(c-c^*)$ (c is the NaCl concentration in the sample, c^* is the NaCl concentration at the onset of the transition at room temperature).

5.3. Phase separation induced by application of a magnetic field

Phase separation induced by the application of a magnetic field has been observed in surfactant coated particle systems [17] and in the case of polydisperse alkaline ionic magnetic fluids [8]. Such a transition is also observed in the case of anionic citrate coated particles, both polydisperse and monodisperse. The transition is observed with an optical microscope at low magnetic field (< 0.1 T) (Fig. 7). If a higher field is needed (0–1.8 T), the samples are placed between coils, lit with a He–Ne laser beam and a diffusion line appears at the transition [8]. The phenomenon is strongly correlated to the particle size distribution and to the salt concentration (c_s) in the sample. Although it is observed for fields of intensity lower than 0.1 T for samples characterized by $\sigma = 0.15$, $D_0 = 12$ nm, $c_s = 0.22$ mol/l or $\sigma = 0.4$, $D_0 = 7$ nm, $c_s = 0.125$ M, higher fields (0.5–1.8 T) are needed as soon as the size or

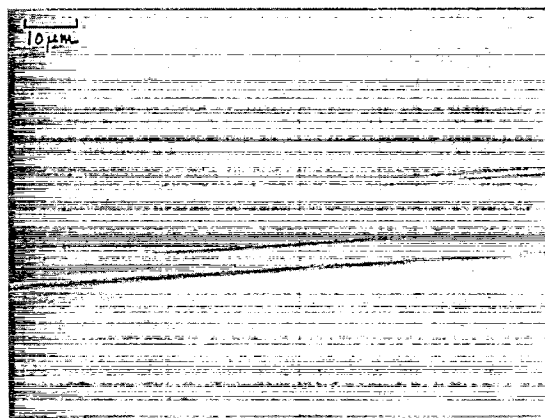


Fig. 7. Transition with magnetic field: long threads of dense phase in a dilute phase.

the NaCl concentration is reduced (about 0.7 T for $\sigma = 0.15$, $D_0 = 9.6$ nm, $c_s = 0.25$ M). With smaller D_0 , it is impossible to observe it even for a field up to 1.8 T.

6. Conclusion

It is possible to produce monodisperse samples with a cheap procedure based on the thermodynamical properties of magnetic fluids. These samples allow the study of the thermodynamical properties of the colloidal solutions, without the influence of polydispersity. The results presented here confirm the thermodynamical aspect of the phase behaviours observed and allow an easier analysis of the influence of particle size and salt concentration on the phenomena.

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