Phase separation in aqueous magnetic colloidal solutions

Abstract Ionic magnetic fluids are aqueous colloidal solutions of magnetic nanoparticles which wear surface charges. Stability of the solution is ensured by screened electrostatic repulsions, and phase transitions "gas-liquid" like are observed when an electrolyte is added to the colloidal solution. The nature and the onset of the transitions are determined as functions of the nature of the particles (maghemite or cobalt ferrite), of the surface charges (anionic oxide particles without or with specifically adsorbed ions), and of the added electrolyte. The onset of the transitions is also related to the particle size distribution parameters.

Key words Magnetic fluids – phase transitions – colloidal solutions

Introduction

Ionic magnetic fluids are colloidal solutions of magnetic nanoparticles dispersed in water without tensioactive molecules [1]. The magnetic particles wear surface charges and the stability of the solution is ensured by screened electrostatic repulsions between grains. A stable colloidal solution is usually compared to a gas of particles, and theories state that a phase separation "gas-liquid" like between a phase dense in particles (liquid phase) and a phase poor in particles (gas phase) may occur [2–8], when some parameters (for example, temperature) are modified. In such ionic solutions, the interparticle interactions are Van der Waals ones, to which screened electrostatic repulsions and magnetic dipolar interactions have to be added. As in any electrostatically stabilized colloid, an addition of electrolyte, which increases the ionic strength, decreases the repulsions and may induce phase transitions. Experimentally, we have found in the case of anionic maghemite $\gamma$-$\text{Fe}_2\text{O}_3$ particles dispersed in alkaline aqueous solutions, that addition of tetramethylammonium hydroxide induces such a phase separation: a liquid phase rich in magnetic particles appears as droplets in another liquid phase poor in particles [9, 10]. An experimental phase diagram has been constructed describing this phase separation in alcaline magnetic fluids when extra base was added [10].

It fact, such results raise many questions. i) The systems are polydisperse and the first problem is to compare the theories, generally dealing with monodisperse systems and our experimental results; another question is if obtaining a liquid phase rich in particles is or is not an artefact due to the polydispersity and then if it really corresponds to a thermodynamic phenomenon. ii) The second problem is to check if this behavior is a universal one, i.e., to study how it depends on the nature of the particles, the parameters of their size distribution, the nature of their surface charges, and the nature of the added electrolyte.

Thus, we present here an experimental work concerning anionic magnetic particles of different nature (maghemite $\gamma$-$\text{Fe}_2\text{O}_3$, and cobalt ferrite $\text{CoFe}_2\text{O}_4$), with different size distributions, dispersed in water (alcaline and pH 7 solutions according to the nature of the adsorbed
species), and to which various electrolytes will be added. The aim of this work is to determine as a function of these parameters, the nature of the phase transition observed by addition of electrolyte (‘‘gas-liquid’’ like or precipitation) and the concentration of electrolyte corresponding to the onset of the transitions.

**Samples**

The ionic magnetic fluids (ferrofluids) that can be obtained are schematized in Fig. 1.

The magnetic nanoparticles are grains of spinel-type ferrimagnetic ferric oxide (MFe$_2$O$_4$) and are synthesized as anionic ones through a chemical process i.e., coprecipitation of mixtures of the metallic salts in alkaline medium as described by Massart [11].

They are dispersable in water as soon as the counterion associated to particles is N(CH$_3$)$_4$ (Na$^+$, NH$_4^+$ induce flocculation of the solution [12]) and stability is a function of the pH as the surface charges are due to surface acid-base equilibria. The pH of the point of zero charge is located for maghemite, as it is for cobalt ferrite particles, around pH 7.5. To modify the pH of this point in case of zero charge, it is necessary to adsorb on the surface small ions, such as for example citrate anions (LNa$_3$, see Fig. 1), which lower the pH of the point of zero charge to 3, allowing to obtain magnetic fluids of pH 7 [13].

The characteristics that allow to describe a magnetic fluid are firstly the **parameters of the size distribution**. The maghemite and cobalt ferrite particles obtained are always polydisperse, the size distribution usually being well described by a log-normal law characterized by the two parameters $D_0$ and $\sigma$ [14]:

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

These parameters are determined either by electron microscopy, either through the analysis of the magnetization curve of the fluid [15]. Usual magnetic fluids obtained in the laboratory have a $D_0$ of the order of 7 nm and a $\sigma$ of the order of 0.4 (Fig. 2).

Another size characteristic useful for the present study, but specific of magnetic fluid is the **average diameter** $D_{bi}$ **determined by relaxation of birefringence**. Its measure is based on the fact that a magnetic fluid, submitted to a magnetic field becomes birefringent because of the alignment of the ferrimagnetic grains [16]. This diameter is of hydrodynamical type and, because of the measure, is an average which gives an important weight to the biggest particles and thus is a characterization of the tail of the distribution [17]. It is thus always found to be much greater than $D_0$, the difference between these diameters being more important when $\sigma$ value is great (Table 1). In the case of the phase separation observed in alkaline sols of maghemite particles, we have shown that this diameter was the relevant parameter which controls the onset of the phase transitions.

The average **number of structural surface charges per particle** has been estimated in the absence of specific adsorption of citrate ions, that means for acid or alkaline fluids, and was found equal to about 200. For these particles, the pH of the point of zero charge is about 7.5, but it is shifted to about 3 by adsorption of citrate [18].

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*Fig. 1 Schematic description of the ionic magnetic fluids synthesized and studied*