

**Experiment title:**

Tuning the aggregates in ferrofluids to control their properties

Experiment number:
SC-2295

Beamline: ID02	Date of experiment: from: 08/02/2008 to: 11/02/2008	Date of report: 28/08/2008 <i>Received at ESRF:</i>
Shifts: 18	Local contact(s): Dr. Michael SZTUCKI	

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Report :

Our aim was the investigation of the microstructure of moderately concentrated magnetic liquids, also called ferrofluids, which are dispersions of magnetic nanoparticles, in various states of interaction, in a liquid matrix. One of the advantages of the home-made ferrite systems electrostatically stabilized that we use is the ability to tune the interparticle potential both in intensity and in range. Indeed modifying the interparticle interaction can lead to the formation of aggregates or thixotropic gels even in dilute systems. We are interested here in these phenomena and their link to the detail of the interparticle potential, especially with the magnetic dipolar interaction.

For this purpose, we prepared several samples modulating the interparticle interaction through different parameters. The Van der Waals attraction is varied through the nature of the ferrite (maghemite or cobalt ferrite). The magnetic dipolar interaction is varied through the diameter d of the nanoparticles : (P) $d = 7.5$ nm; (M) $d = 9$ nm; (G) $d = 11.5$ nm. The repulsive interaction is varied through the charge of the particles (linked to the initial pH of the dispersion, here 2 or 3) and the ionic strength in the solution controlled by added salt (here TMANO₃).

The results we have obtained are illustrated in Figure 1. Firstly, the intensity profile of a typical sample without added salt, given in one set of conditions (nanoparticles (P) and pH3), shows that the nanoparticles are individually dispersed with an interparticle interaction which is repulsive in the initial state (the peak in the structure factor $S(q)$ corresponding to the mean distance between the nanoparticles at their volume fraction, here 1.5%). Then, while increasing the added salt concentration whatever size and pH, the samples whereas remaining liquids, become constituted of small aggregates, and no longer of isolated particles. The size of these aggregates is dependent on the size of the individual nanoparticles (see the three curves for (P), (M) and (G) at pH2 and 0.13 M). For larger salt concentrations, the samples become thixotropic gels, the structure of which depends on the constituting nanoparticles and on the salt concentration (see the curves for pH3 and 0.13M for (P) and (G) nanoparticles). For given nanoparticles, there is a pH-salt equivalence : the decrease of the initial pH is equivalent to an increase of added salt. This is illustrated by an example in Figure 1 (left) with the nanoparticles (G): the curve at pH3 0.065M is superimposed with the one

at pH2 0.13M.

A rotational dynamical probing of these dispersions have been performed, taking advantage of the coupling of optical and orientational properties of the nanoparticles when submitted to a pulse of magnetic field [1,2]. Some examples of the obtained results are presented in Figure 1 (right). The dynamical measurements are coherent with the structural ones: the same trend with the nanoparticles size can be seen as well as the same pH-salt equivalence (see optical relaxation of nanoparticles (G) at pH2 0.13M and at pH 3 0.065M).

While modifying the nanoparticle material from maghemite to cobalt ferrite, a quantitative shift in the results, due to the shift in the van der Waals interaction is observed, however they are qualitatively similar with respect to the influence of nanoparticle size, to the pH-salt equivalence and to the observed structures.

In the gels, the peak of the structure factor corresponds to the size of the particles, meaning that they are at contact and the characteristic correlation length in the gels increases when the particle size increases. The influence of the magnetic dipolar interaction is weak without field and seems to be present only for the largest particles (sample G). As expected, if a field is applied, the scattering becomes strongly anisotropic for sample G while it is only weakly anisotropic for sample P.

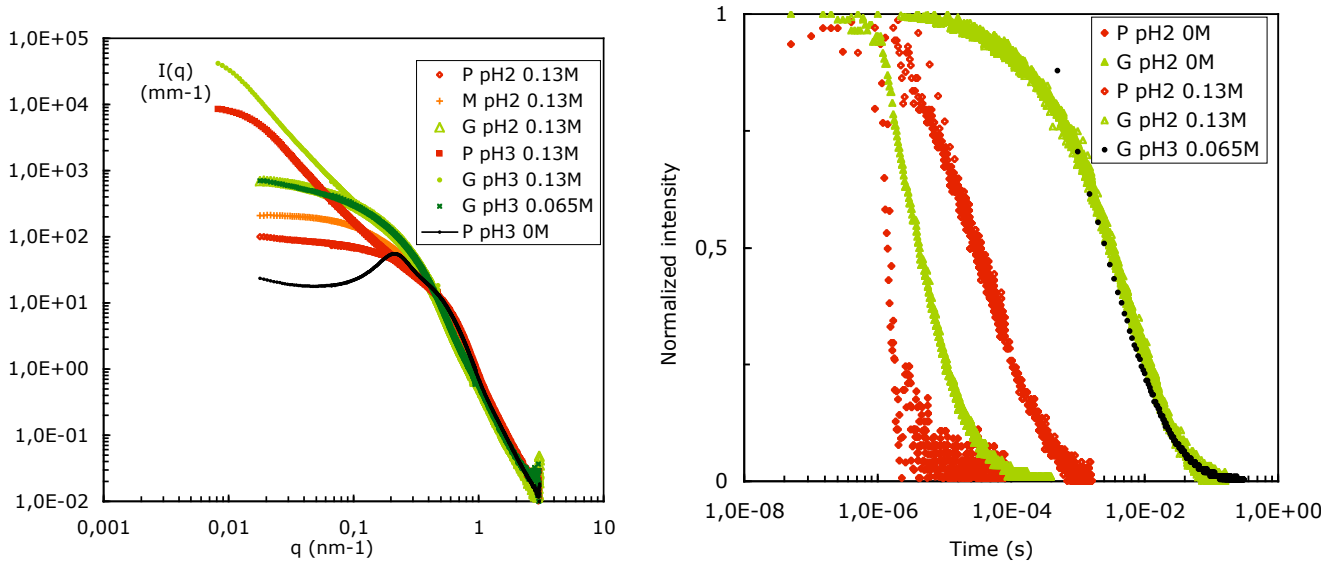


Figure 1: Left : SAXS intensity profiles for several samples of maghemite nanoparticles dispersed in water showing the influence of the particle size, the added salt and the initial pH. The letter indicates the size of the particles ($P = 7,5 \text{ nm}$; $M = 9 \text{ nm}$; $G = 11,5 \text{ nm}$), the second indication is the initial pH before adding salt and the last indication is the concentration of added salt. Right : Temporal relaxation of the optical birefringence induced by a pulse of magnetic field (time = 0 corresponds to the field cut-off) for some of the samples presented in the left figure.

An article based on these measurements is in progress. These results open the perspective to study the kinetics of formation of the dilute gels in a magnetic field (thus leading to anisotropic systems) and the study of more concentrated samples with the possibility of probing the transition between gels and attractive glasses, two different kinds of arrested systems.

References:

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- [2] E. Wanderman, E. Dubois, V. Dupuis, A. Duri, A. Robert, R. Perzynski, *J. Phys.: Cond. Matter* **20**, 204124-1 to 5 (2008)