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CONCENTRATION AND TEMPERATURE EFFECT IN THE MICROSTRUCTURE OF FERROFLUIDS

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Abstract. The spatial correlations in magnetite-based ferrofluids (FF) with pentanol carrier have been investigated by small-angle neutron scattering as dependent on the concentration of the magnetic phase (C = 0.6-20% vol.) and temperature (20-85^{o}C). Some peculiarities in the structure of the FF were detected, such as an anomalous increase of short range order by heating of low concentrated FF (C~0.6-4.0% vol.), the formation of short range order at ambient temperature which weakens at growing concentrations C=7-14% vol., the existence of the stable structure at the highest concentration C~20% vol. when particles shells interpenetrate. Neutron scattering data are discussed regarding to particles intrinsic magnetisation enhancement induced by ordering.

Key words: neutron scattering, ferrofluid, structure.

1. INTRODUCTION

Traditional approaches used in neutron studies of ferrofluids (*e.g.,* Guinier, model of spheres scattering independently) do not give any direct information and real description of structural peculiarities arisen from a fine balance of particles interactions *via* dipole and molecular forces. This balance is influenced by the temperature and concentration of the magnetic phase as well as the changes in the state of the surfactant layers due to both factors. The surfactant shell can be frozen or melted, deformed, weakened or strengthened under external factors and neighbouring particles. The knowledge of the ferrofluids behaviour at the nanoscale level promises a good progress in magnetic colloids technology.

2. EXPERIMENTAL

We have carried out a series of samall angle neutron scattering (SANS) experiments on ferrofluids (FF) of different concentrations (C=0.6-20% vol.) at

temperatures 20°C and 85°C in the range of momentum transfer q = 0.03-4.5nm^{-1} (Budapest Neutron Center "Yellow Submarine" SANS facility)[1]. The samples of pentanol based ferrofluids, stabilised by oleic acid [2], were prepared in the Magnetic Fluid Laboratory (Timişoara Branch of the Romanian Academy). In the experiments no magnetic field was applied and we used the same samples at temperatures of 20°C and 85°C. The raw data were treated in the usual procedures and normalised to the water standard. The detailed analysis was carried out using Inverse Fourier transform (Program package ATSAS).[3]

3. RESULTS AND DISCUSSION

Data treatment in q-space does not allow to distinguish clearly the effects of the particle formfactor and interparticle correlations. These effects are strongly mixed. In order to get more information from the scattering data we performed the Fourier analysis using the regularisation method, giving a real space presentation of the neutron scattering data. This is especially effective in dense ferrofluids where the approximation by the model of independently scattering particles is not correct.

A spherical particle (homogeneous, radius Ro) can be characterised by the individual correlation function [4] $\gamma(r)=1-(3/4)(r/Ro) + (1/16)(r/Ro)^3$ in the range of radii $0 \leq r \leq 2Ro$. Obviously any correlation exists only in the interior particle volume, and at r=2Ro the function γ(r) gets zero value. [3,6]. The function γ(r) can be obtained from the Fourier transform of the scattering intensity distribution I(q) measured in the neutron scattering experiment in the case of diluted system.

It is convenient to use a modified function $P(r)=\gamma(r)\cdot r2$ showing the correlation in the spherical layer. It takes the maximum at rm=1.0494·Ro. So the radius of particle from the position of maximum can be calculated. In dilute systems there are no structural peculiarities at r >2Ro where P(r)≡0. At a high content of the magnetic phase, the interparticle correlations at r > 2Ro come into view and dominate when the average distance between particles is close to their diameter. In concentrated systems at r>2Ro we observe density fluctuations $\gamma(r) \sim \langle \Delta C(0)\Delta C(r) \rangle$ or other possible short range order in particles arrangement. The latter is examined for a series of ferrofluid (FF) samples with magnetic phase concentration C=0.6-20%vol. at ambient (20°C) and high (85°C) temperature.

In Fig.1 (a,b) the scattering intensities distributions and the P(R) correlation function are shown at 20ºC and 85ºC for a magnetite concentration C~0.6 % vol.

Heating destroys random contacts of the particles. At the same time the increased repulsion of the particles creates some additional correlations at middle interparticle distance ~40nm (Fig.1b).

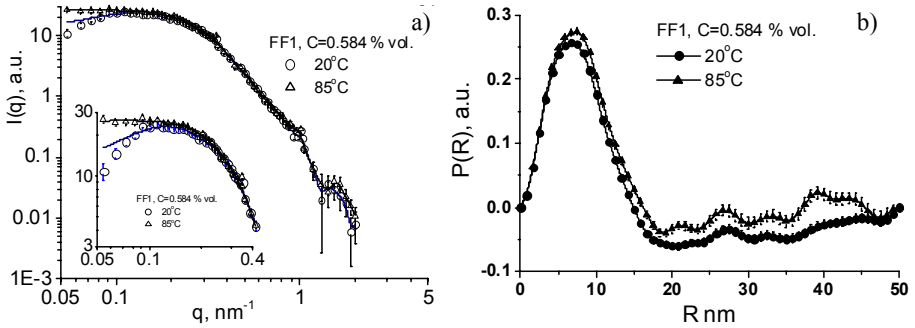

Fig. 1 – a) SANS-patterns, magnetite content C = 0.6%.vol%, T = 20o, 85°C (the part of data at q=0.05-0.4 nm^{-1} is inserted); b) The P(R) function at C=0.6%., T=20°; 85°C.

At a moderate content of magnetite (C~ 4-14% vol., Figs. 2-4) a short range order is more pronounced than at low concentration. However, the ordering is more stable and weakly influenced by temperature.

Correlation functions in all the samples show a strong maximum at R_{m1}~7nm corresponding to the radius of the core R_{m1}~Ro. At a doubled distance ~$2R_{m1}$ the correlation function approaches zero because of the limited core correlation length L≤2Ro~$2R_{m1}$. The core is covered by a double surfactant layer (thickness δ~4nm).

Therefore the forbidden distances are 2Ro < R < 2(Ro+δ)~20nm if shells repulse and do not interpenetrate. Indeed in diluted FF we observe a minimum of correlation function at R~15-20 nm for low and moderate concentrations, C=4-14% vol. (Figs. 2-4). At these concentrations a short range order exists that is proved by well defined maximum at Rmax ~25-30 nm >2(Ro+δ).

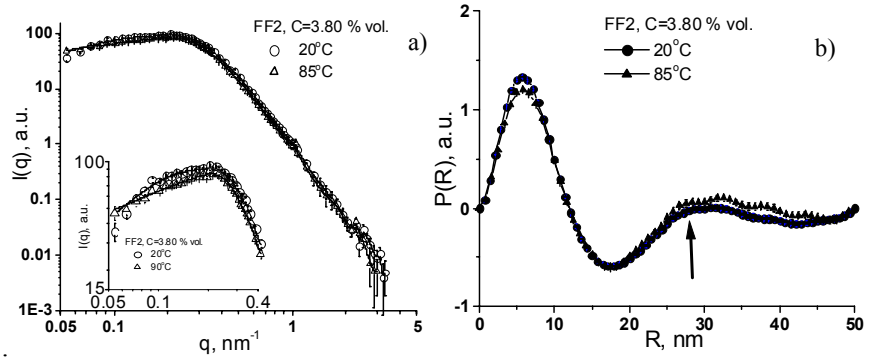

Fig. 2 – a) The SANS-patterns at C = 3.8% vol., T= 20°; 85° C (the part of data at q = 0.05-0.4 nm^{-1} is inserted); b) The P(R) function found at C= 3.8%., vol., T= 20°; 85° C.

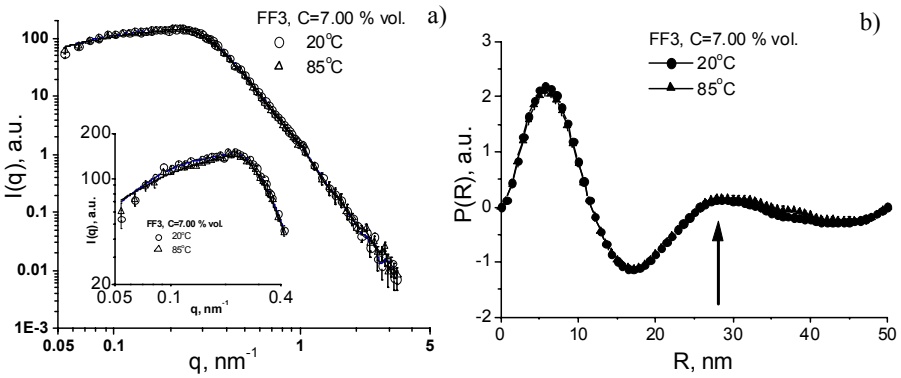

Fig. 3 – a) SANS-data at C=7% , T= 20° and 85°C (insert: data part at q=0.05-0.4 nm^{-1});
b) The P(R) function obtained at C=7%, % vol., T= 20° and 85° C.

At the highest amount of magnetite (C~20% vol.) the interference effects are damped. We interpret this as a result of particles shells interpenetration near the upper limit in the magnetic phase content. The spacing between particles gets a minimum value Rmax ~18 nm < 2(Ro+δ). At C~20% vol. the temperature practically does not disturb the particles arrangement.

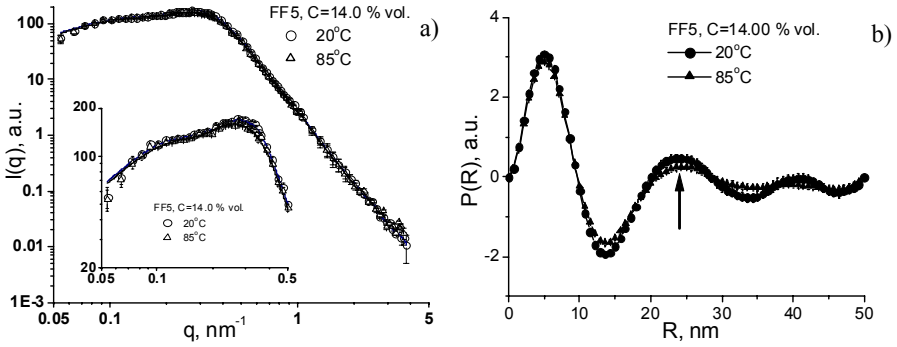

Fig. 4 – a) SANS-patterns at C = 14.0, %, T= 20° and 85°C. (insert: data at q=0.05-0.4 nm^{-1});
b) The P(R) function found at C=14.0, % vol., T= 20° and 85° C.

Oppositely, at low concentration of the magnetic phase we observe a temperature-dependent short range order, but it demonstrates an anomalous behaviour. As we found at the lowest magnetite content, the particles spacing is revealed at high temperature. It means that local interactions (clustering) are destroyed and symmetric repulsive forces (pressure) create an order (C=0.6% vol.). This inverse temperature effect is visible at C=3.8% vol., but at C=7-9% vol. it is not revealed.

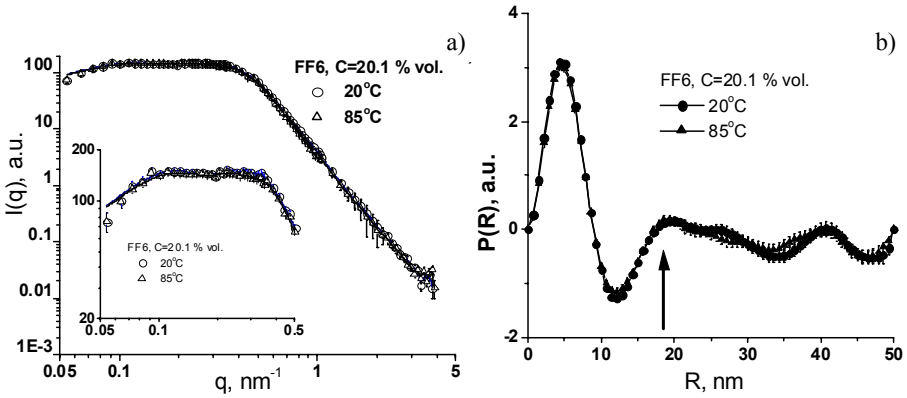

Fig 5 – a) SANS- patterns at C = 20.1vol %, T=20° and 85°C (insert: data at q=0.05-0.4 nm^{-1}); b) The P(R) function obtained at C=20.1 % vol., T= 20° and 85° C.

From the data at high q we found the total surface area of the magnetite cores. At q>>1/Ro in Porod approximation [4] the scattering intensity is equal to $I(q)=A/q^4 + B$. Here the parameter $A \sim 2\pi S_t(\Delta K)^2$ is proportional to the squared contrast factor ΔK and the total surface of particles in the sample. Constant B is an incoherent background. Porod approximation gives Fe_3O_4-particles' surface.

We normalized the measured magnetization of the fluid to the total particles surface and found an anomalous increase of this modified magnetization at C=0.6-7.0% vol. Then at C=9-20% vol. the magnetization maintains at the same level (Fig. 5). This behaviour can be explained by the action of the internal magnetic field, generated by particles ensemble, to each particle. This field induces a higher magnetization of a particle. In weak field (diluted system) the effect of the particles magnetic saturation dependent on their size was observed (surface/volume ratio) and measured by ferromagnetic resonance [5]. As we established, due to the internal field this saturation grows up to a theoretical value (Fig 6).

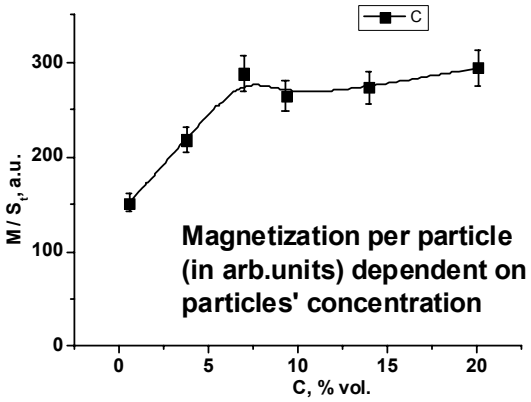

Fig 6 – Magnetization, normalized to the total surface area of particles, vs volume content of magnetite.

4. CONCLUSION

SANS measurements on ferrofluids with different concentrations of magnetite at ambient and high temperature (85°C) showed the evolution of the spatial particles correlations from the rare ensemble of magnetic dipoles slightly correlated to the ordered system of colloidal particles contacting by shells or being tightly packed at the content C~20% vol. when shells interpenetrate. The cross over in the structure leads to anomalous behaviour of the particles magnetisation as dependent on magnetite concentration. Magnetisation reveals the kink at a characteristic concentration C* ~7 % vol. Below the threshold, C<C*, a growth of the particles moment is observed with concentration, while at C≥C* a saturation is achieved.

We proved first the effect of a short range order on the intrinsic magnetic properties of the particles influenced by the internal mean field in magnetised ferrofluid.

REFERENCES

1. L. Cser, L. Rosta, Gy. Török, Neutron Scattering Facilities at Budapest's Modernized Reacto Neutron News 4, No. 2, p. 9–15, (1993).
2. D. Bica, L. Vekas, M. Rasa, Journal of Magnetism and Magnetic Materials, 252 (2002), 10.
3. D. Svergun, J.Appl Cryst 25, (1992).
4. D.I. Svergun L.A. Feigin, *Rentgenovskoe i Neitronnoe Malouglovoe Rasseyanie (Small-Angle X-ray and. Neutron Scattering)*, Moscow: Nauka, 1986. [Translated into English (New York: Plenum Press, 1987)].
5. F. Gazeau, J.C. Bacri, F. Gendron, R. Perzynski, YU.L. Raikher, V.I. Stepanov, E. Dubois, Magnetic resonance of ferrite nanoparticles:evidence of surface effects Journal of Magnetism and Magnetic Materials, 186 (1998), 175–187.
6. O. Glatter; D Orthaber, A. Stradner, G. Scherf, M. Fanun, N. Garti, V. Clement, M E. Leser, Sugar-Ester Nonionic Microemulsion: Structural haracterization//Journal of Colloid and Interface Science 241, 215–225, (2001).