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TEMPERATURE DEPENDENT STRUCTURE OF THE CoFe$_2$O$_4$ COLLOIDAL SOLUTIONS INVESTIGATED WITH SANS

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1.INTRODUCTION

Colloidal solutions , in this case ferrofluids [1], exhibit a remarkably rich variety of behaviors and their study has been and remains very active, beeing perceived to open new technological frontiers [2-4]. To understand the fundamental reasons for the interesting macroscopic properties of these systems, it is necessary to know the structure of the colloidal particles at the microscopic level, and how this structure is influenced by the action of certain external parameters. One of the most powerful techniques which was envolved is small-angle neutron scattering (SANS). This is particularly well suited to the study of magnetic colloids, because of the peculiar features of their magnetic interaction with neutrons which permits the determination of the colloidal dispersion structure under a wide variety of experimental conditions.The neutron scattering methods have largely been used in the last two decades for the determination of structural properties of ferrofluids at a microscopic level [5 - 17] . There were investigated the structure of the particle [5,6,7,8], the aggregation phenomena [5,9,11,13], the ferrofluid dynamics [13,14], particle - surfactant interaction and the surfactant liquid - base interaction [5,16], magnetic dimension of the particles [17].

The ferrofluid is a colloidal dispersion of magnetic subdomain particles of about 100A in diameter in a suitable liquid carrier [1]. For a ferrofluid to remain stable, it is essential that the particles are sufficiently small so that Brownian motion opposes any tendency for particle agglomeration and sedimentation. If these effects take place the desirable characteristics of the liquid will be destroyed. The interparticle interactions which promote agglomeration arise from magnetic and London type Van der Waals forces, whereas sedimentation arises from gravitational fields and magnetic field gradients. In the case of particles in non-metallic carriers as it is in our case, an entropic or steric repulsion can be introduced by coating the particles with long chain
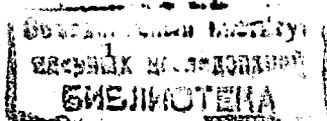
molecules, which overcome the attractive forces at short distances enabling thermal agitation to maintain the particles dispersed.

In this paper we present our preliminary results of the investigation of the modification of the internal structure of the $CoFe_2O_4$ colloidal solution due to the variation of the temperature.

2.EXPERIMENTAL

The cobalt ferrite ($CoFe_2O_4$) ferrofluids were prepared in benzene (C_6H_6) as carrier, with oleic acid ($C_{18}H_{34}O_2$) as surfactant, by the coprecipitation method. The size distribution of cobalt ferrite particles was analyzed by EM. The distribution has a log - normal form with a standard deviation of 6A and the most probable particle diameter of 163A.

The samples were diluted by measured quantities of benzene to give an overall particle volume fractions of 1%. The experiment consisted from two parts:

a) in the first part of the experiment the D-benzene volume fraction in the carrier , x , was produced to take the following three values: 0.0, 0.2 and 0.5. The measurements were made at two values of the temperature: 21.5^0C and 40^0C;

b) in the second part of the experiment there was measured only the magnetic liquid sample based on H-benzene carrier and the temperature values were chosen on the base of the following considerations:

- the temperature of 4.2^0C is below the value of the freezing temperature of the liquid carrier (benzene) and oleic acid in free state;

- the temperature of 9.8^0C is above the value of the melting temperature of the benzene but it is still below the freezing temperature of oleic acid;

- the temperature of 35^0C is above the values of the melting temperature both of benzene and oleic acid.

SANS experiments were performed at IBR-2, JINR- Dubna, using MURN facility with the white beam of incident neutrons and the time of flight detection method.

2.SMALL ANGLE SCATTERING DATA ANALYSIS

The SANS experiments consist in measuring, for each value of x, $I_s(Q)$, the scattered intensity as a function of the momentum transfer, Q:

$$Q = (4\pi / \lambda) \sin(\theta /2),$$

where λ is the neutron's wavelength and θ is the scattering angle.

Runs were also performed on all the compositions of carrier liquids, free of particles, measuring in such a way $I_c(Q)$. According to the procedure described in [18] were obtained $(d\Sigma/d\Omega)_s$ and $(d\Sigma/d\Omega)_c$,the differential elastic coherent scattering cross-sections per unit solid angle and unit sample volume, of the ferrofluids (subscript s) and, respectively, of the carrier liquid (subscript c).The difference between them is the excess scattering power of colloidal particles $d\Sigma/d\Omega$.

In our situation, where colloidal particles are in suspension, we have to consider the scattering length density of the particles and that of the solvent. When the density and chemical composition of the colloidal particles are known and interatomic exchange between particles and solvent are negligible, the important quantity is the difference $K= \rho_p - \rho_0$ (named the contrast) between the coherent scattering lengths densities of the particle (ρ_p) and of the solvent (ρ_0).

If we suppose the situation of N homogeneous, monodisperse and centrosymetric particles, for each particle, a, we can consider its centre of mass, R_a, and the distribution of nuclei in the particle. Taking into account the low spatial resolution of SANS experiments, and that the solvent contribution is taken as a background, the scattering lengths can be replaced by the contrast K. If the intramolecular averages are independent of the intermolecular averages, the nuclear

differential scattering cross-section per particle, $d\Sigma(Q)/d\Omega$ can be separated in three factors:

$$d\Sigma(Q)/d\Omega = \phi\, P(Q)\, S(Q),$$

where $\phi = N/V_0$ is the density of particles in the volume V_0 of the sample. $P(Q)$ concerns each particle and is related to its form factor, $F(Q)$, by:

$$P(Q) = <|\,F(Q)|^2>,$$

with

$$F(Q) = \int (\rho - \rho_0)\exp(iQr)dV$$

and $S(Q)$ is the interparticle term, the structure factor, related to the spatial distribution of the centres of mass:

$$S(Q) = <\Sigma_{a,b}\, \exp[iQ(R_a - R_b)]>.$$

The separation of these factors is not always possible and can be done only within some hypothesis.

2.1.Guinier Approximation

For dilute systems of randomly oriented particles (neglecting size polydispersity), when $S(Q) = 1$, in the region of small Q values ($QR_g < 1.2$), Guinier's law applies and the cross section of the scattering is given by the relation:

$$d\Sigma(Q)\,/d\Omega = [d\Sigma(0)/d\Omega]\,\exp(-R_g^2 Q^2/3), \qquad (1)$$

where $d\Sigma(0)/d\Omega$ is the scattering at zero angle and R_g is the radius of gyration of the particle i.e., the root-mean-square distance of all scattering elements from the center of gravity. If this approximation holds, the plot $\ln[d\Sigma(Q)\,/d\Omega]$ versus Q^2 should show a linear region for small Q.

The characteristic size of a particulate system can be easily obtained within this approximation. For instance, for spherical particles, one can relate the physical radius of the particle R with the radius of gyration by the relation $R = (5/3)^{1/2}R_g$. However, interparticle interference effects should be negligible for this approximation to hold.

3.RESULTS AND DISCUSSION

a) The scattered intensities were extrapolated to zero momentum transfer using the Guinier approximation and subsequently reduced to scattering amplitudes by taking the square root.

The linear dependence of the beginning part of the curve $\ln[d\Sigma(Q)/d\Omega]$ versus Q^2 for the H-benzene magnetic liquid sample allows to obtain the radius of gyration for the temperature of 21.5^0C and 40^0C (Tab.1).

Tab.1

Temperature, ^{0}C	Radius of gyration, Å	Hydrodynamic radius of the particle, Å
21.5	33.63 ± 5.56	43.41 ± 7.17
40	33.91 ± 5.92	43.77 ± 7.64

b) The linear dependence of the beginning part of the curve $\ln[d\Sigma(Q)/d\Omega]$ versus Q^2 allows to obtain the radius of gyration for the temperature of 4.2^0C, 9.8^0C and 35^0C (Tab.2).

Tab.2

Temperature, ^{0}C	Radius of gyration, Å	Hydrodynamic radius of the particle, Å
4.2	30.30 ± 7.25	39.11 ± 9.35
9.8	31.06 ± 3.67	40.09 ± 4.73
35	41.66 ± 5.42	53.79 ± 6.99

It can be seen that the modification of the radius of gyration, consequently of the hydrodynamic radius is very small for the increasing of the temperature from $21.5\ ^0$C to $40\ ^0$C. The variation of R_g and R_h is more significant when the sample
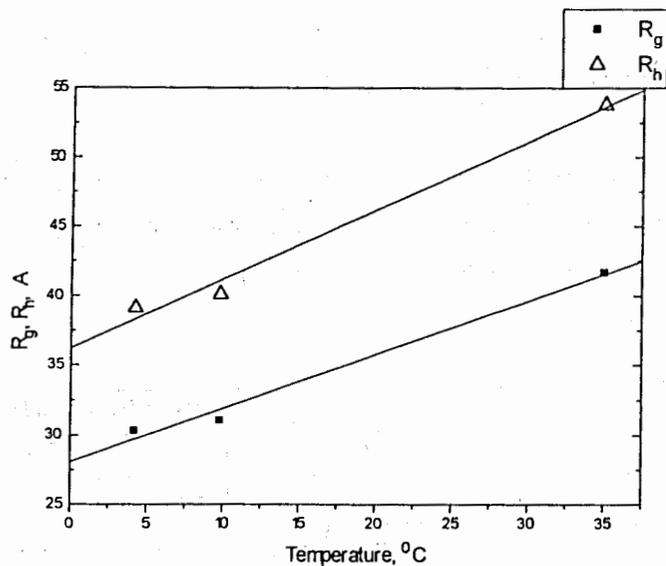
Fig. The linear dependence with the temperature of the radius of gyration, R_g (a) and of the hydrodynamic radius, R_h (b) of the 1% $CoFe_2O_4$ particle volume concentration benzene based magnetic liquid

first is cooled down to 4.2 °C and then the temperature is increased to 9.8 °C and 35 °C.

The variation of the temperature changes the equilibrium of the interactions between the system's components and determines the following effects on the structure of magnetic liquid:

1) The Van der Waals attraction between the chains of the oleic acid molecules chemisorbed on the surface of the same particle, more effective when the temperature is lower, determines the bending of the oleic acid molecules' tails. The result is the fact that the surfactant layer became thinner.

2)The strength of the dipole - dipole interaction between the particles increases with the diminuation of the temperature; the particles come closer one to the other. As result the surfactant shells of the particles interpenetrate and also determine the lowering of the thickness of the surfactant shell, the particles come closer one to the other and it is possible to form clusters.

For the experiment a, the explanation for the obtained different R_g and R_h values for different temperatures consists in the bending or partial bending of the surfactant tails adsorbed on the surface of the same particle due to the Van der Waals attraction between the long chains of the oleic acid molecules.

For the experiment b, first temperatures are so low that both the phenomena occur: the bending and the interpenetration of surfactant chains. This fact explains the obtained smaller values of R_g and R_h at 4.2 °C and 9.8 °C than at 21.5 °C from the experiment a. An explanation for the obtained results at 35 °C in this case is the possibility that with the increasing of the temperature the thermal motion overcomes the attractive forces at short distances and enables to maintain dispersed not particles but dimers.

The linear fit of the values of the radii of gyration obtained for these last values of the temperature gives the possibility to obtain the following relations for the variation of the radius of gyration $R_g(t)$ and the hydrodynamic radius $R_h(t)$ of the system with the temperature (Fig.1):

$$R_g(t) = 28.0569(1 + 0.01371t)$$
$$R_h(t) = 36.2103(1 + 0.01372t) .$$

These experiments help to understand the temperature dependent microstructure dynamics of the magnetic liquids.

To come down to a final conclusion it will be necessary further to make an experiment which will permit to determine the characteristic sizes of the system for a complete cycle on the temperature scale - a " temperature hysterezis ".

4. ACKNOWLEDGEMENTS

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Температурная зависимость структуры коллоидных растворов
$CoFe_2O_4$ по данным малоуглового рассеяния тепловых нейтронов

Представлены предварительные результаты по исследованию изменения структуры коллоидов $CoFe_2O_4$ в связи с вариацией температуры методом малоуглового рассеяния тепловых нейтронов. Измерения были проведены при температуре 21,5; 40; 4,2; 9,8; 35 °C. Изменение радиуса гирации системы, полученного из аппроксимации Гинье, а также гидродинамичного радиуса, с уменьшением температуры можно объяснить двумя эффектами: 1) ван-дер-ваальсовы силы притяжения между длинными хвостами молекул олейновой кислоты, адсорбированных на поверхности одной частицы, искривляют их, и слой сурфактанта становится тоньше; 2) рост дипольного взаимодействия между частицами вызывает проникновение слоев сурфактанта соседних частиц.

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Temperature Dependent Structure
of the $CoFe_2O_4$ Colloidal Solutions Investigated with SANS

In this paper we present our preliminary results of the investigation of the modification of the structure of the $CoFe_2O_4$ colloids due to the variation of the temperature by means of small angle neutron scattering. The modification of the radius of gyration of the system obtained in the Guinier's approximation, consequently of the hydrodynamic radius, with the variation of the temperature is explained by two phenomena: the Van der Waals attraction between the long tails of the oleic acide molecules adsorbed at the surface of the same particle, determining the surfactant layer to became thinner, and the interpretation of the surfactant shells due to the increasing of the dipole-dipole interaction between the particles with the lowering of the temperature.