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Structural Studies of Ferrofluids by Small-Angle Neutron Scattering

M.Balasoiu[a,b], M.V.Avdeev[a], V.L.Aksenov[a], V.Ghenescu[b], M.Ghenescu[b], Gy.Torok[c],
L.Rosta[c], D.Bica[d],
L.Vekas[d], D.Hasegan[b]

[a]Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia
[b]Institute of Space Sciences, Bucharest, Romania
[c]Research Institute for Solid State Physics and Optics, Budapest, Hungary
[d]Center for Fundamental and Advanced Technical Research, Timisoara, Romania

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Abstract. The aim of this paper is to present method to investigate the properties of magnetic fluids by means of small angle neutron scattering. Ferrofluids are dispersions of small, single-domain magnetic particles suspended in a fluid carrier.

The neutron scattering methods have been largely used the last two decades for the determination of structural properties of magnetic liquids at microscopic level. There can be investigated the structure of the particle, the aggregation phenomena, the magnetic liquid dynamics, particle-surfactant interaction, surfactant liquid-base interaction and structure, magnetic behavior of the samples.

Experiments on small angle neutron scattering were carried out on SANS instrument YuMO in function at IBR-2 high-pulsed reactor at the Frank Laboratory of Neutron Physics, Joint Institute of Nuclear Research, Dubna, Russia.

Keywords: Neutron, Ferrofluids, SANS, Magnetic particles

INTRODUCTION

Colloidal suspensions of single domain magnetic particles of about 100Å in diameter, stabilized with a surfactant shell in a suitable liquid carrier, known as Ferro fluids [1], exhibit a remarkably rich variety of behaviors and their study remains very active [2]. 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 were involved, 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. There can be investigated the structure of the particle, the aggregation phenomena, the magnetic liquid dynamics, particle-surfactant interaction and the surfactant liquid-base interaction, magnetic dimension of the particles [3].

We present our investigations on ferrofluids performed for several years at different small-angle facilities including the YuMO time-of-flight diffract meter at the IBR-2 pulsed reactor at the Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research (Dubna, Russia), SANS instrument at VVR-SM steady-state reactor at the Research Institute of Solid State Physics and Optics (Budapest, Hungary).

EXPERIMENTAL

The general theory of the scattering of thermal neutrons (see [4]) shows that the differential scattering cross section $d\Sigma/d\Omega$, can be considered with good approximation, a function of momentum transfer, **q**.

$$d\Sigma(\mathbf{q})/d\Omega = (1/V)\, \Sigma_{kl}\, b_k\, b_l < e^{i\mathbf{q}\mathbf{r}_k}\, e^{-i\mathbf{q}\mathbf{r}_l} > \qquad (1)$$

In the small angle neutron scattering experiment we measure $d\Sigma/d\Omega$, the differential scattering as a function of q, the momentum transfer:

$$q = (4\pi / \lambda) \sin(\theta /2) \qquad (2)$$

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

From the relation (2) it can be seen that to obtain the dependence $d\Sigma(\mathbf{q})/d\Omega$ there can be measured or the scattering angle θ, or the wavelength λ, or both parameters. So, there can exists two possibilities to measure $d\Sigma/d\Omega$:

1) with q variation, by the variation of angle θ for λ kept constant;

2) with q variation, by the variation of wavelength λ (meanning variation of the speed of the incident neutrons on the sample, for θ kept constant.

In our experiments we have used both these methods to measure $d\Sigma(q)/d\Omega$, using a steady reactor (VVR-SM) and a pulsed source (IBR-2). Besides the high level characteristics of the neutron sources, also the used experimental instruments (Fig.1 and. Fig.2) presented performant parameters as shown in Tab.1 and Tab.2.

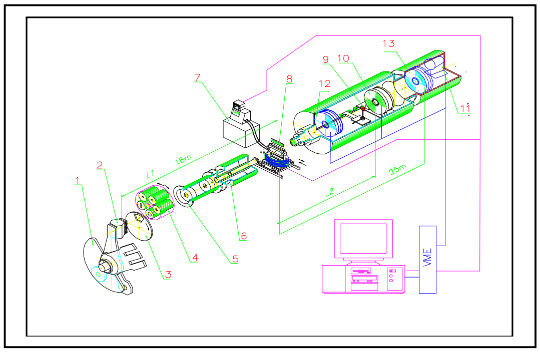

Fig.1 - YuMO SANS TOF diffractometer in function at IBR-2 reactor [5, 6]: 1) movable reflector; 2) moderator/cold moderator; 3)

chopper (adapted to cold moderator); 4) first collimator; 5) vacuum tube; 6) second collimator; 7) liquid bath thermostat; 8) V, graphite, H_2O standards; 10) second circular detector (PSD) of thermal neutrons; 11) detector of direct beam; 12) first circular detector of thermal neutrons; 13) third circular detector of thermal neutrons.

The parameters characterizing the diffractometer are collected in the Table 1

Table 1

Monochromatization:	Time of flight method
Used wavelength	0.5A to 8A $^{\#}$
Q-resolution	Low, 5-20%
Size of beam on the sample	8-22 mm^2 $^{\Sigma}$
Transferred momentum range:	7x10^{-3} - 0.5 A^{-1}
Flux on the sample (thermal neutrons)	10^7-4x10^7 n/(s cm^2) [1]
Detectors	He^3 -fulfiled, home made preparation, 8 independent wires
Detector (direct beam)	^{6}Li-convertor (home made preparation)
Sample environment	Thermostatted sample changer, electromagnet, pressure camera

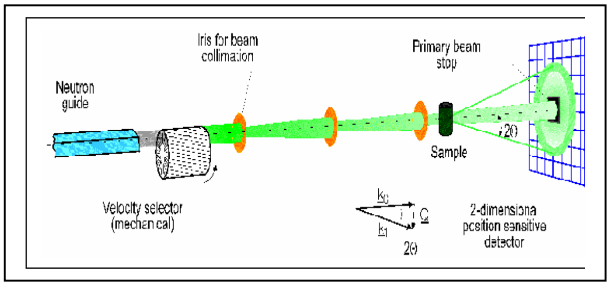

Fig.2 - SANS diffractometer in function at VVR-SM steady reactor [7].

The parameters characterizing the diffractometer are collected in the Table 2:

Table 2

Monochromator:	Mechanical velocity selector
Incident wavelength:	3 - 24 Å
Wavelength spread:	usually 12 – 30%
Maximum beam size at sample:	16 mm diameter
Transferred momentum range:	0.004 - 0.5 Å^{-1}

The studied ferrofluid was produced at the Laboratory of Magnetic Fluids, CFATR, Timisoara, Romania [8,9].

RESULTS AND DISCUSSIONS

The contrast variation method, applied in a small angle scattering (SANS) experiment, was used to simultaneously obtain information about molecular and magnetic structure of diluted magnetite/C_6D_6 ferrofluids. There it was shown that the separate determination of the contribution of nuclear and magnetic interactions to scattering patterns may be accomplished even with unpolarized neutrons, i.e. in the absence of any perturbation produced by an external magnetic field, otherwise involved in the usual methods with polarized beams [10, 11].

The effect of the colloidal particle concentration on the structure of the magnetite/C_6D_6 ferrofluid stabilized by oleic acid was investigated by SANS (Fig.3). The thickness of surfactant shell is the key parameter, which determines the stability of the fluids. It was shown that in the case of the magnetite/oleic acid/benzene ferrofluid the thickness of the surfactant layer (monolayer of oleic acid around magnetite particles) changes significantly when changing the magnetite concentration. A significant decrease in the thickness of the surfactant layer with increase in the magnetite concentration was observed when the concentration of particles increases within an interval of 0.1-19 vol. %. The magnetic scattering in the system was not taken into account, but the model curves fitted well to experimental ones, which points to a small effect of the magnetic scattering in the studied systems[12-15].

The situation is more complicated in ferrofluids based on polar solvents [13, 16-18], in particular, water.

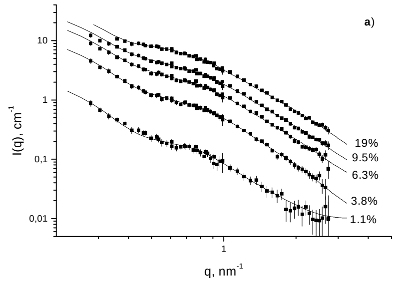

Fig.3 - Experimental (points) and model (lines) scattering curves at different magnetite concentrations indicated to the right of the graph. Magnetic scattering was not taken into account when fitting.

In the case of the magnetite/dodecylbenzenesulphonic acid/water ferrofluid the large interpenetration between sublayers of the double surfactant layer (dodecylbenzenesulphonic acid around magnetite particles) was detected which does not change much with the concentration [15].

Further, it was also studied in this systems the magnetic scattering by the analysis of the anisotropic SANS patterns from ferrofluids in a magnetic field. The isotropic A(q) and anisotropic B(q) contributions to two-dimensional scattering patterns were separated according to the expression:

$$I(q, \varphi) = A(q) + B(q) \sin^2\varphi, \qquad (3)$$

where φ is the angle between the direction of the applied magnetic field and scattering vector[15,19].The specific anisotropy appears in the scattering and in the case of magnetization saturation the isotropic and anisotropic parts of the scattering correspond to nuclear and magnetic contributions, respectively.

The comparison of the nuclear and magnetic scattering from the benzene-based ferrofuid with the magnetite concentration c_m=5 vol. % is presented in Fig.4. It was surprising that the *B*(*q*) function is not fitted by the model of simple polydisperse spheres corresponded to the magnetic core of the colloidal particles in ferrofluids. The reason for this is unclear for us at the moment, which requires the further analysis and experiments.

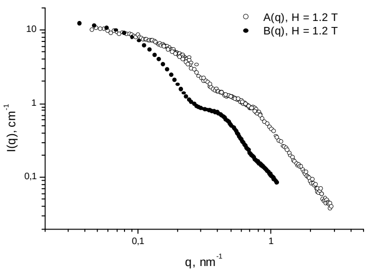

Fig.4 - A(*q*) and B(q) functions at saturation magnetization for the the benzene-based ferrofuid with the magnetite concentration c_m=5 vol. %. In this case A(q) and B(q) correspond to nuclear and magnetic scattering, respectively.

The analysis of the effect of interparticle interaction, as well as of the magnetic scattering, on the accuracy of the structural parameters require additional experiments and special preparation of samples.

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