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USE OF SMALL-ANGLE NEUTRON SCATTERING IN TESTING THE STABILITY OF FERROFLUIDS

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Использование малоуглового рассеяния нейтронов
в тестировании стабильности магнитных жидкостей

Стабильность магнитных жидкостей — дисперсий магнитных частиц в жидкостях, стабилизированных поверхностно-активными веществами (ПАВ), — является главной характеристикой, которая определяет возможность эксплуатации данных систем в различных индустриальных и биомедицинских приложениях. В настоящей работе предложено использовать метод малоуглового рассеяния тепловых нейтронов (МУРН) для выявления агрегации коллоидных частиц в магнитных жидкостях и ее изменения со временем при воздействии внешнего магнитного поля. Несмотря на то, что в большинстве случаев детальное описание рассеяния довольно сложно, об устойчивости магнитной жидкости при включении/выключении внешнего магнитного поля можно судить по изменению в средней интенсивности рассеяния. Преимущества МУРН при тестировании стабильности магнитных жидкостей состоят в том, что промышленные образцы могут быть проверены без любых дополнительных модификаций. Также могут быть легко реализованы эксперименты в реальном времени с любой магнитной нагрузкой. Предлагаемая методика иллюстрируется на примере нескольких магнитных жидкостей.

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Use of Small-Angle Neutron Scattering
in Testing the Stability of Ferrofluids

Stability of ferrofluids — colloidal solutions of magnetic particles covered with surfactants — is the main characteristic that determines the possibility to exploit ferrofluids in different industrial and biomedical applications. Small-angle neutron scattering (SANS) can be effectively used to reveal the aggregation and its change with time in ferrofluids under the action of magnetic field. Despite the fact that in most cases the detailed description of scattering is complicated, one can judge whether a ferrofluid is stable or not by simple analysis of changes in the mean scattering intensity. The advantages of SANS are that industrial samples can be tested without any additional modifications, as well as the real-time experiments with any magnetic load can be easily performed. Examples for a number of ferrofluids are given.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

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Ferrofluids, fine stable dispersions of magnetic materials in liquids, find a wide range of applications in many technical and industrial fields [1] such as mechanical devices (dampers, high vacuum seals, bearings, actuators, valves, switches), separators, technical acoustics, measuring devices and sensors, printing equipments, electromagnetic defectoscopy and others. Much promises are connected with the development of their applications in medicine [2] for magnetic drug targeting and delivering, magnetic fluid hyperthermia, magnetic resonance imaging. Stability under different regimes of external magnetic load in a specific device determines the possibility to exploit ferrofluids during long periods of time. In this connection the development of methods which could test the ferrofluids in what concerns the presence of aggregates and their changes in time is of current interest. In our paper the method of small-angle neutron scattering (SANS) is proposed to be used for this purpose. From the analysis of the change in the mean SANS intensity one can check out whether the significant aggregation effects take place in a fluid and at what time and how fast they appear.

Ferrofluids (Table 1) with magnetite dispersed in nonpolar and polar carriers for SANS experiments were synthesized [3] at the CFATR (Timisoara, Romania). SANS experiments at RT were carried out on the small-angle diffractometer at the Budapest Neutron Center (Hungary).

Table 1. Investigated fluids with single/double stabilization by oleic acid (OA), dodecylbenzenesulphonic acid (DBS), lauric acid (LA)

Sample	Carrier	Stabilizers	Magnetite
1	Benzene	OA	5.0 vol. %
2	Pentanol	OA + DBS	6.5 vol. %
3	Water	LA + LA	4.2 vol. %
4	Water	DBS + DBS	2.1 vol. %
5	Water	LA + DBS	6.5 vol. %
6	Sap	OA + OA	4.4 vol. %

Measurements were made in the stages «no field» (initial sample in the absence of magnetic field), «field on» (magnetic field of 1.2 T is turned on), «field off» (magnetic field is turned off after some period). No special control over the field rise and reduction was accomplished, they were performed manually during several seconds.

The comparison of the SANS curves (Fig. 1) obtained at the stage «no field» for different ferrofluids with the curves calculated according to the fit of spherical core-shell model (quasispherical magnetic particles covered by surfactant shells) reveals that only the benzene-based ferrofluid (sample *1*) satisfies the model (Fig. 1, sample *1*). It was shown [4] that for the given fluid this model works well in a wide interval of momentum transfer ($0.05 \div 5$ nm^{-1}), and no significant effects of aggregation and interparticle interaction are observed for the magnetite fraction up to 5 vol. %.

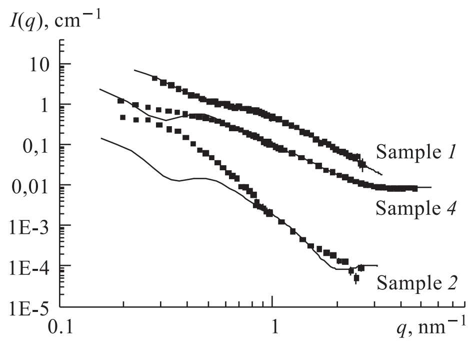

Fig. 1. Experimental SANS curves and model curves calculated according to the core-shell model. Intensities of samples *4* and *2* are divided by factors 10 and 100, respectively

The magnetic scattering contribution was found to be small [4] in comparison with the nuclear one. In the absence of the magnetic field it is isotropic like nuclear scattering. In the stage «field on» a specific anisotropy over the radial angle φ in the magnetic scattering results in a decrease in the mean scattering intensity (Fig. 2, a). Using 2D scattering pattern for the saturated sample the nuclear and magnetic scattering contributions can be separated [4, 5]. Their summation in the proportion [5] corresponding to the state «no field» coincides with the experimental scattering curve obtained in this state, which means that there are no changes in the structure of the fluid under magnetic field. The multiple repetition of the magnetic load results in the same behavior of the scattering intensity (Fig. 2, a). So, such behavior distinguishes highly stable ferrofluids.

For the polar carriers, alcohol and water, the situation is more complicated, since a significant difference between the expected and observed scattering curves exists (Fig. 1, samples *2*, *4*). The reason for this can be connected either with a specific, preexisting aggregation in initial samples or with interaction between colloidal particles in ferrofluids, whose origin is to be clarified. The scattering in the magnetic field is quite different for different samples. For the alcohol-based (sample *2*) and two water-based ferrofluids (samples *3*, *4*) these are similar to the previous case, which indicates to the high stability of these fluids. For other water-based ferrofluids (samples *5*, *6*) in the stage «field on» the scattering is still isotropic and the mean scattering intensity increases (Fig. 2, b, c). It can be interpreted [6] as a reflection of the formation of aggregates caused by the magnetic field, which means that the given fluids are less stable than the previously discussed samples. The absence of the anisotropy in the scattering when the fluid is under the magnetic field means that the additional scattering from aggregates is significantly larger than the magnetic scattering contribution. This fact allows one to detect definitely the formation of aggregates in the fluids in the stage «field on». From Fig. 2, b, c one can judge that the changes in the scattering in the stage «field on» have two regimes. Fast increase takes place in the first minutes, and then it slows significantly. In our previous work it was shown [6] that such behavior can be interpreted in terms of formation of elongated aggregates. It is concentration dependent [6] (Fig. 2, b). Right after the magnetic field is turned off (the stage «field off») the mean scattering intensity shows again an increase in the aggregation (Fig. 2, c).

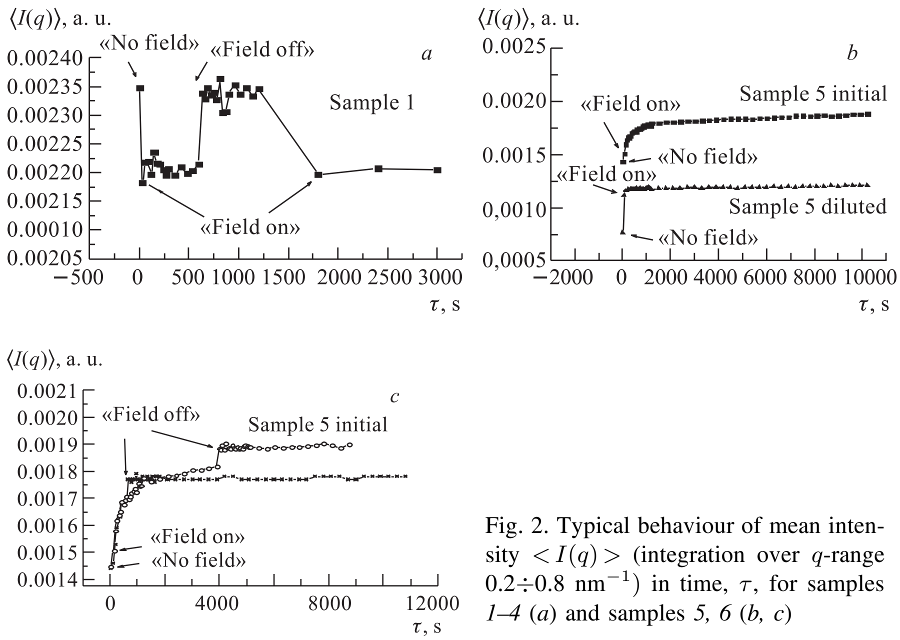

Fig. 2. Typical behaviour of mean intensity $< I(q) >$ (integration over q-range 0.2÷0.8 nm^{-1}) in time, τ, for samples *1–4* (a) and samples *5, 6* (b, c)

So, two characteristic behaviors of the mean scattering intensity allows one to separate stable and unstable ferrofluids with magnetic particle fraction of less than 7 vol. %. For higher concentrations it may happen that the effect of aggregation will be compensated by that of magnetic scattering. To clarify this question the design of water-based ferrofluids with higher concentration is in progress.

Comparison [7] of the presented technique to test the stability of the ferrofluids with other methods, such as magnetometry and rheology, shows the consistence of the results obtained by all methods. In respect to neutron scattering we should note that in the course of experiments the regimes of magnetic load close to those used in practice can be easily attained. Along with it no effects but of the magnetic field which could result in structural changes in ferrofluids take place. All this makes the SANS technique promising for nondestructive tests of stability of industrial ferrofluids.

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