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The microstructure of ferrofluids and their rheological properties

L. M. Pop[1]*, J. Hilljegerdes[1], S. Odenbach[1] and A. Wiedenmann[2]

[1]ZARM, Universität Bremen, Am Fallturm, 28359 Bremen, Germany
[2]Hahn-Meitner Institute, Glienickerstr. 100, 14109 Berlin, Germany

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One of the most important features of ferrofluids is the possibility to change their physical properties, especially their viscosity, by means of moderate magnetic fields. This capability makes ferrofluids very useful in the fields of engineering, medicine and fundamental research. Rheological experimental results, as well as theoretical studies, correlate the change of the viscosity of a sheared ferrofluid under the influence of a magnetic field, the so-called magnetoviscous effect, to the internal structure formation under certain external conditions. To obtain information about the microstructure of ferrofluids, experiments using the small-angle neutron scattering (SANS) technique have been carried out. Three magnetite-based ferrofluids with different particle–particle interactions, and thus various magnitudes of the magnetoviscous effect, were investigated. Using a specially designed rheometer, SANS experiments were performed for different shear rates and magnetic field strengths in order to observe the modification of the microstructure in ferrofluids and to associate the SANS information with their macroscopical behaviour. The scattering patterns obtained show a good agreement with the qualitative model that explains the magnetoviscous effect. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: ferrofluids; magnetoviscous effect; microstructure; small-angle neutron scattering; scattering patterns

INTRODUCTION

Experimental investigations[1] of field-induced changes of the viscosity of ferrofluids under shear flow have shown that an increase of the magnetic field strength yields an increase of the fluid's viscosity, the so-called magnetoviscous effect, as seen in Fig. 1a. In the classical theory of rotational viscosity,[2] this behaviour is explained by the hindrance of the free rotation of particles in a shear flow by means of magnetic fields. This theory applies for highly diluted ferrofluids, assuming vanishing interactions between the particles. Furthermore, the particles should be large enough to have the magnetic moments fixed within.

However, the commercial ferrofluids used for most applications are generally concentrated and, therefore, the interaction between the particles cannot be ignored. Rheological measurements show that even ferrofluids having the same volume concentration of the magnetic material, in this case 7.2% of Fe_3O_4, exhibit considerably different magnitudes of the magnetoviscous effect, as seen in Fig. 1a–c. Therefore, the dominant factor that causes the magnetoviscous effect is not the volume concentration; the magnitude of the effect should, moreover, mainly be influenced by the microstructure of the ferrofluid.

To prove the connection between the magnetoviscous effect and the particle–particle interaction in the fluid sample, ferrofluids with different contents of large particles were produced,[3] using the method of magnetic separation. It has been shown that a high content of large particles, i.e. strong interaction between the particles, leads to a high magnetoviscous effect. The large particles are more susceptible to form structures in the ferrofluid than the small ones and, therefore, the influence of their concentration on the magnetoviscous effect can be correlated to the formation of chain-like structures in ferrofluids.[4] Considering the increase of the viscosity with magnetic field strength to be an effect of the hindrance of the free rotation of chain-like structures in the shear flow by means of magnetic fields, the theoretical model shows a good agreement with the experimental results.[3,4] A reduction of the magnetoviscous effect (field-dependent shear thinning), which is found with increasing shear rate, can also

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*Correspondence to: L. M. Pop, ZARM, University Bremen, Am Fallturm, 28359 Bremen, Germany.
E-mail: pop@zarm.uni-bremen.de

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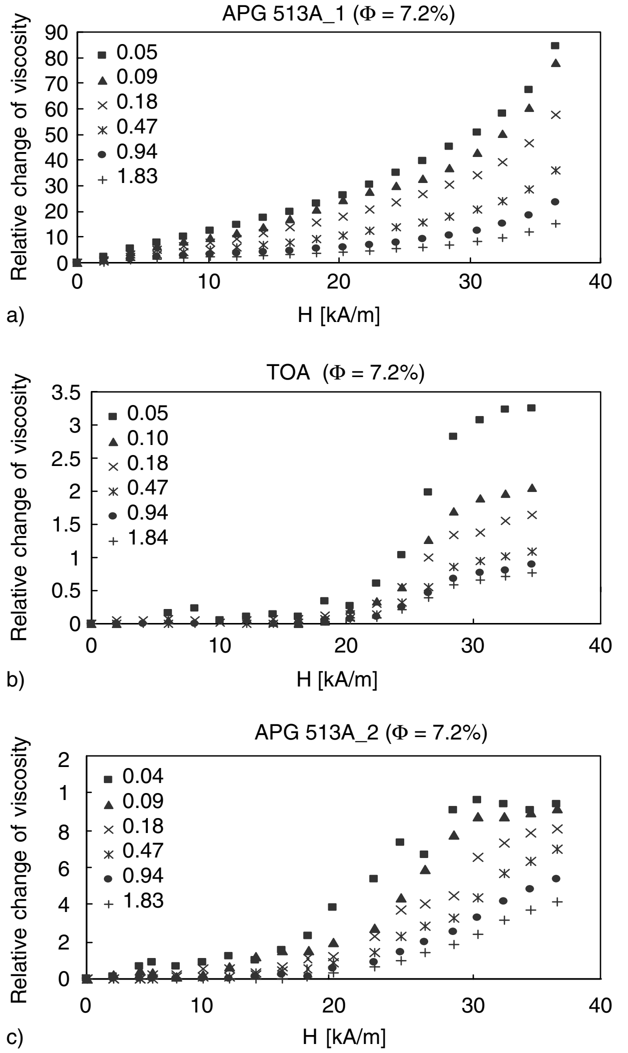

Figure 1. Magnetoviscous effect in the ferrofluid sample used for the SANS experiment.

be explained by this model as a breakage of the chains in the flow. In this model the different magnetoviscous behaviour of the fluids in Fig. 1 can be explained by a different ability for chain formation and, therefore, by a significant difference in their microstructures in the presence of a magnetic field and shear flow.

The aim of this paper is to show that the modification of the microstructure of ferrofluids governs their macroscopical behaviour. To prove the correlation between the formation of chains and the magnetoviscous effect, small-angle neutron scattering (SANS) was used as a direct observation tool.

EXPERIMENTAL SETUP

To point out the connection between the rheological behaviour of ferrofluids and their microstructure, a special rheometer, which can be used for viscosity measurements as well as for the investigation of the microscopic structure of the fluids using SANS, was developed. The rheometer (Fig. 2) is a cone–plate system, which has the advantage of ensuring a constant shear rate overall in the flow, eliminating the problem of the influence of shear rate gradients to structures formed in the ferrofluid. A magnetic field up to 180 kA m^{-1} can be applied perpendicular to the vorticity of the flow, an arrangement in which the magnetoviscous effect is maximal.[4] The shear rate can be varied from 0 up to 450 s^{-1} by rotating the plate while the cone is fixed. The most important feature of the rheometer is given by the fact that SANS experiments can be performed under the same experimental conditions, i.e. magnetic field strengths and shear rates, as the rheological measurements. This enables a determination of the change of the microstructure giving rise to the magnetoviscous behaviour.

QUALITATIVE MODEL

During the SANS experiments, the neutron beam passes the fluid layer perpendicular to the cone–plate system (Fig. 3). The neutrons scattered around the primary beam are registered in a two-dimensional detector. The structure of the scattering pattern obtained at the detector is mainly determined by two components. The nuclear scattering results from the interaction between neutrons and the nucleus of the magnetic particles, while the magnetic scattering is due to the interaction between their magnetic moments and the magnetic moments of the neutrons. The magnetic component of the scattering depends on the azimuth angle between the direction of the magnetic moment of the structures formed and the scattering vector.[5]

Previous rheological investigations of ferrofluids under shear flow and magnetic field strength,[3,4] together with theoretical studies,[6] have established the model of chain formation to explain the magnetoviscous effect. Combining this with SANS theory, a qualitative model to interpret the macroscopical behaviour of the ferrofluid sample and the SANS results is proposed (Fig. 4).

In the static case (Fig. 4a), an applied magnetic field will induce chain-like structures in the ferrofluid, where the chains are aligned with the magnetic field. Since the chains are aligned parallel to the beam, the neutrons will detect the cross-section of the chains' first particle only. A shear flow applied to the fluid sample (Fig. 4b) causes a mechanical torque that diverts the chains from their initial direction while a magnetic torque resulting from the misalignment between the magnetic moment and the field direction counteracts this misalignment.[4] In this situation, the neutrons will detect the projection of the chains and, thus, the nuclear component of the scattering pattern will change. Owing to the deviation of the total magnetic moment of a chain from the initial direction, a modification of the magnetic component of the scattering is expected. A higher shear rate will increase the mechanical torque, resulting not only in an increased misalignment of the

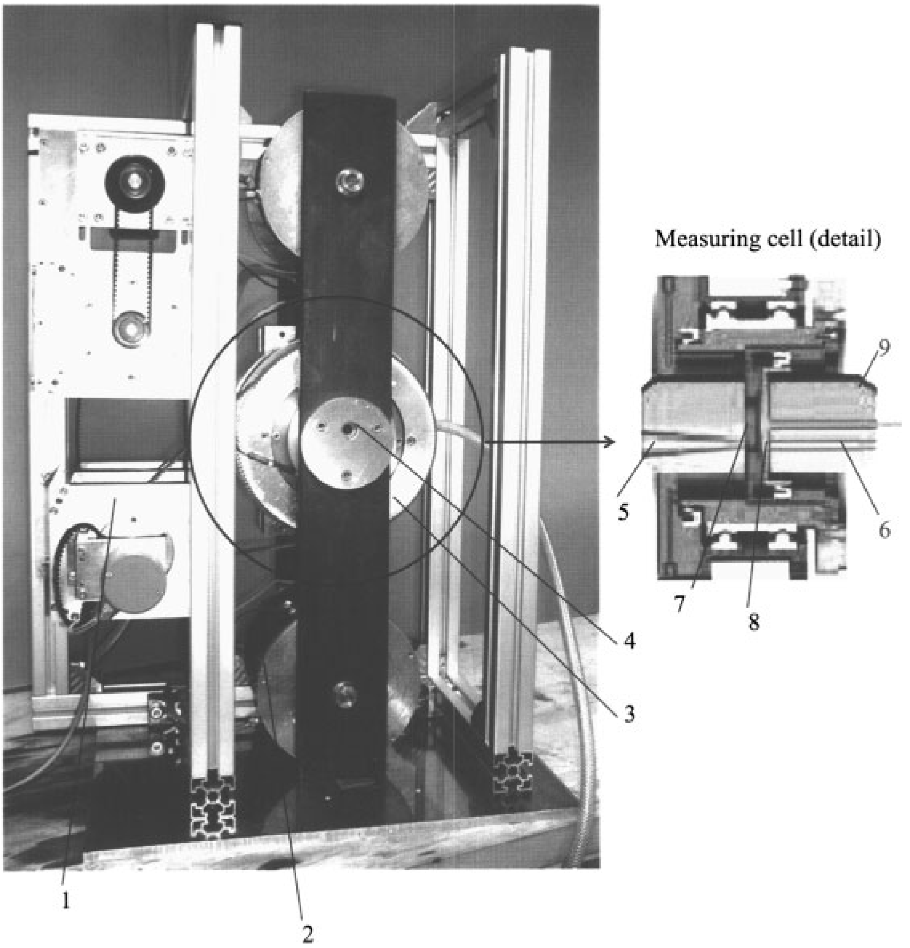

Figure 2. Photograph of the experimental setup for the SANS experiment. 1: drive unit; 2: coil; 3: measuring cell; 4, 5, 6: channels; 7: plate; 8: cone; 9: pole shoe.

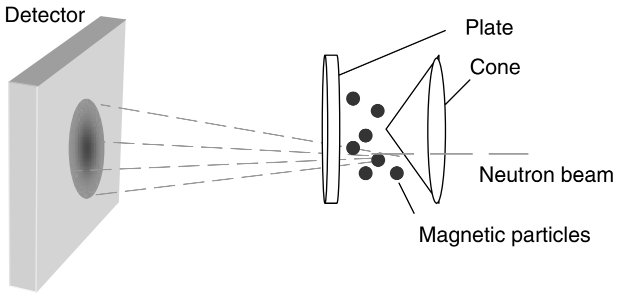

Figure 3. Sketch of the arrangement for the SANS experiment in the rheometer.

chain direction with the direction of the magnetic field but also in a breakage of the chains. Thus, a further change of the scattering pattern is also expected.

We emphasize that other types of particle arrangement, such as field-induced ordered lamellar structures, as observed recently in cobalt ferrofluids,[7] would show qualitatively the same behaviour in the present scattering geometry.

EXPERIMENTAL RESULTS

The first SANS investigations of ferrofluids subjected to a shear flow and a magnetic field were performed with three magnetite-based ferrofluids, two commercial ones (Ferrotec APG513A from two production lines) and an experimental one (TOA, supplied by the Technical University of Timisoara). All three fluids have the same magnetic volume concentration, but a different content of large particles and, therefore, different magnitudes of the magnetoviscous effect, as seen in Fig. 1. The SANS experiments were carried out in a magnetic field range from 0 to 160 $\mathrm{kA\,m^{-1}}$, directed parallel to the neutron beam. Rheological measurements of all three ferrofluids have shown no change of viscosity with magnetic field strength for high shear rates. According to the theoretical model, all chains are broken in this situation and the particles are homogeneously distributed in the fluid. Thus, the fluid can be assumed as being a single particle system here. Therefore, the high shear rate ($\dot{\gamma} = 200\ \mathrm{s^{-1}}$) situation, i.e. the single particle system, has been considered as a reference. To eliminate the contributions of the small

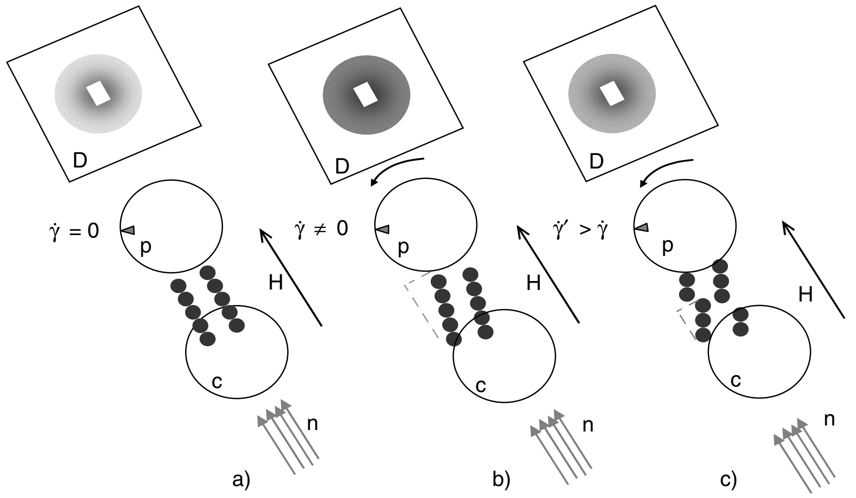

Figure 4. Qualitative behaviour of a ferrofluid assuming formation of chain-like segments under the influence of a magnetic field (a), their misalignment under increasing shear flow (b), ending in disruption at high shear rates (c). D: detector; C: cone; P: plate; *H*: magnetic field; n: neutron beam.

particles, the surfactant and the carrier liquid to the scattering, the reference was subtracted from the scattering patterns obtained for shear rates varied within a range from 0 to 200 s^{-1}. The additional scattering, due to the components which do not influence the magnetoviscous effect, has been removed in this way. The difference pattern will thus only contain information about relevant changes in the structure factor corresponding to the chain-like ordering. The difference patterns obtained for the fluid with high magnetoviscous effect, APG513A_1, indicate a dependence of the scattered intensity on the shear rate and the magnetic field strength (Fig. 5). For a high magnetic field strength and a low shear rate (Fig. 5a) the difference pattern is almost zero. Owing to the high magnetic field, longer segments of chains are formed, but their deviation from the initial direction is very small. Thus, the situation is similar to the static case. Since the cross-sections have almost the same size as those in a single particle system, the difference between this situation and the reference scattering pattern is merely given by a lower concentration of the scattering centres, due to the structure formation in the ferrofluid sample. For higher shear rates (Fig. 5b–d), the deviation of the chains from the magnetic field direction becomes larger and, therefore, their projection, as seen by neutrons, increases. Additional to various nuclear components of the scattering, the magnetic component, due to different projections of the total magnetic moment on the detector plane, will also vary and, therefore, the difference between the scattering patterns and the reference becomes larger. The difference is maximal for the highest shear rate shown here (Fig. 5d), where the field is still strong enough to keep the particles together. The chains are long and, at the same time, due to the high shear rate, strongly deviated from the magnetic field direction. Therefore, the cross-sections of the scattering centres will be significantly different from those in a single particle system, leading to a strong change in the difference scattering pattern. For lower magnetic field strengths and low shear rate (Fig. 5e and i), according to the qualitative model presented above, the influence of the magnetic torque on the chains is weaker than in Fig. 5a. The chains formed due to the influence of the magnetic field strength are shorter. The magnetic torque that acts on the chains, as well as the mechanical torque that diverts the chains from the field direction, will change. An alteration of the ratio between the two effects, the magnetic and the mechanical one, leads to a different deviation angle of the chains in the flow. Therefore, the difference between the scattering patterns and the reference becomes non-zero and shows a minimum for the lowest magnetic field strength presented here (Fig. 5i). Keeping the magnetic field strength constant and increasing the shear rate (Fig. 5j and k) the deviation of the chains increases, resulting in a change in the difference scattering patterns. For low magnetic field strength and high shear rate (Fig. 5l) the chains are broken, the particles are homogeneously distributed in the sample, and hence the difference scattering pattern is again almost zero. At intermediate values of the magnetic field strength (Fig. 5e–h) an increase of the shear rate leads only to increased differences of the scattering patterns; the magnetic field is strong enough to avoid the breakage of the chains but too weak to reach the same effect as in the case of high magnetic field strength.

The experimental ferrofluid (TOA) shows a low magnetoviscous effect (Fig. 1b). This indicates a low content of large particles and, therefore, almost no structure formation is expected. The weak increase of the viscosity appears due to the hindrance of the free rotation of single particles, i.e. small structures, in the flow, by means of magnetic fields. This is also confirmed by the SANS results. In the difference scattering

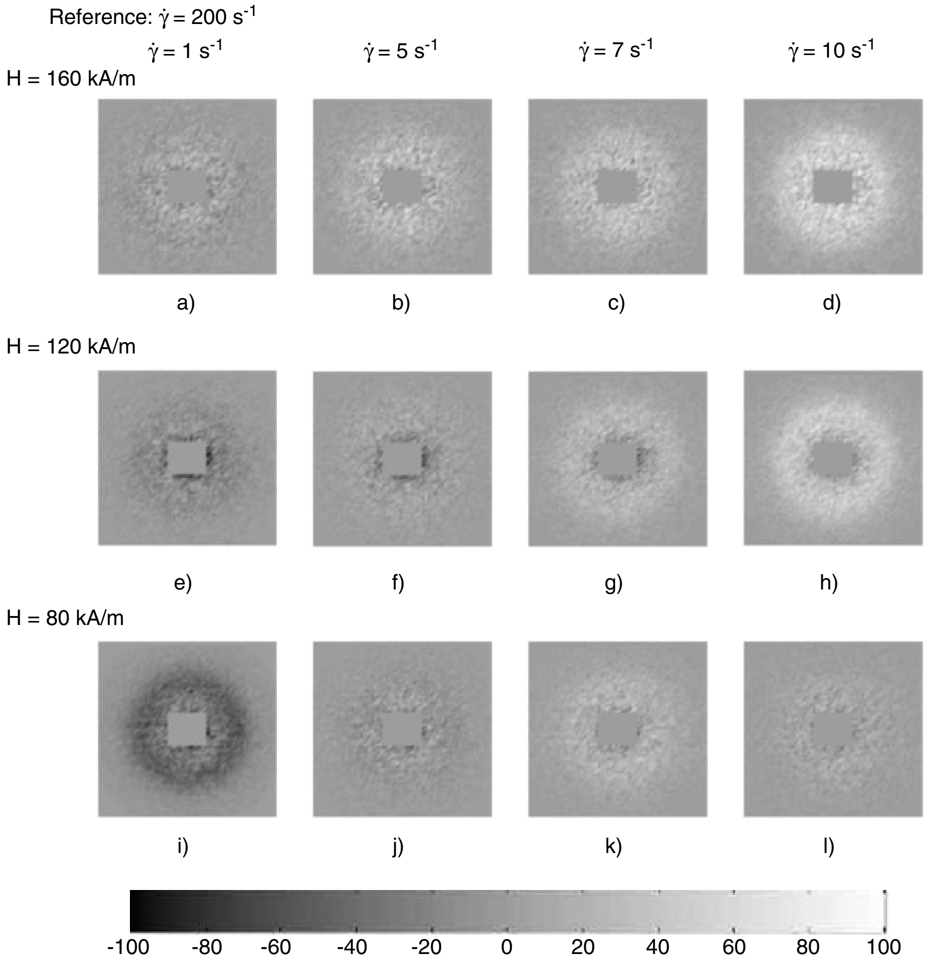

Figure 5. Difference scattering patterns obtained for APG 513A_1 (high magnetoviscous effect) using SANS.

patterns, obtained as explained above, no modification of the microstructure can be observed.

The slight modification of the difference scattering patterns with the magnetic field strength that can be observed (Fig. 6a, e, and i), is most likely only an orientation effect of the magnetic moments. For a low magnetic field strength (Fig. 6i), the magnetic moments of the particles are randomly distributed in the ferrofluid sample. For higher magnetic field strength, the magnetic moments of the single particles tend to be orientated closer to the direction of magnetic field. This orientation process induces a change of the resulting magnetic moment of the sample and, therefore, a marginal modification of the difference scattering patterns with the magnetic field strength can be observed (Fig. 6a, e, and i).

These results were confirmed by SANS measurements performed with the commercial fluid obtained from a second production line, APG513A_2. This fluid also shows a low magnetoviscous effect comparable to TOA. As in the case of TOA, the scattering patterns indicate no modification of its microstructure with magnetic field and shear rate. Altogether, a direct connection between the strengths of the magnetoviscous effect and the structure formation in ferrofluids which can be observed using SANS could thus be established.

OUTLOOK

The qualitative model presented above is in good agreement with the experimental results obtained using SANS. Subtracting the reference from the scattering patterns eliminates the non-relevant contributions to the scattering and gives information concerning the modification of the internal structure.

It was shown above that each difference scattering pattern depends on the ratio between magnetic field strength and shear rate, which influences the length of the chains and their orientation. This determines both the nuclear component of the scattering and the magnetic component, due to its dependency on the orientation of the magnetization, whereas the direction of the magnetization is determined by the ratio between the magnetic field strength and the shear rate. For a

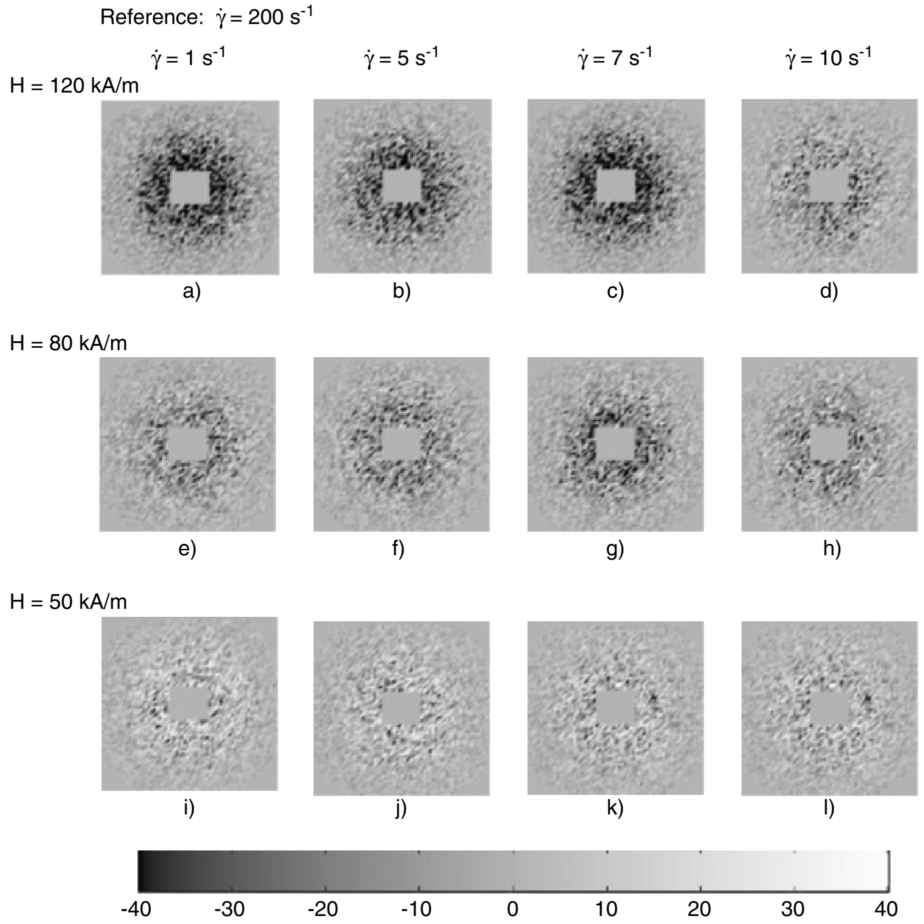

Figure 6. Difference scattering patterns obtained for TOA (low magnetoviscous effect) using SANS.

quantitative evaluation, the length of the chains and the ratio between the magnetic and the mechanical torques (for each magnetic field strength and shear rate) should be calculated, as well as the deviation angle between the magnetization of the chain and the direction of the magnetic field. Using this information, the structure and the form factors can then be calculated and the scattering pattern for each situation could be simulated.[8,9] A comparison between the theoretical and experimental results should, therefore, be possible.

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