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THE INFLUENCE OF LARGE PARTICLES AND AGGLOMERATES ON THE MAGNETOVISCOUS EFFECT IN FERROFLUIDS

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Investigations were made to prove the influence of large particles and agglomerates on the magnetic field induced changes of viscosity in suspensions of magnetic nanoparticles. Magnetic liquids from one production batch were subjected to a stepwise refinement process providing samples with different agglomerate content. From magnetic field dependent rheological properties, a clear relation between magnetoviscous effects and the content of large particles and particle agglomerates was obtained.

Introduction

Suspensions of magnetic nanoparticles (commonly called magnetic fluids or ferrofluids) show normal liquid behavior coupled with superparamagnetic properties. This enables magnetic control of their flow and other physical characteristics by means of magnetic fields with a strength of about 50 mT. The magnetic particles, having a mean diameter of about 10 nm, are usually magnetite (Fe_3O_4). They are covered with a surfactant made from long chained organic molecules, prohibiting agglomeration due to v.d.-Waals attraction. Since magnetic agglomeration and sedimentation of the particles are prevented by thermal energy, stable suspensions can be produced. The volume concentration of the magnetic component is usually about 2–10 vol.% and various carrier liquids like oils, kerosene, or water can be used. (for information on magnetic fluids see, e.g., [1, 2, 3]). The most famous field induced change of the properties of ferrofluids is the change of their viscous behavior. In 1970 McTague discovered a field induced increase of viscosity in a suspension of nanosized Co-particles [4]. An explanation for this phenomenon was given by Shliomis [5] with the concept of hindrance of free rotation of the particles due to the action of the magnetic field, commonly called rotational viscosity. The ensuing theory provides a relation for an increase in viscosity in the magnetic field $\eta_{r(H)} = \eta_{(H)} - \eta_0$ over the zero field value as:

$$\eta_{r(H)} = \frac{3}{2}\eta_0\phi' \frac{\alpha - \tanh\alpha}{\alpha + \tanh\alpha} < \sin^2\beta >, \qquad \alpha = \frac{\mu_0 m H}{kT}, \tag{1}$$

where ϕ' is the volume fraction of the magnetic particles including the surfactant coating, β the angle between magnetic field direction and vorticity of the flow (<..> denotes spatial averaging), m the magnetic moment of the particles, k Boltzmann's constant, and T the absolute temperature.

Applying this theory to experimental results requires recalling the basic assumptions made to establish (1). First of all the theory assumes that the relaxation of the magnetization of the ferrofluid is dominated by the Brownian process and not by Néel relaxation, i.e., it changes its direction by a rotation of the particles rather than by a rotation of the moment inside the particles.

In reality the process with the smaller time constant will dominate the process of relaxation of magnetization. Since both time constants depend on the size of the particles [6, 7], a critical particle size exists for which transition from the Néel process to the Brownian process occurs. For particle sizes below this critical size, the relaxation follows the Néel–process, i.e., the moment rotates freely inside the particle. Such particles - usually called magnetically weak - will not contribute to a field dependent increase of viscosity since their free rotation cannot be hindered by a magnetic torque produced by the interaction between the applied field and the magnetic

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moment. Only those particles following the Brownian process, i.e., having a moment fixed inside the particle, will feel such a magnetic torque and will therefore contribute to rotational viscosity. Beside this assumption one assumes further that the particles will not interact, and that the concentration of the magnetic component will be small enough to neglect cooperative phenomena. But the most important point is the claim that the particles need to be magnetically hard.

For Co-particles the critical size for transition from weak to hard particles is in the order of 5 nm; thus most of the particles in suspensions as used in [4] will contribute to the viscosity increase. In contrast, magnetite particles with a diameter below 14 nm will relax by the Néel process. Thus only larger particles may contribute to η_r. Various authors [8, 9, 10] have shown that the mean particle size in commercial ferrofluids is about 10 nm and thus only a negligible portion of particles could contribute to rotational viscosity. Therefore the results on viscosity changes reported (e.g., in [11, 12]) cannot be explained by a single particle theory applying (1) under compliance of the measured size distribution. Moreover, effects like field dependent shear thinning [13] or the appearance of normal stress differences [14] observed in commercial ferrofluids require the formation of large structures like chains, which cannot be formed by the magnetic dipole-dipole interaction between magnetite particles with a size of about 10 nm. Therefore it has been assumed in [13, 14] that large particles and primer agglomerates, i.e., agglomerates of two particles with a surfactant layer, which are formed during the fluid production process [15], dominate the viscous behavior of the fluid in the presence of a magnetic field. These particles would have higher Néel relaxation times and could thus relax by the Brownian process. Further on the coupling coefficient of single particles,

$$\lambda = \frac{2\mu_0 m^2}{(d+2s)^3 kT} \tag{2}$$

(with s the thickness of surfactant coating and d the diameter of the particles), is high enough to explain chain formation for particles with a diameter about 16 nm. In various theoretical approaches it has been shown that this would give rise to pronounced field dependent effects on the rheological properties of ferrofluids [16, 17, 18]. In the following we will use the term "large particles" for all magnetic structures relaxing by the Brownian relaxation process.

1. Magnetic fluids with various content of large particles

To prove the above-mentioned assumption of the dominating influence of large particles on the viscous properties of ferrofluids in a magnetic field, we have performed experiments on fluids with different contents of large particles. To avoid changes in the rheological behavior due to a different makeup of the ferrofluids and to isolate the effect of the large particles, we have used fluids from a common batch, stepwise reducing the content of the large magnetic structures by means of a magnetic refinement process.

As known from former work [19], the change of concentration of magnetic particles $\partial c/\partial t$ in a magnetic field gradient ∇H can be approximately written as

$$\frac{\partial c}{\partial t} \propto \frac{d^6}{d+2s}\, c \nabla H^2, \tag{3}$$

where c denotes the concentration of the magnetic component.

Equation (3) shows that the time change of concentration of the magnetic particles depends on the fifth power of the magnetic diameter. Thus a size dependent sedimentation can be induced by subjecting a sample of the fluid to a magnetic field gradient.

We have prepared samples of magnetic fluid containing magnetite particles with a mean diameter of 10 nm in a petroleum oil. The volume concentration of the magnetic component in all specimens was about 7.2 vol.%. The stock fluid was obtained from an early stage of the production process, i.e., before it was subjected to refinement

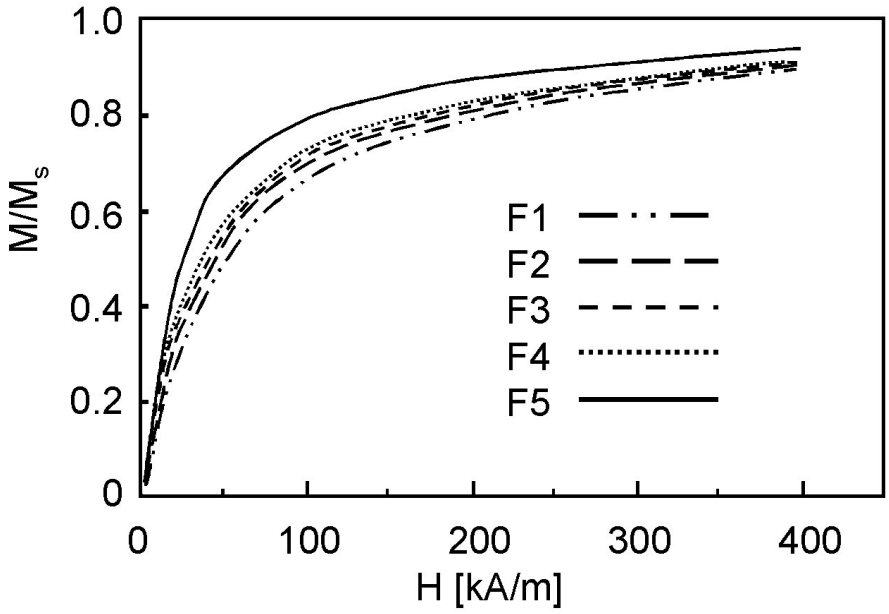

Fig. 1. Normalized magnetization curves for fluids F1 to F5, showing significant differences in curve shape, indicating a different size distribution of the suspended particles.

techniques. A part of this fluid was treated in a magnetic field gradient for a certain length of time to reduce the content of large particles. This procedure was repeated several times, resulting in a series of fluid samples with decreasing content of large particles. All these fluids were adjusted to the same volume concentration of the magnetic component to avoid effects due to variation of concentration. In total, 5 samples were produced which were designated F1 to F5, with F5 being the sample with the highest amount of large particles, i.e., the initial sample. Decreasing amounts of large particles, i.e., an ongoing refinement process, is indicated by decreasing ordinal.

The purity of fluid F3 is comparable to that of usual commercial ferrofluids. All ferrofluids have been characterized magnetically and the results are shown in Table 1 and Fig. 1. As seen the saturation magnetization of all fluids is identical within an accuracy of 1%, thus eliminating a change of interaction due to variation of concentration. The mean particle size decreases with progressive purification, indicating a decrease in the number of large particles and agglomerates. Furthermore it can be seen that the mean particle size is quite similar for fluids F1 and F2 as well as for F3 and F4. This subdivides the fluids into three major groups: F5 with a high content of large particles, F3 and F4 with mean content, and F1 and F2 with a low content. To get a better picture concerning possible changes of the particle size distribution, we have plotted the normalized magnetization curves (Fig. 1). They show significant differences in curve shapes between fluids F1 and F5. The steeper increase of magnetization with magnetic field observed in F5 indicates a significant amount of relatively large particles, e.g., agglomerates, as is also evident from the calculated mean particle size (Table 1). While the observed differences indicate qualitatively a reduction of large particles and agglomerates due to the refinement process, the differences are nevertheless not strong enough to obtain a reasonable insight into the size distribution by a magnetogranulometric analysis [20].

Table 1. Magnetic properties of the samples

Fluid	F1	F2	F3	F4	F5
M_s[kA/M]	32.41	32.34	31.54	32.17	32.06
$\bar{d}$ [nm]	8.3	8.8	9.2	9.2	10.1

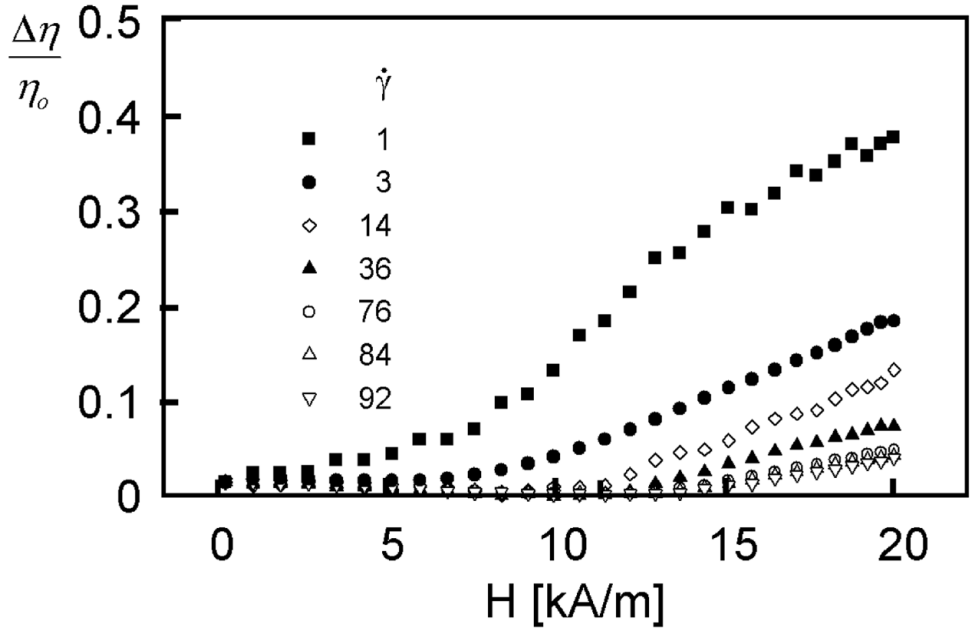

Fig. 2. The relative magnetoviscous effect for various shear rates measured for the fluid with the highest content of agglomerates.

2. Rheological Investigations

With the fluids described above we have carried out a series of experiments to determine the shear dependence of the magnetoviscous effects. For these experiments we used a specialized cone plate rheometer, designed for the investigation of magnetic fluids under the influence of magnetic fields [21]. The experiments were carried out in the rotating mode of the rheometer, with shear rates from 1 s^{-1} to 100 s^{-1}. The magnetic field was oriented parallel to the axis of rotation and thus perpendicular to vorticity of the flow. The magnetic field strength ranged from 0 kA/m to 35 kA/m. With a demagnetization factor of approximately 1 for the flat fluid layer, the internal field in the fluid ranged from 0 kA/m to approximately 21 kA/m. For all experiments the fluids were maintained at 20°C with an accuracy of $\pm$ 0.05°C. Figure 2 shows the field induced increase in viscosity for various shear rates for the fluid with the highest content of large particles, F5. It is seen that a strong magnetoviscous effect occurs which decreases with increasing shear rate. At high shear rates the magnetoviscous effect becomes nearly independent of the shear rate. This indicates that field induced structures of magnetic particles or agglomerates are broken down by shear. At high shear rate all larger structures are fragmented and thus the magnetoviscous behavior is determined by the influence of the large particles alone.

For low magnetic field strength, i.e., for small values of α, (1) can be approximated by

$$\frac{\eta_{r(H)}}{\eta_0} = \frac{1}{4}\frac{\mu_0^2}{k^2T^2}\phi' m^2 H^2. \tag{4}$$

Thus a fit of the relative magnetoviscous effect against H^2 can provide some approximate information about the relevant structures dominating the viscous behavior of the fluid. Figure 3 shows the relative magnetoviscous effect as a function of H^2 for Fluid F5 measured with $\dot{\gamma} = 92\ \mathrm{s}^{-1}$. From the slope of the linear relation between $\eta_{r(H)}/\eta_0$ and H^2 one can obtain the product $\phi' m^2$.

Assuming that all chains are broken, and that the dominating portion of the agglomerates are dimers, we can fix the equivalent diameter of the large particles to approximately 16 nm, as was also found in [11]. We thus find that the plot of $\eta_{r(H)}/\eta_0$ against H^2 leads to the volume concentration of the magnetic agglomerates, f = 0.8 %. This fits well with the order of magnitude of the agglomerate content calculated by Zubarev [22]

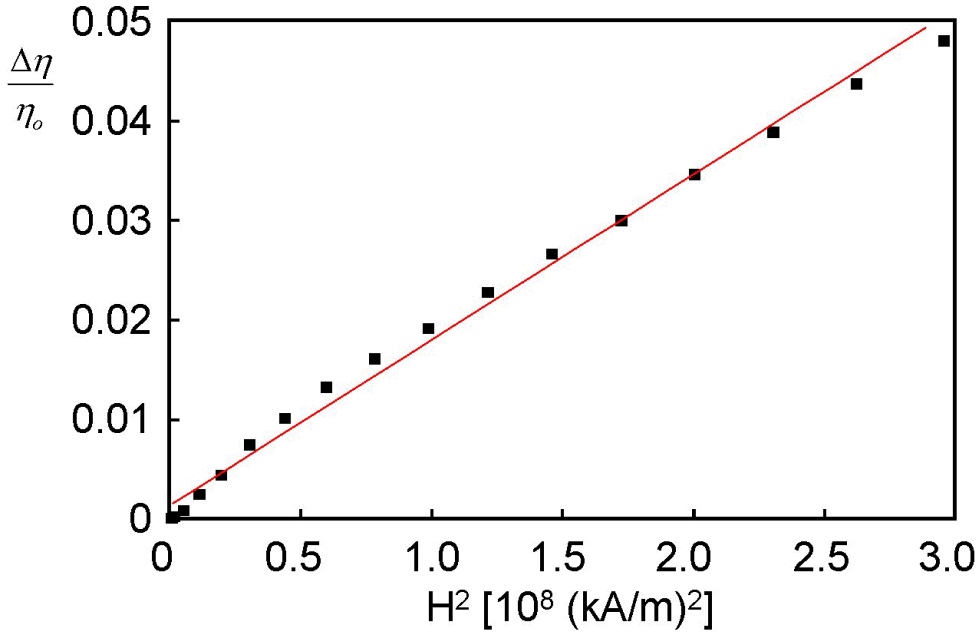

Fig. 3. The relative change of viscosity plotted against the square of the internal field. From the linear fit the product $\psi' m^2$ can be obtained following the theory by Shliomis [5].

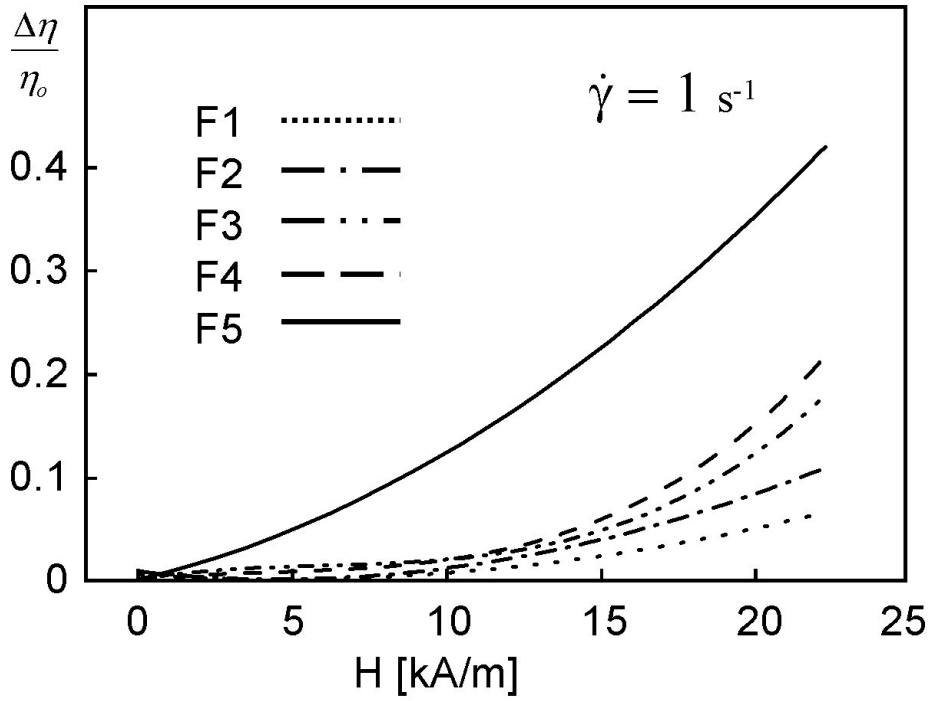

Fig. 4. Comparison of the magnetoviscous effect for samples with different content of agglomerates for $\dot{\gamma} = 1\,\mathrm{s}^{-1}$.

using the data of [11]. In Fig. 4 we have compared the magnetoviscous effect of all five samples for $\dot{\gamma} = 1\ \mathrm{s}^{-1}$. It can be seen that a strong difference between F5 and F4 exists, while F3 and F4 as well as F1 and F2 are relatively similar. Between F2 and F3 a slightly stronger difference appears, compared to that between F1 & F2

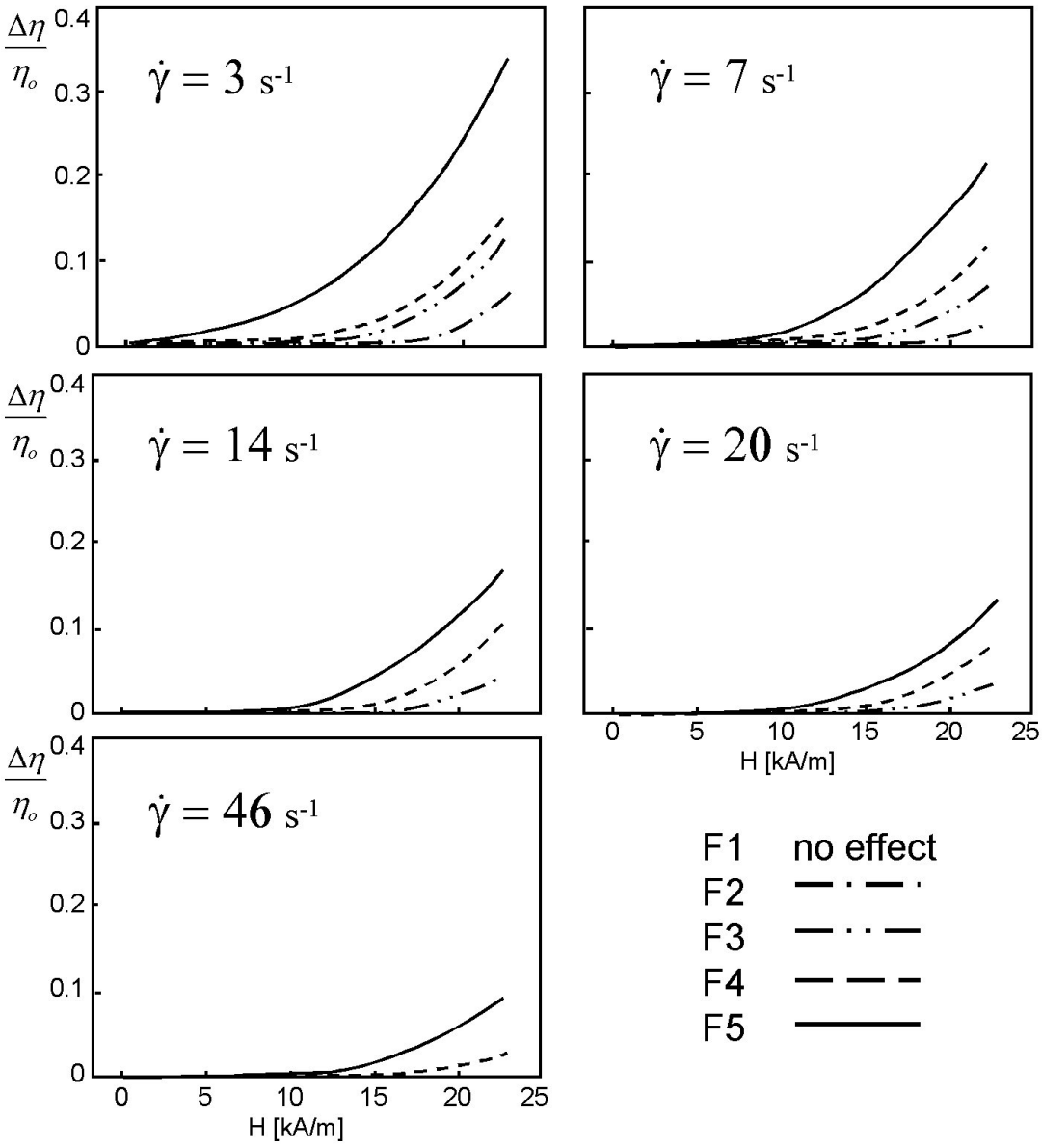

Fig. 5. Same as Fig. 4 for different shear rates ranging from $\dot{\gamma} = 3\ \mathrm{s}^{-1}$ to $\dot{\gamma} = 46\ \mathrm{s}^{-1}$. Fluid F1 shows only for $\dot{\gamma} = 1\ \mathrm{s}^{-1}$ (Fig. 4) a measurable effect.

and F3 & F4. This agrees well with the magnetization measurements discussed above. Focusing on the shear dependence of the magnetoviscous effect, Fig. 5 shows that for all fluids the magnetoviscous effect decreases with increasing shear rate and the relation between different fluids is conserved. For Fluid F1 the magnetoviscous effect is detectable only for $\dot{\gamma} = 1\ \mathrm{s}^{-1}$. With increasing shear rate the magnetoviscous effect falls below the detection limit successively for the various fluids. Only for F5 can a significant signal be obtained up to $\dot{\gamma} = 100\ \mathrm{s}^{-1}$, the highest shear rate tested (Fig. 2).

To obtain an estimate of the reduction of the amount of agglomerates in samples F1 through F4 we have used the relationship $(\eta_{r(H)}/\eta_0)$ versus H^2 as discussed earlier with the same assumptions for the size of large particles as for F5. For this determination we have always used the highest shear rate at which a magnetoviscous effect could be observed. This is a good approximation for fluids F3 and F4, which show a convergence of the magnetoviscous effect for high shear rates as also noted for F5 (Fig. 2). For F1 and F2, where only low shear

rates are available, the calculated values just provide an order of magnitude since it must be assumed that the chains are not broken for these low shear rates. Therefore the size of the relevant structures is underestimated in our calculations since not only the large particles themselves but larger structures like chains should have to be considered. This results finally in an overestimation of the amount of large particles involved. Nevertheless the resulting values given in Table 2 give a good idea of the change of the large particle content as obtained from the rheological data. Between F5 and the fluids with mean large particle content (F3 and F4), the amount of large particles increases by a factor of 3 while fluids F1 and F2 contain only about 10% of the initially existing large particles.

Table 2. Content of agglomerates deduced from the viscosity variation at low field strength under the assumption of dimer agglomerates with $d = 16$ nm

Fluid	F1	F2	F3	F4	F5
$\phi_{\mathrm{agglomerate}}$ [vol.%]	0.09	0.14	0.22	0.26	0.8

Conclusions

From our results we can draw the following conclusions concerning the magnetoviscous effect in ferrofluids. First of all it has been shown that the viscosity is influenced by an applied magnetic field. This variation depends on shear rate in the same way that an increase in shear rate reduces the magnetoviscous effect. Furthermore it is observed that the viscosity increase depends on the purity of the fluid. Ferrofluids with a high content of large particles show a strong increase in viscosity with applied magnetic field while in fluids with a high level of refinement the magnetoviscous effect is negligible. Since all fluids had similar overall content of magnetic material, we can draw the conclusion that small particles with diameters around 10 nm do not contribute directly to the magnetoviscous properties of a ferrofluid, which is consistent with the fact that the particles are not magnetically hard. They may have a certain importance as a magnetic background medium, enhancing the interaction between the large particles, but this is not within the scope of this investigation. The observed field dependence of viscosity in magnetite ferrofluids is thus mainly due to the existence of large particles. The higher the content of large particles, the greater the magnetoviscous effect. The change in the amount of large particles has also been supported by magnetization measurements on the fluids, where the shape of the curves as well as the mean particle size indicate a corresponding variation of the content of large particles.

Finally we could deduce the approximate content of large particles under the assumption that dimers and single large particles of comparable size are the type of large particles. The calculated content is less than 10 % of the total magnetic concentration for the fluid with the highest amount of large particles. The refinement process is able to reduce the large particle content by approximately one order of magnitude.

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