

Scaling between Viscosity and Hydrodynamic / Magnetic Forces in Magnetic Fluids*

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The aim of this work is the investigation of the magnetorheological behavior, under both simple steady- and oscillatory-shear flow regimes, of fluids composed by micron-sized iron particles (average diameter 930 ± 330 nm) dispersed in silicone oil. Magnetic fields ranging from 279 A/m (0.35 mT) to 1727 A/m (2.17 mT) were applied to the suspensions. The effect of silica nanoparticles as stabilizer of the suspensions has also been considered. The study has been made by the scaling between the viscosity of the suspension and the ratio of hydrodynamic to magnetic forces acting on the dispersed particles, given by the dimensionless Mason number (Mn), and interpreted in terms of the chainlike model taken from the theory of Martin and Anderson (*J. Chem. Phys.* **104** (1996) 4814-4827). The model is quite well accomplished for iron suspensions of different (20 % and 30 %) volume fraction without any stabilizing agent. The presence of added silica nanoparticles in the suspension hinders the formation of regular iron structures induced by the magnetic field, especially at the lowest applied magnetic fields. Thus the model becomes not applicable to these cases. Viscometry has been shown to be more adequate than oscillometry for scaling the viscous properties of magnetorheological suspensions with microscopic interparticle forces in terms of Mn number.

Keywords
magnetic colloids
viscosity
magnetorheology

INTRODUCTION

Magnetic colloids are a group of materials that exhibit the remarkable property of changing their flow properties under the application of an external magnetic field.¹ They can be classified into: (i) ferrofluids (FF), which are stable colloidal dispersions of ferro- or ferrimagnetic nanoparticles in a carrier liquid² and (ii) magnetorheological (MR) fluids, which are dispersions of micron-sized magnetic particles.¹ Nano-sized particles (diameter ≈ 10 nm) used in FF are magnetically single-domain and, therefore, they possess a permanent magnetic dipole moment.

In the absence of a magnetic field, MR fluids typically behave as nearly ideal newtonian liquids. The application of a magnetic field induces magnetic dipole and multipole moments on each particle, which interact, leading to the formation of columnar structures parallel to the field.³ These structures can largely affect their flow behavior. In particular, their rheological behavior can change from that of a newtonian fluid to a plastic one, with appearance of measurable yield stress and a plastic viscosity depending on the applied field strength. These modifications are known as magnetorheological or magnetoviscous effects. However, even under the application

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of high magnetic fields, FF manifest only a relatively modest magnetoviscous response and do not develop a yield stress.^{4,5,6} On the contrary, micron-sized ferro- or ferrimagnetic particles are magnetically multidomain and attain large magnetic moments under the application of rather weak magnetic fields. As a consequence, MR fluids manifest a high magneto-viscous response characterized by a high yield stress.^{3,7} Due to these properties, MR fluids are field-responsive materials with a broad range of technological applications. MR fluids are typically formulated using high density materials such as iron, iron alloys or metal oxides (ceramic ferrites) dispersed in low-density liquids. Therefore, their stabilization against sedimentation arises as an important challenge, facing the technological applications of these field-responsive materials.⁸ Approaches to improve the stability include: (i) addition of thixotropic agents (*e.g.* carbon fibers and silica nanoparticles),^{7,9,10} (ii) addition of surfactants (*e.g.* oleic acid or stearate salts),^{11,12,13} (iii) adding magnetic nanoparticles^{14,15,16} and (iv) use of viscoplastic media or water-in-oil emulsions as continuous phases.^{17,18}

In a previous work¹⁰ we have found that the use of silica nanoparticles as a stabilizing agent is especially adequate. The two mechanisms invoked to explain how silica particles influence the stability of MR fluids are: (i) silica-silica interparticle hydrogen bonding, which facilitates the formation of a thixotropic network that prevents the sedimentation and eventually reduces the redispersion difficulties, and (ii) the adhesion of silica to iron particles by acid-base reactions in non-polar media. In the presence of the field, the shell of adsorbed silica will partially screen the magnetic interactions between iron particles, thus reducing the magnetorheological effect. Because of both reasons, a precise control of silica concentration is needed to avoid an excessively thickening of the carrier fluid or a too thick silica layer on iron, as both circumstances would hinder the chaining of magnetic particles under the action of the external magnetic field. In agreement with Ref. 7, a low volume fraction 2%–3% of silica is recommended, sufficient to impart a low yield stress to the suspensions so that they can flow easily under a small agitation.

On the other hand, the interpretation of the measurements of shear-flow of confined MR fluids needs of the knowledge of the fundamental forces acting on the particles: they are the responsible of the formation of the internal structures which originate the non-linear properties (yield and flow behavior) of field-responsive fluids. Discussion in terms of the Mason number, Mn , (proportional to the ratio between hydrodynamic and magnetostatic forces) allows the interpretation of different types of aggregates between the suspended particles. Other factors dealing with the nature of the solid boundaries (gap) in the measuring cell have also to be taken into account when performing rheological measurements. Amongst

them, corrections for wall slip are needed to determine the true deformation experienced by the bulk of the sample. An in depth review of apparent wall slip is given by Barnes.¹⁹

Usually, the magnetically-induced structures in MR fluids present a length distribution in the field direction. When changing the gap thickness it is necessary to ensure that the average chain length distribution still predicts gap spanning structures in order to develop the MR effect. The combined use of different rheological techniques and the interpretation of the measurements in terms of a well-founded model could be applied to gain more insight on the correlation between the macroscopic shear behavior and microscopic structure of these systems.

The aim of this work is just the investigation of the non-linear behavior in both simple steady- and oscillatory-shear flow regimes, using a fluid composed by micron-sized iron particles dispersed in silicone oil. This has been made by means of the scaling between the viscosity of the suspension and the ratio hydrodynamic/magnetic forces acting on the dispersed particles. The presence in the fluid of silica gel as stabilizer was also tested. The results are analyzed in the light of the non-linear model essentially taken from the theory of Martin and Anderson.²⁰

FLOW REGIME: VISCOSITY AND MASON NUMBER

Different models (see Ref. 7) have been devoted to predict the relation between the viscosity in steady shear flow and the Mason number (Mn), which expresses the ratio of hydrodynamic to magnetic forces between two vicinal particles in shear. These models assume that the aggregates induced by the magnetic field deform affinely with the shear flow and find their equilibrium angle when the hydrodynamic torque equilibrates the magnetic restoring torque. When the Mason number increases, a critical angle is reached at which the aggregates break into equal parts, and further increase in shear rate (or Mn) will decrease the equilibrium length until all the aggregates are destroyed. A scaling of the viscosity (in fact the normalized viscosity, see below) with $Mn^{-\nu}$ is predicted in models based on ellipsoidal aggregates or on particle chains. The parameter ν can vary from 0.68 to 1 when the ratio of magnetic to brownian forces increases (λ); in the limit of $\lambda \rightarrow \infty$ the model based on ellipsoidal aggregates or on particle chains predicts an exponent $\nu = 1$. In particular, the model proposed by Martin and Anderson²⁰ assumes that the magnetic and hydrodynamic forces dominate the shear in suspensions of spherical particles gathered into chains by dipolar magnetic interactions. These chains form a cubic network in which the chain-chain interaction is neglected.

The following relationship between the viscosity, η , and the Mason number, Mn , is predicted in steady-state shear:²⁰

$$\frac{\eta - \eta_\infty}{\phi \eta_0} \equiv \eta_F \approx C Mn^{-1} \quad (1)$$

where C is a constant which value depends on the microscopic structure induced by the field, η_F is the dimensionless field-specific viscosity, η_∞ is the suspension viscosity at infinite Mn , *i.e.*, at infinite shear rate (at infinite shear rate the viscosity is independent on the magnetic field strength applied since there are not any magnetically induced structures); η_0 is the solvent viscosity, and ϕ is the particle volume fraction.

Different values of constant C can be found in the literature for field responsive-fluids: Martin and Anderson²⁰ proposed $C = 8.82$; de Gans *et al.*²¹ (1999), $C = 5.25$, and Volkova *et al.*,⁹ $C = 1.91$. In this work we have used that proposed in Ref. 20 (linear chain model). Several different definitions of the Mason number also appear in the literature, and in this model the Mason number is given by:

$$Mn = \frac{\eta_0 \dot{\gamma}}{2\mu_0\mu_f\beta^2 H_0^2} \quad (2)$$

where H_0 is the external magnetic field strength and $\beta = (\mu_p - \mu_f) / (\mu_p + 2\mu_f)$ is the magnetic contrast factor. μ_p is the relative magnetic permeability of the ferromagnetic particles (iron in this work) and μ_f the relative permeability of the continuous medium (silicone oil); consequently, as $\mu_p \gg \mu_f$, $\beta \approx 1$. Therefore, a scaling $\eta_F \approx Mn^{-1} \approx (\dot{\gamma} / H_0^2)^{-1}$ is predicted by Eqs. (1) and (2). Hence, a collapse among graphs at different magnetic field strengths will be expected when η_F is plotted *versus* Mn or $(\dot{\gamma} / H_0^2)$ if there are no other forces acting on the particles than

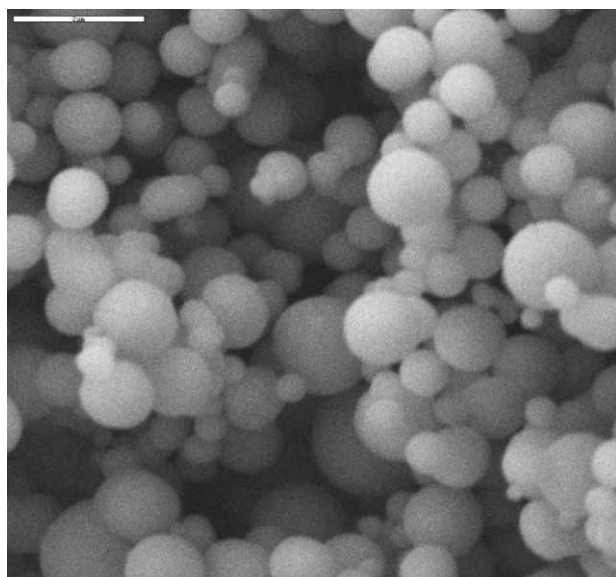


Figure 1. SEM picture of iron particles. Bar length 2 μm .

those assumed by the model (hydrodynamic and magnetic forces).

The relationship between the viscosity, η , and Mn , can be obtained in shear-oscillatory experiments by changing in Eqs. (1) and (2): the shear rate, $\dot{\gamma}$, by $\gamma_0\omega$ (γ_0 is the strain amplitude, ω is the frequency of the oscillatory shear); the viscosity, η , by the magnitude of the complex viscosity, $|\eta^*|$; and similarly η_∞ by $|\eta_\infty^*|$ (for $\gamma_0\omega \rightarrow \infty$).

EXPERIMENTAL

Materials

Iron powder, originally obtained from carbonyl iron precursors, was supplied by BASF (Germany). It was a HQ quality powder of micrometer size. SEM pictures (Figure 1) were taken to analyze the size and shape of the iron particles, showing that they are spherical and polydisperse, with average diameter 930 ± 330 nm. Silicone oil (polidimethylsiloxane) with viscosity $\eta_0 = 0.031$ Pa s and density 954 kg m^{-3} (Fluka, Germany) was used as dispersing medium. The dielectric constant of silicone oil is $\epsilon_r = 2.6$, as measured with a Dekameter DK 300 apparatus (WTW, Germany).

Silica nanoparticles 7 nm in diameter (Aerosil-300®, Degussa-Hüls, Germany) were added to the suspensions and used as stabilizing agent.

Iron-silica suspensions were prepared as follows: (1) iron, silica and silicone oil were mixed in a polyethylene container; (2) the mixture was stirred firstly by hand, and then in a ultrasonic bath; (3) step (2) was repeated several times, and finally the sample was immersed in a sonifier (Branson model 450, USA) to ensure the required final homogeneity. The gradual homogenization of the samples was checked by the disappearing, in the successive mixing cycles, of the initially observed aggregates in the container bottom. The suspensions used were of 20 and 30 % iron volume fraction, and the concentrations of added silica were 7.3 and 14.6 g/L. No significant changes in the viscosity of the carrier were observed as silica nanoparticles content increased in the concentration range employed.

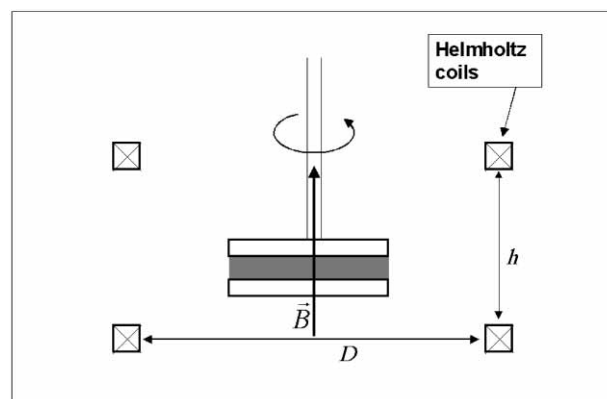


Figure 2. Schematic drawing of the rheometer used in magnetorheological experiments. Coil diameter $D = 39.5$ cm; distance between the two coils $h = 19.5$ cm.

Rheological Measurements: Apparatus and Methods

The magnetorheological properties of the suspensions were measured at a temperature of 25.0 ± 0.1 °C in a Bohlin CS10 controlled stress rheometer using a parallel-plate measuring cell (radius of the rotating plate $R = 2$ cm) (Bohlin PP-40) for gap width of 0.15 mm. The magnetic field was generated using a pair of Helmholtz coils (Phywe, Germany). The coils were placed so that their axes coincided with that of the measuring plates (see a scheme in Figure 2), thus producing a magnetic field in the vertical direction. A Hall-effect teslameter (Phywe, Germany) was used to measure the magnetic flux density B in the air gap between the plates. Variations in B throughout the gap were always below 10 %. We checked that the electronics of the rheometer is not affected by the magnetic field, by measuring, in steady-state and dynamic experiments the rheological behavior of four newtonian liquid samples (glycerine, the silicone oil used

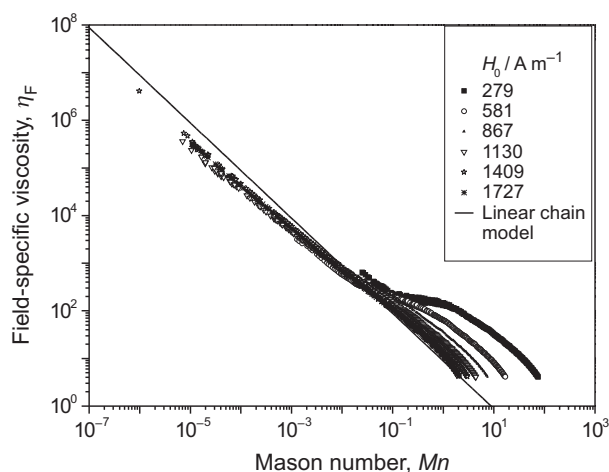


Figure 3. Field-specific viscosity as a function of Mason number, obtained from steady state experiments, for 30 % iron volume fraction in silicone oil and the values of magnetic field strength shown in the graph. The solid line corresponds to the prediction of the linear chain model.

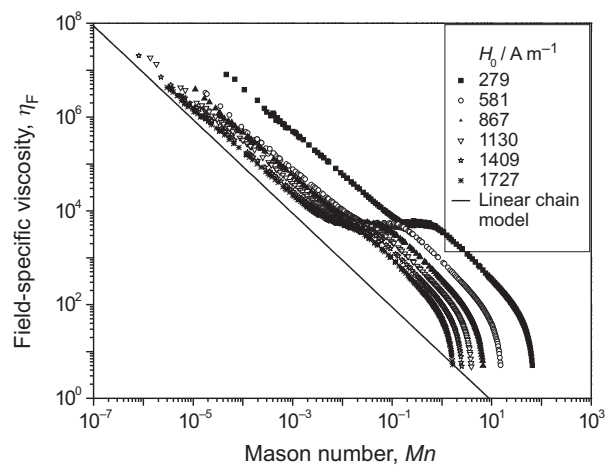


Figure 4. Same as in Figure 3 but in the presence of 14.6 g/L of silica particles.

in this work, and two standard silicone oils –4940 and 100800 mPa s from Brookfield) in presence and absence of applied magnetic field in the range $B = 0$ –2.5 mT. In this range the same results were obtained whatever the field applied, thus demonstrating that no effect exists on the rheometer components.

Two rheological techniques were used for the characterization of the suspensions: (a) steady-state flow (viscometry); samples were subjected to a shear stress ramp in the range from 0.05 to 100 Pa (the time elapsed between two consecutive steps was 2 s) and the corresponding shear rate was measured for the different suspensions in order to obtain the viscosity of the suspensions, η ; η_∞ is the viscosity corresponding to the highest value of the shear rate in the η vs. $\dot{\gamma}$ plots; since the (apparent) shear rate in the plate-plate geometry depends on the radial coordinate, r , the software of the rheometer calculates the real shear rate at $r = 0.75 R$ applying the Weissenberg-Rabinowitsch correction.²² (b) Dynamic oscillatory shear; an oscillatory shear stress at constant frequency $\omega = 1$ Hz and variable amplitude, σ_0 (ranging between 0.5 and 10 Pa) was applied to the suspensions and the magnitude of the complex viscosity, $|\eta^*|$, recorded.

The rheological measurements were performed both in the absence and in the presence of external magnetic field. The field ranged from $H_0 = 279$ A/m ($B = 0.35$ mT) to $H_0 = 1727$ A/m ($B = 2.17$ mT).

In order to ensure reproducible results, and taking into account the time-dependent behavior of thixotropic suspensions, samples were pre-sheared during 30 s at a large shear rate and zero magnetic flux density. Then, the magnetic field was applied during a 30 s waiting time with no shear applied, both in viscometry and oscillometry tests. Finally, rheological measurements were started maintaining the presence of the magnetic field.

RESULTS AND DISCUSSION

Steady-state Measurements: Field-specific Viscosity and Mason Number

In Figure 3 is shown the field-specific viscosity, η_F , as a function of the Mason number, Mn , for suspensions at 30 % iron volume fraction and at different magnetic field strengths. Figure 4 shows the results obtained for the same values of magnetic field, but for a system containing, in addition to the iron particles (30 %), silica gel at concentration 14.6 g/L. Results were also obtained for suspensions containing different iron content (20 % volume fraction) and lower silica concentration (7.3 g/L). The trends obtained were similar to those shown in Figures 3–4 and are not shown here, although the data will be used below.

The solid line in Figures 3 and 4 correspond to the theoretical prediction according to Eq. (1). It is noteworthy that the curves corresponding to the different applied magnetic fields collapse for $Mn < 0.1$ (Figure 1) and $Mn < 10^{-2}$ (Figure 3) (in this case, except at the lowest magnetic

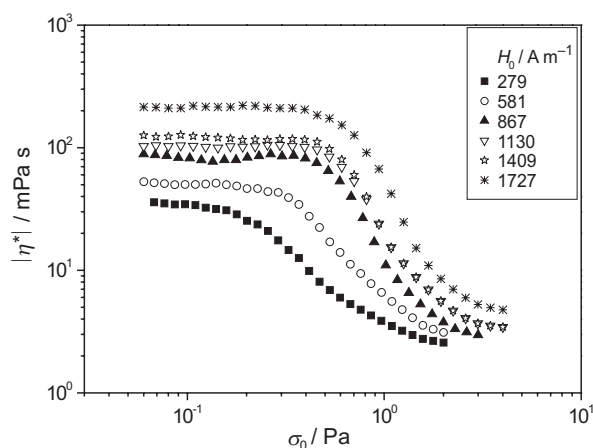


Figure 5. Magnitude of the complex viscosity as a function of shear stress amplitude for 30 % iron volume fraction in silicone oil at the indicated magnetic field strengths.

TABLE I. Average values (\pm standard deviation) of the Mason number exponent (ν) obtained by fitting the experimental rheological data (in viscometry and oscillometry) to Eq. (1) for the different magnetic fields applied (see text and Figures 3, 4, 6 and 7). The composition of the MR fluids studied is indicated

Suspension composition	ν (viscometry)	ν (oscillometry)
20 % Fe + 0 g/L silica	-0.93 ± 0.07	-1.15 ± 0.22
20 % Fe + 7.3 g/L silica	-0.93 ± 0.21	-0.97 ± 0.07
30 % Fe + 0 g/L silica	-0.95 ± 0.06	-0.97 ± 0.10
30 % Fe + 7.3 g/L silica	-0.93 ± 0.16	-1.10 ± 0.13
30 % Fe + 14.6 g/L silica	-0.94 ± 0.12	-1.13 ± 0.16

field). In all cases, the slope of the experimental η_F vs. Mn plots, below those critical Mason values, are close to that predicted by the chain model (slope equal -1). The average values of these slopes for the different suspensions used in this work are included in Table I. Note that they are not significantly different than -1 . For higher values of Mn , the curves do not coincide for the different magnetic fields and the slopes are not constant.

According to Ref. 20, the chain formation becomes important when $Mn = 0.1$ for »chains« of two particles, *i.e.* the magnetic interactions are at least ten times higher than the hydrodynamic ones. Thus the condition of stability for longer chains is that Mn must be even lower than 0.1 (magnetic interaction strong enough, as compared to hydrodynamic one, as to prevent the rupture of the chains). The comparison of results in Figures 3 and 4 indicates that the chain model is quite well accomplished for iron suspensions without any stabilizing tixotropic agent. The presence of added silica nanoparticles in the suspension must hinder the formation of regular iron structures induced by the magnetic field. Note that the chain model fails in this case for $Mn > 10^{-2}$ (Figure 4).

Oscillatory rheological techniques were also used to check the validity of the chain model. As mentioned in

the experimental section of this work, the magnitude of the complex viscosity was measured as a function of the shear stress amplitude at a constant frequency of 1 Hz. In Figure 5 are presented, as an example, the results obtained for 30 % iron volume fraction (no silica added). It can be seen in it that there is an initial viscosity plateau (linear viscoelastic region), followed by a sudden decrease as σ_0 increases, which corresponds to the transition to a non-linear viscoelastic behavior of the suspension. The values of $|\eta^*|$ used in Eq. (1) (modified for oscillatory-shear regime) were obtained from the plots $|\eta^*|$ vs. σ_0 and employed to calculate the field-specific viscosity, η_F , under oscillatory shear. This quantity is represented in Figures 6 and 7 as a function of the Mason number for 30 % iron volume fraction suspensions without (Figure 6) and with added silica (14.6 g/L, Figure 7).

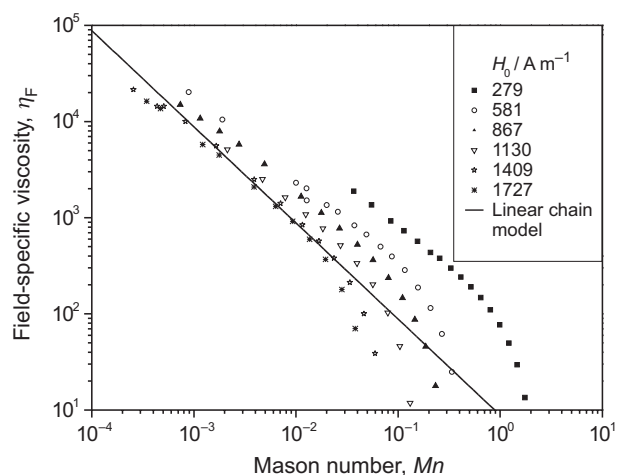


Figure 6. Field-specific viscosity as a function of Mason number, obtained from oscillatory experiments, for 30 % iron volume fraction in silicone oil at the values of magnetic field strengths shown in the graph. The solid line corresponds to the prediction of the linear chain model.

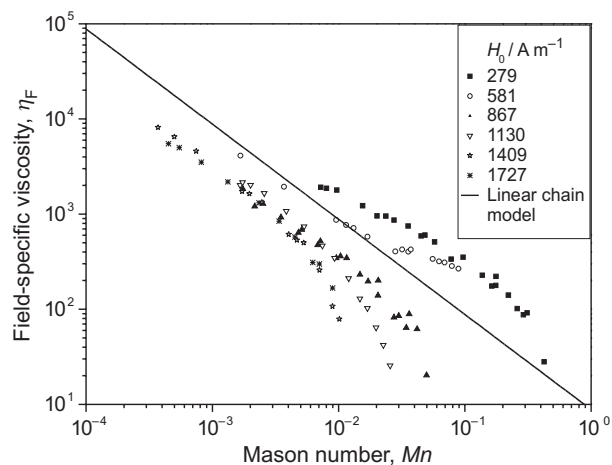


Figure 7. Similar to Figure 4 but in the presence of 14.6 g/L of silica nanoparticles.

Now, the curves do not collapse so sharply as with viscometric measurements (Figures 3 and 4). In iron suspensions (30 %) and in the absence of silica (Figure 6), some joint trend of the curves could exist at Mn numbers below 0.01. The slope is -0.97 ± 0.10 (see Table I; see also results obtained for other suspensions). The addition of silica to 30 % iron suspension (Figure 7) results in a decreasing trend of η_F as Mn increases that does not match with the predictions of the chain model: the linear region is much more reduced and only exists in the range of very low Mason number and for the higher magnetic fields. The comparison of data obtained from viscometric measurements (Figures 3 and 4) with those obtained from oscillometry (Figures 6 and 7) shows that the later technique, as far as it is used for the purpose of scaling the viscous properties of magnetorheological suspensions with microscopic interparticle forces (the chain model discussed in Eq. (1)), is less adequate than the former one. The scattered data shown in Figures 6 and 7 could be due to the uncertainties in the determination of $|\eta_\infty^*|$, the complex viscosity at infinite shear rate, from sets of data as those presented in Figure 5: $|\eta_\infty^*|$ is a property of the suspension »working« under strong, non-linear conditions. In the case of viscometric measurements, from the experimental point of view η_∞ is a much better defined quantity.

The chain model allows the estimation of the stiffness of the chains in terms of the scaling between hydrodynamic and magnetic interactions between the particles. This, in turn, is interpreted macroscopically in terms of the dimensionless viscosity of the suspension, field-specific viscosity, η_F . It could be now compared the theoretical value of η_F predicted by the chain model, with the real values of η_F obtained through the rheological measurements. For that purpose, one can select a Mn value in the η_F vs. Mn plots, low enough in the linear region, although not too close to the lowest measurable shear-rate by the rheometer. For $Mn = 10^{-3}$, the linear chain model (Eq. (1)) predicts $\eta_F = 8820$. In Figure 8 there are plotted the values of η_F obtained for $Mn = 10^{-3}$ from data in Figures 3 and 4 (as well as from data in other set of results using suspensions of different composition, not shown in this work). In the absence of silica in the suspension, η_F is practically independent of H_0 (see data in Figure 8 for 20 % and 30 % iron content). However, when silica is added at different concentrations, there exists a strong dependence between the field-specific viscosity and the strength of the magnetic field, especially for the lower H_0 applied. Concerning the magnitude of experimental η_F , the values obtained for pure iron suspensions and magnetic fields larger than approximately 600 A/m ($B_0 = 0.75$ mT) range from: 5440 (30 % iron, $H_0 = 1727$ A/m) and 11924 (20 % iron, $H_0 = 581$ A/m). These values are of the order of the values predicted theoretically by the chain model. Thus, it could be assumed that the struc-

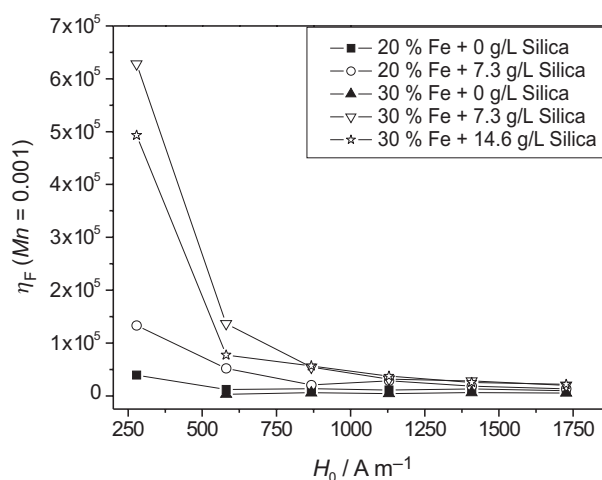


Figure 8. Field-specific viscosity (for $Mn = 0.001$) as a function of magnetic field strength obtained from steady-state experiments.

tures formed in iron suspensions under the action of external magnetic field agree with those linear, stable, chains predicted by the model.

On the contrary, when silica is added to the iron suspensions, the magnitude of η_F goes far away from the values predicted by the model, and the deviation increases as the field decreases and the silica concentration increases. Broadly, the big values of η_F must be related to the effects that provoke in the internal structure of the suspension the presence of nanoparticles, which act as a tixotropic agent. To explain this behavior, it could be considered that: (i) the aerosil particles dispersed in oil media form a tixotropic gel by silica-silica H-bonding, that increases the viscosity of the oil media, thus hindering the migration of iron particles by the action of the applied magnetic field; (ii) as demonstrated in previous works,^{10,23} the silica nanoparticles adhere to suspended micron sized iron particles, originating a cloud of the former particles around the latter ones, the so-called »halo« structure. This »halo« significantly diminishes the magnetic interaction between the iron particles, because they cannot approach themselves up to the close contact. The existence of silica-silica and silica-iron interactions does not match with the main assumption of the chain model, *i.e.*, the existence of only hydrodynamic and magnetic interactions to explain the particle chaining originated by the action of external fields.

CONCLUSIONS

In this work we have investigated the behavior of iron-based magnetorheological suspensions under steady-shear and oscillatory-shear regimes, as well as the effect of silica nanoparticles as stabilizer of the suspensions. A scaling between viscosity and the ratio of hydrodynamic to magnetic forces given by the dimensionless Mason num-

ber (Mn) has been made and interpreted in terms of a chainlike micro-structural model.²⁰

It has been concluded that the chain model is quite well accomplished for iron suspensions without any stabilizing tixotropic agent. The presence of added silica nanoparticles in the suspension must hinder the formation of regular iron structures induced by the magnetic field. The chain model fails in this case for $Mn > 10^{-2}$, *i.e.*, for magnetic interactions not strong enough to provide stability for the structural silica-iron chains against the shear forces. The chain model has been shown to be more adequate for viscometry results than for oscillometry ones for scaling the viscous properties of magnetorheological suspensions with microscopic interparticle forces in terms of Mn number.

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SAŽETAK

Relacija između viskoznosti i hidrodinamičko/magnetskih sila u magnetskim tekućinama

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Cilj je ovog rada istraživanje magnetoreološkoga ponašanja tekućina, sastavljenih od mikrometarskih čestica željeza (prosječni promjer 930 ± 330 nm), pri jednostavnom stalnom i oscilirajućem protoku. Primijenjena su magnetska polja jakosti od 279 A/m (0,35 mT) do 1727 A/m (2,17 mT). U obzir je uzet i učinak nanočestica silicijeva oksida kao stabilizatora suspenzije. Istraživanje je rađeno uspoređivanjem viskoznosti suspenzije i omjera hidrodinamičkih i magnetskih sila koje djeluju na dispergirane čestice, izraženih u obliku Masonovoga broja (Mn). Interpretacija je izvedena prema tzv. lančanom modelu preuzetom iz teorije Martina i Andersona (*J. Chem. Phys.* **104** (1996) 4814–4827). Slaganje s modelom je dobro u slučaju suspenzija željeza različitih volumnih udjela (20 % i 30 %) u kojima nema stabilizirajućeg agensa. Dodatak nanočestica silicijeva oksida u suspenziju priječi nastajanje pravilnih željeznih struktura induciranih magnetskim poljem, posebno pri najnižim magnetskim poljima primijenjenim u ovom radu. U tim slučajevima model više nije primjenljiv. Pri određivanju viskoznih svojstava magnetoreoloških suspenzija s mikroskopskim međučestičnim silama, izraženih kao Mn broj, viskozimetrija se pokazala prikladnijom metodom od oscilometrije.