Concentration and composition dependence of the rheological behaviour of some magnetic fluids

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Abstract

The particle concentration dependence of the dynamic viscosity of various mono- and double-layer sterically stabilized magnetic fluids was investigated in the absence of an external magnetic field. Fits of the relative viscosity data to various approximating relationships show that the flow properties are influenced by chemical composition details, but do not depend significantly on dipolar interactions between particles. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Rheological properties are essential to describe the flow characteristics of many magnetic fluids in the absence and under the influence of an external magnetic field. These properties are dependent on the particle size and shape, particle size distribution, as well as on the interactions between particles and agglomerate formation.

Previous works on the subject [1–3] revealed various aspects specific to magnetic fluids, especially the relevance of the particle concentration and the degree of colloidal stability on their rheological behaviour. Recent measurements on the concentration dependence of the sedimentation velocity of magnetic fluids [4,5] clearly evidenced the significant influence of particle interaction details, in particular of the type of surface covering of magnetic nanoparticles.

The aim of this paper is to evidence some effects of the composition and concentration on the dynamic viscosity of several sets of magnetic fluids with mono- and double-layer sterically stabilized magnetite nanoparticles dispersed in nonpolar and polar carrier liquids.

2. Preparation of samples

Two large samples of petroleum-based magnetite magnetic fluids were prepared by the same chemical coprecipitation method, described in Ref. [6], the only difference being related to the quality of the chemisorbed surfactant layer (technical grade (TOA) and chemically pure oleic acid (POA)). Excess oleic acid was eliminated by repeated flocculation – redispersion of magnetite particles. Highly

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concentrated nonpolar (transformer oil (TR-30)) and polar (pentanol (PENT), heptanol (HEPT), dioctylsebacate (DOS)) magnetic fluid samples were prepared by carrier liquid exchange, using dodecylbenzenesulphonic acid (DBS) and poly-isobutylenesuccineanhydride (PIBSA), as secondary (physically adsorbed) surfactant for the polar carriers. Except for TR-30 samples, prepared both with TOA and POA surfactants, the samples with polar carriers (PENT, HEPT, DOS) have POA as the primary chemisorbed surfactant.

The maximum volume fraction of magnetite in concentrated samples attained $\phi_\rho = 0.22$. Various samples with lower particle volume fraction were obtained by subsequent dilution of the original stock magnetic fluids.

TEM analyses of the two petroleum-based stock magnetic fluids, stabilized with TOA and POA, respectively, showed only a small difference between the mean diameters of particles. There were 1591 particles measured with TOA and 1203 with POA, giving the values of 11.1 and 10.9 nm for the mean physical diameter.

3. Viscosity measurements

Viscosity measurements were performed using an Ubbelohde capillary viscosimeter and a RHEOTEST-2 Couette-type rotary rheometer at shear rates up to 1400 s^{-1} (i.e. at very low Peclet number values, $\text{Pe} \ll 1$), in the temperature range -10–$50°C$. Non-Newtonian rheological behaviour was not observed in the investigated ranges of particle volume fraction, temperature and shear rate.

4. Main approximating relationships

The data concerning the dynamic viscosity η of magnetic fluids and of their carrier liquids, η_0, were fitted to several approximating relationships with one adjustable parameter, depending on the particle volume fraction ranges considered. Considered, among others, were the well-known relationships of Einstein, Batchelor, Rosensweig–Nestor–Timmins, Vand, Krieger–Dougherty and Quemada [1–3,7].

Recently, Chow [8,9] performed a detailed theoretical analysis of concentrated suspensions, especially of the influence of many-body particle interactions on the effective viscosity. Based on a liquid lattice model, the low shear limiting viscosity resulted as

$$\eta = \eta_0\left[\exp\left(\frac{2.5\phi_h}{1-\phi_h}\right) + \frac{A\phi_h^2}{1-A\phi_h^2\phi_m}\right], \tag{1}$$

where A is the coupling coefficient.

The parameters examined in this paper, considering the shape of particles to be approximately spherical, were the following: (1) the ratio $p = \phi_h/\phi_\rho$ (or ϕ_h) (ϕ_h – hydrodynamic volume fraction, ϕ_ρ – solid volume fraction) in Einstein and Vand-type relationships; (2) the coefficient c of ϕ_h^2 in dependencies of the type given by Batchelor (c_B) and by Rosensweig et.al. (c_R); (3) the maximum packing fraction ϕ_m in the relations of Krieger and Dougherty and Quemada; and (4) the coupling coefficient A of Eq. (1).

5. Results and discussion

The values of coefficient p for the magnetic fluids investigated were determined by fitting the viscosity data to the Einstein and Vand relationships. Involving the viscosity data for the whole particle concentration domain considered, up to $\phi_\rho \approx 0.2$, the values of p obtained from good quality fits to the Vand formula are significantly lower than those found from Einstein's relationship for very diluted samples ($\phi_\rho < 0.02$) (see Table 1). This tendency was observed for each type of magnetic fluid, but the difference between the two fits is much lower for TR30 + POA samples than for those with technical-grade surfactant or with double-surfactant layer. For the TOA-stabilized samples the parameters p_E (found from fit to Einstein formula) and p_V (found from fit to Vand formula) are significantly greater than those found for TR-30 samples with chemically pure surfactant (POA), which denote the presence of a large amount of agglomerates in TOA-stabilized samples, evidenced also by dichroism measurements [10]. Taking into account the p values found and the mean physical diameter

Table 1
Parameter values obtained from fits to three approximating relationships, for low-volume fraction (Einstein and Batchelor) and for the whole-volume fraction domain investigated (Vand and Rosensweig et al.) ($t = 20°$C)

Magnetic fluid	p_E	δ_E (nm)	p_V	δ_V (nm)	c_B	c_R
TR30 + POA	2.87	2.31	2.54	2.10	9.87	1.42
TR30 + TOA	8.10	—	3.70	—	11.90	1.35
PENT	6.02	4.50	3.83	3.10	10.77	1.49
HEPT	—	—	3.41	2.78	—	1.19
DOS	7.56	5.30	4.10	3.30	10.45	1.26

of particles, the effective surfactant layer thickness δ was evaluated (Table 1), from p_E and p_V values for good-quality POA stabilized samples, without agglomerates. Note, for example, that the δ values found for TR-30 samples are consistent with the POA surfactant used. As also observed, $\delta_V < \delta_E$, i.e. the resulting surfactant layer thickness is smaller when the fit involves the data for the whole concentration domain investigated. Concentration dependence of the effective surfactant shell thickness was also observed in small angle neutron-scattering investigations on D-benzene magnetic fluids [11] (see also Ref. [12]), or in dynamic light scattering measurements on PENT magnetic fluids [4,5] (in these works the PENT sample is denoted MaS) prepared by the same method [6].

The particles considered were of spherical shape. This is a good approximation since from birefringence measurements and electron micrography analyses a relatively small mean ellipticity (≈ 1.3) was found [10]. Also a fit of TR30 + POA samples viscosity data at 20°C to the Krieger–Dougherty formula with two parameters, ϕ_m and $[\eta]$ (intrinsic viscosity), gave $[\eta] = 2.73$ very close to $[\eta] = 2.5$ valid for spherical particles. In subsequent fits to various other data sets $[\eta] = 2.5$ was considered. The low concentration viscosity data were fitted to the Batchelor type function (Fig. 1). The fitted values of the coefficient c_B of the second-order term are greater than the theoretical value 6.2 for hard spheres (Table 1), the most pronounced deviation corresponding to TR30 + TOA samples. In the case of particles with a double layer of surfactants in polar carriers (PENT, DOS), the formation of agglomerates is practically absent [10,13],
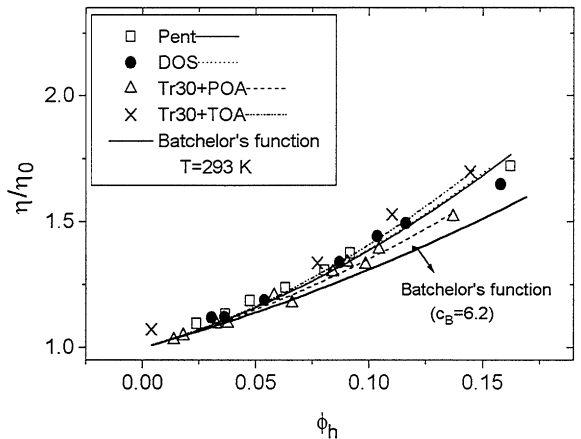

Fig. 1. Relative viscosity vs. hydrodynamic particle volume fraction fitted to Batchelor's-type function: $\eta/\eta_0 = 1 + 2.5\phi_h + c_B\phi_h^2$.

probably due also to the contribution of electrostatic repulsive interactions (evidenced for PENT magnetic fluids in Refs. [4,5]). The resultant overall repulsion between particles impedes their agglomeration, but also increases the viscosity [14] of these magnetic fluids. The lowest deviation from the behaviour of a hard sphere suspension was evidenced in the case of TR30 + POA samples.

Viscosity data for each set of samples were fitted with good results to the approximating relationships considered, as illustrated in Fig. 2 for TR30 + POA and DOS samples at 20°C. The fitted values of the coupling coefficient A of Eq. (1) are generally close to the theoretical result $A = 4.67$ found for nonmagnetic suspensions [9]. Some particular values are presented in Table 2.

Table 2
Fitted values of the coupling coefficient A of formula (1) for TR30 + POA and DOS magnetic fluids at 20°C (see also Fig. 2) using $\phi_m^{(KD)}$ and $\phi_m^{(Q)}$ which are the maximum hydrodynamic fractions obtained from fits to the formulas of Krieger–Dougherty and Quemada, respectively

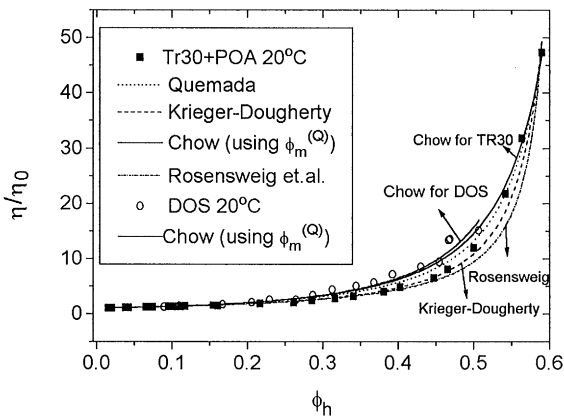| Magnetic fluid	ϕ_h	ϕ_m^{KD}	A^{KD}	ϕ_m^{Q}	A^{Q}
TR30 + POA	$\leqslant 0.45$	0.55 ± 0.0006	4.94 ± 0.28	0.66 ± 0.004	4.54 ± 0.20
TR30 + POA	$\leqslant 0.60$	0.65 ± 0.0012	3.83 ± 0.055	0.69 ± 0.0008	3.65 ± 0.047
DOS	$\leqslant 0.45$	0.56 ± 0.006	4.87 ± 0.25	0.66 ± 0.006	4.39

Fig. 2. Relative viscosity vs. hydrodynamical volume fraction for TR30 + POA and DOS samples (fits to approximating relationships).

6. Conclusions

The rheological behaviour of magnetic fluids is very sensitive to composition details, in particular to the type of stabilisation and quality of surfactants used. The particle concentration dependence of the relative viscosity is well described especially by formula (1) and shows that in the absence of an external magnetic field the flow properties of the investigated magnetic fluids are not influenced significantly by dipolar interactions.

Acknowledgements

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