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Effect of centrifugation on dynamic susceptibility of magnetic fluids

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ABSTRACT

The dispersive composition, dynamic susceptibility and spectrum of times of magnetization relaxation for six samples of magnetic fluid obtained by centrifuging two base colloidal solutions of the magnetite in kerosene was investigated experimentally. The base solutions differed by the concentration of the magnetic phase and the width of the particle size distribution. The procedure of cluster analysis allowing one to estimate the characteristic sizes of aggregates with uncompensated magnetic moments was described. The results of the magnetogranulometric and cluster analyses were discussed. It was shown that centrifugation has a strong effect on the physical properties of the separated fractions, which is related to the spatial redistribution of particles and multi-particle aggregates. The presence of aggregates in magnetic fluids is interpreted as the main reason of low-frequency (0.1–10 kHz) dispersion of the dynamic susceptibility. The obtained results count in favor of using centrifugation as an effective means of changing the dynamic susceptibility over wide limits and obtaining fluids with the specified type of susceptibility dispersion.

1. Introduction

It has been well known that nano-sized colloidal particles in the magnetic fluid are subject to intensive thermal (Brownian) motion, which realizes their distribution throughout the accessible fluid space. Due to application of a special procedure which prevents particle coagulation (by ionic or surfactant stabilization), the magnetic fluids avoid stratification and can preserve for years the spatial homogeneity in the gravitational field of the Earth (if the characteristic height of the cavity does not exceed a few centimeters). The situations drastically changes in the case when the magnetic fluid has a sufficient amount of coarse particles (with magnetic core 20–25 nm in diameter) and/or aggregates formed under the action of van der Waals and magnetodipole interparticle interactions. Sedimentation of coarse particles and aggregates is responsible for the formation of a peculiar type of particle "atmosphere" in the fluid with inhomogeneous distribution of particles throughout the thickness of the fluid layer, which resembles the barometric distribution. The spatial inhomogeneity increases, if the magnetic fluid is subject to centrifugal forces or gradient magnetic fields. In these cases, the characteristic height of the "barometric" distribution proves to be compatible with the size of the cavity, which gives rise to the formation of inhomogeneous particle distribution with large concentration gradients. The characteristic concentration differences (i.e., the degree of inhomogeneity) can change by several orders of magnitude depending on the size of cavity, the size and concentration of particles and aggregates [1,2]. Note that the presence of coarse particles in the magnetic fluid is not necessarily a negative factor, because these particles (all other things being equal) increase the saturation magnetization and the initial magnetic permeability of the solution. We are certainly speaking about some "acceptable" concentration of coarse particles, which has inessential effect on the sedimentation stability of the magnetic fluid.

The centrifugation process is one of the important stages of magnetic fluid preparation [3–6]. It is commonly used to remove the non-magnetic admixtures and accidentally formed large aggregates from the colloidal solution, as well as to check the mixture for stability under conditions of centrifugal fields. The objective of the present work is to obtain qualitative data on the effect of centrifugation on the granulometric composition of colloidal particles and aggregates, spectrum of relaxation times and dynamic susceptibility of the magnetic fluid – the parameter, which is most sensitive to the particle size distribution [7,8]. The obtained results are the reflection of the fact that the centrifugation can be used as a means of affecting the dynamic susceptibility over wide limits and preparing the fluid with a prescribed type of the dynamic susceptibility dispersion.

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2. Theoretical basis and data processing method

It has been well known that in magnetic fluids there are two mechanisms of magnetic moment relaxation – the Neel [9] and Brownian [10] mechanisms. The former is typical for small-sized particles. The essence of this mechanism is that the magnetic moment rotates inside the magnetic particles about their crystallographic axes in the wake of the external magnetic field, while the particles themselves remain immovable. In this case, the magnetization reversal of the Neel particle is related to overcoming the energy barrier of height KV_m (K is the constant of magnetic anisotropy, V_m is the volume of the magnetic core of the particle), and therefore the time of magnetic moment relaxation increases exponentially with an increase of the reduced energy of magnetic anisotropy $\sigma = KV_m/kT$, where kT is the energy of thermal motion. According to Ref. [11] the Neel relaxation time is described quite adequately by the interpolation formula

$$\tau_N(\sigma) = \tau_D \frac{e^\sigma - 1}{2\sigma}\left[\frac{1}{1+1/\sigma}\sqrt{\frac{\sigma}{\pi}} + 2^{-\sigma-1}\right]^{-1} \quad (1)$$

where $\tau_D \approx 10^{-9}$ s is the characteristic time of the Larmor precession damping. At $\sigma \leqslant 1$ the time of magnetic moment relaxation is rather small and at the frequency of the probing field $f \leqslant 10^5$ Hz, the magnetization reversals are quasi-static. So, the Neel particles have no effect on the low frequency magnetic susceptibility dispersion. The Brownian mechanism of the magnetic moment relaxation is related with the mechanical rotation of particles in a liquid matrix. The corresponding (Brownian) relaxation time depends on the size of the particle and is given by

$$\tau_B = \frac{3\eta V}{kT} \quad (2)$$

where η is the dynamic viscosity of colloidal solution, V is the hydrodynamic volume of the colloidal particle including that of the protecting shell. The mechanism operating in real solutions is the mechanism, which is able to provide the shortest relaxation time. The equality of characteristic times $\tau_N = \tau_B$, solved for the anisotropy parameter σ specifies the crucial diameter x^* of the magnetic core of the particle suspended in the fluid [10]. At $x < x^*$ the Neel mechanism of magnetic moment relaxation prevails and at $x > x^*$ the Brownian mechanism becomes dominant. For a magnetite particle with the effective anisotropy constant $K \approx 2 * 10^5$ erg/cm^3 (for example, [7]), suspended in the colloidal solution with the volume concentration of magnetite particles of several percent, this value according to the obtained estimates is $x^* \approx 17$ nm. In dilute solutions such diameter of the magnetic core corresponds to the Brownian time τ_B of about of 10^{-5} s and strong dispersion of the dynamic susceptibility at the frequencies of order of 10–100 kHz. The dispersion of dynamic susceptibility at lower frequencies is associated with more coarse Brownian particles and/or particle aggregates considered as independent kinematic units. Using the known from experiment low-frequency susceptibility $\chi = \chi(\omega)$, we can approximately estimate the characteristic times of magnetization relaxation, the sizes of Brownian particles and aggregates.

In the case of idealized monodisperse fluid the time of magnetization relaxation can be readily determined from the dispersion curves describing the dependence of the real $\chi'(\omega)$ and imaginary $\chi''(\omega)$ parts of susceptibility on the frequency of the sounding field. The dynamic susceptibility in this case is described by the Debye formula

$$\chi' = \frac{\chi_0}{1+\omega^2\tau_B^2}, \quad \chi'' = \frac{\chi_0\omega\tau_B}{1+\omega^2\tau_B^2}, \quad (3)$$

where χ_0 means the static susceptibility. The condition $\omega^*\tau_B = 1$ specifies the frequency ω^*, at which the real part of susceptibility decreases by a factor of two and the imaginary part reaches the maximum value. The estimation of the relaxation time and characteristic size of the particle (or cluster) by formula (2) is reduced to determination of the characteristic frequency ω^*, corresponding to the maximum point on the $\chi''(\omega)$ – curve [12].

Polydispersity of magnetic fluids and the existence of aggregates cause the spectrum of dynamic susceptibility to "extend" by several orders of magnitude [7], and the location of the maximum $\chi''(\omega)$ become uncertain. In this case, all coarse particles and aggregates can be formally subdivided into rather narrow fractions differing in times of relaxation of the magnetic moments while the dynamic susceptibility can be represented as a superposition of the Debye functions:

$$\chi'(\omega) = A_0 + \Sigma_{i=1}^N \frac{A_i}{1+\omega^2\tau_i^2}, \quad \chi''(\omega) = \Sigma_{i=1}^N \frac{A_i\omega\tau_i}{1+\omega^2\tau_i^2}. \quad (4)$$

where τ_i is the time of magnetization relaxation, corresponding to the ith fraction. The spectral amplitude A_i has the meaning of contribution of the above to the equilibrium susceptibility of the system. For the some of the Neel particles $\omega\tau_N \ll 1$ in the examined frequency range and their contribution A_0 to the dynamic susceptibility is independent of frequency.

The relaxation times τ_i and the spectral amplitudes A_i were found from the spectral $\chi'(\omega)$ – and – $\chi''(\omega)$ curves by the least square method using the Levenberg–Marquardt algorithm, which was realized with the use of the LMFIT library [13]. The solution of the reverse problem obtained in such a way is obviously not unique, because it depends on the selected number of fractions N in the right-hand-side of Eq. (4). In the present study, with increase of N the error of the experimental curve approximation first decreases reaching some irreducible level determined by the error of measurements. In all cases we chose the minimal number of fractions (from 5 to 7) capable of sustaining this irreducible level. An increase in the number of fractions above this minimum appears to be unjustified leading to a simultaneous increase of the error of computation of the amplitude A_i. Thus, the selection of the number of fractions N in series expansion Eq. (4) cannot be considered unambiguous – it involves a compromise. A desire to obtain more comprehensive information on the relaxation times and granulometric composition by increasing the number of fractions is restrained by a growth of the error in the spectral amplitude A_i – the larger is the number of fractions the greater is the error. For the number of fractions chosen for our calculations the spectral amplitudes A_i are determined from Eq. (4) with the error of about 20%, which, however, decreases by a factor of 1.5–2 after averaging over the fractions relating to individual particles or clusters.

Eq. (4) has been written under the assumption that the interactions between individual clusters and particles not entering the clusters (steric, hydrodynamic, van der Waals and magnetodipole interactions) have inessential effect on the relaxation time of the magnetic moment. Apparently, this assumption holds true for diluted solutions but is invalid for concentrated magnetic fluids. However, even in the case of concentrated fluids Eq. (4) are expected to lead to insignificant errors, because the steric and hydrodynamic interparticle interactions can be taken into account (at least partially) by the replacement of the dispersion medium viscosity in Eq. (2) with the effective viscosity of the magnetic fluid. The influence of the magnetodipole interactions on the dynamics of individual particles is recently analyzed in [14,15]. It has been shown that magnetodipole interactions lead to a shift of the maximum on the $\chi''(\omega)$ –curve in the direction toward low frequencies (approximately by 30–40%) and increase in the length of the $\chi'(\omega)$ – curve plateau. This implies that the spectrum of relaxation times formally determined from Eqs. (4) is inconsistent