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Magnetoviscous effect in ferrofluids with different dispersion media

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ABSTRACT

Ferrofluids based on magnetite nanoparticles dispersed in different carrier media (dialkyldiphenyl and polyethylsiloxane) have been synthesized using mixed surfactants (oleic acid, stearic acid and alkenyl succinic anhydride). Magnetic properties of the samples and a change of their shear viscosities in an applied magnetic field have been studied in order to evaluate an influence of the carrier medium on a magnetoviscous effect. A significance of the interaction of the carrier medium and surfactant with a consideration of the magnetic and rheological behavior of ferrofluids was demonstrated.

1. Introduction

Ferrofluids are unique magnetic colloidal systems, whose disperse phase is represented by magnetic nanoparticles. The particles are usually coated with a mono- or bimolecular layer of the surfactant and suspended in an organic or non-organic carrier liquid. The character of the surfactant, the carrier liquid and the size of the magnetic particles are determining parameters for the stability of ferrofluids. A mean size of classical magnetite particles used in ferrofluids is about 10 nm and they have a nearly spherical shape [1]. This size provides the gravitational and magnetic stability of these colloids. Previous researches have shown that commercial samples of ferrofluids often represent polydisperse systems which contain particles fractions with much higher sizes [2,3], which lead to a change of the ferrofluids viscosity in an externally applied magnetic field. It is usually referred as the magnetoviscous effect for colloids with single domain ferromagnetic particles and magnetorheological effect for suspension with non-Brownian particles [2,3]. A change of the particles material, e.g. cobalt instead of magnetite, will lead to a changed interparticular interaction and to a modified rheological behavior of the ferrofluid respectively. The possibility to tune and control the rheology of ferrofluids is of a high practical importance [3]. Due to a high magnetization and liquidity, ferrofluids are used in divers technical applications, e.g. as a liquid sealing in chemical and biochemical reactors and vacuum feedthroughs, as well as a working body in tilt sensors etc [1,3–5]. Furthermore, ferrofluids based on conventional lubricating oils show improved tribological characteristics [6,7].

A targeted synthesis of stable magnetic colloids with desired physical and chemical properties is a challenging scientific task, which requires exhaustive studies and, particularly, magnetorheological characterization. A detailed viewpoint on a flow behavior of ferrofluids can significantly expand an area of their applications. Many studies are focused on commercial ferrofluid samples, for which scarcely ever an exact composition or synthesis procedure is known. Furthermore, a systematical analysis of the surfactant influence on magnetoviscous effect in ferrofluids is as well rather poor published. More attention is usually given to the nanoparticles material and morphology [8–16] as well as to the fluid stability [17–20]. Recently, a magnetoviscous effect in a pure biocompatible ferrofluid and a sample diluted with blood has been experimentally evaluated, while significantly higher effect was measured in the diluted samples [21]. Theoretical predictions of the ferrofluid rheology based on the rotational viscosity and chains/droplets formation approaches are not able to give an explanation of the enhanced magnetoviscous effect [22–24]. Assumably, in this case a complex interaction between a carrier medium and magnetic nanoparticles should be taken into account. This requires special investigations.

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In this study stable magnetic colloids based on magnetite nanoparticles suspended in different dispersion media have been synthesized. A primary goal was to evaluate an influence of the carrier medium and surfactant on the magnetoviscous effect in ferrofluids. Synthesized samples in this work contain magnetite nanoparticles from one batch and are based on dialkyldiphenyl and polyethylsiloxane, while combinations of the oleic acid, stearic acid and alkenylsuccinic anhydride are used as a surfactant to cover the particles. These compositions makes these ferrofluids very attractive for engineering oriented application, e.g. at low and high temperatures, under vacuum condition etc. Magnetic behavior and magnetoviscous effect are experimentally studied and an influence of the synthesis conditions on a rheological behavior of these colloids is evaluated.

2. Materials

The following commercial grade components from Acros Organics have been used: iron sulfate ($FeSO_4{\cdot}7H_2O$, 99%), iron chloride ($FeCl_3{\cdot}6H_2O$, 98%), aqueous ammonia (NH_4OH, 25%), oleic acid ($C_{17}H_{33}$, 97%), alkenylsuccinic anhydride ($C_{76}H_{145}O_3$, 80%).

2.1. Nanoparticles

Magnetite nanoparticles have been synthesized using an intensive mixing of the iron sulfate salt (II) and iron chloride (III) salt with an excess amount of the aqua ammonia solution (NH_4OH) in a thermostatically controlled vessel at a temperature of 298 K.

Similar methods are reported elsewhere and protected with patents [25–28].

Obtained suspension has been repeatedly flushed out with distilled water up to pH=7–8. A cleaning grade of the suspension from sulfate and chloride ions was proved verifying the specific electrical conductivity of the flush water (1.77 μSm cm^{-1}) as it has been reported in [29].

To characterize a crystal structure and specific surface of the nanoparticles an X-Ray analysis of a water suspension of the synthesized magnetite was conducted using a method presented in [25]. The X-Ray diffractometer 'Dron-3' has been used (diffraction at small-angels of $2\theta = 1 - 30°$). Results of the XRD analysis have shown that most of magnetite crystals have a size of 7.5 ± 3.5 nm.

2.2. Dispersion medium

As dispersion medium dialkyldiphenyl (Alkaren D24S) and polyethylsiloxane (PES-5^{tm}) were used. Dialkyldiphenyl has a low viscosity, low vapor pressure, high thermal oxidation stability, good tribological characteristics and is not affected by the hydrolysis. Moreover, it is non toxic and nonreactive. Polyethylsiloxane is a molecular species, whose molecules consist of interlacing silicon and oxygen atoms with cut in hydrocarbonic chemical groups via unlinked silicon bonds. A polyethylsiloxane liquid used in this study (PES-5) is known for its low saturated vapor pressure, low melting point, good dielectric and hydrophobic properties, low temperature viscosity coefficient and low surface tension. Additionally, it has a good thermal conductivity and thermal oxidation stability. Such polyethylsiloxane liquid can be used as a carrier medium of ferrofluids utilized for the liquid sealing and is especially suitable at low temperatures and vacuum conditions. Alkaren D24S and PES-5 are considered as Newtonian liquids with viscosities of 0.046 Pa s and 0.250 Pa s at 20 °C respectively.

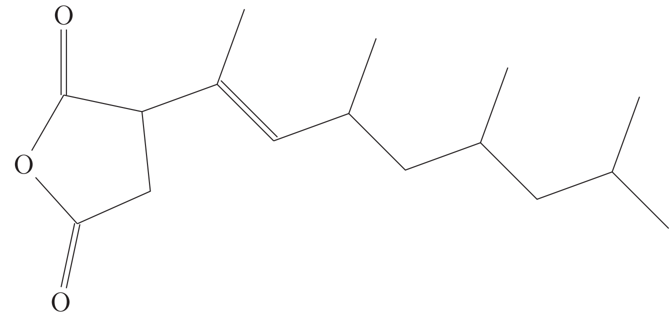

Fig. 1. Schematic of the molecular structure of alkenylsuccinic anhydride [30].

2.3. Ferrofluid samples

Ferrofluid samples have been produced in two basic stages: synthesis of magnetic nanoparticles with colloidal sizes and their stabilization in a liquid medium.

Magnetite was centrifuged and, afterwards, the surface of the particles was stabilized with a monomolecular absorbing layer of surfactant followed by a peptizing of the stabilized magnetite in a disperse medium at T=85 °C during 6–10 h under vacuum. The protective absorbing layer guaranties an aggregation stability of the ferrofluids. This layer must have a certain thickness in order to limit an interparticle attraction. Moreover, the coating has to be sturdy against effects of electrolyte, temperature and mechanical vibrations. A mixture of oleic acid and alkenylsuccinic anhydride (Fig. 1) has been used as a surfactant. Alkenylsuccinic anhydride is intended to enhance a protection of magnetite nanoparticles from corrosion. It is expected that this mixed surfactant will expand an applicability of the ferrofluid.

A composition and basic properties of the samples synthesized within the study are given in Table 1.

3. Experimental

3.1. Magnetic measurements

Magnetic measurements were conducted using a vibrating sample magnetometer (Lake Shore 7407). An effective applied magnetic field H was calculated taking into account the geometrical demagnetizing factor N

$$H = H_{ext} - M(H){\cdot}N, \quad (1)$$

where H_{ext} is the strength of an externally applied field, $M(H)$ is the magnetization of the fluid. The geometrical demagnetizing factor is N=0.44 for the given geometry of the sample holder.

Results of magnetic measurements are presented in Fig. 2 and Table 2. All samples show for ferrofluids typical superparamagnetic behavior without magnetic hysteresis. The saturation magnetization is estimated comparing experimental results with a spontaneous magnetization of the magnetite (446 kA/m [1]). The initial magnetic susceptibility is calculated using a linear approximation of the magnetization curve (H) in the range of the low values of an applied field. It is possible to estimate the size of magnetite cores for monodomain nanoparticles dispersed in a ferrofluid using the initial susceptibility which is approximated from the measurements as given by [1]:

$$\chi_i = \frac{\pi}{18}\phi\mu_0\frac{M_0^2 d^3}{kT}, \quad (2)$$

where χ_i denotes the initial magnetic susceptibility, μ_0 the vacuum permeability, M_0 the spontaneous magnetization of the magnetic material, d the diameter of the nanoparticles, k_B the Boltzmann's