Magnetic and structural investigations on barium hexaferrite ferrofluids

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Abstract

Barium hexaferrite $BaFe_{12-2x}Ti_xCo_xO_{19}$ ferrofluids have been prepared using oleic acid as surfactant and Isopar M[®] or dodecane as carrier liquid. The ferrite particles were prepared by glass crystallization. Hysteresis parameters, the initial susceptibility versus temperature and the magnetic particle size were obtained by VSM. Ferrofluids with a partly deuterated carrier liquid were investigated by small angle neutron scattering (SANS). SANS curves lead to a bimodal size distribution consisting of single magnetic particles with an organic shell and aggregated particles with an incomplete organic layer.
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1. Introduction

In contrast to magnetite, which is the predominating magnetic material of commercial ferrofluids (FF), barium hexaferrite has an intrinsic anisotropy one order higher. On the other hand, saturation magnetisation of Ba-ferrite (BaF) is not significantly smaller than that of magnetite. From these facts consequences are expected: For magnetite based FFs the anisotropy barrier—which determines the Néelian relaxation—is not defined by the particle volume only. Small random deviations from spherical particle shape will induce an additional shape anisotropy and therefore significantly inflect the overall anisotropy barrier. In contrast, for BaF FFs the influence of shape anisotropy is less severe due to its high intrinsic anisotropy. Therefore, Néelian relaxation is mainly defined by the size distribution of the core particles. It is expected that Néelian relaxation is significantly suppressed by the high intrinsic anisotropy of BaF compared to magnetite FFs with the same particle size distribution. Magneto-rheological effects

will be much more significant in the case of BaF FFs. Numerical calculations (local-equilibrium magnetic state model) of the effect [1,2] show a much higher specific viscosity gain for BaF FFs compared to magnetite FFs.

2. Preparation

Nanocrystalline Ba-ferrite $BaFe_{12-2x}Ti_xCo_xO_{19}$ particles were prepared by the glass crystallization method [3]. The particles grow isolated in a glass matrix and were leached out by dissolving the matrix. BaF FFs have been prepared using oleic acid as surfactant and Isopar[®] M or dodecane as carrier liquid [1]. K-oleate was added to the ferrite to adhere at the particle surface. The oleate was converted to oleic acid. The substance was washed, the coated particles were separated and carrier liquid was added. Aggregates in the FF were reduced by centrifugation at $5000g$. The supernatant liquid is the initial FF, which usually will be diluted. For SANS investigations from the initial fluid different diluted FFs in mixtures of protonated and deuterated dodecane were prepared.

A water-based Ba-ferrite FF with oleoyl sarcosine as surfactant was prepared for the first time (without the

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centrifugation step, volume fraction $\approx 0.8\%$) from the same initial powder [4].

3. Magnetic characterization

An analysis of the size distribution of the magnetic cores of the ferrite particles was done by magnetic granulometry as described in Ref. [5] by calculating the superparamagnetic volume fraction at different temperatures according to $V = \ln(t_o/\tau)k_B T/K(T)$ in the range from 5 up to 300 K. The time constant t_o is determined by the sweep rate in the magnetization loops of 100 Oe/s. $\tau = 1/2\pi f \approx 10^{-9}$ s is determined by the attempt frequency of the thermally activated remagnetization processes. Stoner–Wohlfarth behaviour was assumed for non-superparamagnetic particles. The ratio of anisotropy $K(T)/K(295\,\mathrm{K})$ was determined experimentally from $H_c(T)$- and $M_S(T)$-data of a coarse non-superparamagnetic powder (mean size ≈ 50 nm, for $K_1(295\,\mathrm{K})$ value cf. Ref. [6]). Deviations of an effective K is due to differences in the particle shape (coarse particles are platelets whereas the nanoparticles are roughly spherical (by TEM)) and surface anisotropy of the nanocrystalline powder. Magnetic granulomety data are shown as a histogram in Fig. 1. The first value (for $d_{\mathrm{Core}} < 1.63$ nm) is uncertain because (i) the temperature range below 4.2 K is experimentally not accessible and therefore assumptions for the 0 K-values have to be made. (ii) The relative remanence M_R/M_S is lower than $1/2\ (=0.41)$ even at 5 K, in contrast to the Stoner–Wohlfarth theory.

Particle size distributions were reconstructed as well from magnetization data at room temperature by solving the Langevin integral equation (Eq. (1)) under the assumption of a lognormal particle size distribution [7]

$$M = M_S \int_0^\infty \rho(V) L\left(\mu_0 \frac{M_{\mathrm{S\ Bulk}} V}{k_B T} H\right) \mathrm{d}V. \tag{1}$$

The normalized lognormal particle size distributions obtained by this method are also plotted in Fig. 1 for an FF prepared from the same batch of BaF nanopowder (b) and for the case of the nanopowder suspended in gel (c). As can be easily seen there is no significant difference between these two distributions. Therefore, we conclude that significant loss of larger particles due to sedimentation during FF preparation does not occur.

Median particle core diameter were calculated from the initial DC-susceptibility data according to

$$d_{\mathrm{Core}} = 2 \sqrt[3]{\frac{3}{4\pi} \frac{3k_B T}{\mu_0 M_{\mathrm{S\ Bulk}} M_S} \chi_{\mathrm{DC}}} \tag{2}$$

and on the other hand from magnetization behaviour $(\mathrm{d}M/\mathrm{d}(1/H))$ close to saturation according to

$$\frac{\pi}{6} d_{\mathrm{Core}}^3 = \frac{M_S}{M_{\mathrm{S\ Bulk}}} \frac{k_B T}{\mu_0} \frac{\mathrm{d}(1/H)}{\mathrm{d}M}. \tag{3}$$

From these two methods we obtained for the FF of Fig. 1(b) core diameters of 4.7 and 7.9 nm, respectively. Frequency dependent AC-susceptibility measurements revealed a linear decrease of the real part of the susceptibility with the logarithm of frequency.

Specific AC-susceptibility data for the water-based Ba-ferrite FF [4] are shown in Fig. 2. Due to the linear fit of $\chi'\,(\ln f)$ in Fig. 2, a constant χ''-value is predicted by the so-called $\pi/2$-law [8,9] which is also plotted in Fig. 2 as a full line parallel to the ordinate, in good agreement with the experimental χ'' data. A constant χ'' value is explained by a broad distribution of relaxation barriers in Refs. [9,10].
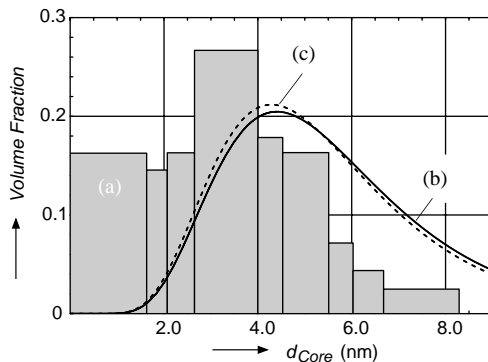

Fig. 1. Core size distribution of BaF nanopowder obtained by magnetic granulometry (a) compared with the lognormal distribution calculated from magnetization data for an FF from the same batch of powder (b) and powder suspended in gel (c).
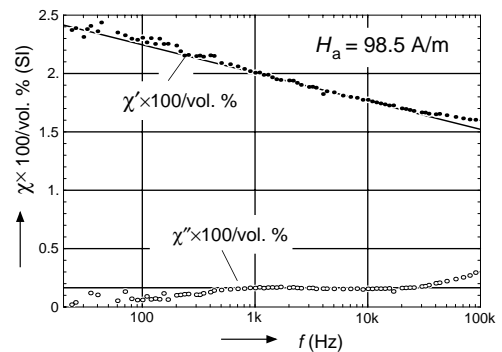

Fig. 2. Specific AC-susceptibility data (i.e. AC susceptibility related to the volume fraction of Ba-ferrite) of the water-based BaF FF in dependence on the frequency of the external AC magnetic field with constant amplitude of 98.5 A/m.

4. Structural properties

FF with a partly deuterated carrier liquid ($C_{12}H_{26}$ and $C_{12}D_{26}$) and a particle content between 1 and 4 vol% were investigated directly in the fluid state by SANS. In connection with an applied magnetic field SANS allows to distinguish between single magnetic particles and agglomerates in the range up to about 50 nm. The deuteration causes the scattering contrast between the organic surfactant and the carrier liquid. SANS curves lead to a bimodal size distribution (Fig. 3) consisting of single magnetic particles (mean diameter 8 nm) with an organic shell and aggregated particles. The single particle diameter (surfactant not included) corresponds with values found by magnetic measurements as well as former TEM investigations [1]. About 2/3 of the particles are separated. The agglomerates have a mean diameter of about 22 nm and consist of ferrite particles with an incomplete organic layer. There was no significant influence of the total particle concentration on the relative volume fraction.

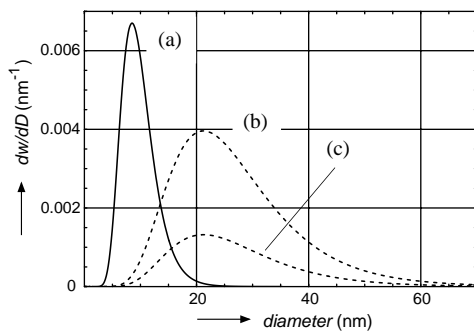For further details on SANS investigations see in Ref. [11].

Fig. 3. Relative volume size distribution of an FF by SANS of single particles calculated without organic layer (a) and agglomerates including surfactant material (b). (c) shows the magnetic particle fraction in the agglomerates estimated from the scattering length density.

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