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DETERMINATION OF FERROFLUID MAGNETISATION CURVE BASED ON THE MEASUREMENT OF PARTICLE DISTRIBUTION OBTAINED BY THE DLS METHOD

WYZNACZANIE KRZYWEJ MAGNETYZACJI FERROCIECZY NA PODSTAWIE POMIARU ROZKŁADU CZĄSTEK OTRZYMANEGO METODĄ DLS

Key words: ferrofliud, magnetic fluid, DLS measurement, particle distribution.

Abstract: Ferrofluid is a colloid with particles of about 10nm that show magnetic properties. These fluids are used in a variety of applications. Their application is affected by the type of carrier base liquid, the magnetic properties of the particle's material, and their size and shape. In practical applications, the magnetisation curve and the initial magnetic susceptibility are the most important characteristics of any ferrofluid. There are many methods for determining magnetic characteristics, e.g., using magnetometers. The magnetisation curve can also be determined on the particle distribution obtained using a transmission electron microscope (TEM). However, the cost of these devices and tests is relatively high. This paper describes a method for determining the magnetisation curve based on particle size measurements using the dynamic light scattering (DLS) method. Also, it is necessary to know the saturation magnetisation of the ferrofluid. The obtained magnetic characteristics were compared with magnetisation curves described in other publications. The purpose of this paper is to present the method and determine the influence of various particle distribution parameters on ferrofluid characteristics. The advantage of the method is that a small volume of ferrofluid is required in measurements using the DLS method. The measurement can be performed quickly, and the result can be used to estimate the magnetic properties of ferrofluids quickly. These characteristics can be used in analyses (mathematical or numerical calculations) of different devices such as magnetic seals, magnetic couplings, magnetic dampers, etc.

Słowa kluczowe: ferrociecz, ciecz magnetyczna, Pomiary DLS, rozkład cząstek.

Streszczenie: Ferrociecz to koloid o cząstkach rzędu około 10 nm, który wykazuje właściwości magnetyczne. Ciecze te znalazły zastosowanie w różnych aplikacjach. Na ich potencjalne zastosowanie wpływa rodzaj bazy nośnej, magnetyczne właściwości cząstek oraz wielkość i kształt. W praktycznym zastosowaniu krzywa magnetyzacji oraz wartość podatności magnetycznej są najważniejszymi parametrami ferrocieczy. Istnieje wiele metod wyznaczenia charakterystyk magnetycznych np. za pomocą magnetometrów lub krzywą tę można wyznaczyć na podstawie znajomości rozkładu cząstek otrzymanego z wykorzystaniem transmisyjnego mikroskopu elektronowego (TEM). Koszty tych urządzeń oraz badań są jednak relatywnie wysokie. W pracy opisano metodę wyznaczenia krzywej magnetyzacji na podstawie pomiaru wielkości cząstek z wykorzystaniem metody dynamicznego rozpraszania światła (DLS) oraz znajomości wartości magnetyzacji nasycenia ferrocieczy. Otrzymane charakterystyki magnetyczne porównano z krzywymi magnetyzacji opisanymi w innych publikacjach. Celem pracy jest przedstawienie metody oraz określenie wpływu różnych parametrów rozkładu cząstek na otrzymywane charakterystyki magnetyczne. Zaletą metody jest to, że wymagana jest mała objętość ferrocieczy w pomiarach z wykorzystaniem metody (DLS). Pomiar można wykonać w krótkim czasie, a wynik może zostać wykorzystany do szybkiego oszacowania właściwości magnetycznych ferrocieczy. Uzyskane charakterystyki mogą być wykorzystane w analizach (obliczeniach matematycznych lub numerycznych) różnych urządzeń takich jak uszczelnienia magnetyczne, sprzęgła magnetyczne, tłumiki itp.

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PREFACE

Magnetic fluid (ferrofluid) is one of the so-called controllable fluids because a magnetic field change influences its rheological properties and can be kept at a given location. It is not susceptible to sedimentation and is stable even under a high magnetic field. This is related to the small size of the particles and the fact that they are covered with a surface-active agent (surfactant) to prevent their agglomeration. The surfactant has a chain structure of about 2 nm in length. One end is adsorbed on the surface of the particles, while the other floats in the carrier liquid, providing repulsive forces between the particles. The most commonly used surfactants include oleic acid, linoleic acid, lecithin, and others **[L. 1]**. The size of magnetic particles is usually between 5 and 20 nm. They are made from materials that contain iron, cobalt, and nickel. The most commonly used material is Fe_3O_4 magnetite due to its higher saturation magnetisation value **[L. 2]**. The volume share of particles in the carrier liquid is usually about 10%. These fluids have applications in seals, speakers, dampers, and cooling systems **[L. 3]**. They are also used as a lubricant, and medicine is a very promising field of application **[L. 4]**. The magnetisation value is an important magnetic parameter that determines the application of a magnetic fluid. This determines the value of the magnetic field that is created in the material as a result of an external magnetic field. Ferrofluids are classified as superparamagnetic fluids, where magnetisation is similar to that of paramagnetic materials. At the same time, their initial magnetic susceptibility is high **[L. 5]**. The change in the magnetic properties of the fluid is a function of many parameters, in particular: the volume fraction of particles in the carrier fluid, the magnetic properties of the particle material, and the size and shape of the particles. Often the comparative parameter between fluids is the saturation magnetisation value. This is the value at which a further increase in magnetic field causes magnetic permeability to attain a characteristic value for vacuum. In the case of ferrofluid, saturation magnetisation is often given for a magnetic field intensity of 800 kA/m **[L. 6]**.

There are many instruments to measure magnetisation, and one of them is the magnetometer. However, this method often fails when measuring the magnetisation of magnetic fluids. This is related to the fact that these devices can usually perform measurements for very high values of magnetic induction on the order of 42 T. Magnetic fluids reach magnetic saturation already at a magnetic induction of 0.5 T. Other methods have also been developed over the years. Magnetisation can be determined, for example, by measuring the magnetic mass **[L. 7]**. This method involves measuring the attraction force of a fluid to a magnetic field source as a result of moving a magnet closer to a sample of magnetic fluid. The method for measuring magnetisation in an alternating magnetic field is described in the paper **[L. 8]**. There is also an iterative method based on measuring magnetic induction and then performing a series of numerical simulations to adjust the magnetisation curve **[L. 9]**.

Another method is measuring the carrier liquid's particle size distribution and determining the magnetisation curve based on known mathematical relationships **[L. 10]**. At the same time, the only direct and accurate method for obtaining the particle size distribution in ferrofluid is by measuring it with a transmission electron microscope (TEM). The problem with this method is that it is not always possible to make a simple dependence between the magnetic moment of the particles and their volume because, from these measurements, we will not get accurate information regarding the anisotropy of the surface, the degree of oxidation of the particles, the presence of, i.e., "dead layers," etc. **[L. 11]**. Measurements (TEM) are also complicated and time-consuming. An alternative and less precise method for determining the particle size distribution is atomic force microscopy (AFM) **[L. 12]**. An intermediate method between (TEM) and (AFM) can be Dynamic Light Scattering (DLS). This method is often used to measure the size of nanoparticles dispersed in a fluid. In recent years there have been significant developments (decreasing equipment prices and increasing measurement accuracy) **[L. 13]**. The measurement itself takes several minutes. The method is based on determining particle movements occurring due to Brownian motion. The laser light scattered by the particles contains information about the diffusion rate and, thus, the particle size distribution. This allows the analysis of particles ranging from 0.3 nm to 10000 nm. This paper presents a method for determining the magnetisation curve on particle size measurements. For this purpose, it is also necessary to know the saturation magnetisation value, which is often the only magnetic parameter provided by ferrofluid manufacturers.

THEORETICAL BASIS

The size and shape of the particles are among the most important parameters that directly affect the magnetic properties of ferrofluids. However, the distribution of characteristic particle sizes is not a less important factor. This distribution can be obtained numerically $f_N(D)$ or volumetrically $f_V(D)$. In the latter case, the volume fraction containing diameters between D and dD is $f_V(D)\mathrm{d}D$. Particles with diameters between *[D; D+dD*] "generate" magnetization $dM = M_S f_V(D)\mathrm{d}D$. Based on this, the magnetisation of a polydispersity system without taking into account the interaction of particles for the case of "weak" magnetic anisotropy (KVkT) can be described by a Langevin function:

$$M(H) = M_s \int_0^\infty L\left(\frac{\mu_0\mu(D)H}{kT}\right) f_V(D)dD \qquad (1)$$

where:

M_S – saturation magnetisation of ferrofluid;

$\mu(D)$ – magnetic momentum;

$L(\xi) = \coth(\xi) - \frac{1}{(\xi)}$ the dimensionless Langeven function;

H – magnetic field intensity;

K – the Boltzmann constant;

T – temperature.

If the diameter distribution is described by a number-weighted distribution, the product $Nf_N(D)dD$ determines the number of particles in the interval [$D;D+dD$], where N-the total number of nanoparticles in the ferrofluid. For number-weighted and volume-weighted distributions:

$$\frac{dV}{dD} = \frac{dN}{dD} D^3. \qquad (2)$$

Then the relationship between the probability density of a number-weighted distribution and the volume-weighted distribution can be written in the form

$$f_V(D) = \frac{D^3 f_N(D)}{\int_0^\infty D^3 f_N(D)dD} \qquad (3)$$

Equation (1) transforms to

$$M(H) = \frac{M_s}{\langle D^3 \rangle} \int_0^\infty L\left(\frac{\mu_0\mu(D)H}{kT}\right) D^3 f_N(D)dD, \qquad (4)$$

where

$$\langle D^3 \rangle = \int_0^\infty D^3 f_N(D)dD. \qquad (5)$$

The logarithmic normal distribution and the gamma distribution are most commonly used to describe the distribution of the diameters **[L. 6, 10]**. In this work, the logarithmically normal distribution is used:

$$f(D) = \frac{1}{D\sqrt{2\pi}\sigma} \exp\left(-\frac{(\ln(D) - m)^2}{2\sigma^2}\right), \qquad (6)$$

where *σ, m* parameters of the distribution, which can be calculated from the data obtained by the DLS method.

RESEARCH METHOD

Four fluids were selected for these studies, the properties of which are shown in **Tab. 1**. The parameter (M_S) was obtained from the manufacturer's information. The magnetic particles are made of magnetite, and the carrier fluid is synthetic oil. The other parameters, such as density (ρ) and dynamic viscosity (η) without a magnetic field, were determined based on our own research.

The particle size distribution was determined using the (DLS) method on a Litesizer 500 instrument. The magnetic fluid sample was dissolved in petroleum ether, a solvent with highly nonpolar properties. The solvent's dynamic viscosity (525.2 MPas) was adopted in the instrument software. This value was determined using an MCR301 rheometer using the two-coaxial cylinder method at 25°C. The refractive index was adopted with a value of 1.3533. Each measurement was repeated at least three times. The graphs show the average values. When the diameter distribution is measured, we can obtain a result indicating the number-weighted and volume-weighted distribution.

Table 1. Physical properties of examined ferrofluids
Tabela 1. Właściwości fizyczne badanych ferrocieczy

Label	Saturation magnetization M_S kA/m	Density ρ_F g/ml	Viscosity η (B=0 T, t=25°C) Pa·s
FF1	7	1.029	0.36
FF2	17.2	1.058	1.07
FF3	35.1	1.33	0.36
FF4	47.7	1.415	0.19

The number-weighted distribution is consistent with results obtained on a microscope, such as a TEM, and will give an even representation of small as well as large particles. The volume-weighted distribution corresponds to results obtained from laser diffraction or X-ray diffraction and will be more sensitive to the presence of larger particles. Measurements of particle size distributions (number-weighted and volume-weighted) and their theoretical curves obtained from the log-normal distribution (6) are shown in **Fig. 1**. **Table 2** shows the calculated parameters of the log-normal distribution (6) for the results with number-weighted and volume-weighted. The median, mean value, mode (most frequent value), and standard deviation were chosen as comparative parameters.

As shown in **Fig. 1**, a trend toward a rightward displacement of the peak of the theoretical curve is noticeable for all fluids. The difference between the mode value calculated from the DLS data and the theoretical distribution in percentage is given in **Table 3**. The NDLS label means that the total number of diameter intervals measured by DLS

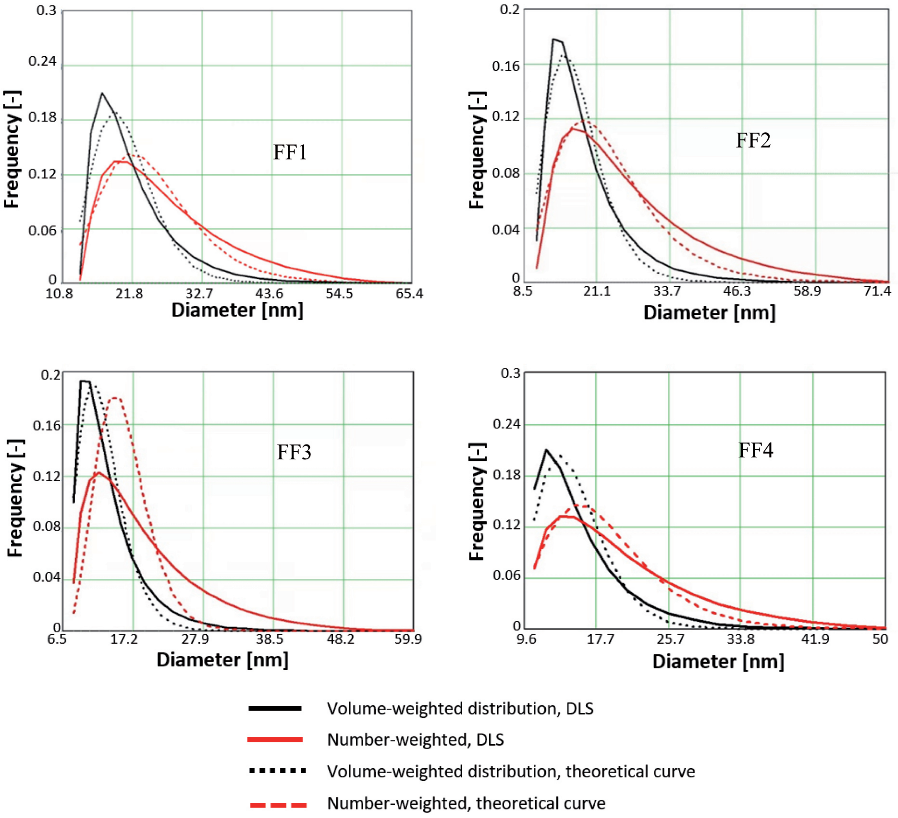


Fig. 1. Measurements of particle size distributions (number and volume weighted) and their theoretical curves
Rys. 1. Pomiary rozkładów wielkości cząstek (ważone liczbowo oraz objętościowo) oraz ich teoretyczne krzywe

Table 2. Parameters of log-normal distribution
Tabela 2. Parametry rozkładu logarytmicznego

Label	Number weighted distribution				Volume weighted distribution			
	Median value, nm	Mean value, nm	Mode, nm	Standard deviation, nm	Median value, nm	Mean value, nm	Mode, nm	Standard deviation, nm
FF1	19.99	20.05	18.93	12.81	23.75	25.24	21.68	15.77
FF2	16.88	17.56	15.61	11.08	21.57	23.14	18.74	15.06
FF3	12.03	12.52	11.11	7.905	15.28	15.77	14.35	9.867
FF4	14.47	14.95	13.56	9.364	17.55	18.55	15.71	11.89

Table 3. Percentage difference of the mod value obtained from the measurement and the logarithmic distribution

Tabela 3. Procentowa różnica wartości mody otrzymanej z pomiaru oraz rozkładu logarytmicznego

Label	Number weighted distribution,%			Volume weighted distribution,%		
	N_{DLS}	N_{DLS}-1	N_{DLS}-2	N_{DLS}	N_{DLS}-1	N_{DLS}-2
FF1	11.5	11.4	7.7	14.6	13.5	27.6
FF2	15.3	14.4	10.7	10.4	11.1	57.5
FF3	19.1	18.7	17.5	19.4	5.3	22.3
FF4	12.8	10.6	0.7	16.0	15.6	74.2

is considered. However, the label NDLS-1 and NDLS-2 implies that the one and two largest diameters are not considered.

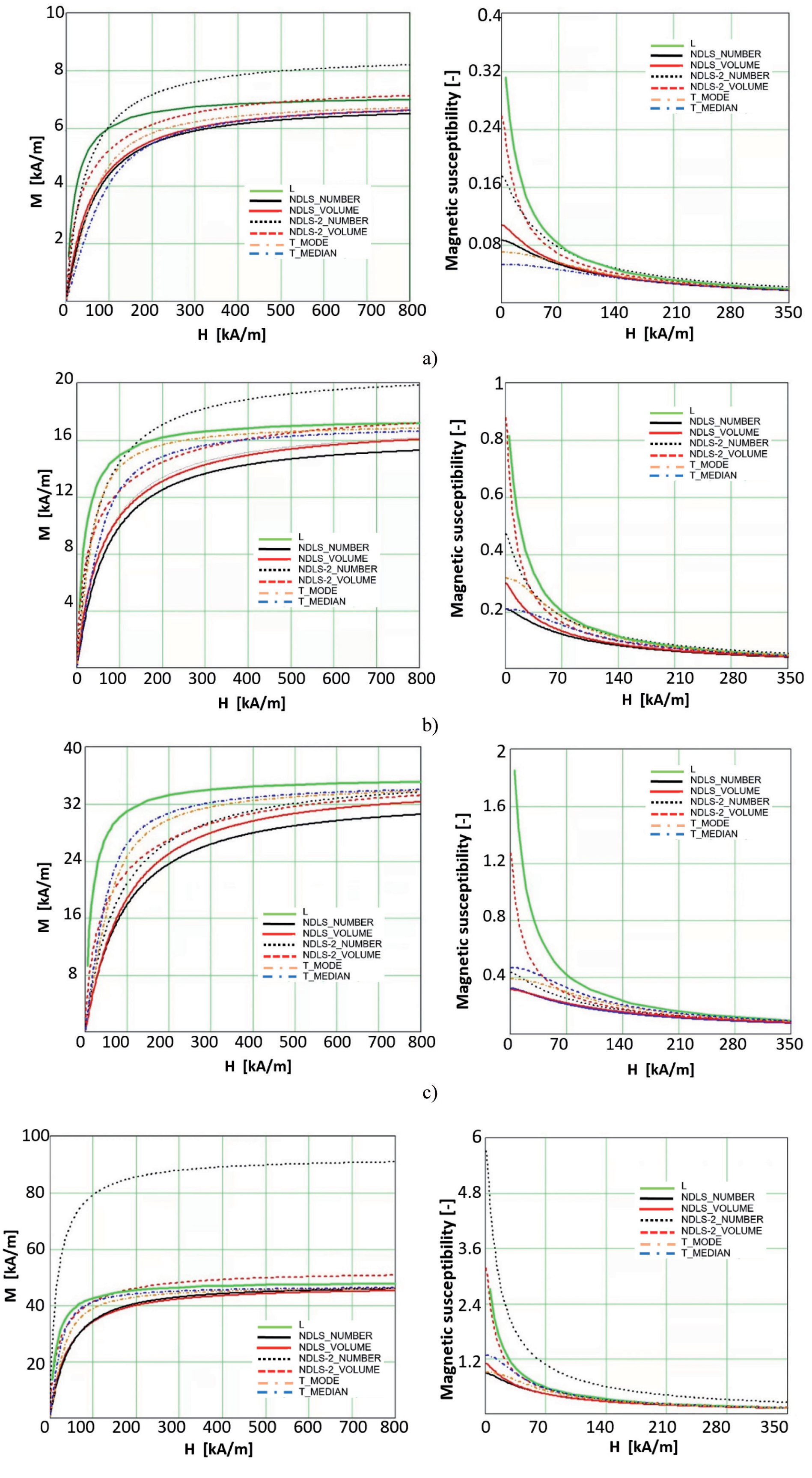
The data presented in **Table 3** shows that the particles with the largest diameters significantly affect the mode values for both the number- and volume-weighted distributions. Not including the single largest diameter (NDLS-1) for most fluids (except for liquid FF2) results in a smaller difference in mode values; that is, there is a better fit of the peak position between the theoretical curves and those obtained from measurements. Not including the two largest diameters (NDLS-2) increases the difference and the volume-weighted distribution is up to 75% (for FF4 fluids), while for the number-weighted distribution for all fluids, the difference is even smaller than for (NDLS-1).

RESULTS

Magnetisation curves of ferrofluids obtained from theoretical number-weighted and volume-weighted particle size distributions are shown in **Figure 3**. The designation "L" refers to magnetisation curves determined from experimental data presented in the paper [L. **L.10]**. The designations "NDLS_Number" and "NDLS_Volume" refer to magnetisation curves determined from theoretical equations (1), (4), (6), which take into account the total number of diameter intervals obtained under the DLS measurement for the number- and volume-weighted distributions, respectively. The designations "NDLS-2_Number" and "NDLS-2_Volume" refer to the magnetisation curves calculated from the theoretical data, which do not take into account the two largest diameters values obtained by the DLS measurement. In addition, curves determined based on the value of only one parameter, such as the mode "T_MODE" and the median value "T_MEDIAN", are shown in **Fig. 3**. Since the magnetic susceptibility parameter (χ) is an important parameter for mathematical or numerical calculations, its values are also presented on the graphs for comparison purposes. It was calculated using the equation:

$$\chi = \frac{M}{H} \tag{7}$$

Analysing the results shown in **Fig. 2**, it can be seen that the curves determined from DLS number-weighted data for the whole sample (NDLS) have the largest fit error and significantly deviate from the values determined from experimental data over the entire range of the change in the value of the magnetic field intensity H. Better results are obtained for volume-weighted data. In the case of FF2, FF3, and FF4 liquids, considering only the mode or median values results in a better fit, especially for magnetisation curves. At the same time, for magnetic susceptibility values, the curves still deviate significantly from the experimental. Sample reduction (elimination of the two largest diameters determined by DLS measurement – NDLS-2) leads to a better fit of these curves in the range of small values of H=0-200 kA/m for all tested fluids. The best result is obtained for volume-weighted data. The coefficient of determination R2 is calculated to verify the magnetisation curves' fit. For the FF1 fluid, this coefficient is in the range [L. 0.9301;0.9835**]**; for the FF3 fluid is in the range [L. 0.9301;0.9835**]** and for the FF4 fluid [L. 0.964;0.9575**]**. The lowest value of the determination coefficient for liquids FF1, FF3, and FF4 is obtained from the theoretical curve, for which a number-weighted particle size distribution without sample reduction was used. The highest R2 values are obtained for volume-weighted data with sample reduction. For fluid FF2, the lowest value of the determination coefficient is 0.3674 for the number-weighted distribution with a reduced sample. **Fig. 2** shows the difference in magnetisation values, which may be due to the



a)

b)

c)

d)

Fig. 2. Magnetization and magnetic susceptibility curves of the FF1 (a), FF2 (b), FF3(c) and FF4(d) ferrofluids

Rys. 2. Krzywe magnetyzacji oraz podatności magnetycznej FF1 (a), FF2(b), FF3 (c) oraz FF4 (d) cieczy magnetycznych large proportion of diameters with large values in the distribution. On the other hand, R2 =0.9845, which can be considered a good fit for the reduced sample and the volume-weighted distribution.

CONCLUSIONS

This paper presents a method for determining magnetisation curves using measurements of particle distributions by the DLS method. This method allows us to determine the particle size distributions of ferrofluid particles weighted by number and volume. A logarithmic normal distribution expresses the obtained diameter values according to equation (6). The magnetisation curves are calculated based on the particle distributions and the known values of the ferrofluid saturation. The analysis of the obtained results allows us to formulate the following conclusions:

- For all studied ferrofluids, the particle size distribution is unimodal, and the value of the mode and other distribution parameters (mean value, median value, and standard deviation) largely depends on the measurement method: by volume or by number.
- Reducing the measured diameter values by excluding the largest diameters allows a better fit of the theoretical distribution to the DLS results, especially in the case of a number-weighted distribution.
- A better fit of the theoretical particle size distribution to the DLS results did not lead to a better agreement of the obtained magnetisation curves. This may be because, in the DLS measurement, the diameter values for which the particles are counted were constant (by volume or number).
- Sample reduction (elimination of the two largest diameters determined by the DLS – NDLS-2_Volume) made it possible to obtain a very good agreement of saturation magnetisation values with experimental results reported in the literature: the minimum disagreement is 0.05% for the FF2 fluid and the maximum – 6.3% for the FF4 fluid.

Presented in this work results do not cover all the subjects. Further research should include a comparison of magnetisation curves obtained from direct measurements for the studied ferrofluids rather than referring to experimental magnetisation curve data from the literature. A correction factor can be imposed into the equations to get a better fit.

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