MEASUREMENTS OF PARTICLE SIZE DISTRIBUTION PARAMETERS IN FERROFLUIDS

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ABSTRACT

A method is presented by means of which (for a ferrofluid with a lognormal distribution of particle size) it is possible to determine the standard deviation (σ) and median particle diameter (D_v) from the room temperature magnetisation curve. The method has been applied to several commercial ferrofluids, containing ferrite particles, and to fluids consisting of cobalt particles in toluene prepared by the method of Hess and Parker[1]. The particle size distributions have also been measured by using an electron microscope. It has been found that the magnetic data gives estimates of the 'magnetic size distribution' parameters D_{vm} and σ_m, which differed from the 'physical size distribution' parameters D_{vp} and σ_p obtained from electron microscope data. It is found that $D_{vp} > D_{vm}$, and $\sigma_p < \sigma_m$. These observations are consistent with the results of Kaiser and Miskolczy[2] and Granqvist and Buhrman[3].

INTRODUCTION

A ferrofluid is a suspension of very fine magnetic particles, with typical sizes of the order of 100 Å. For particles of this size, Brownian motion is sufficient to prevent sedimentation in a gravitational field. To prevent particle agglomeration through Van der Waals attractive forces and magnetostatic inter-particle interactions, the particles are generally coated with long chain polar molecules.

The magnetisation curves for ferrofluids at room temperature are generally superparamagnetic (having zero coercivity and remanence). If the particles are all of the same size, the magnetic behaviour is described by the Langevin function

$$L = \coth b - 1/b \tag{1}$$

Where $b = \mu H/kT$, μ ($=I_s' V$) is the particle magnetic moment, V is the particle volume, I_s' is the saturation magnetisation of the bulk material. I_s, the saturation magnetisation of the ferrofluid is equal to $\epsilon I_s'$ with ϵ the volumetric particle packing fraction.

Ferrofluids, however, invariably contain a distribution of particle sizes. This is conveniently characterised by a distribution of volume fraction f(y), where the reduced diameter $y = D/D_v$ (D is the particle diameter and D_v is the median diameter of the distribution). f(y)dy is defined as being the fraction of the total magnetic volume having reduced diameters between y and y+dy.

The magnetic properties of a ferrofluid are modified by the presence of a particle size distribution. The magnetisation is now given by the sum of the contributions from each particle diameter, weighted by the distribution function, thus

$$I = I_s \int_0^\infty L\, f(y)\, dy \tag{2}$$

In the limit of small fields, the Langevin function may be written

$$L = I_s' VH/kT$$

Hence equation (2) becomes

$$I = \frac{I_s H I_s'}{3kT} \int_0^\infty V f(y) dy$$

Since $D = D_v y$, $V = \pi D_v^3 y^3/6$ and

$$I = \left[\epsilon I_s'^2 H \pi D_v^3 \int_0^\infty y^3 f(y) dy\right] / 18\, kT$$

The initial susceptibility of the system is given by

$$\chi_i = \left[\frac{dI}{dH}\right]_{H\to 0} = \frac{\epsilon I_s'^2 \pi D_v^3}{18\, kT} \int_0^\infty y^3 f(y) dy \tag{3}$$

For large H, the Langevin function may be written

$$L = 1 - 1/b = 1 - 6kT / (I_s' H \pi D_v^3 y^3) \tag{4}$$

Substituting for L from equation (4) into equation (2)

$$I = I_s \int_0^\infty (1 - 6kT/(I_s' H \pi D_v^3 y^3))\, f(y) dy$$

$$= I_s \left[1 - \frac{6\, kT}{I_s' H \pi D_v^3} \int_0^\infty y^{-3} f(y)\, dy\right] \tag{5}$$

Equation (5) follows from the fact that the distribution function must obey the normalisation condition:

$$\int_0^\infty f(y)\, dy = 1$$

From equation (5), the relationship between I and 1/H for large H should be a straight line, which will cross the I = 0 axis at a point $1/H_0$ given by

$$1 = \frac{6\, kT}{I_s' \pi D_v^3} \cdot \frac{1}{H_0} \int_0^\infty y^{-3} f(y) dy \tag{6}$$

It is possible to evaluate the integrals of equations (3) and (6) if the form of the distribution function is known. There is evidence to suggest[3] that the lognormal distribution function

$$f(y) = \frac{1}{y\sigma\sqrt{2\pi}} \exp(-(\mathrm{Ln}(y))^2/2\sigma^2)$$

occurs in fine particle systems (σ is the standard deviation). Using the lognormal distribution function, the integrals of equations (3) and (6) can be written

$$\int_0^\infty y^n f(y) dy = \int_0^\infty y^n \frac{\exp(-(\mathrm{Ln}(y))^2/2\sigma^2)\, dy}{y\sigma\sqrt{2\pi}}$$

where n = 3 or - 3

0018-9464/78/0900-0975$00.75

Making the substitution

$$z = (\mathrm{Ln}(y))/\sigma - n\sigma$$

$$\int_0^{\infty} y^n f(y)\,dy = \exp(n^2\sigma^2/2)\int_{-\infty}^{\infty}\frac{\exp(-z^2/2)\,dz}{\sqrt{2\pi}} = \exp(n^2\sigma^2/2)$$

Since $\int_{-\infty}^{\infty} \exp(-z^2/2)/\sqrt{2\pi} = 1$

Substituting the values of the integrals into equations (3) and (6), and solving the equations for D_v and σ,

$$\sigma = \left[\mathrm{Ln}(3\chi_i/(\epsilon I_s'.1/H_0))\right]^{1/2}/3 \qquad (7)$$

$$D_v = \left[\frac{18kT}{\pi I_s'}\cdot\sqrt{\frac{\chi_i}{3\epsilon I_s'}\cdot\frac{1}{H_0}}\right]^{1/3} \qquad (8)$$

Equations (7) and (8) give D_v and σ in terms of the parameters χ_i, $1/H_0$, and $\epsilon I_s'$ which can be determined experimentally.

RESULTS

The distribution parameters were determined for several ferrofluids obtained from Ferrofluidics Corp.* in addition to a cobalt/toluene fluid prepared by the method of Hess and Parker[1]. The fluids were a diester based ferrofluid with a saturation magnetisation M_S ($=4\pi I_S$) of 200 G, a water based fluid with M_S = 120G, and a petroleum fluid with M_S = 80G. These fluids contained Fe_3O_4 particles. The cobalt/toluene ferrofluid had a saturation magnetisation of 90G. The same fluid was also measured after concentration by forced evaporation of the toluene. This had a value of M_s = 370G.

The size distribution of each fluid was measured using an electron microscope. It was found that the 'magnetic diameter' D_{vm} calculated from the magnetisation curve was invariably less than the 'physical diameter' D_{vp} obtained by electron microscopy. The results are given in Table 1.

Fluid	Magnetic Measurements		Electron Microscopy	
	D_{vm}(Å) ($\pm$5)	σ_m	D_{vp}(Å) ($\pm$15)	σ_p
Diester Based M_s = 200 $\pm$ 10G	110	0.44	140	0.22
Water Based M_s = 110 $\pm$ 10G	120	0.63	205	0.22
Petroleum Based M_s = 50 $\pm$ 10G	75	0.455	90	0.4
Cobalt/Toluene 1	47	0.187	75	0.10
2	45	0.195		

TABLE I

1. As prepared M_s = 90 $\pm$ 10G
2. Concentrated M_s = 370 $\pm$ 10G

The fact that $D_{vm} < D_{vp}$ is in agreement with the observations of Kaiser and Miskolczy[2], who made magnetic measurements on several commercial ferrofluids. They found that I_s was always less than $\epsilon I_s'$ (with ϵ the calculated packing fraction) which is the expected value of the saturation magnetisation of the system. The low observed value of I_s was interpreted as arising from a chemical reaction between the stabilising surfactant and the ferrite particles. The reaction results in the formation of non magnetic surface layers, which makes the magnetic diameter of the particles smaller than the physical diameter.

For the Fe_3O_4 ferrofluids it was found that the standard deviation σ_m (from magnetic data) > σ_p (from the electron microscope data). This is consistent with the results of Granqvist and Buhrman[3] who measured the median diameter and standard deviation (σ_1), by bright field electron microscopy of aluminium particles which had undergone surface oxidation. The dark field mode was used to obtain the median diameter and standard deviation (σ_2) of the unoxidised aluminium cores of the particles, they found $\sigma_1 > \sigma_2$.

The values of D_{vm} and σ_m obtained from equations (7) and (8) give a good estimate of the magnetic size distribution parameters. This is demonstrated in fig 1 where the magnetisation curve as computed

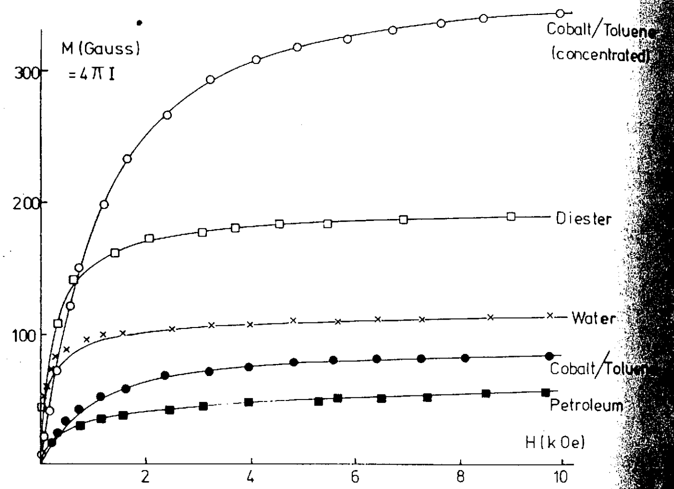

FIG 1

Theoretical and experimental room temperature magnetisation curves.

from the values of D_{vm} and σ_m are compared with the experimental data, and good overall agreement found for all except the water based fluid. It must be expected that the computed curves fit the data at high and low fields, since D_{vm} and σ_m were calculated from these portions of the magnetisation curve. However, if the lognormal distribution is a bad representation of the actual distribution within a sample, the experimental data would deviate from the computed curve at intermediate values of field. These values of field are those around the 'knee' of the magnetisation curve, and the fit in this region gives a measure of the applicability of the lognormal distribution. The agreement for the water based fluid was poor. However, this fluid has a large median diameter and standard deviation, which re[illegible] in a significant amount of magnetostatic particle interaction, of which no account is taken in deriving equations (7) and (8).

The distribution of particle sizes for the diester based fluid was found to be approximately Gaussian determined from electron microscopy. However, magnetic data appears to fit a lognormal distribution. This may be due to the fact that the analysis using magnetic measurements is insensitive to the differences between these distributions. An alternative explanation is that after the surface reaction has taken place, the lognormal distribution is a satisfactory distribution for the magnetic cores whereas the Gaussian distribution is a better fit for the physical diameter.

By simply equating the magnetostatic interaction energy of two particles in contact, with the thermal energy kT, one can obtain a critical diameter ($\sim$100 Å for ferrite particles), above which the particles should form agglomerates and hence sediment out of suspension. However, the presence of the non magnetic surface layers and the addition of a surfactant reduce the interaction energy, and this probably explains the stability of the water based fluid, which has D_{vp} = 200 Å. Stability in a magnetic field gradient is also increased since D_{vp} (from which the viscous drag is calculated) is greater than D_{vm} (from which the force on the particle is calculated). This results in an increase in the time taken to reach equilibrium, and hence increased stability in a magnetic field gradient.

From the measured values of χ_i and $1/H_o$ it is possible to make two estimates of the diameter. These will only be equal if the system has a uniform particle size. If the fluid has a distribution of particle size, the two diameters will differ, and in general, D_i (from χ_i) $>$ D_u (from $1/H_o$), since χ_i is more sensitive to the larger particles, whilst the approach to saturation is more sensitive to the smaller particles. In the case of the concentrated cobalt/toluene ferrofluid, the diameters are D_i = 48Å, and D_u = 42Å. In fig 2 the experimental results for the concentrated cobalt toluene ferrofluid are compared to results calculated

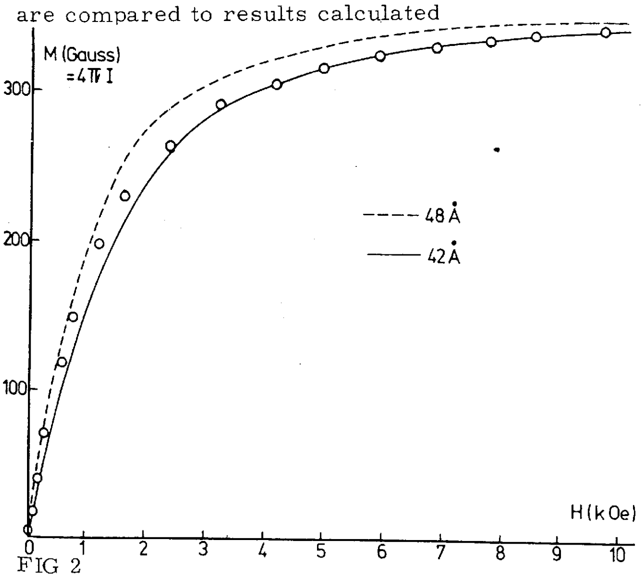

FIG 2

Experimental results for the concentrated cobalt/ toluene ferrofluid compared with theoretical single particle volume curves for 42 and 48 Å particles.

for single particle diameters of 42 and 48 Å. It can be seen that as expected the calculated curve for 48Å fits the low field data but not the high field data, whilst the reverse is true for the 42Å curve. At intermediate values of field, the agreement between the experimental data and both calculated curves is poor. This shows that it is not possible to obtain a good fit between the experimental points and a theory assuming a single particle size.

CONCLUSIONS

The method of determining size distribution data from the magnetisation curve of a ferrofluid has been found to give good estimates of the magnetic size distribution parameters D_{vm} and σ_m. It has been found that for all ferrofluids examined, $D_{vm} < D_{vp}$ (D_{vp} is the physical diameter from electron microscopy) and $\sigma_p < \sigma_m$. These results are consistent with the work of Kaiser and Miskolczy[2] and Granqvist and Buhrman[3].

An appreciation of the difference between magnetic and physical distribution parameters is important in analysing experimental results. This is demonstrated in fig 3, where the experimental results for the diester based ferrofluid are seen to be in evident disagreement with the curve calculated from the distribution parameters as determined by electron microscopy.

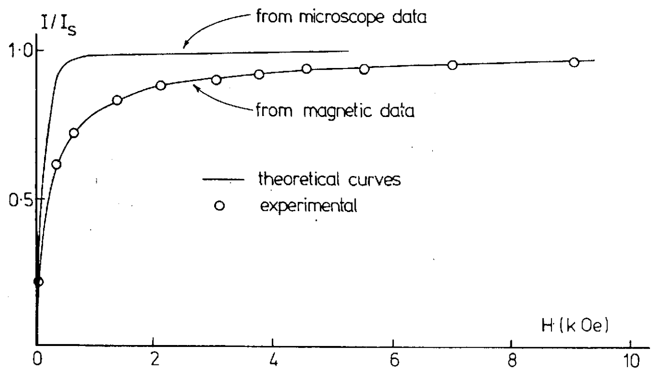

FIG 3

Experimental and theoretical magnetisation curves for the diester based ferrofluid.

ACKNOWLEDGMENTS

The financial support of the Science Research Council and the AERE (Harwell) is gratefully acknowledged.

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