Particle size determination: Viscosity study

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Magnetic and rheological properties of the laboratory synthesized three different magnetic fluids are reported. Using log-normal size distribution the magnetisation data were fitted and the particle size, domain magnetisation and the size distribution are obtained. The particle size were also determined from the viscosity measurement and it was found that the size corresponds to the median diameter of the number distribution. The effect of polydispersity on the viscosity is also discussed.

The particle size and its distribution play an important role to determine the various physical and magnetic properties of the magnetic fluid. There are various techniques to determine the size of particles, like, X-ray, magnetisation, viscosity, etc., but each experiment measures different aspect of the particle size: a solid content, a magnetic content and an equivalent hydrodynamic size which includes the effect of surfactant coatings. If a system is a mono-dispersed, the particle size obtained from viscosity will be greater than that obtained from magnetisation measurement. But a magnetic fluid is a polydispersed system, therefore, to determine the particle size distribution, one has to consider various size distribution functions and choose the one which gives the best fit to the observed characteristics. For a magnetic fluid the most widely used function is a log-normal distribution function which is given as

\[
P(D) \, dD = \frac{1}{\sqrt{2\pi} \sigma D} \exp\left[-\frac{(\ln(D/D_m))^2}{2\sigma^2}\right] dD
\]  \hspace{1cm} (1)

where, \(D\) is particle size, \(\sigma\) is standard deviation and \(\ln D_m\) is mean of \(\ln D\).

For a polydispersed system it was observed that the particle size obtained from the viscosity is sensitive to the peak size diameter of the log-normal volume distribution function\(^1\). To understand this result three kerosene based magnetic fluids were synthesized. The study reported here shows that viscosity gives the size of the particle which corresponds to the median diameter of the number distribution of log-normal distribution function which is same as a peak size of the log-normal volume distribution function.

In the present paper, the results obtained from viscosity measurement for three different fluids prepared in kerosene having particles of (i) Mn-Zn (50%) ferrites, (ii) Mn-Fe (50%) ferrites and (iii) Fe-Zn (50%) ferrites have been reported.

**Experimental Procedure**

**Preparation of magnetic fluids**—The standard co-precipitation technique has been used to prepare the fine magnetic particles. The starting materials of GPR grades, FeCl\(_3\) 6H\(_2\)O, MnCl\(_2\) 4H\(_2\)O, ZnSO\(_4\) 7H\(_2\)O and FeSO\(_4\) 7H\(_2\)O were used to obtain ions of Fe\(^{3+}\), Mn\(^{2+}\), Zn\(^{2+}\) and Fe\(^{2+}\) in an aqueous solution. The detailed procedure and conditions for preparation of fine particles are given elsewhere\(^2,3\). The particles obtained are then coated with oleic acid and dispersed in kerosene. The resulting fluids are stable and are liquid at room temperature and solid below 200K.

**Structural characterization**—X-ray patterns were recorded on a Philips PW 1130/90 X-ray diffractometer using CuK\(\alpha\) radiation (\(\lambda = 1.5414\)Å). The X-ray diffraction pattern for Mn-Zn, Mn-Fe and Fe-Zn systems were analysed by X-ray Rietveld refinement programme and it confirms the formation of single phase spinel (i.e. fcc with a space group of Fd3m) structure. The parameters derived from the fit are given in Table 1.

**Magnetisation measurement**—The magnetisation measurements were carried out using search-coil method. Fig. 1 shows the reduced magnetisa-
Table 1—Parameters obtained from X-ray, magnetisation and viscosity measurements

<table>
<thead>
<tr>
<th>Sample</th>
<th>(a, \text{Å} )</th>
<th>(\sigma )</th>
<th>(M_d, \text{emu/cc} )</th>
<th>Particle size (Å) determination</th>
<th>X-ray</th>
<th>Magnetisation</th>
<th>Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(D)</td>
<td>(D_m)</td>
<td>(D_a)</td>
<td>(D_s)</td>
</tr>
<tr>
<td>Mn-Zn</td>
<td>8.450</td>
<td>0.36</td>
<td>205</td>
<td>67</td>
<td>71</td>
<td>48</td>
<td>41</td>
</tr>
<tr>
<td>Mn-Fe</td>
<td>8.445</td>
<td>0.28</td>
<td>410</td>
<td>70</td>
<td>80</td>
<td>63</td>
<td>62</td>
</tr>
<tr>
<td>Fe-Zn</td>
<td>8.412</td>
<td>0.40</td>
<td>150</td>
<td>50</td>
<td>60</td>
<td>37</td>
<td>43</td>
</tr>
</tbody>
</table>

\(^*\)Average

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Fig. 1—Reduced magnetisation with field for three magnetic fluids at room temperature. The lines through the data points are calculated using Eq. (3).

In magnetic fluids, the dispersed particles are not usually mono-dispersed, therefore, one has to consider the contribution of all the particles to the magnetisation, i.e.,

\[ M = \int_{D} M'(D) P(D) dD \]

where, \(P(D)\) is a volume distribution of log-normal distribution for spherical particles given by Eq. (1).

\[ P(D) = \frac{1}{\sigma \sqrt{2\pi}} \exp\left[-\frac{(\ln(D/D_m))^2}{2\sigma^2}\right] \]

In magnetic fluids, the dispersed particles are not usually mono-dispersed, therefore, one has to consider the contribution of all the particles to the magnetisation, i.e.,

\[ M = \int_{0}^{\infty} M'(D) P(D) dD \]

where, \(P(D)\) is a volume distribution of log-normal distribution for spherical particles given by Eq. (1).

\[ P(D) = \frac{1}{\sigma \sqrt{2\pi}} \exp\left[-\frac{(\ln(D/D_m))^2}{2\sigma^2}\right] \]

where, \(P(D)\) is a volume distribution of log-normal distribution for spherical particles given by Eq. (1).

Solid lines in the Fig. 1 were generated using Eq. (3). The parameters corresponding to the best fit obtained for all the three fluids are given in Table 1. It is evident from Table 1 that the substitution of Zn and Mn enhances the domain magnetisation of the particles but at the same time there is a change in particle size.

**Viscosity measurement**—Viscosity measurements were made using a wells-Brookfield cone/plate viscometer. The temperature of the sample cup was maintained up to an accuracy of ±0.01°C with the help of a EX-100 constant temperature bath. The instrument was calibrated using a Brookfield viscosity standard fluid.

**Results and Discussion**

The viscosity of a magnetic fluid in absence of an externally applied magnetic field is same as that of a nonmagnetic colloidal suspension. Fig. 2
\[ \eta = \eta_0 \left(1 + \frac{5}{2} \phi_m \right) \] \hspace{1cm} (4)

where, \( \eta \) and \( \eta_0 \) are viscosity of fluid and carrier respectively, and \( \phi_m \) is the magnetic volume fraction. For moderately high concentration a two-constant expression is assumed, i.e.,

\[ \eta = \eta_0 \left(1 + a \phi_m + b \phi_m^2 \right)^{-1} \] \hspace{1cm} (5)

where Eq. (5) should reduce to Eq. (4) for low concentration with \( a = -2.5 \). At concentration, \( \phi_c \), the colloid solidifies and \( \eta_0/\eta \) goes to zero. Hence the second constant \( b = (2.5\phi_c-1)/\phi_c^2 \). The closest packing for spherical particles is for \( \phi_c = 0.74 \). In case of a magnetic fluid, each of the particles is coated with a surfactant layer of thickness \( \delta \) nm, which occupy a fractional volume \( \phi_h \) in the fluid given by

\[ \phi_h = \phi_m \left(1 + \frac{\delta}{r} \right)^3 \]

using this, Rosensweig \(^4\) obtained the expression

\[ \frac{\eta - \eta_0}{\phi_m \eta} = \frac{5}{2} \left(1 + \frac{\delta}{r} \right)^3 \left(\frac{5/2 \phi_c - 1}{\phi_c^2} \right)(1 + \frac{\delta}{r})^{\phi_m} \] \hspace{1cm} (6)

A plot of measured value of \( (\eta - \eta_0)/\phi_m \eta \) versus \( \phi_m \) yields a straight line (Fig. 3). The values of particle diameter obtained from the intercept, \( D(i) \), at \( \phi_m = 0 \) and from the slope, \( D(s) \), using \( \phi_c = 0.74 \) for all samples are given in Table 1. The Eq. (6) is true for mono-dispersed system. Using geometric packing consideration, which is different for poly-dispersed system, Mooney \(^5\) has shown that,

\[ \eta = \eta_0 \exp \left(\frac{2.5 \phi}{1 - K \lambda \phi} \right) \] \hspace{1cm} (7)

where \( K \) is a constant factor dependent on the packing fraction. In the present case \( K \phi_c = 1 \), so that Eq. (7) becomes,

\[ \eta = \eta_0 \exp \left(\frac{2.5 \phi}{1 - \lambda (\phi/\phi_c)} \right) \] \hspace{1cm} (8)

where, \( \lambda \) is a factor depending on polydispersity. Using Eq. (8) the viscosity was calculated for all the fluids (Fig. 4). It was observed that \( \lambda \) is different for each fluids. The relation between \( \lambda \) and \( \sigma \) is not known so it is not possible to fit the log-normal distribution to the viscosity data, but it can be seen from Table 1 that the particle size obtained

![Figure 3](image-url)  
Fig. 3—\((\eta - \eta_0)/\phi_m \eta \) versus \( \phi_m \) for Mn-Zn, Mn-Fe and Fe-Zn magnetic fluids. The lines are fit to the Eq. (6).

![Figure 4](image-url)  
Fig. 4—Effect of polydispersity on the variation of viscosity with hydrodynamic volume fraction using Eq. (7). The values of \( \lambda \) for each fluids are given.

shows the variation of viscosity with magnetic volume fraction for three different fluids. It can be seen from the figure that it obeys Einstein’s relation at lower concentration as
from the viscosity are matched with the median
diameter of number distribution \( D_{nm} \) of the log-
normal distribution function which is equivalent to
the peak diameter of volume distribution, \( D_{pv} \),

\[
D_{pv} = D_{nm} = D_{vm} \exp(-3\sigma^2)
\]  ... (9)

where, \( D_{vm} \) is the particle diameter obtained from
magnetisation measurement using log-normal vol-
ume distribution function and \( \sigma \) is the standard
deviation. This directional variance shows that the
viscosity is sensitive to the number of particles
rather than the volume of the particles for the same
magnetic volume fraction.

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