CHAPTER 6

EFFECT OF CAPILLARY SIZE AND MAGNETIC FIELD ON ROTATIONAL VISCOSITY OF FERROFLUIDS: A PHYSICAL SIMULATION STUDY

6.1 INTRODUCTION

Colloidal dispersions of magnetic nanoparticles in a passive liquid matrix are known as ferrofluids.\(^1\) Remote control of the fluid flow by an externally applied magnetic field leads to certain attractive applications in biomedicine and biotechnology\(^2\)-\(^7\). Magnetic drug targeting (MDT) and magnetic cell separation (MCS) are the two examples of such applications\(^8\). A phenomenological theory for hydrodynamics of MDT system is developed by Voltairas et al\(^9\) and an experimental simulation study was carried out by Ganguly et al\(^10\). Theory of MCS is discussed by Pankhurst et al\(^2\). Transport properties of a drug/cell carried by ferrofluid are expected to be modified by the direction of the applied field as well as by the diameter of the vesicles\(^11\). In these applications a parameter called ‘magnetophoretic mobility’ (\(\xi\)) of the particles, which decides, how manipulable a magnetic particle is, plays an important role in the above mentioned applications\(^2\). In this research, effect of variation of capillary diameter on the field induced rotational viscosity (\(\eta_r\)) of water and kerosene based ferrofluids is described. The effect of direction of the applied field on \(\eta_r\) is also studied. We have analyzed results in the light of Shliomis’ theory of ferrohydrodynamics\(^12,13\) and examined its effect on \(\xi\).

6.2 SYNTHESIS OF IRON OXIDE NANOPARTICLES

Nanomagnetic particles of iron oxide are synthesized by chemical co-precipitation technique\(^14\). Analytical grade \(\text{FeSO}_4 \cdot 7\text{H}_2\text{O}\) and \(\text{FeCl}_3 \cdot 6\text{H}_2\text{O}\) are used to obtain the ions of \(\text{Fe}^{2+}\) and \(\text{Fe}^{3+}\) in the stoichiometric ratio of 1:2 in aqueous solution. This solution of iron salts is added to 25% ammonia solution under continuous mechanical stirring. A
black precipitate of Fe$_3$O$_4$ is instantly formed. The pH of the mixture is brought to 10.5 with the help of excess ammonia solution, under continuous stirring pH is maintained at 10.5 for 20 min. Iron oxide particles are obtained by magnetic decantation. Several water washes are given by magnetic decantation in order to remove water soluble impurities. Water wet slurry are preserved for further process.

6.3 **SYNTHESIS OF KEROSENE AND WATER BASED FERROFLUID**

![Diagram](image)

**Figure 1** Schematic representation of process used to prepare water base as well as kerosene base ferrofluids

To synthesize kerosene-based ferrofluid, bare iron oxide particle has to be coated with small chain length surfactant (oleic acid). As shown in the schematically in **Figure 1**, first of all, ammonium oleate is prepared by adding oleic acid in ammoniated water under constant stirring at 40 °C until crystal clear solution is obtained. It is then added slowly to the water wet iron oxide particle slurry under continuous stirring at room temperature. The reaction is continued for one hour after which, the temperature is raised to 92 °C. At this stage oleic acid gets chemi-adsorbed on the surface of the iron oxide nanoparticles. After that, the solution is allowed to cool to room temperature. When the solution temperature reaches to room temperature, it is flocculated with the help of dilute HCl. Coated particles are washed several times with water followed by
a wash with acetone. Finally, this particle slurry is dispersed in kerosene under mechanical stirring at 50 °C. Thus a stable colloidal suspension of iron oxide is ready, which is highly stable at room temperature even in the presence of a gradient magnetic field of 0.6 T.

In order to produce effectively stable water base magnetic fluid, as shown in Figure 1, the particles are coated with bi-layer of surfactants (oleic acid) using a two-step process\textsuperscript{14,15}. In the first step, oleic acid is chemi-adsorbed on the surface of nanoparticles, leaving the particles surface hydrophobic, which cannot be dispersed in water. Secondary coating is required to make them water loving. In order to get the secondary coating, oleic acid coated nanoparticle slurry is centrifuged at 12000 rpm for 10 min to remove access oleic acid from the slurry. Extracted nanoparticles are wash with water for several times and then dispersed in a mixture of ethanol and water. Freshly prepared ammonium oleate is added drop wise to this solution under constant stirring at 50 °C in order to achieve secondary coating. Secondary coating is physically adsorbed on the surface of coated particles. A stable water-based ferrofluid is ready, which is preserved at room temperature for further investigation.

6.4 INVESTIGATION OF NANOPARTICLES

X-ray diffraction pattern of as-synthesized Fe\textsubscript{3}O\textsubscript{4} nanoparticles are shown in Figure 2.

![XRD pattern of Fe\textsubscript{3}O\textsubscript{4} nanoparticles produced by chemical coprecipitation](image)

Figure 2 XRD pattern of Fe\textsubscript{3}O\textsubscript{4} nanoparticles produced by chemical coprecipitation
All the six peaks in the pattern are indexed to the fcc inverse spinel structure. The value of lattice parameter obtained from the highest intense reflection (311) is 0.837 nm. This result is in good agreement with that reported in the powder diffraction database (card No. 19-0629). The average crystallite size obtained by classical Scherrer equation with a geometric factor of 0.9 over (311) reflection is 10.5 nm.

Magnetization of the ferrofluids is determined on vibrating sample magnetometer. **Figure 3 (A and B)** shows the reduced magnetization curve of the magnetic fluid measured at room temperature. The experimental observations are fitted with modified Langevin theory\textsuperscript{16}.

According to this model, magnetization $M$ is a function of applied field $H$.

\[
M = \phi M_d \int_{0}^{\infty} L(\alpha)P(D)dD
\]

(1)

**FIGURE 3A** Reduced magnetization curve of water based magnetic fluid. The curve is fitted with modified Langevin theory. Fitting parameters obtained are domain magnetization ($M_d$) = 320 kA/m, magnetic median particle diameter ($D_m$) = 10.4 nm and standard deviation of logarithmic of particle diameter ($\sigma$) $\approx$0.34.
FIGURE 3B Reduced magnetization curve of kerosene based magnetic fluid fitted with modified Langevin theory. Fitting parameters obtained are domain magnetization ($M_d$) = 320 kA/m, magnetic median particle diameter ($D_m$) = 10.4 nm and standard deviation of logarithmic of particle diameter ($\sigma$) = 0.28.

Where $\phi$, $M_d$, $L(\alpha)$ and $P(D)$ are respectively the volume fraction, domain magnetization, the Langevin function and the lognormal distribution function.$^{17}$

$L(\alpha) = \coth(\alpha) - \frac{1}{\alpha}$ and $\alpha = \frac{\mu H}{k_B T}$. Here $\mu$ and $H$ are the magnetic moment of the particle and applied external magnetic field, respectively. Parameters derived from the fit are domain magnetization ($M_d$), magnetic median particle diameter ($D_m$) and standard deviation of the logarithmic of particle diameter ($\sigma$), which are shown in Figure 3. $k_B$ and $T$ has their usual meaning.

6.5 PHYSICAL SIMULATION STUDY

Capillary viscometers each having length 40 mm and diameters 0.5, 1 and 2 mm are calibrated at 25°C by using water, benzene and kerosene. Each viscometer is filled with the diluted magnetic fluid with $\phi = 0.64\%$ and placed horizontally between the poles of an electromagnet in such a way that the direction of the fluid flow is parallel to the direction of external magnetic field. Flow rate as a function of magnetic field is
measured and viscosity $\eta_r$ is determined from the measurements. Angular dependency of the flow rate is determined in a viscometer having 1 mm capillary diameter by tilting the viscometer with respect to the direction of the applied magnetic field (Figure 4). These measurements are carried out for four specific angles ($\beta = 0^\circ$, $15^\circ$, $45^\circ$, $90^\circ$) between the vorticity of flow and the direction of applied magnetic field. The angle between vorticity of flow and field direction ($\beta$) is related to the angle between direction of fluid flow and magnetic field ($\phi$) by $\beta = 90^\circ - \phi$.

![Figure 4. Schematic representation of particle motion in capillary vessel. $H$ represents the direction of external magnetic field, $v$ is velocity of fluid flow, $\Omega$ represents the vorticity and $\mu$ is the magnetic moment of the particle.](image)

When the angular velocity of the magnetic particles does not coincide with the angular velocity of the fluid, then an additional frictional force arises. Taking this into consideration the rotational viscosity will be given by

$$\eta_r (\alpha) = \frac{3}{2} \eta_0 \frac{aL^2(\alpha)}{\alpha - L(\alpha)} <\sin^2\beta>$$

where,

$$<\sin^2\beta> = \frac{1}{2\pi} \int_0^{2\pi} \sin^2\beta$$

Here $\beta$ is the angle between the vorticity of flow and the direction of magnetic field and $\phi_h$ is hydrodynamic volume fraction of magnetic particles. For $\beta = 0$ equation (2) reduces to
\( \eta_r(\alpha) = \frac{3}{2} \eta \alpha \frac{L^2(\alpha)}{\alpha - L(\alpha)} \)  

(4)

Figure 5 (A and B) shows the variation of rotational viscosity as a function of applied magnetic field for three different capillary diameters.

Figure 5A. Field induced rotational viscosity of water based magnetic fluid having magnetic volume fraction 0.64% measured for three different capillary diameters.

It is observed from the curves that as magnetic field increases, rotational viscosity increases gradually and then reaches to saturation. It is interesting to note that the zero field viscosity is independent of the capillary diameter, but field induced viscosity increases sharply as the capillary diameter of the viscometer decreases.

Figure 5 (A and B) shows that in the case of water based magnetic fluid, change in rotational viscosity is quite larger than that observed for the case of kerosene based magnetic fluid. This may be attributed to the presence of aggregates in water-based ferrofluid\(^ \text{20} \). All the three curves are fitted with the modified Shliomis relation given by equation (4)\(^ \text{13,19} \). The fitted curves are shown in Figure 6 (A and B). In both the figures Y scale is shifted for the sake of clarity, and fitting parameters thus obtained are presented in Table 1.
Figure 5B. Field induced rotational viscosity of kerosene based magnetic fluid having magnetic volume fraction 2.24% measured for three different capillary diameters.

Figure 6A. Reduced rotational viscosity of water based magnetic fluid having magnetic volume fraction 0.64% measured for three different capillary diameters (A) 0.5 mm, (B) 1 mm and (C) 2 mm. The solid lines are the theoretical curves generated using equation (5).
FIGURE 6B Reduced rotational viscosity of kerosene based magnetic fluid having magnetic volume fraction 2.24 % measured for three different capillary diameters (A) 0.5 mm, (B) 1 mm and (C) 2 mm. The solid lines are the theoretical curves generated using equation (5)

Table 1 Hydrodynamic parameters of water and kerosene based Fe₃O₄ ferrofluid

<table>
<thead>
<tr>
<th>Carrier</th>
<th>Parameter</th>
<th>Capillary diameter (mm)</th>
<th>Angle (β)</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>Water</td>
<td>D (nm)</td>
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<td>15.3</td>
</tr>
<tr>
<td></td>
<td>η(∞) (mPa.S)</td>
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<td>1.92</td>
</tr>
<tr>
<td></td>
<td>φₜ</td>
<td>0.42</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>ξ(mm³/sec/kg)x10⁻⁹</td>
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<td>0.88</td>
</tr>
<tr>
<td>Kerosene</td>
<td>D (nm)</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>η(∞) (mPa.S)</td>
<td>1.42</td>
<td>0.78</td>
</tr>
<tr>
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<td>φₜ</td>
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<td></td>
<td>ξ(mm³/sec/kg)x10⁻⁹</td>
<td>1.02</td>
<td>1.87</td>
</tr>
</tbody>
</table>

When $H \to \infty$, $L(\alpha) = 1$. Therefore, equation (4) takes the form
\[ \eta_r(\infty) = \frac{3}{2} \eta \phi_h \]  \hspace{1cm} (5)

Here \( \eta \) is fluid viscosity when \( H = 0 \). By substituting the value of \( \eta_r(\infty) \) and \( \eta \) in equation (5), effective hydrodynamic volume fraction \( (\phi_h) \) is determined for each capillary. The variation of the effective hydrodynamic volume fraction \( (\phi_h) \) as a function of the capillary diameter (\( d \)) is shown in Figure 7 for both the carriers. \( \phi_h \) is found to be inversely proportional to \( d \) (Table 1). This is due to the increase in local density of particles within the capillary region of the viscometer, which leads to the increase in the hindrance to the flow by friction force acting between the adjacent layers.

**Figure 7.** Plot of effective hydrodynamic volume fraction \( (\phi_h) \) as a function of capillary diameter (\( d \)) for water and kerosene based ferrofluid

In earlier studies rotational viscosity was measured for two special cases when \( \beta \) assumed the value 0 (direction of magnetic field parallel to the vorticity of flow) and \( \pi/2 \) (direction of magnetic field perpendicular to the vorticity of flow)\textsuperscript{13,19}. However, no measurements for \( \beta\neq0 \) or \( \pi/2 \) are available in the literature. It is not always possible to orient the direction of the applied field perpendicular or parallel to the axis of capillary in MDT systems. Hence, it will be useful to study the effect of field orientation on rotational viscosity \( \eta_r(H) \). **Figure 8 (A and B)** shows angular
variation of rotational viscosity as a function of applied magnetic field for four specific directions of magnetic field with respect to fluid vorticity.

![Graph](image_url)

**Figure 8A.** Angular dependent rotational viscosity as a function of applied magnetic field for different angles ($\beta$) between field direction and vorticity of the flow for water based ferrofluid

![Graph](image_url)

**Figure 8B.** Angular dependent rotational viscosity as a function of applied magnetic field for different angles ($\beta$) between field direction and vorticity of the flow for kerosene based ferrofluid
When the field direction is parallel to the fluid vorticity, the magnitude of the change in rotational viscosity is lowest. On the other hand, when field is perpendicular to the fluid vorticity, the change in rotational viscosity is twice that for the parallel case. This is in agreement with the prediction made by Shliomis\textsuperscript{12} and observed by other authors\textsuperscript{18,19}. For any other angle $\beta$, $\eta_r(H)$ should fall between these two extremes (Figure 8 A and B). The goodness of fit in Figure 8 (A and B) indicates that Shliomis relation holds true for any arbitrary angle $\beta$ between field and vorticity. While fitting the experimental results with equation (2), it is assumed that all the constituent particles of ferrofluid are monodispersed in size. The results of experimental fits are shown in Table 1.

**Figure 9** shows the variation in the effective hydrodynamic volume fraction ($\phi_h$) as a function of the angle ($\beta$).  

![Figure 9](image)

**Figure 9.** Plot of effective hydrodynamic volume fraction ($\phi_h$) as a function of angle between the direction of magnetic field and vorticity of flow for water based ferrofluid. The inset shows the same plot for kerosene based ferrofluid

It shows that the increase in the angle $\beta$ results into the sharp decrease in the effective hydrodynamic volume fraction. The exponential nature of decrease of the effective volume fraction is attributed to the sine square dependence of $\beta$ in equation (2).
observed decrease in effective hydrodynamic volume fraction with rise in $\beta$ is due to the decrease in the local density of magnetic nanoparticles aligning in the direction of magnetic field. Further, the magnitude of the effective hydrodynamic volume fraction ($\phi_h$) for water based magnetic fluid is found to be higher than that of kerosene based magnetic fluid. In water-based ferrofluid, particles are coated with a double layer of surfactants. In water-based ferrofluid the presence of aggregates have already been reported\textsuperscript{20}. This could be responsible for the observed larger size of effective hydrodynamic volume fraction in water-based ferrofluid.

Magnetophoresic mobility $\xi$ is an important parameter for designing an MDT system. $\xi$ is determined by using the following relation\textsuperscript{21}

$$\xi = \frac{R_m^2 \Delta \chi}{9 \eta}$$

Here $\eta$ is the viscosity of the medium, $R_m$ is the radius of the magnetic particle and $\Delta \chi = \chi_m - \chi_w$ where $\chi_m$ is the susceptibility of magnetic nanoparticles and $\chi_w$ is the carrier susceptibility. As the magnitude of $\chi_w$ is negligible compare to $\chi_m$, only susceptibility of magnetic nanoparticles is taken into the account in calculation of magnetophoretic mobility. When a ferrofluid is flowing through a capillary then it will be more appropriate to replace $\eta$ by $\eta_r$ in calculation of $\xi$. The percentage contribution of rotational viscosity for water and kerosene based ferrofluids are found to be 32, 28, 16% and 16.3, 13, 8.3% respectively for 0.5, 1.0 and 2.0 mm diameter capillary respectively. This contribution is quite large and cannot be neglected while determining magnetophoretic mobility of magnetic nanoparticles. Therefore $\eta$ should be replaced with $\eta_r$ in equation (6). By substituting the values of radius of magnetic nanoparticles, its magnetic susceptibility and rotational viscosity in equation (9), we have computed magnetophoretic mobility for three capillary diameters and four specific angles between the direction of field and vorticity of flow. Obtain values are shown in Table 1.

6.6 CONCLUSIONS

The present work brings out the importance of contribution of the field induced rotational viscosity when a ferrofluid is flowing through a capillary placed in a magnetic field. It also shows that orientation of the capillary vis - a - vis the field
direction affects significantly to the rotational viscosity. These results in turns affect the magnetophoretic mobility and local density, which are important parameters in magnetic drug targeting. Therefore, the present physical simulation study may provide useful information in designing an MDT experiment.

REFERENCES

12. M Shliomis (1972) J of Exp and Theoretical Phys 34:1291

CHAPTER 7

MULTIFUNCTIONAL Fe₃O₄-Ag NANOCOLLOIDS