Silica anchored colloidal suspension of magnetite nanorods
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Abstract
This study focuses on the interaction of colloidal silica nanoparticles with the magnetite (Fe$_3$O$_4$) magnetic fluids (MF), which eventually forms nanorod like structure. The aqueous magnetic fluid consists of magnetite nanoparticles having double layers of lauric acid surfactants. This surfactant provides stability towards short-range van der Waals attractive and steric repulsive forces, as well as long-range dipole-dipole interactive force. Whereas, in the colloidal silica, the sodium ions provide stability to the silica nanoparticles. To understand the interaction among the silica and magnetite nanoparticles, both, colloidal silica and magnetic fluid, were mixed in different proportions. Thus, the interaction present in the system is studied using FTIR, TGA, and magnetic field induced microscopy. The FTIR and TGA data reveal that silica interacts with the outer layer of lauric acid through the Si-O bond and eventually provides stability to the system. The length of the lauric acid sheath varies with the concentration of silica nanoparticles. The SEM images indicate nanorod formation, and its structure dimensions vary with the silica concentrations, which is also reflected in the magnetic field-induced structure formations. The structure observed using microscopy correlated with the interaction derived from FTIR and TGA data analysis.

1. Introduction
The growing interest in the magnetic nanoparticles and its fluid has attracted many researchers working in its facets from synthesis to applications [1][2][3][4][5]. Moreover, interest is always due to understanding the basic mechanism in the absence and presence of the applied magnetic field, and subsequently, its effects [6] [7][8]. Starting from the use of transition metal ions for the synthesis of magnetic nanoparticles, it has now expanded to the composite nanostructures, which includes some of the vital parameters like size, shape, crystal structure composition, etc. [9][10]. The stable colloidal suspension is an interesting material owing to its tunable properties viz. rheological, magnetic, optical, electrical, etc.[11][3]. This stable suspension made of nanoparticles can be either prepared in single carrier (e.g., hydrocarbon oil, water, solvent, etc.)
or emulsions (water in oil or oil in water), mixed with micron sized non-magnetic or magnetic materials [1][12][13][4]. One such non-magnetic material, which is well reported and used, is silica [4][9]. The silica is known for its non-toxicity, adsorption properties, surface functionalization, thermal and chemical stability, and various biological and environmental applications [14][15].

Researchers are focusing on the magnetic fluid (ferrofluid - a stable colloidal suspension of magnetic nanoparticles decorated by surfactant layer(s) suspended in magnetically passive medium) due to various promising engineering and biomedical applications [16][12][17][18]. The modulation of magnetic properties by doping/mixing other non-magnetic material (e.g., silica, graphene oxide, latex, polymer, gold, etc.) became subject of interest due to ability to tune other allied properties, viz. optical, rheological, electrical, biomedical, etc.[19][20][21][22][23][24][25]. The modulation of these properties is attributed to the interaction (direct/indirect) between the magnetic and non-magnetic particles. Moreover, the nature of interaction usually depends on (i) the composition and sizes of particles, (ii) types of stabilizing ions or surfactant, and (iii) carrier of suspension. It is always important to understand the nature of the interaction between magnetic and non-magnetic particles, which eventually helps to explore further for various applications. In various studies, the non-magnetic material is either used to form a core-shell structure or mixed in the magnetic fluid externally[15][26]. The inclusion of micron-sized silica particles in the magnetic fluid demonstrates magnetorheological properties and illustrates the formation of field-induced column-like structure [27][28]. Hence, the effect of inclusion of (i) micron-sized silica particles as well (ii) silica decorated particles in the magnetic fluid are well reported. However, the effect of the addition of nanosized (< 50 nm) silica particles are studied less [15].

Here, we report the interaction of the addition of 12 nm-sized silica nanoparticles in the aqueous magnetic fluids. The interaction is studied using Fourier transform infrared spectroscopy and thermogravimetric analysis. The Scanning electron microscopic (SEM) images indicate the formation of nanorod like structure consists of magnetic nanoparticles covered with silica. Interestingly, superparamagnetic nature retains even after the addition of silica and in-spite of forming nanorod like structure. The magnetic field induced microscopy demonstrates microstructure formations with controlled inter-chain spacing.
2. Experimental

2.1 Sample Preparation:

Analytical grade chemicals used were Iron (II) chloride (98%), Iron (III) chloride (97%), ammonia solution (28-30%), lauric acid (≥98%), and LUDOX HS-40 colloidal silica (40 wt.% suspension in H₂O) (all from Sigma-Aldrich (Merck)).

The synthesis of magnetic fluid has been carried out as follows [29][30]. Iron (II) chloride (6 g) and Iron(III) chloride (12 g) each dissolved in 25 ml water. The particles were precipitated by adding 30 ml NH₄OH in iron chloride solutions at 300K with vigorous stirring (450 RPM). After 5 minutes, to remove the chlorine impurities, luke-warm water (T~308 K) wash was given twice. Followed by 5% ammoniated water to provide charge to the freshly prepared particles. Ferrite slab magnets (surface magnetization 1000 G) were used for the magnetic decantation process. Finally, thick magnetic slurry obtained was kept on a pre-heated hot plate while continuously stirring. Once the temperature of slurry reached around 353K, 2.4 g lauric acid (LA) added and gently stirred for 1-1.5 minutes. This results in double layers of lauric acid stabilized magnetite magnetic fluid (MF). As the extra quantity of surfactant is added, it makes this fluid dilution insensitivity (can dilute 50-60 times). Here we dialyzed this fluid (to remove extra free surfactant) overnight and used for the present work and coded here as F100 magnetic fluid (MF).

Colloidal silica (HS-40) is a suspension of silica nanoparticles (size ~ 12 nm) stabilized using sodium counter ions. This suspension was mixed with the magnetic fluid to study the effect of silica nanoparticles on the magnetic fluid properties. Three samples were prepared by mixing X ml of F100 MF and Y ml of HS-40, whereas the total volume of the system kept constant (i.e., 1 ml). The first sample F80H20 consists of 0.8 ml F100 MF and 0.2 ml HS-40 suspension. The F75H25 contains 0.75 ml F100 MF and 0.25 ml HS-40 suspension. The F70H30 fluid has 0.7 ml F100 MF and 0.3 ml HS-40 suspension. The F80 fluid has 0.8 ml F100 MF, and 0.2 ml ammoniated water (5% NH₄OH solution).

2.2 Characterization Techniques

Fourier Transform Infrared (FTIR) spectroscopic measurements were carried out using NICOLET 6700 spectrophotometer (Thermo). Each spectrum was recorded in the range of 400-
4000 cm⁻¹ in an interval of 1 cm⁻¹ at 300 K. The sample pellet was prepared by thoroughly mixing the sample in KBr powder (IR grade, Sigma-Aldrich).

Thermogravimetric Analysis (TGA) (TGA/DSC-1, Mettler Toledo) was used to determine the thermal decomposition and phase transition temperatures. Hot air oven-dried (@ 100 °C - 16 hours) samples (~15 mg) was placed in an alumina crucible and scanned in a temperature range of 50-1000 °C (under N₂ atmosphere). Initially, all the samples were scanned with 10 °C/minute step size. After identifying the region of interest, the temperature range was segmented as follows: a) 50-200 °C -10 °C/min. step size, b) 200-360 °C - 5 °C/min. step size, c) 360-690 °C - 10 °C/min. step size, d) 690-750 °C - 5 °C/min. step size, e) 750-820 °C - 2 °C/min. step size, and f) 820-1000 °C - 5 °C/min. step size.

Magnetic field-induced light transmission set-up was aligned as follows. A randomly polarized He-Ne laser (632.8 nm, 5 mV power) beam could pass through a polariser. This polarized light was incident on a fluid sample kept in a glass cell having thickness ~120 μm. The direction of the magnetic field generated using electromagnet was perpendicular to the sample cell. Photodiode (DET 10A/M, Thorlabs) connected to a multimeter (8808A, Fluke) was used to measure the magnetic field induced change in the transmitted light intensity. The magnetic field was measured using Gaussmeter (DGM-20, Raman Scientific Instruments).

Magnetic field-induced microstructure formations were studied using an inverted metallurgical microscope (IM7100, Meiji Techno). Using a 20X objective lens (0.4 NA), a ProgRes C3 CCD camera (Jenoptik) could capture the field of view. A drop of a magnetic fluid, sandwiched between a glass plate and a coverslip, was subjected to a gradient magnetic field of 0.055T. Thus, the magnetic field applied was at right angles to fluid and incident light. Using the ImageJ program, microstructure formation was studied.

3. Result and Discussion:

The interaction of silica nanoparticles (HS-40) with the magnetite nanoparticle in the magnetic fluid stabilized using double layers of lauric acid (LA) surfactant is studied using the FTIR spectra. Figure 1 shows FTIR spectra (% transmission) of F70H30, F75H25, F80H20 fluids along with its parent systems, i.e., F100 MF and silica suspension (HS-40). General observation of all spectra suggests the presence of all major peaks, while detailed analysis is as follows.
Figure 1: FTIR spectra illustrating influence of silica nanoparticles on F100, HS-40, F80H20, F75H25, F70H30 magnetic fluids.

In F100 MF, the IR band observed at 3440 cm\(^{-1}\) is attributed to the stretching vibration of H\(_2\)O molecules. Due to the lauric acid (LA) coating, H-C-H stretching vibrations are evident. The antisymmetric (\(\nu_{as}\)) and symmetric (\(\nu_s\)) modes of CH\(_2\) seen at 2919 cm\(^{-1}\) and 2850 cm\(^{-1}\), respectively, whereas the signature bands of CH\(_3\) observed \(\nu_{as}\) at 2955 cm\(^{-1}\) and \(\nu_s\) at 2870 cm\(^{-1}\), respectively. The vibrational modes corresponding to carbonyl C=O chains usually observed in LA at 1712 cm\(^{-1}\) disappeared here. Instead, two new vibrations corresponding to carboxylate symmetric (\(\nu_s\)COO\(^-\)) and asymmetric (\(\nu_{as}\)COO\(^-\)) modes of vibrations appeared as a broad band centered around 1635 and 1442 cm\(^{-1}\), respectively, which result as wavenumber separation, \(\Delta\) (= \(\nu_{as}\) COO\(^-\) – \(\nu_s\) COO\(^-\)), around 234 cm\(^{-1}\). The \(\Delta\) depicts monodentate interaction between the carboxylate head and the magnetite nanoparticles of magnetic fluid. In other words, it confirms the chemi-adsorption of lauric acid on the surface of magnetite nanoparticles [31]. Herrera et al. reported similar interaction of magnetite nanoparticles with lauric acid and oleic acid [32]. The magnetite is having an inverse spinel structure, where Fe\(^{+2}\) occupies B site, while Fe\(^{+3}\) occupies both A and B-sites. In the FTIR spectra, the band observed at 589 relates to the tetrahedral (A) site, whereas bands observed at 420 & 411 cm\(^{-1}\) relates to the octahedral (B) site [33][34].
In the silica suspension (HS-40), the band observed at 3454 cm\(^{-1}\) attributed to the stretching vibration of H\(_2\)O molecules. Correspondingly, the band at 1636 cm\(^{-1}\) is due to the bending vibrations of H\(_2\)O molecules. A shoulder around 3248 cm\(^{-1}\) is due to the stretching vibrations of Si-OH (bonded water). The characteristics transverse optical (TO) frequency and longitudinal optical (LO) frequency bands of SiO\(_2\) nanoparticles falls in the fingerprint region 700–1350 cm\(^{-1}\) [35]. The TO and LO modes of the Si-O-Si asymmetric stretching vibrations are evident from the sharp band at 1111 cm\(^{-1}\) with a shoulder around 1188 cm\(^{-1}\), respectively. Correspondingly, band at 800 cm\(^{-1}\) attributed to the symmetric stretching vibrations of Si-O-Si and band at 471 cm\(^{-1}\) assigned as O-Si-O bending vibrations. The observed band agreed with that of synthesized amorphous SiO\(_2\) [14].

The bands observed at 3439 cm\(^{-1}\), 3435 cm\(^{-1}\), and 3427 cm\(^{-1}\), respectively of F70H30, F75H25, and F80H20 of H\(_2\)O stretching vibration indicate a redshift compared to both the parent fluids. Similarly, H\(_2\)O bending vibrations observed at 1639 cm\(^{-1}\), 1635 cm\(^{-1}\) and 1627 cm\(^{-1}\) for respective F70H30, F75H25 and F80H20 fluids. The observed band varies compared to HS-40 silica suspension. The antisymmetric and symmetric modes of CH\(_2\) remains constant around 2922 cm\(^{-1}\) and 2852 cm\(^{-1}\) in all three fluids, which agrees with the parent F100 fluid. The TO and LO modes of the Si-O-Si asymmetric stretching vibrations remain constant at 1111 cm\(^{-1}\), whereas variation in the shoulder position observed around 1214 cm\(^{-1}\), 1221 cm\(^{-1}\), and 1221 cm\(^{-1}\) respectively for F70H30, F75H25 and F80H20 fluids. Corresponding symmetric stretching vibrations of Si-O-Si as a band remains invariant at 801 cm\(^{-1}\) along with O-Si-O bending vibrations at 471 cm\(^{-1}\) for all the three fluids. Shoulder band in HS-40 silica at 966 cm\(^{-1}\) shifts to 973 cm\(^{-1}\), 974 cm\(^{-1}\), and 975 cm\(^{-1}\), respectively, for F70H30, F75H25, and F80H20 fluids, which is associated with Si-O stretching vibration. The shift indicates the interaction of silica with the lauric acid coated magnetite. Also, A-site of Fe-O stretching vibrations shifts from 589 cm\(^{-1}\) to 576 cm\(^{-1}\), 585 cm\(^{-1}\), and 587 cm\(^{-1}\), respectively, for F70H30, F75H25, and F80H20 fluids, while B-site Fe-O stretching vibration remains invariant. Here, we recall that the silica suspension is added to the ferrite magnetic fluid (without any chemical process); hence, it is unlikely to expect any change in the figure print region of ferrite particles (i.e., cation distribution band positions). However, as per the present spectral analysis, we can conclude that silica NPs interacts with the lauric acid coated magnetite’s. However, the observed variation in the cationic A-site of magnetite is surprising. In order to understand and further confirm the interaction of silica with F100 fluid, TGA experiments were carried out.
Thermogravimetry Analysis:

Figure 2: First order derivative of thermal decomposition of F100, F80H20, F75H25, and F70H30. Inset: Variation in the mass loss (normalized) with increasing temperature.

Thermogravimetric data used to determine the decomposition temperature of the surfactant and phase-transition temperature of ferrite and silica nanoparticles. Figure 2 shows the first derivative $\frac{dM}{dT}$ of F100, F70H30, F75H25, and F80H20 magnetic fluids. As discussed below, spectra show five peaks, corresponding to the transition temperature. The mass loss observed at $\sim 120 \, ^{\circ}C$ is attributed to the absorbed moisture and/or water crystallization temperature. In F100 MF, assigned transition temperatures 255 (± 5) $^{\circ}C$ and 346 (± 5) $^{\circ}C$ corresponds to the decomposition of secondary and primary layers of chemi-adsorbed lauric acid present on the magnetite nanoparticles. The synthesis route adopted here lead to form double layers of surfactant on the magnetic nanoparticles [29][30]. A third peak corresponding to free/un-bound lauric acid surfactant is absent here. Hence, it confirms our analysis of FTIR spectra, where peak $\sim 1712 \, cm^{-1}$ corresponding to physi-adsorbed / unbound lauric acid peak is absent. Albeit, the surfactant remains only as a double layer of chemi-adsorbed lauric acid on the surface of magnetic nanoparticles. The addition of silica in the F70H30, F75H25, and F80H20 fluids varies the first peak from 255 (± 5) $^{\circ}C$ (i.e., F100) to 262 (± 5) $^{\circ}C$. We attribute this variation to the interaction of silica nanoparticles with the second layer of LA. The result of TGA supports the interaction observed in the FTIR spectra. As expected, the first layer of LA does not alter on the addition of silica NP and remains constant, i.e.,$\sim 346$ (± 5) $^{\circ}C$. Further, the
increase in the temperature from 500 – 1000 °C illustrates the phase transition of magnetite. The peak observed in F100 at 700 ± 5 °C is attributed to the phase transition from FCC spinel ferrite \( \text{Fe}_3\text{O}_4 \) to wustite \( \text{Fe}-\text{O} \) [36][37]. Noticeably, we observed a redshift in the first phase transition from 700 (± 5) °C, 734 (± 5) °C and 724 (± 5) °C in the F70H30, F75H25, and F80H20 respectively, and correlated with the reduction in the silica NP concentration. The secondary transition seen in F100 at 864 (± 5) °C is due to further transformation to metallic Fe [38]. This peak moves to 799 (± 2) °C, 795 (± 2) °C, and 776 (± 2) °C in respectively F70H30, F75H25, and F80H20 possibly reveals degradation of some different structure. Perhaps during the heating cycle \( \text{Fe-C/Fe-Si} \) or similar composite forms and degraded [36].

**Table-1:** The mass loss (%) and the decomposition temperature of F100, F80H20, F75H25, and F70H30 fluids. It also shows the number of the secondary and primary layers of lauric acid ligands bound on a magnetite nanoparticles derived using equation (1), and increment in the ratio of primary: secondary with the increase in the silica nanoparticles.

| Sample | Layer   | \( T(°C) \) (± 5) | % Wt loss \( dM/dT \) | No. of Ligands | The ratio of primary to secondary |
|--------|---------|-------------------|------------------------|----------------|----------------------------------|
| **F100** | Secondary | 255 | 8.3 | 421 | 2.10 |
|         | Primary   | 346 | 16  | 886 |        |
| **F80H20** | Secondary | 262 | 4.4 | 214 | 2.35 |
|         | Primary   | 346 | 9.8 | 505 |        |
| **F75H25** | Secondary | 262 | 5.5 | 271 | 2.79 |
|         | Primary   | 346 | 14  | 757 |        |
| **F70H30** | Secondary | 262 | 4.4 | 214 | 3.21 |
|         | Primary   | 346 | 12.9| 689 |        |

The TGA analysis of F100, F70H30, F75H25, and F80H20 magnetic fluids are used to calculate the number of organic ligands (molecules) bound with the magnetite surface using the relation [33][39], \( p = \frac{m_2}{m_1+m_2} \times 100 \% \). Here, sample mass \( m_1 = \rho_1 \times V_1 \), with \( \rho_1 \) the density of bulk magnetite \( (5.17 \times 10^3 \text{ kg/m}^3) \), the volume of each magnetite crystals \( V_1 = \pi D^3 / 6 \), with D
the particle diameter of magnetite obtained from Scherrer’s formula. The total mass of the organic molecules bound to one nanoparticle, \( m_2 = n\mathcal{M}_2 \times 10^{-3} \times 6.022 \times 10^{-23} \text{kg/mol} \) measured as mass-loss during carbonization process, with \( \mathcal{M}_2 \) the molecular of lauric acid \((200.318 \times 10^{-3} \text{kg})\). Thus, the number of ligands (molecules) bound at each mass-loss peak is calculated as,

\[
n = \frac{\pi \times D^3 \times \rho \times \rho \times 6.022 \times 10^{23}}{6 \times \mathcal{M}_2 (100-p)} \quad \text{……… (1)}
\]

Table -1 shows the number of ligands bound as the secondary and primary layers of lauric acid surfactant on a single magnetite nanoparticle derived from the equation (1). In F100 fluid, the number of primary and the secondary molecules on single magnetite are 886 and 421 respectively, and hence the ratio of primary: secondary is 2.1. It infers that around each magnetite nanoparticle, there will be 2.1 lauric acid molecule in the first layer with corresponding one lauric acid molecule in the second layer. In F80H20 fluid, the number of lauric acid molecules in the primary and secondary layers are comparatively less than F100 fluid; however, the ratio (primary: secondary) increases. Whereas, in F75H25 and F70H30, the number of ligands and overall primary: secondary ratio increases to 2.79 and 3.21, respectively. The increase in this ratio may affect the energy ratio, namely magnetic and thermal energies. Moreover, the F75H25 is having a relatively higher number of lauric acid molecules in inner layers compared to the other two fluids (i.e., F70H30 and F80H20). Which in-turn may affect on the size parameter of silica-magnetic cluster/aggregates.

Figure 3 shows SEM images of (a) F80H20, (b) F75H25, and (c) F70H30 fluids. It emerged from the images that the addition of silica leads to form rod-type aggregates. The number density of this elongated/rod-shaped structure is higher in F80H20 fluid, while it relatively decreases with increasing silica concentrations. Also, the background becomes more whitish with increasing silica concentrations (i.e., a to c). General observation of all the images indicates formations of rod-like structure, but the presence of spherical and other shapes is evident. The average length of these rods are 1.43 µm, 1.49 µm, and 1.53 µm, while the average width 0.24 µm, 0.42 µm, and 0.64 µm respectively for F80H20, F75H25, and F70H30 fluids. Based on this, roughly, it can be estimated that the thickness of the rod-like/elongated structure increases with the increase in silica concentrations. This observation supports our TGA findings. Similarly, adding CMC in-situ and ex-situ in Fe3O4 nanoparticles leads to form two different types of structure[40].
A recent report discussed the preparation of magnetic silica microbeads using the water-in-oil emulsion method [15]. STEM resembles core-shell like structure, where magnetic nanoparticles layered inside silica microbeads. The surface porosity varies with span 80 (surfactant) concentrations. In the present work, magnetic fluid and silica suspension are mixed (unlike emulsion), which produces nanorods or rod-like structures. The white color spherical-like aggregates formed of either silica or silica-magnetite composites. To understand the magnetic nature of the observed nanorods, we performed magnetic measurements. Figure 4 shows magnetization data of magnetic fluids F100, F80H20, and F30H70. We noted here that the saturation magnetization, initial susceptibility, mean magnetic size, and log-normal particle size distribution (σ) varies linearly with the magnetic volume fraction of F100 (see table 2).
Supplementary S1 discusses the analysis of magnetic properties. The fact that nanorods possess uniaxial anisotropy and relatively high magnetic susceptibility compared to single-domain magnetic nanoparticles. In spite of forming nanorod structure, we assume here that magnetite particles stuck in each rod behave like single-domain magnetite. In order to have a clear understanding of this behavior, we performed the magnetic field induced microscopy.

Table 2: Parameters derived from the data are initial susceptibility ($\chi_i$), and saturation magnetization ($M_s$). The magnetic volume fraction ($\varphi_m$) calculated assuming constant $M_d$. Other parameters derived are mean particle diameter ($D_m$), volume-weighted mean magnetic diameter ($D_{mv}$), number weighted mean diameter ($D_{mn}$) & log-normal size distribution ($\sigma_D$). (refer supplementary S1 for detail)

| Sample   | $\chi_i$ ($\pm 0.001$) | $M_s$ ($kA/m$) ($\pm 0.0045$) | $\varphi_m$ | $D_m$ (nm) ($\pm 0.1$) | $D_{mv}$ (nm) ($\pm 0.01$) | $\sigma_D$ |
|----------|------------------------|-------------------------------|-------------|------------------------|---------------------------|-----------|
| F100     | 0.305                  | 8.1843                        | 0.00169     | 11.3                   | 8.09                      | 0.47      |
| F80H20   | 0.241                  | 6.3953                        | 0.00132     | 11.4                   | 8.29                      | 0.46      |
| F70H30   | 0.214                  | 5.5224                        | 0.00114     | 11.5                   | 8.64                      | 0.44      |

Figure 5: Microscopic images of F80, F80H20, F75H25, and F70H30 fluids at different times after applying the 0.055T magnetic field. Scale 400 μm.
The microscopic images were captured from 0 to 5 minutes (300 seconds) with 30 seconds interval of applying 0.055T magnetic field for F80, F80H20, F75H25, and F70H30 fluids. Figure 5 shows representative microscopic images from 1 to 5 minutes. The structure formed in the F80 is relatively scattered, whereas silica added fluids exhibit a relatively large and continuous structure. Moreover, the structure formed in the silica added fluids tends to stabilize over the period. Figure 6 shows the chain length and width determined using ImageJ software.

It depicts that on the application of magnetic field, in initial 30 seconds, field-induced structure formation takes shape. In the water-based magnetic fluid, the existence of pre-agglomerates helps to form a relatively stable field-induced structure [23][26]. Interest in understanding field-induced self-assembly in the superparamagnetic colloids in the presence of nano/micron non-magnetic particles also increases [41]. In the F80, F80H20, F75H25, and F70H30, the average length of the chains is 42.5, 47.5, 42.5, and 40 µm, while average width 4.75, 3.75, 4.00, and 3.5 µm respectively. This shows that the addition of silica inhibits the growth of the chains. Based on the data of average length and width of the nanorods (based on SEM), one can estimate the numbers of nanorods to form field-induced chains. The average number of nanorods to form vertical chains are around 35, 29, and 26, respectively, in the F80H20, F75H25, and F70H30 fluids. Similarly, the number of nanorods estimated for the width of the chains is 16, 10, and 5, respectively, for the F80H20, F75H25, and F70H30 fluids. We propose the following hypothesis to explain the reduction in the chain dimensions while correlating with the FTIR and TGA analysis.

Figure 6: Weighted average length and width of the chains as well as successive interchain distance as a function of time.

The lauric acid (surfactant) and silica nanoparticles both are non-magnetic in nature. The silica nanoparticles used here are stabilized using sodium ions. In other words, sodium counter ions...
prevent silica from aggregation. On adding silica suspension in the magnetic fluid, it is reacting with the outer (second) layer of lauric acid. The double-layer of surfactant interacting with silica nanoparticles should influence on the short-range (van-der Waals and steric repulsion) and long-range (dipole-dipole) interactions. The van der Waals attractive force between the spheres is given by [42],

\[
V_{ij}^{vdw}(r_{ij}) = -\frac{A}{6} \left[ \frac{2}{l^2+4l} + \frac{2}{(l+2)^2} + \ln \left( \frac{l^2+4l}{(l+2)^2} \right) \right]
\]

Here \( A \) is the Hamaker Constant, \( l = \frac{2s}{D_{core}} = \frac{2r_{ij}}{D_{core}} - 2 \), where \( s \) is the surface to surface distance of the particles reduced by the diameter \( D_{core} \) of the magnetic particles, \( r_{ij} \) the distance between their centers. The steric repulsion of the non-magnetic surfactant is described by,

\[
V_{ij}^{ster}(r_{ij}) = \frac{\pi D_{surf} k_B T}{2} \left[ 2 - \frac{l+2}{t} \ln \left( \frac{1+t}{1+l/2} \right) - \frac{l}{t} \right] \quad 0 < l < 2t
\]

Where, \( \xi \) is the surface density of the surfactant, \( k_B \) the Boltzmann Constant (= 1.38 \( \times \) 10\(^{-23} \) J/K), \( T \) the absolute temperature, \( t = \frac{2\delta_{surf}}{D_{core}} \), with the length of the surfactant chain \( \delta_{surf} \) (typically 2 nm). Rosensweig showed that the short-range potential in the magnetic fluid is expressed as, \( V^{SR} = V_{ij}^{vdw} + V_{ij}^{ster} \). [42][16]. A long-range interactive field that exerts due to the presence of an external magnetic field is expressed as,

\[
U_{dd} = \frac{\mu_0 m^2}{4\pi r^3} [1 - 3 \cos^2 \theta]
\]

Where, \( \mu_0 \) is the magnetic permeability of free space (4\( \pi \times 10^{-7} \) N/A\(^2 \)), \( m \) the dipole moment induced by the external magnetic field, \( r \) the separation distance between the two superparamagnetic particles, \( \theta \) the angle between the direction of the magnetic field and the line joining the centers of the two particles. The distance between the two particles is subject to the intensity of the applied magnetic field compared to thermal energy (\( k_B T \)).

The interaction energy of magnetic fluid comprises of magnetic and non-magnetic particles (here silica) is represented by [43],

\[
U_{ij} = -\frac{\mu_f m_1 m_2}{4\pi r_{ij}^3} [1 - 3 \cos^2 \theta]
\]

Where, \( m_1 = \left| V_{p1} \frac{3(x_{p1} - x_f)}{(x_{p1} - x_f) + 3(x_f + 1)} H_a \right| \), and \( m_2 = \left| V_{p2} \frac{3x_f}{2x_f + 3} H_a \right| \) represents the absolute values of the equivalent magnetization for the magnetic and non-magnetic particles, respectively. The magnetic interaction force is given by [43],
\[ F_{ij} = -\nabla U_{ij} = -\frac{3\mu r^{m_{1}m_{2}}}{4\pi r_{ij}^{3}} \left[ (1 - 3\cos^{2} \theta) e_{r} + 2\sin \theta \cos \theta e_{\theta} \right] \]  

(5)

Recall here that \( \theta \) represents the angle between the linking line of the two particles and the direction of the applied magnetic field, \( e_{r} \) the coordinate variable along the linking line of the two particles, and \( e_{\theta} \) the cylindrical coordinate system. According to the equations (4) & (5), the trends of the interactive energy and the magnetic force varies with the angle \( \theta \), and both the magnetic and non-magnetic particles exhibit opposite direction of the magnetization. Additionally, the particle interaction is repulsive when \( 0^\circ \leq \theta < 54.73^\circ \) [7], and attractive when \( 54.73^\circ < \theta \leq 90^\circ \) [43]. Which is contrary to the magnetic fluid comprises of only magnetic particles, which shows that the interparticle interaction is positive when \( 0^\circ \leq \theta < 54.73^\circ \). The effect of magnetic and non-magnetic particles are discussed in detail in the Ref.[43]. In the present fluids, we approximated numbers of particles/aggregates in a chain based on the nanorod dimensions observed using SEM. As it is observed that in all three fluids, magnetic field induced structure stabilizes after 1 min (60 sec), numbers reported here are after 1 minute only. In the F80H20, F75H25, and F70H30 fluids, the average nanorods assembled are longitudinal (and transverse) 34 (16), 29 (10), and 26 (7), respectively. As shown in Figure 2 of Ref.[43], the magnetic and non-magnetic particles parallel to the field lines experience a repulsive force, whereas perpendicular to the field lines experiences an attractive force. Similar is reflected in the present fluids, where higher silica concentration leads to form short and thin chains, whereas for low concentration it forms long and thick chains. Figure 6(c) shows the successive interchain distance for all the fluids. In the magnetic fluid F80 large change is observed with the increase in time, while in silica added fluids the interchain distance decreases relatively. The estimated number of lines in a grating per meter \( (N = l/d) \) \( (l = \text{length of a grating (say 1 m), and } d = \text{interchain distance (in meter)) is in the range of 150-350, 350-670, 450-600, and 550-1150 respectively for the F80, F82H20, F75H25 and F70H30 fluids. Although we need to achieve better control on these deviations, but resultant range of F75H25 is relatively less. The diffraction angle \( (\theta_r) \) is calculated as, \( \sin \theta_r = m\lambda /d \), where \( m = \text{order to diffraction, and } \lambda = \text{wavelength of incident light (here 650 nm). It infers that in case of first order diffraction (m=±1), } \theta_r \text{ ranges from } 0.56^\circ - 1.41^\circ, 1.3^\circ - 2.5^\circ, 2.0^\circ - 3.0^\circ, \text{ and } 1.87 - 4.3^\circ \text{ respectively for he F80, F82H20, F75H25 and F70H30 fluids. These preliminary results are encouraging. Further, field dependent experiments will throw some more light to develop tunable diffraction grating.}
Conclusion:

Articles providing indirect interaction of nonmagnetic particles with the magnetic nanoparticles in terms of optical, magnetic, rheology, etc. properties are reported in the literature [8][27]. However, papers reporting evidence of direct interaction and its influence on various properties are less [15]. Here, we demonstrate that adding silica nanoparticles suspension (Ludox HS-40) with the aqueous magnetic fluid (magnetite nanoparticles stabilized using double layers of lauric acid surfactant) results in chemically interactive fluid. The chemical interaction is derived using FTIR and TGA. The analysis of the FTIR spectrum suggests that silica nanoparticles interact with the lauric acid through Si-O stretching vibrations. The intensity of the Si-O-Si band increases with increasing silica concentrations. The interaction of silica nanoparticles with lauric acid is further confirmed using TGA. TGA data reveals that silica bind with the outer (second) layer of lauric acid attached to the magnetite nanoparticles. The ratio of primary to secondary layer ligands increases with increasing silica concentration. However, the number of lauric acid ligands observed is relatively more in F75H25 fluid compared other two fluids containing high and low silica concentration. This indicates that surfactant layer thickness is subject to the concentration of nonmagnetic silica nanoparticles. The scanning electron microscopy reveals formation of silica decorated magnetite nanorods. Despite of forming nanorod structure, the magnetic fluid exhibits superparamagnetic behaviour. The magnetic field assisted assembly indicates the formation of long, thick and scattered chains in the aqueous magnetic fluid. Whereas, relatively short, dense chains with controlled interchain distances are observable in the silica added magnetic fluids. As these soft chains behaves like diffraction grating lines, grating angle range is calculated. The preliminary results of grating parameters are encouraging and has potentiality to develop as tunable diffraction grating.

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