Chapter VIII  Probing the Effect of Temperature on Magnetic Field Induced Structural Transitions in Ferrofluids

8.1 Introduction

Particle aggregation changes the physical properties in colloidal systems [261, 378-380]. The fundamental understanding of the influence of aggregation parameters such as particle size, temperature, viscosity on aggregation process in colloidal systems is important from practical applications point of view [375, 381]. The field induced aggregation in magnetic nano-colloidal systems is mainly due to dipolar interaction between the dispersed magnetic nanoparticles [235, 274, 275]. Though numerous studies have considered the effect of dipolar interaction on field induced aggregation in magnetic nano-colloidal systems, the effect of temperature on field induced aggregation and related magneto-optical properties has not been systematically studied earlier. In this chapter, we have systematically studied the effect of temperature on the external field induced light transmission in kerosene based ferrofluids.

8.2 Experimental Details

The kerosene based ferrofluid samples used in this study is a disordered magnetic medium as explained in Chapter II (section 2.2). The detailed procedure of acquiring the transmission spectra through the samples as a function of $B$ has been explained in Chapter II (section 2.4). Here, the direction of incident light was kept parallel to the direction of $B$ and the ferrofluid was taken in a cuvette of path length, $L = 10$ mm and kept inside a Peltier based temperature controlled cuvette holder. The specimen temperature was varied using a programmable temperature controller. The $\phi$ was kept constant at 0.00155 throughout the experiments.
8.3 Results and Discussions

8.3.1 Wavelength Dependent Behavior of Magnetic Field Induced Light Transmission in Ferrofluids at Fixed Sample Temperature

Figure 8.1 shows light transmission through the ferrofluid as a function of $\lambda$ at five different $B = 0, 62, 130, 196$ and 264 G. The specimen temperature is kept constant at 278 K. The light transmission increases with $\lambda$ for all $B$. As the Fe$_3$O$_4$ nanoparticle size is much lower than $\lambda$ ($a \ll \lambda$) the light scattering can be described using Rayleigh’s theory, where the scattering efficiency is inversely proportional to the fourth power of the incident wavelength, i.e. $Q_{\text{scat}} \propto \frac{1}{\lambda^4}$ [286]. Hence, the observed decrease in the scattering intensity with increasing $\lambda$ is in good agreement with Rayleigh’s theory and this explains the increase in the transmission of incident light with increasing $\lambda$ in the ferrofluid. It can be further observed from Figure 8.1 that the transmission of incident light is highest at $B = 0$ G and it decreases with increase in $B$. 
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Fig. 8.1 Light transmission as a function of light wavelength ($\lambda$) at different external magnetic fields ($B = 0, 62, 130, 196, 264$ G) in a ferrofluid. Range of $\lambda$ is 675-750 nm and specimen temperature ($T$) was kept constant at 278 K.

In the absence of $B$, the oleic acid coated Fe$_3$O$_4$ nanoparticles are randomly dispersed in the carrier liquid due to Brownian motion of particles. On application of $B$, the magnetic moments of the individual nanoparticles orient themselves along the direction of $B$ and form linear chain like structures [59, 273]. When the magnetic coupling constant ($A_{\text{Coup}}$) between two nanoparticles is greater than one ($A_{\text{Coup}}>>1$), the dispersed magnetic nanoparticles undergo a disorder to order transition leading to the formation of linear chain like structures due to head-on aggregation of the dispersed nanoparticles along the direction of $B$ [172, 284, 382]. The interaction of incident light with such linear chain like structures with their axis parallel to the direction of propagation of light gives rise to a ring like transmission spectrum [282]. The aggregation of nanoparticles increases with $B$ due to increase in the dipolar interaction leading to a larger scatterer size [376]. On application of $B$, the magnetic nanoparticles form single chain like structures along the direction of $B$ up to $B_{C1}$ and beyond that zippering of chains takes place due to lateral aggregation resulting in bundles of nanochains [172]. The length of these chains increases with $B$ and the aggregation process depends on the strength of the field and exposure time. When the scatterer size is comparable with the $\lambda$ the scattering regime changes from Rayleigh to Mie region.

The transmission, absorption and distribution of the scattered light, during passage through a magnetic nanofluid depend on the nature of the dispersed scatterers [256, 285]. The total extinction efficiency ($Q_{\text{ext}}$) is the sum of scattering efficiency ($Q_{\text{sca}}$) and absorption efficiency ($Q_{\text{abs}}$) and can be expressed by the following equation [285].
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\[ Q_{\text{ext}} = Q_{\text{sca}} + Q_{\text{abs}} \]  

The mathematical expressions of \( Q_{\text{ext}} \) and \( Q_{\text{abs}} \) have been provided in Chapter VII (Equation 7.1) and Chapter VI (Equation 6.4), respectively and

\[ Q_{\text{sca}} = \frac{2}{\chi^2} \sum_{n=1}^{\infty} (2n+1)(|a_n|^2 + |b_n|^2) \]  

where, \( a_n \) and \( b_n \) are the Mie scattering parameters which depend on the scatterer size parameter \( (\chi = ka, \text{where } a \text{ is the radius of the nanoparticle and } k = 2\pi/\lambda) \).

The magnetic permeability (\( \mu \)) increases with increasing \( B \) for ferromagnetic scatterers [289]. At certain values of the external magnetic field the scatterer sizes are such that Mie resonances occur leading to a buildup of standing waves inside the scattering medium resulting in subsequent delay in light propagation causing the light transmission to decrease with increasing magnetic field as shown in Figure 8.1 [225].

Figure 8.2 shows the theoretical plot of \( Q_{\text{ext}} \) at lower values of the \( ka \) for four different \( \lambda \) (= 675, 700, 725 and 750 nm). It can be seen from the figure that the peak value of the extinction efficiency decreases with increasing \( \lambda \) and hence, light transmission increases with \( \lambda \) for a constant \( B \) as shown in Figure 8.1. As discussed earlier, in the absence of field, the increase in light transmission with increasing \( \lambda \) can be described by the Rayleigh scattering theory, whereas, in presence of an external field the individual nanoparticles form linear chain like structures due to dipolar interaction leading to a larger scatterer size and the system can be described by Mie scattering theory where the extinction efficiency decreases with increasing \( \lambda \) resulting in an increase in field induced light transmission with \( \lambda \).
Fig. 8.2 $Q_{ext}$ as a function of $ka$ at different $\lambda \sim 675, 700, 725, 750$ nm. Variation of $Q_{ext}$ is shown at lower values of $ka$. 
8.3.2 Temperature Dependent Field Induced Light Transmission and Possible Reasons of Temperature Effect on Transmission

![Graph depicting the normalized transmitted light intensity as a function of external magnetic field (B) at different sample temperature (T = 278, 288, 298, 303, 318K) in ferrofluid. Light wavelength, λ = 700 nm. Solid lines correspond to the linear regression analyses of the experimental data. The adjusted R² for the linear regression analyses are 0.97, 0.99, 0.99, 0.99 and 0.96 for T = 278, 288, 298, 303 and 318K, respectively.](image)

Fig. 8.3 Normalized transmitted light intensity as a function of external magnetic field (B) at different sample temperature (T = 278, 288, 298, 303, 318K) in ferrofluid. Light wavelength, λ = 700 nm. Solid lines correspond to the linear regression analyses of the experimental data. The adjusted R² for the linear regression analyses are 0.97, 0.99, 0.99, 0.99 and 0.96 for T = 278, 288, 298, 303 and 318K, respectively.
Figure 8.3 shows the variation of normalized transmitted light intensity as a function of $B$ for ferrofluid at five different specimen temperatures viz. $T = 278$, 288, 298, 303 and 318 K. For all the cases the $\lambda$ is kept constant at 700 nm. It can be seen from the figure that for all values of $T$, the normalized transmitted light intensity decreases with increasing $B$ owing to the Mie resonance induced buildup of standing waves inside the scattering medium due to enhancement of $ka$ with $B$. It can be further observed from Figure 8.3 that the field induced light extinction occurs at lower $B$ for lower $T$. The solid lines in Figure 8.3 indicate the linear regression analyses on the experimental data points where the slopes provide the rate of field induced light extinction ($R_{\text{trans}}$). Figure 8.4 shows the variation of $R_{\text{trans}}$ as a function of $T$ and it can be seen that $R_{\text{trans}}$ linearly decreases with increasing $T$. The normalized transmitted light intensity shows linear dependence with $B$ for all five $T$ and does not show critical field like behavior [376] or saturation in the transmitted intensity profile due to extremely low $\phi$ of the ferrofluid used in the present study.

The coupling constant, which determines the strength of the dipolar interaction with respect to the thermal energy of the specimen, is inversely proportional to $T$ and hence, aggregation kinetics will vary with $T$. In the absence of $B$, the dispersed nanoparticles undergo random Brownian motion and the diffusion coefficient can be expressed by the Stokes-Einstein equation (Chapter II, Equation 2.7).
Fig. 8.4 Rate of extinction of normalized transmitted light intensity ($R_{\text{Trans}}$) as a function of sample temperature ($T$). Solid line corresponds to linear regression analysis of the experimental data and adjusted $R^2$ is 0.96.

From the Stokes-Einstein equation it is evident that the diffusivity linearly increases with $T$ (as shown in the inset of Fig. 8.5). Moreover, the root mean square velocity ($V_{\text{RMS}}$) of the dispersed
nanoparticles undergoing random Brownian motion also increases with $T$ ($V_{RMS}$ is directly proportional to $T^{0.5}$) and can be expressed by the following equation [383].

$$V_{RMS} = \frac{1}{d_h} \sqrt{\frac{18k_B T}{\pi \rho d_h}}$$

(8.3)

Here, $\rho$ is the density of the nanoparticles. It has been reported earlier that for kerosene based ferrofluid, the variation in absolute viscosity with $T$ is not significant for the ferrofluid and the base fluid. Hence, with increase in $T$, the root mean square velocity and diffusivity of dispersed nanoparticles increases because of an enhancement of Brownian motion. On application of $B$, the dipolar attraction between the magnetic nanoparticles causes the particles to form linear chain like structures along the direction of $B$. The aggregation process is hindered by the enhanced Brownian motion for higher $T$ leading to slower aggregation kinetics at higher $T$. Figure 8.5 shows the variation of coupling constant as a function of $T$ (using Eq. 3.3,) for three different values of $B (= 100, 150$ and $200$ G). It can be seen that for all values of $B$, the coupling constant decreases with increasing $T$ indicating a slower aggregation kinetics at higher $T$.

With increasing $T$, the Brownian motion of the dispersed nanoparticles increases and hence, higher $B$ is required to form linear chain like structures, causing the extinction of transmitted light intensity to shift to higher $B$ values as shown in Figure 8.3. The rate of extinction of light transmission also decreases linearly with $T$ (Figure 8.4) indicating an increase in the time scale of aggregation kinetics at higher $T$ due to a linear increase of diffusion coefficient with $T$. 


Fig. 8.5. Coupling constant ($A_{\text{Coup}}$) as a function of sample temperature ($T$) at three different external magnetic fields ($B = 100, 150, 200$ G). (Inset) Diffusion coefficient ($D_T$) as a function of $T$.

Such temperature dependent field induced extinction of normalized transmitted light intensity is possible only under the influence of $B$ and not under thermo-optical effects as the rate of
change of refractive index as a function of $T$ is extremely low in nano-colloidal systems without external fields. Thermo-optical effect occurs due to modulation of refractive index of a medium as a function of $T$. For nano-colloidal systems the rate of change of refractive index with respect to the $T$ is very low ($-10^4$) [384]. Hence, the change of refractive index is negligible for nominal variation in $T$ (278 – 318 K in the present study). On the other hand, in the presence of $B$, ferrofluids exhibit magneto-optical effects due to spatial anisotropy caused by external field induced structural reorganization which ultimately causes enhancement of size parameters and an extinction of transmitted light intensity at a certain value of $B$ and $T$. With increase in $T$, the field induced extinction of transmitted light intensity occurs at a higher field giving rise to temperature dependent magneto-optical properties.

Figure 8.6 shows the variation of light transmission as a function of $\lambda$ at four different $T$ (=278, 288, 303 and 318 K) and at $B = 130$ G. As discussed earlier, the light transmission increases with $\lambda$ due to decrease in extinction efficiency with increasing $\lambda$. It can be seen from the figure that the light transmission is higher at higher $T$ due to the higher contribution from the thermal energy, which hinders the aggregation process to form field induced linear chain like structures along the direction of $B$. Due to increase in diffusivity of the suspended nanoparticles, the size parameter decreases which results in an increase of light transmission at higher $T$ as depicted in Figure 8.6. It can be further observed from Figure 8.6 that the field induced light transmission (at 750 nm) increases by 11, 25 and 33% when the temperature is increased by 10, 25 and 40 K, respectively from 278 K. This shows that there exist possibilities of temperature sensitive tuning of field induced light transmission in ferrofluids which can be used for temperature sensitive optical sensors.
Fig. 8.6. Light transmission as a function of incident wavelength ($\lambda$) at different sample temperature ($T = 278, 288, 303, \text{ and } 318 \text{ K}$) for the ferrofluids. Here, external field, $B = 130 \text{ G}$. 
8.3 Conclusions

The effect of temperature on field induced light transmission in a kerosene based ferrofluid containing oleic acid coated Fe$_3$O$_4$ nanoparticles of average size 6.5 nm is studied. At a fixed specimen temperature the light transmission monotonically increased with wavelength in the presence of an external magnetic field due to reduced extinction efficiency at higher wavelength. It is further observed that the light transmission decreased with increasing external magnetic field due to enhancement of size parameter and the resulting buildup of standing waves in the scattering medium. The normalized transmitted light intensity decreased with increase in external magnetic field and the extinction occurred at lower value of external magnetic field for lower specimen temperature. Moreover, the rate of light extinction is found to decrease linearly with increasing temperature due to the linear increase in diffusivity of the dispersed magnetic nanoparticles. With increase in temperature the coupling constant decreases and hence, the field induced aggregation occurred at a slower rate leading to an increase in light transmission.